

What makes a material function? Let me compute the ways...

Modelling in FP7 NMP Programme Materials projects



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Third version

Edited by

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Introduction

This is the third and more complete brochure presenting modelling projects funded under FP7. The publication of the first and second brochure has received extensive appreciation and the European Commission has received numerous statements and inputs that have been taken into account to prepare this second brochure.

Modelling is a powerful tool that supports materials research in the development of novel or improved applications. It provides the key information for identifying new materials, tailoring materials and design materials for structures and systems.

To foster dialogue and mutual understanding between industrial end-users, software developers and theoreticians, this publication presents the scope and achievements of the modeling in about 80 projects funded in the 7th Framework Programme (2007-2013) by the NMP Programme, unit Materials.

Importance of the projects to the European Industry

The use of materials modeling in industries is very versatile. Application addresses fields like Energy, Environment, Transport, Health, ICT and Manufacturing. It is supporting the creation of products like solar cells, sensors, car parts, tissues, computers, tools, coatings. Industrial application is the target of the FP7 NMP program and the projects show the continuous effort to move from model development to model application and finally upscaling for industrial application. It is important to note that, in general, models become most useful to industry when they have reached an advanced maturity. This requires strong interaction between the code developers and industry, and, because of the complexity and long timescale of the code development and validation process, the support of programmes such as NMP makes an important contribution to competitiveness.

The most crucial issue related to modeling in industrial applications is in the formulation of models that produce realistic results. In general, modeling and simulations can be the eyes of the experimentalists, helping them to access information that would not be available otherwise and interpret the experimental results. Modeling provides also invaluable predictions on the evolution of a system in a quicker or cheaper way than with trial and error methods. Industry uses modelling for:

- Saving costs by establishing a strategy for testing and by screening new material candidates, when a
 "try and fail" approach cannot be carried out in the industry or it would be too complicated,
 dangerous or expensive.
- Understanding results of measurements. This is particularly important at the nanoscale and at femtoscale where access to materials properties and processing methods is often difficult. The simulation can provide this information for every point in the sample at every time.
- Reducing the time to market, by accelerating the time scales of understanding and developing new materials.
- Suggesting new materials and experimental procedures to create them. Materials design by
 modeling is about investigation of relations between chemical and physical composition,
 microstructure and effective properties at a macroscale, so that a material can be designed with
 desired macro-properties. Modeling can be used to examine the properties of materials and
 devices that have not or cannot yet be created.

Questions that can be answered by modelling

To show the value of modeling, the achievements of the models beyond experiments have been listed. The models can answer questions like:

- •What is the influence of the automotive catalytic converter's shape on its performance?
- •Which hydrogen-microstructure interactions play a critical role in the degradation of materials and components?
- •Which are the dissipation mechanisms that contribute to the macroscopic adhesion between a metal and a polymer?
- •What is the role of thermodynamics and what are the reversal processes involved in ultrafast magnetisation processes?
- Is it possible to control the parameters of the excitation process and of the metal oxides to create long-lived metastable phases with tailored physical properties?
- Which is the role of the size of the systems in realistic nanometric devices? How is the dynamics influenced when the length scale is reduced to the nanometer size of devices (<20 nm)?
- •Which are the parameters that control the final state in a solar cell reached after the photo-excitation?
- Which is the influence of biomedical devices on the surrounding tissues?
- What is the most adequate stiffness and permeability of an intervertebral disc substitute?
- Which is the increase of electrical conductivity in composites upon addition of carbon nanotubes?

What are models? What are simulations?

Materials are complex systems and the equations that describe the physical and chemical behaviour of real systems are often too complicated to be solved easily. In order to save computer time, which is a precious and limited resource, the description of phenomena has to be simplified. Fortunately, often not all details need be taken into account in order to reproduce and predict experimental results. Key assumptions about reality can be made ignoring the complexity that is not necessary to describe the given situation. In this brochure, these approximations are called "models"¹.

With "simulation software and numerics" it is meant instead the implementation of the model in a computational code and the numerical methods that are used to solve the equations. In this publication, modelling is considered to be the establishing of relations between physical or chemical



Fig 1 Simulation gives the numerical solution to the model applied to a specific situation (Hans Fangohr, University of Southampton, UK)

¹ Note: the word "model" is used in many other situations (e.g. geometrical model of the sample, car model or fashion model), but different words will be used here for those instances.

quantities. The tuning of constants in an existing relation (parameterisations like force fields or engineering rules) are not considered to be modelling.

Model application and model development

Application of models

A model is strong if it is transferable from one materials system to another within the limits of the model. Many NMP projects are applying existing physics and chemistry models to new materials and manufacturing processes. This has generated a wealth of new information². When applying an existing model to a new situation, unexpected results or new phenomena may be discovered, but these results are obtained with existing equations. An overview of the extensive fields of model application in FP7 NMP projects will be described in Chapter 8 in more detail.

Development of new models

At times, models cannot be transferred from one physical situation to another (say from energy conversion to spin-dynamics). In such cases, research projects may want to increase the complexity of the model, by incorporating new physics and chemistry. This happens when complete new physics and chemistry is to be described. Modellers start from the simpler equations, and gradually add complexity to it (e.g. more transition metal orbitals, ligand orbitals, Coulomb exchange, spin-orbit, phonons) until a satisfactory agreement with experiments is reached. For example, it has been necessary to develop new models in femtosecond dynamics: at the femto-scale new dynamics, physics or chemistry takes place and new optoelectronics/magnetics/bio/chemistry models have been developed. Alternatively, modelers apply the model first at a small scale and transfer the results into a larger scale model in the form of constitutive equations. Constitutive equations are necessary to close the equations describing the system. Together they form the governing equations. This allows them to identify what are the critical relevant processes that lead to experimental results. Another typical case of the necessity to develop new models are the constitutive equations for continuum processes at the macro-scale. Existing macro-scale models consider processes at a smaller scale approximately and thus, by their nature, do not incorporate all necessary physics/chemistry. This often happens in mechanical modeling e.g. when considering how to build a structural model of an amorphous material in some smart way.

Chapter 7 will briefly describe the situations in which new physics and/or chemistry equations have been developed. In this chapter, adhering to the above definition of the word "model", only new equations are discussed. For example, the fine tuning of an existing force field to better reproduce results of a new material but using the same established equations is not considered as a new model in this text but as a new application of the same model. On the other hand, developing a new force field by adding new terms to include physical or chemical properties previously excluded will be considered as a new model. New constitutive equations linking physical or chemical parameters in a new empirical equation, found as results of modeling or as results of experiments, are also included as new modeling. The basic phenomenon might not be completely understood but this new relation can at least be called a 'hypothesis'.

² Please note that the physical/chemical knowledge about the system or process needed to perform the model application goes beyond purely computational skills.

Intermezzo: Some philosophy

The conservation equations are the foundations of physics and chemistry. Modeling starts with an approximation which at first is seen as a good balance between complexity and computability. Development of models may either make the crude model more complex (and in principle the perfect conservation equations is retrieved) or reduce the complexity of the model.





Fig 2 Model development works by moving along the arrow upwards or downward. (based on Kersti Hermansson, Uppsala University, SE)

Method development

The word "method" is reserved to indicate the way in which models are used. For example, the development of a smart way to compute long-range interactions in materials quickly and accurately is considered here method development rather than model development (although at the same time it certainly allows the use of more advanced interaction models because the simulation goes faster).

Other examples of method development are the methods to improve the sampling of complex potential energy landscape and phase space; this is called metadynamics. Since it can be particularly difficult to sample efficiently the phase space of a material for realistic conditions, improvements on current methods are valuable for the materials community, see Chapter <u>2</u> and <u>6</u> for more information.

Choosing the right model

When several (validated) models exist, the scientist/industry has to choose which one to use. This "testing of models" is also a valuable part of modelling. This consists in trying to answer questions like "which model gives properties that are closest to measurements for this material?" Here the researcher is investigating which physics is needed to describe the given situation. So a model that "approximate reality by considering the neighbours as point charges and ignore temperature effects" states what is the necessary physics to describe the measurements with. Sometimes the choice of a model depends on the balance between accuracy and simplicity. The outcomes of such testing might also be important because if none of the models are adequate the result of testing is that more physics/chemistry needs to be added to existing models.

<u>MONAMI</u> has been testing two models to calculate the electronic structure of V_2O_3 : a so called N-th order Muffin-Tin Orbital (NMTO) model, with features like massive down folding and generation of Wannier combined, and full-potential software using dynamical mean field theory for strongly correlated systems.

In <u>MORDRED</u>, large-scale atomistic simulations of oxide interfaces using dynamic charge transfer models were benchmarked against first principles simulations. Calculations of structure and charge for a large set of cluster, bulk and interface cases with both models were compared to undertands the limits of the faster and more approximated method.

<u>OXIDES</u> has been doing comparative tests of two first-principles methodologies, PSIC and B1-WC, by applying them to structural, electronic, and magnetic properties of a known 2-dimensional electron gas system: LaAlO3/SrTiO3. They evaluated the reliability of PSIC and B1-WC, comparing them with theoretical results presented in literature or obtained with other methods. This way, they explored the limits and capabilities of the two approaches. This testing is essential in selecting the most adequate band energy description to be exploited for transport properties, but it is not stricto sensu a new model development.

Numerical power needed and up-scaling for the industry

Simulation of models applied to new materials involves finding a solution to the equations of the model. This can become very complicated and the computational power needed may become an issue. Design environments should be developed that balance accuracy and speed. To this end, many models are solved with parallel algorithms, which allow the load to be distributed among computer processors.

Upscaling to industry should build on the progress made in High Performance Computing (HPC), theoretical models and faster numerical processes.

Part of the effort should be directed towards the key and transverse issues of software code modularity and reusability. An integrated and user-friendly design environment must be created.

This might require vertically integrated communities with theoretical modelers, experimental data generation and validation experts, software and hardware integrators and industry end-users.

Introduction of model types

A convenient way of approaching materials modeling consists in separating the models according to the entity whose behaviour is described (electrons, atoms, nanoparticles and grains and continuum unit cell). The description involves different physics or chemistry. This is often related to the time and length scale of the processes and determines the size of the systems that can be simulated with certain available computer resources. For example, diffusivity may be simulated modelling electrons diffusion, ion transport at atomistic level and electrical current with continuum models. Another example is modelling of chemical reactivity using molecular simulations at the atomistic scale and continuum reaction kinetics thereafter.

The four natural categories consist of three discrete types and one continuum type of model:

Method	Entity whose behaviour is described	Number of units	Length scale	Time scale
Electronic models	electron	10-100	0.1 - 1 nm	-
Atomistic models	atom	10 ² -10 ⁹	0.1 - 100 nm	fs - μs
Mesoscopic models	nanoparticle, grain	10 ⁶ -unlimited	100 nm - mm	ms - s
Mesoscopic magnetism models			1 nm - 100 mm	1 ps - 1000 ns
Continuum approaches	continuum unit cell	unlimited	nm-m	s - ks



Fig 3 An illustration of entities in the different model types. The length and time scales to which the models can be applied is indicated by ellipses. (Pierre Severin, Coexpair and Olaf van der Sluis, Philips)

Electronic models: These models describe the behaviour of electrons. Quantum mechanical methods are used to describe the behavior of the electrons which determine the properties and structures of the material. Ab initio models calculate electronic structures "from first principles" (i.e. based on fundamental principles of physics) expressed in the Schrödinger's equation within a set of approximations that do not include fitting the model to experimental data. These models thus rely on basic and established laws of nature without ad hoc parameterisation. Here, the material is explicitly represented by nuclei and electrons. From the model results at these shortest atomic time/length scales, electronic transitions and chemical reactions can be derived.

Examples of electronic model results: electronic band structure giving conductive/dielectric and optical properties force fields parameters, (magnetic) anisotropy, diffusion coefficient, activation energies thermodynamic stability and kinetic elementary processes for atomic defects and dopants

Atomistic models: These models describe the behaviour of atoms. When the electronic degrees of freedom are ignored, molecular mechanical models and classical mechanics are applied to describe the behavior of atoms and molecules. In addition to quantum mechanics based techniques, atomistic modeling uses effective interactions between atoms, called interatomic potentials (also empirical potentials or force

fields). Interatomic potentials do not treat the quantum nature of electrons explicitly, which allows models using these potentials to be enormously faster than models using quantum methods. Such interatomic potential based modeling may not be as accurate as full quantum mechanical approaches, but can be used to simulate complex materials processes as radiation damage in nanocrystalline materials and friction between surfaces.

The most common technique here is Molecular Dynamics simulations, now routinely carried out on systems including up to tens of thousands of molecules (consisting of many atoms) over tens of nano seconds. At these longer time scales e.g. lattice motion is described.

Examples of atomic model results: trajectories, packing, stiffness, dynamical properties, surface and interface energies, constitutive equations parameters, spectral properties

Mesoscopic models: These models describe the behavior of nanoparticles or grains. At the supra-atomic scale where uninteresting or fast details of the atomic motions are averaged out or replaced by stochastic terms, mesoscopic models concentrate on essential motions and large-scale structures. Examples are thermodynamics models. Also the so-called coarse-grained models fall in this category and here the fundamental unit is a "bead" that interacts with other "beads" via effective soft potentials. This category of models also includes the magnetism models based on macro-spin approaches that combine atomic spins into a macro-spin.

Examples of mesoscopic model results: morphology, domain formation and growth kinetics, thermal stability, magnetic behaviour

Continuum models: These models describe the behavior of a continuum unit cell. At this level material is assumed to be continuously distributed throughout its volume. Models at this scale disregard the discrete particle-based structures and smaller detail. This level describes how materials are seen and touched. Modelling at this scale can predict material decomposition, defect formation, crack propagation, solidification of liquids and other important variables for industrial manufacturing. At these macroscopic length scales e.g. thin films and realistic nano-devices with metallic contacts are described.

Examples for macroscopic model results: macroscopic structural behaviour, heat and mass transport, permeation times, chemical reaction kinetics, electromagnetic behaviour

The large majority of the in FP7 NMP materials projects performed modeling at different scales. The models in each scale will be introduced and it will be described how they are used.



Fig.4 Number of projects in the FP7 NMP Programme performing modelling of the fours different types.

Linking of models (multi-scaling and multi-physics/chemistry modeling)

In order to increase their predictive capability and applicability to a wide range of applications, continuumscale models need to include processes, which originate at the electronic, atomistic and nanoparticle-scale. This lies in the very nature of the continuum-scale models, where such effects are neglected. For example, continuum-scale models that approximate interfaces by a set of effective band offset parameters have no predictive power over interface related effects as the detailed electronic and atomistic structure near the interfaces is not taken into account.

The great challenge in creating accurate and predictive models is that materials form a true multi-scale problem. A consistent hierarchy of simulations at different levels of representation is needed.

Multi-scaling is linking codes describing the behavior of different entities, each code dealing with part of the physics/chemistry. We reserve the word multi-scaling for linking of different type of models (electrons, atoms, nanoparticles or continuum), where the linking is based on new models for the interaction physics.

Note however that the notion multi-scale modelling has two interpretations:

- Applying the same physics model to different length and times scales: e.g. continuum model applied to the nm structure and at mm-scale (fine and coarse grids).
- Linking models with different physics.

The first interpretation is quite common in material engineering (micromechanics) and the difficulty is linking of datafiles at different grid points.

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Note that also the notions "**Multi-physics/chemistry modeling**" is often used. This usually means connecting different codes describing different physics/chemistry at the <u>same</u> scale.

An example is describing micromechanics and fluid mechanics, both at continuum scale.

A major issue in linking models is the reduction, extraction and transfer of data from one model to another and this is a very active subject of research. For example, semi-empirical pseudo-potentials, which can be used to calculate the accurate electronic structure, are based on first principles calculations at a smaller scale (Hartree-Fock, density functional theory, and higher level QM methods). In continuum modeling often the results of models applied at mesoscale (nm) are fed into the macro-scale model (μ m) in the form of constitutive equations or as boundary conditions and represents a big challenge in contemporary modeling.

Finally, last but not least, in a multi-scale multi-physics approach not only models should be connected but also integrate experimental data in a clever way.

The linking of the models represents a considerable challenge and of the projects performed modelling at different scales, and 67% linked the different models.

Coupling of models

Especially at continuum level different physics and chemistry models are solved simultaneously and this is called coupling of models.

Modelling for interpretation of experimental results/characterisation

The interpretation of experimental data as material properties relies on models as well. In Fig 1 "experimental results" contains BOTH the "getting the signal" phase and "making the interpretation" phase. This includes deciding which formula (model) to use to convert the signal into a property. It can also involve the post-processing of measured quantities into other physical/chemistry properties.

<u>METACHEM</u> is processing transmission, reflection and ellipsometry spectra of metamaterials measured at different angles of incidence (ellipsometric data) to extract values of optical constants of metamaterial. This is done with the help of electromagnetic wave propagation models, but the interpretation model used is at the moment a debated research topic discussing the existence of concepts like "refractive index".

Chapter 1 Electronic models

Electronic models describethe behaviour of electrons. The theoretical framework of electronic models is the Schrödinger equation, with which the evoluation at the quantum level of any atomic or molecular system with time can be calculated. The Schrödinger equation is defined by two elements: the so called wavefunction of the quantum system, and H, the Hamiltonian operator. The wavefunction is a function which represents, at each moment in time, the positions, momenta and spins of all particles in the system. However, the spin part of the wavefunction is often not explicitly carried in calculations that do not focus on magnetic properties. The most crucial element is H, the Hamiltonian operator, which represents the total energy of any given wavefunction and takes different forms depending on the external forces acting on the material. In magnetics, the Hamiltonian includes terms expressing energy due to exchange interaction, spin-orbit interaction, and Zeeman interaction.

In practice, quantum mechanical models are finding suitable approximations of the full Hamiltonian and/or of the molecular orbitals, in order to simplify the numerical calculations of the electronic degrees of freedom without compromising the quality of the simulated results. Further approximations and semi classical approaches may also be used.



Fig.1.1 Number of projects that used one of the four main types of electronic models treated here.

1.1. Ab initio quantum mechanical (or first principle) models

The Schrödinger equation can be solved exactly only for a few problems of limited interest. To solve the equation for systems of practical use, approximations are in general required. *Ab initio* models may be based on a series of approximations that do not include fitting the model to experiments. This is also called a first principle approach because the model is using the Schrödinger equation and is still based purely on fundamental principles of physics.

Quantum mechanical chemistry models are routinely used to calculate the ground state of atomic and molecular systems and the energy and configurations (electronic structure) of the excited states. This can be applied to several problems of practical use.

Ab initio models are applied, to calculate the mechanism of new catalysts and proton conductance in proton exchange membranes (<u>HYPOMAP</u>), surface energies and activation energies of catalytic nanoparticles (<u>NEXT-GEN-CAT</u>) and to calculate the formation energy of inclusion complexes in layered magnesium oxides, HTLC, which is relevant for the synthesis of quasi-solid electrolytes (<u>MINOTOR</u>).

Interface processes can be studies at the quantum level, for example adhesion of metal-ceramic interfaces and internal grain boundaries in realistic conditions (<u>ROLICER</u>); interfacial hydrogen bonding and adsorption of water and carbohydrates on cellulose surfaces (<u>SURFUNCELL</u>); the energy barriers and binding energies of hydrogen in normal interstitial sites and around point defects (<u>MULTIHY</u>).

In solar cell material development, ab initio models are used to calculate changes in the work functions of metal electrodes upon deposition of self-assembled monolayers (<u>MINOTOR</u>) and the energy, electronic distribution and properties of nanostructures in PV excitonic solar cells (<u>INNOVASOL</u>).

These models can also cover superconducting systems and are then used to predict electronic and superconducting properties at interfaces of layers with different axis orientation (<u>SUPER-IRON</u>).

Given the challenges of solving the Schrödinger equation, quantum mechanical calculations can only be performed for isolated systems (in vacuo) and at zero temperature. However, often the output of ab initio quantum mechanical models is used as input to develop parameters for models at higher scales, in the development of interatomic potentials or to calculate partial atomic charge distribution. This ensures the incorporation of crucial quantum effects and properties for larger, more realistic, systems simulations at a reduced computational costs and time.

The Schrödinger equation can be solved for small molecular systems if one considers that the mass of the nuclei is much larger than the mass of the electrons, the Born-Oppenheimer approximation. This assumption is valid if the electrons move much faster than the nuclei and the electrons feel the electric field of the nuclei *as if* the nuclei are in a fixed position. The electronic wavefunction of the electrons depends then only on the position of the nuclei and not on their momenta.

Basis sets

To solve the Schrödinger equation numerically the concept of basis sets of wavefunctions is introduced. The orbitals are expanded as a linear combination of such functions with the weights or coefficients to be determined.

Often a simple and effective basis set is made of linear combinations of atomic orbitals (LCAO) centered on the nuclei. Basis sets composed of Gaussian functions centered on the nuclei are also popular because of their flexibility in implementation and, only if needed, functions centered on bonds or lone pairs are added. In solids and other systems with periodic boundary conditions, it is common, and sometimes more appropriate to use basis sets composed of plane waves up to a cutoff wavelength. These functions are naturally periodic and independent of the atom positions and are therefore appropriate to describe the delocalized electrons in solid crystal (electron gas).

In all cases, the choice of the most appropriate basis functions depends on the system under consideration and the level of accuracy that is needed in the final result. A large number of ready-made basis sets are available and implemented in commercial codes, but new basis set are sometimes generated to study systems that present new challenges.

1.1.1 Hartree-Fock (HF) method

In so-called wave-function based approaches, the Hartree–Fock (HF) method is the conceptual the starting point of molecular poly-electron structure calculations. The orbitals of the system are expressed in a set basis functions (discussed in the previous section) and the coefficients of this expansion are obtained numerically using a variational procedure that iteratively refines the individual electronic solutions to obtain the configuration that yields the lowest total energy (also known as the SCF, self-consistent field method).

Several approximations are applied in a Hartree-Fock calculation. First, the Born-Oppenheimer approximation is assumed and relativistic effects are neglected. Moreover, each particle is thought to be subjected to the mean field created by all other particles. This means that the method is neglecting the electron-electron correlation terms in the Hamiltonian. This method thus fails to represent strongly correlated systems, and systems close to the dissociation limit, as well as the weak dispersion interactions between molecules.

Ab initio Hartree-Fock electronic calculations have been used to calculate structures, electronic density distribution and mobilities, partial atomic charges and electric dipoles (<u>INNOVASOL</u>, <u>MUST</u>, <u>ONE-P</u> and <u>ORAMA</u>).

1.1.2 Higher level ab initio methods

The Hartree-Fock method has fundamental limitations. It provides a localised representation of molecular orbitals which is not appropriate in highly dispersive systems and electron correlation is neglected. Higher level quantum chemical methods have been developed to overcome these simplifications and provide the most accurate calculation results of electronic structure.

These methods include: Configuration Interaction (CI), which includes the excited states in the description of the electronic state. Coupled Cluster (CC) takes the basic Hartree–Fock molecular orbital method and constructs multi-electron wavefunctions using the exponential cluster operator to account for electron correlation. Møller–Plesset perturbation theory (MP2, MP3, MP4, etc.) improves on the Hartree–Fock method by adding electron correlation effects as a second order perturbation of the Hartree-Fock Hamiltonian. These methods devise schemes which can, at least in principle, be infinitely refined by the addition of higher level terms. For example, a CCSD(T) calculation simply means a calculation done using a coupled-cluster method, which includes singles and doubles fully and triples are calculated non-iteratively.

Note that due to their higher computational cost, these methods can only be applied to systems very limited in size.

Traditional post-Hartree-Fock methods (e.g. MP2 or CCSD(T) methods) on cluster models has been used to study the catalytic activity of MOFs by modelling reactions catalysed by Lewis acid sites (<u>MACADEMIA</u>); and to study the proton conductance in the proton exchange membranes (<u>HYPOMAP</u>).

1.1.3 Density Functional Theory

A popular and versatile quantum mechanical method that includes (some of) the effect of electron correlation (albeit approximately) is Density Functional Theory (DFT).

DFT is based on the Hohnberg-Kohn theorem that states that ground-state energy is uniquely defined by the electron density. The properties of a many-electron system are then determined by using functionals, i.e. functions of the spatially dependent electron density. DFT calculations usually consist in solving the Kohn–Sham equation which is the Schrödinger equation of a fictitious system (the "Kohn–Sham system") of non-interacting particles (typically electrons) that generate the same density that the real system of interacting particles would generate. This simplifies the formulation greatly because instead of explicitly including the real potential of many interaction electrons, the Kohn–Sham equation contains a local effective (fictitious) external potential of non-interacting particles.

Typically, the biggest additional modeling necessary in DFT is the formulation of the exchange-correlation functionals, which need to model not only the electron exchange and correlation energy terms but also the difference between the kinetic energy of the fictitious non-interacting system and the real one. The equations are then solved using an iterative self-consistent approach based on the variational principle.

The simplest way to implement DFT is using the local density approximation (LDA) where the functional depends only on the density at the coordinate where the functional is evaluated. A further refinement is obtained considering the generalized gradient approximation (GGA) which is still local but also takes into account the gradient of the density at the same coordinate.

However, for many solid-state systems, and in molecular calculations, more sophisticated functionals are often needed, and a huge variety of exchange-correlation functionals have been developed for chemical applications. For molecular systems the so-called B3LYP functional is widely used, and is mentioned as an example of a hybrid functional in which the exchange energy, in this case from Becke's exchange functional, is combined with the exact energy from Hartree–Fock theory. The adjustable parameters in hybrid functionals are generally fitted to a 'training set' of molecules. Although the results obtained with these functionals are sufficiently accurate for many applications, there is no obvious systematic way of improving them (in contrast to some of the higher level ab initio methods like configuration interaction or coupled cluster theory). In the current DFT approach, error is estimated comparing the results to other methods or experiments.

Computational costs are relatively low when compared to higher level ab initio methods based on the complex many-electron wavefunction. However, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces and strongly correlated systems; and

there are inaccuracies in DFT calculations of the band gap in semiconductors, to mention a few examples. Improving DFT calculations by modifying the functional or by the addition of terms to overcome this problem is an active research topic.

Spin polarized DFT is an extension of DFT which includes both the electron density and the up and down spin densities explicitly in the Kohn-Sham equations.

Density functional theory (DFT) has been used to perform quantum mechanical electronic calculations in a large number of projects (GOFAST, GRENADA, HIPERSOL, HYPOMAP, INNOVASOL, LEMSUPER, MONAMI, MORDRED, NAMASTE, NEXT-GEN-CAT, ONE-P, ORAMA, SURFUNCELL). DFT has been applied to model non-collinear magnetism, electric fields applied to surfaces, electric polarization and the mapping of the electronic structure to tight-binding Hamiltonians (IFOX). The catalytic activity of MOFs is explored modelling reactions catalysed by Lewis acid sites, using periodic DFT calculations and toi characterise the chemisorption processes occurring at the surface of open metal centres of metal organic frameworks (MOFs) (MACADEMIA). DFT has been used to calculate electronic properties (critical temperatures and magnetic anisotropy) of thin polycrystalline magnetic films and to study the influence of the electronic correlations at the interface in hybrid metal/oxide-based magnetic bilayers in a nanocomposite system (NANOPYME). DFT has also been used to calculate the adhesion of metal-ceramic interfaces and internal grain boundaries in realistic conditions (ROLICER). Spin polarized DFT is used to calculate to calculate the magneto-crystalline anisotropy and the exchange interaction between atomic spins (ULTRAMAGNETRON, REFREEPERMAG, MAGNONICS, DYNAMAG, ATHENA, CRONOS). In <u>ROMEO</u> the role of the specific structural distortion near grain boundaries on the magneto-crystalline anisotropy and magnetization will be determined by means of first principles DFT calculations.

1.2. Many body models and effective Hamiltonians

The many-body problem is a general name for a vast category of physical problems where a large number of equations for a large amount of particles need to be solved in order to provide an accurate description of the system. This is e.g.the case in a large many-electron system or when it is necessary to include the effect of the surroundings on the system of interest (for example, in solvation models the weak interactions of the (small) quantum system with the (many) solvent molecules are treated approximately to keep the computational costs limited).

A large number of many-electrons systems can be studied theoretically by the models that have been discussed in the previous paragraph. However, when the system size increases the calculations required by full ab initio methods and DFT methods become very quickly unfeasible.

In addition, ab initio methods are commonly solved through approximations which limit their accuracy. For example, in highly correlated systems and in solids where electrons may be considered as nearly localised, solving the Schrödinger equation within an independent electron scheme fails to reproduce experimental results.

There are several ways to approach a many-body quantum problem, depending on the characteristics of particular system at hand, however it most often relies on more drastic approximations on the Hamiltonian or wavefunctions representation.

Effective Hamiltonians

Except in few simple cases, models that treat many-body electron interactions require the definition of an "effective" Hamiltonian. This is a simplified representation of the true Hamiltonian where some parameters are derived from empirical data. These methods are very popular because they allow to treat large systems (up to millions of non-equivalent atoms), where a full ab-initio method without the approximations would often be computationally too expensive.

Dynamic Mean Field Theory

The many body Dynamical Mean Field Theory (DMFT) is a method to approximate many body Hamiltonians and it is designed to deal with strongly correlated materials. In such materials, the approximation of independent electrons, which is used in Density Functional Theory band structure calculations, breaks down. DMFT adds the contribution of the local interactions between electrons and bridges the gap between the nearly-free electron gas model and dense condensed-matter models. DMFT can be used to model the phase transition between a metal and a Mott insulator, a process where the strength of electronic correlations increases.

DMFT has been successfully applied to real materials to calculate material properties of strongly correlated systems like high temperature superconductors (<u>MONAMI</u>, <u>GOFAST</u> and <u>LEMSUPER</u>)

1.2.1 Nearly-free electron model

The electronic band structure of metals can be described by the simplest effective Hamiltonian, which treats electrons in a solid as moving almost freely through the crystal lattice.

1.2.2 Pseudopotentials

Pseudopotentials provide an approximation of the full Hamiltonian. They can be developed to approximate the core (i.e. non-valence) electrons of an atom and its nucleus with an effective potential, or pseudopotential. This approach considers the nuclear charge as effectively screened by tightly bound core electrons. As a consequence, only the chemically active valence electrons are treated quantum mechanically, thereby reducing the number of electrons in the Schrödinger equation and the size of basis sets.

Semi-empirical pseudopotentials have been used to calculate electronic energies and lifetime of charge carriers in large structures (10-100nm) with up to millions of non-equivalent atoms (<u>HIPERSOL</u>).

1.2.3 Semi-empirical tight binding potential (TB) model

The opposite extreme to the nearly-free electrons is the case where the electrons in the crystal are tightly bound and behave much like the atoms, as in the tight binding model (TB). The method is closely related to the LCAO method used in ab initio models. Electrons are viewed as occupying the standard orbitals of their atoms, and then 'hopping' between atoms during conduction.

Tight binding models are applied to a wide variety of solids. The approximation often works well in materials with limited overlap between atomic orbitals and limited overlap between potentials on

neighbouring atoms. Band structures of materials like Si, GaAs, GaN, SiO₂ and diamond for instance are well described by TB-Hamiltonians.

This model can be used to perform finite-temperature simulations, and calculate thermoelectric properties and electronic transport calculations (*OXIDES*), to evaluate hydrogen trapping at extended crystal defects such as grain boundaries and dislocations (*MULTIHY*) to explore effects connected to finite temperature and disorder (*ATHENA*) and to describe electronic and optical properties of GaN based nanowires (*SMASH*). Effective tight-binding Hamiltonians will be constructed starting from first-principles to describe the electronic properties of defects, superlattices and grain boundaries and simulate the superconducting properties (*Jc*, *Hc*, *Tc*) by means of Bogoliubov-De Gennes equations. This will give information on the superconducting properties: order parameters in real space across the boundary, superconducting current flow at the boundary and critical currents (*Jc*° and how the superconducting properties of *FeSCs* are affected by the mis-orientation angle will be predicted. First-principles models of effective interactions between electrons, including spin fluctuations, will be elaborated to provide fundamental information on the superconducting properties will be done extending the ab-initio SuperConducting Density Functional Theory with electronic pairing interactions (*SUPER-IRON*).

1.2.4 Hubbard model

The Hubbard model is the simplest model of interacting particles in a lattice, with only two terms in the Hamiltonian: a kinetic term allowing for tunneling ('hopping') of particles between sites of the lattice and a potential term consisting of an on-site interaction, which stems from the Coulomb repulsion between electrons occupying the same atomic orbital. For electrons in a solid, the Hubbard model can be considered as an improvement on the tight-binding model, which includes only the hopping term. The Hubbard model is actually the simplest model able to describe the interaction-driven transition from a metal to an insulator, commonly known as the Mott transition. Mott insulators are commonly found within transition metal oxides and organics, where the Coulomb repulsion overwhelms the very narrow bandwidth--More recently, the Bose- and Fermi-Hubbard models has been used also invoked to describe the behavior of ultra-cold atoms trapped in optical lattices. The Hubbard model is a good approximation insofar the effect of all other bands but the conduction ones can be neglected, which corresponds to low enough temperature and energy so that all interband transition are uninfluential. If interactions between particles on different sites of the lattice are included, the model is often referred to as the 'extended Hubbard model'.

The fact that the Hubbard model cannot be solved analytically in arbitrary dimensions has led to intense research into numerical methods for strongly correlated electron systems.

The Hubbard model can also be studied within the Monte Carlo statistical method for example to study the electronic exchange interaction in non-equilibrium situations (FEMTOSPIN). Molecular Hubbard models for ground state and low temperature properties of strongly correlated materials have been used to calculate long ranged electron-electron interaction and insulator-superconductivity transitions in lattices under pressure (LEMSUPER) and to model the Hamiltonian of inorganic metal nanoparticles embedded in matrices of conjugated organic materials (HYMEC).

1.2.5 k·p effective Hamiltonian

This is a technique that allows a band structure to be approximately described in terms of just a few parameters. The technique is commonly used for semiconductors, and the parameters in the model are often determined by experiment.

This model can be used to calculate conduction and valence band valence band structure around a point of symmetry and effective masses of the charge carriers. Thereafter these values can e.g. be used as input to a drift diffusion model calculating the electron and hole transport (<u>SMASH</u>) or to micromagnetic models for magnetisation (<u>NAMASTE</u>).

1.2.6 Polarisable continuum model

The polarisable continuum model (PCM) is commonly used to model a solvent-mediated chemical reaction. For a system with very many solvent molecules, the computational cost of modeling would grow prohibitively high, if it were necessary to consider each solvent molecule as a separate molecule. Instead the solvent reaction field is simulated by a set of apparent charges self-consistently determined on the basis of the electric potential generated by the solvated molecules. The solvated molecules electronic field is modelled with one of the available electronic models.

This model has been used to simulate the effect of surrounding solid electrolyte weakly interacting with the conductive molecules in excitonic solar cells (<u>INNOVASOL</u>).

1.2.7 Envelope function approximation for continuous media

This is a model that proposes an approximation of the wavefunction, based on the fact that the wavefunction varies very quickly close to the cores of the atoms of the lattice. In the he *envelope approximation* only the slowly varying "envelope" modulating the rapidly varying part of the wavefunction is considered. The boundary conditions are applied to the envelope function directly, rather than to the complete wavefunction.

This method is used to calculate the quantum states of confined particles in nanostructures (<u>SMASH</u>).

1.3. Quantum mechanical in response to time dependent fields

To study electronic and spin dynamics under the effect of external time dependent potentials, such as electric or magnetic fields, time dependent models are needed.

1.3.1 TD-DFT and TD(Spin)DFT

Time-dependent density functional theory (TDDFT) is a quantum mechanical model used to investigate the properties and dynamics of many-body systems in the presence of time-dependent potentials, such as electric or magnetic fields. The effect of such fields on molecules and solids can be studied with TDDFT to extract features like excitation energies, frequency-dependent response properties, and photo-absorption spectra.

As TDDFT is an extension of DFT, the conceptual and computational foundations are analogous and use the effective potential of a fictitious non-interacting system which returns the same density as any given

interacting system. Numerically, this TDDFT model is much more complex then DFT, most notably because the time-dependent effective potential at any given instant depends on value of the density at all previous times. Note however that at present most of the implementation assume a local time-dependence of the potential (adiabatic approximation).

TDDFT is able to account correctly for magnetic fluctuations in the paramagnetic state of iron and other itinerant ferromagnets, the effects of vibrations (electron-ion dynamics) on photo-energy conversion (<u>CRONOS</u>, <u>INNOVASOL</u>) and it is used to calculate transport properties in systems with a strong correlation term between particles (<u>HYMEC</u>).

If needed, the equation of motion for the spin degrees of freedom can be derived with timedependent spin-density-functional theory TD-SDFT, which includes the spin density interacting with the external magnetic field. This can then be used to calculate non-linear interactions between spin, conducting electrons and laser light (<u>FEMTOSPIN</u> and <u>CRONOS</u>).

1.3.2 The time-dependent k·p-model

This quantum kinetic model describes the time evolution of the multi-band electronic state and is a linear coupled system of Schrödinger equations. The evolution is governed by the k·p Schrödinger operator which as an extension to the single-band models describes a system of bands of the band structure, usually the four topmost valence bands.

1.3.3 Other time-dependent models

The time-dependent approach based on the Gutzwiller wave function and approximation is a very simple tool that allows simulating for quite long times the non-equilibrium evolution of correlated electron models. It is in essence an improvement of the time-dependent Hartree-Fock approximation, endowing a Hartree-Fock Slater determinant with local many-body correlations that better capture the collective nature of the Mott localization phenomenon. It is a rigorous variational approach in the limit of large lattice-coordination, but seems to provide qualitatively correct results also beyond that limit.

The time-dependent Gutzwiller approach is able to model the temporal evolution of correlated materials brought out-of-equilibrium by ultra-fast laser pulses (<u>GOFAST</u>).

The Blonder-Tinkham-Klapwijk model is used to describe the normal-superconducting microconstriction contacts at the crossover from metallic to tunnel junction behavior. The Blonder-Tinkham Klapwijk (BTK) model in its simplest form does not require any input from other models. In its 3D extension, the BTK model requires in input the shape of the Fermi surface. In any case, this model allows fitting the gap features of the point-contact Andreev-reflection (PCAR) spectra and thus obtaining the amplitude and the symmetry of the superconducting gap(s).

The multiband Eliashberg theory includes interband spin-fluctuation interactions and describes superconductivity-induced infrared optical anomalies. The multiband Eliashberg model requires some input from band structure calculations (normal DOSs at the Fermi levels) and contains 2 free parameters (namely the coupling strengths) that can be adjusted to reproduce the gaps provided by the BTK fit of the spectra and the experimental critical temperature.

In particularly good contacts, the point-contact spectra also contain electron-boson structures that cannot be fitted by the simple BTK model; in these cases, since one of the outputs of the Eliashberg model is the

whole energy-dependent gap function, this may be put in the extended BTK model to calculate theoretical point-contact spectra that feature electron-boson structures that can be compared to the experimental ones.

These models have been used to calculate the intrinsic physical parameters (superconducting transition temperature, penetration depth, upper critical field) and superconductance energy gaps (<u>IRON-SEA</u>), which are very important intrinsic physical parameters in superconductors.

1.4. Statistical charge transport model

To describe the transport of charge carriers in solids or liquids, statistical methods can be used, like the drift-diffusion and the percolation method described below. It should be noted that the underlying methodology can be applied at many scales, see Chapter 2.5 and 3.4.

1.4.1 Semi-classical drift-diffusion model

This is a popular semi-classical model to describe the transport of charge carriers in solids. This can be described by a hopping model on a lattice of sites (hopping rate equation). To arrive at the behaviour at longer time and length scales a process of averaging is applied so that the complicated microscopic structure of transport dynamics is replaced by a continuum drift-diffusion equation with a diffusivity specific for the material. The carrier density distribution can be modelled using quantum mechanical Fermi-Dirac statistics or Boltzmann statistics. The necessary input parameters like band gap, carrier mobility and diffusion coefficient are obtained empirically or with separate theoretical calculations, using the Einstein relation. When the underlying lattice is disordered the situation is much more difficult. Disorder has to be taken into consideration if the sites of lattice are randomly distributed and hopping rates might depend on energy states on the sites. In general, the continuum description of disordered lattices cannot be represented by a diffusion equation with a well-defined diffusivity coefficient. Monte Carlo simulations have been performed in order to approximate the diffusivity for certain disordered systems.

In some cases, the average velocity field exists because of a force; for example, the equation might describe the flow of ions dissolved in a liquid, with an electric field pulling the ions in some direction (as in gel electrophoresis) or in semiconductor devices the electrons and holes are subject to electrical potentials. In this situation, it is usually called the drift-diffusion equation or the Smoluchowski equation. The word "drift" is related to drift current and drift velocity.

The drift diffusion model has been used to simulate electronic transport in large diameter heterojunction nanowires with tunnel junctions (<u>AMON-RA</u>), to calculate electron transport across oxides interfaces (<u>MORDRED</u>), electron and holes transport in Gallium Nitride based nano-rod structures (<u>SMASH</u>) and to calculate steady state conductivity (high and low state) in organic semiconductor device (<u>HYMEC</u>).

1.4.5 Percolation models

Statistical approaches for electrical conductivity are also applied in percolation models. Transport due to percolation is represented as movement through a three-dimensional network of vertices in which the edge or "bonds" between two neighbors may be open (allowing the particles through) or closed with a certain defined probability. Electron tunnelling is described with quantum mechanical percolation models which assume the charge transport between carbon nanotubes are partly through physical contacts and partly through electron tunnelling between carbon nanotubes with a given probability.

Electron tunneling percolation models are used to predict electron percolation thresholds for polymer/CNT composites and electrical conductivity of polymers reinforced with CNT (IMS & CPS).

Chapter 2 Atomistic models

Most molecular systems and phenomena of interest in physics and chemistry are too large to be treated by quantum mechanics simulations, even if semi-empirical approximations are used. Atomistic models describe the behavior of atoms and aim at simulating the behaviour of larger molecular systems (typically between 10^2 and 10^9 atoms, length scale 0.1-100nm, timescale fs-µs) maintaining individual atomistic detail, but often removing an explicit representation of the electrons. Although these systems are not large enough to be considered macroscopic, they are often sufficiently large to reproduce experimental results within the desired accuracy and at the same time detailed enough to detect their microscopic origin. Atomistic simulations are based on statistical mechanics, statistical thermodynamics and other probabilistic theory. They consist in treating the many-atoms system as a large statistical population, whose behaviour is determined by the forces applied to each single atom. Simulations are performed keeping the number of particles, temperature and total energy constant (the so-called microcanonical ensemble); the number of particles, temperature and volume constant (the so-called canonical ensemble) or the chemical potential, temperature and pressure (the so-called grand canonical ensemble). Statistical mechanics provides the mathematical framework for relating the microscopic properties of individual atoms and molecules to the macroscopic bulk properties of materials that can be observed in everyday life. These models explain macroscopic structural, thermodynamical and dynamical observables (e.g. temperature, pressure, work, heat, free energy, entropy and spectra of these variables) based on classical and quantum-mechanical descriptions of statistics and mechanics at the microscopic level. For example, a macroscopic observable like temperature is due at microscopic level to the collisions between particles and can therefore be mathematically derived sampling the velocities of the atoms.

For the statistical mechanics formulation to be valid, the averaging has to be done over all possible configurations of the system, i.e. all possible positions and momenta of all particles (ergodic condition). This is true if the simulation is infinitely long, and approximately true if the system is allowed to evolve for a sufficient amount of time. The ergodic condition may be more difficult to achieve in systems with many degrees of freedom, or with large energy barriers between possible configurations, as the systems may be trapped in one local energy minimum. Methods to overcome this problem and speed up the configurational sampling are an active field of research.

To determine whether or not to use continuum models or statistical mechanics, the Knudsen number may be evaluated for the problem. The Knudsen number is defined as the ratio of the molecular mean free path length to a certain representative physical length scale. This length scale could be, for example, the radius of a body in a fluid. More simply, the Knudsen number is how many times its own diameter a particle will travel on average before hitting another particle. Problems with Knudsen numbers at or above unity are best evaluated using fine scale (atomistic and mesoscopic) statistical mechanics for reliable solutions.

In general, atomistic models need input describing the interactions between the atoms and equations that are used to obtain the macroscopic properties that can be compared with experiments.



Fig.2.1 Number of projects that used one of the four main types of atomistic models treated here.

Input to atomistic models:

Interatomic potentials

In molecular simulations, the interaction forces between atoms are given by interatomic potentials. These are usually represented by simple analytical parametrical expressions. This input to the atomistic models (interatomic potential functions and parameter sets) can be derived from experiments or calculated by smaller scale electronic models (see Chapter <u>1</u>) for a small number of appropriate test molecules. Validation of parameter sets is done against experimental results on larger and more diverse systems. Often an iterative procedure for the refinement of the parameters is needed. The most important aspect in the development of the interatomic potentials is to ensure transferability of parameters across a diverse range of systems and test the accuracy limits of the parametrisation.

Force Fields

A force field is a system of potential energy functions and parameters used in molecular mechanics, Molecular Dynamics or Monte Carlo simulations. In all-atoms force fields, each atom is represented explicitly, including the light and small hydrogen, while in united-atom force fields some atoms, like hydrogen and carbon atoms in methyl and methylene groups, are treated as a single unit. Grouping of larger atomic moieties may be necessary to simulate larger systems for longer times and this is treated in the next chapter under coarse-grained mesoscopic models. Typically, first each atom is modelled by assigning a radius (usually the van der Waals radius), a polarisability and a constant net charge (generally derived from quantum calculations and/or experiment). The next step is to model the force field. Force fields usually consist of a sum of additive terms, which represent both bonded interactions (between atoms that are actually covalently bonded) and non-bonded interactions. Terms between bonded atoms include: bond terms between 2 atoms, bend terms between 3 atoms, and torsional (dihedral) terms between 4 atoms. Bond and bend terms are often treated as springs with an equilibrium distance equal to the experimental or calculated value. The dihedral or torsional terms have multiple minima and cannot be modeled as springs, and their specific functional form varies in different force fields. Additionally, "improper torsional" terms may be added to enforce the planarity of aromatic rings and other conjugated systems, and "cross-terms" may be added that describe coupling of different internal variables, such as angles and bond lengths. Some force fields also include explicit terms for hydrogen bonds. 26

The non-bonded terms are much more computationally costly to calculate in full, since a typical atom is bonded to only a few of its neighbors, but interacts with every other atom in the system. The electrostatic force between charged particles is a typical non-bonded interaction and is given by Coulomb's law. Longrange electrostatic interactions are often important features of the system under study (especially for proteins) but the electrostatic terms are notoriously difficult to precisely calculate well because they do not fall off rapidly with distance. A variety of methods are used to address this problem; the simplest approximation consists in using a cut-off range for these interactions and atom pairs whose distances are greater than the cutoff have a van der Waals interaction energy of zero.

Other more sophisticated but computationally intensive methods are known as particle mesh Ewald (PME) and the multipole algorithm. To account for electronic polarisability and produce better agreement with experimental observations, parameters can be buffered or scaled by a constant factor.

Other non-bonded forces are London dispersive interatomic forces (attractive) and electron-electron short range forces (repulsive). These are typically modelled together using the so-called Lennard-Jones potential.

Notwithstanding their simplicity, force fields can reproduce quite well a wide variety of chemical and biological problems, including drugs binding, protein folding kinetics and protonation equilibria.

Bond Order Potentials (BOP)

Bond order potentials belong to a class of analytical potentials which is used in molecular simulations. Examples include the Tersoff potential, the Brenner potential, the Finnis-Sinclair potentials, ReaxFF, and the second-moment tight-binding potentials. They have the advantage over conventional molecular mechanics force fields in that they can, with the same parameters, describe several different bonding states of an atom, and they may thus, to some extent, be able to describe chemical reactions correctly. The potentials were developed partly independently of each other, but share the common idea that the strength of a chemical bond depends on the bonding environment, including the number of bonds and possibly also angles and bond length.

2.1 Molecular Mechanics

Molecular mechanics uses classical mechanics to model molecular systems in order to calculate molecular geometry, energy, and various molecular properties. It does this by finding the lowest energy conformation of a molecule. The potential energy is calculated using force fields. The (local) minimum is searched for by an appropriate algorithm (e.g. steepest descent). Global energy optimization can be accomplished using simulated annealing, the Metropolis algorithm and other Monte Carlo methods, or using different deterministic methods of discrete or continuous optimization. Molecular mechanics can be used to study small molecules as well as large biological systems or material assemblies with many thousands to millions of atoms.

2.2 Statistical Mechanics models: Molecular Dynamics (MD)

The first important aspect of atomistic models concerns the descriptions of the forces between the atoms. The second important aspect of atomistic model is what equations can be used to obtain the macroscopic proprieties that are then compared with experiments. The equations used in Molecular Dynamics to obtain macroscopic properties are the Newton equations of motion for all atoms in the system. Molecular Dynamics consists in simulating molecular trajectories by integrating the equations of motion. The time evolution of the simulation is broken down in small time steps. Using a numerical integration scheme, the dynamics of each atom in the system under the effect of the interatomic forces is calculated for each time step. The length of the time step chosen is a compromise between a value large enough to allow a reasonably long simulation time for the purpose of the study and a value small enough to capture all the required fundamental frequencies of motion in the system and conserve the energy between integrations steps. Typically this is in the range of 1-10 fs, but depends on the range of motions allowed in the system. Multiple time scale calculations, where rapidly changing forces are updated more frequently than slowly changing forces, are also possible in order to reduce the required computational time.

Large systems which are repetitive at a certain scale can be simulated using periodic boundary conditions. In these, forces are calculated only for atoms contained in a unit cell and then replicated across 1, 2 or 3 dimensions to simulate the effect of particles entering and leaving the unit cell. The size of the unit cell needs to be large enough so that each particle does not feel the influence of its mirror image in one of the replicated cells.

Temperature and pressure can be controlled using numerical methods that simulate the effect of a thermostat or barostat or using stochastic methods like Langevin dynamics that add friction and random forces to account for molecular collisions.

The main advantage of molecular dynamics with respect to some other molecular simulation methods is that not only does it allow obtaining macroscopic properties (e.g. temperature, pressure, work, heat, free energy, and entropy) that can be compared with experiment, but also the trajectory of the system during the simulation from which dynamical and structural quantities can be obtained.

Simulations with molecular dynamics can reproduce conditions in real life experiments and even experiments that are not possible, safe or wise to perform.

2.2.1 Classical Molecular Dynamics

Molecular Dynamics (MD) calculations performed using force fields and integrating the classical Newton's equations of motions for atoms are called classical MD. Several software packages are available (see <u>Annex II</u>) and several implement their own force field. If the force fields parameters are derived from experimental data, classical Molecular Dynamics is often called empirical Molecular Dynamics.

Classical molecular dynamics has been used for the calculation of the trajectories of guest molecules within the metal-organic frameworks and then the calculation of the guest diffusivity by means of the Einstein mean squared displacment plots (AMCOS). Molecular Dynamics (Garofalini force field) has been used to model cement hydration (CODICE). Classical molecular dynamics has been used to model morphological properties of solar cells, light emitting diodes, transistors, batteries and ultra capacitors. They are used to generate the Si/Ag and Si/Ni interfaces accounting for strain and misfit dislocations to investigate influence of N content and gradients on the trap density at the interface (<u>HIPERSOL</u>). Classical molecular dynamics has also been used to calculate the interface dipole at organic/organic interface (<u>MINOTOR</u>), to predict the bulk organization and simulate realistic interfaces between the insulating layer and the organic semiconductor at the nanometre scale (<u>ONE-P</u>). Classical molecular dynamics has been used to calculate physical properties of nanostructured materials (<u>MONAMI</u>), to calculate dynamic charge transfer in nanoelectronics devices (<u>MORDRED</u>) and to calculate properties of branched polymers as host matrices for Li-ion battery solide polymer electrolytes (<u>SUPERLION</u>).

Classical molecular dynamics has been extensively used to study interface problems in matrices, composites, coatings, cracks and defects structures. In particular, it has been used to simulate deposition of atoms and formation of lattice structures of coatings and layer interfaces in thermodynamic process in multi-layered films as input for micromechanical models (M3-2S) to calculate the selectivity and transport properties of different materials for industrial separation processes in different mixtures and state (MACADEMIA) to determine average confirmation, chain stiffness, degree of counterion condensation of polyelectrolyte chains, formation of surfactant polyelectrolyte complexes and adsorption of single electrolyte chains, formation of polyelectrolyte layer (MUST), to study large scale defect structures in the ceramics such as dislocation and incoherent grain boundaries (ROLICER), to calculate strength of hydrogen bonding and dispersion interactions and adsorption of water or carbohydrate in cellulose surfaces (SURFUNCELL). In surface engineering of reinforced and nanostructured composite and polymers, classical molecular dynamics has been used to simulate the effect of functionalization of the mechanical properties of the CNT and calculate the stress strain slope as well as the interfacial interactions between CNTs and polymeric matrices (<u>POCO</u>), to extract local traction and crack opening displacement data and calculate densities, glass transition temperature, volumetric coefficient of thermal expansion and isotropic mechanical properties to validate the simulation of the polymer network formation in the epoxy resin (<u>NANOINTERFACE</u>). In hydrogen storage and fuel cells development, it has been used to simulate adsorption in proton exchange membranes (HYPOMAP). Large scale molecular dynamics will be used to study the crystallization dynamics and thermal properties of several phase change compounds amorphous phase in the bulk and in nanowires, by using empirical interatomic potentials (SYNAPSE).

2.2.2 Ab initio molecular dynamics

With the progress of computational speed and memory, it is possible to perform calculations of Molecular Dynamics which take into consideration explicitly the effect of the electrons in the calculation of the forces (ab initio MD). Although still limited to smaller systems and shorter periods of time than classical MD, a significant advantage of using ab-initio methods is the ability to study, without empirical parameters, reactions that involve breaking or formation of covalent bonds, tunneling and proton transport mechanisms.

The main challenge consists in calculating efficiently and accurately the forces acting on the nuclei due to the electrons. Since many electrons are in the system their potential energy is represented by a multidimensional surface for each nuclei configuration. Assuming that it is possible to decouple the motion of the electrons from the motion of the nuclei (Born-Oppenheimer approximation), the classical equations of motion for the nuclei are integrated using the sum of the interatomic potential and the forces derived from the electron potential energy surface. At each time step, the ground-state electronic potential surface can be calculated using standard quantum mechanical methods (Born-Oppenheimer Molecular Dynamics) or introducing fictitious dynamics for the electrons which follow adiabatically the nuclei and are subjected to small readjustments "on the fly" during the nuclei evolution to keep them close to the ground state potential surface **(**Car-Parrinello Molecular Dynamics).

Car–Parrinello and Born–Oppenheimer first principle Molecular Dynamics simulations were conducted for the calculation of the charge distribution in metal-organic frameworks (<u>AMCOS</u>). Ab initio MD has been used to model mechanical, magnetic and electrical properties of graphene (<u>GRENADA</u>), to calculate pressure induced metallisation of potential high pressure superconductors (<u>LEMSUPER</u>), to calculate ab initio surface and interface energies in metal alloys and electric active materials (<u>MINTWELD</u>), and to calculate magnetic properties, solvatochromism, non-linear optical properties, like hyper-polarisability and two-photon absorption of large solvated systems including more than 10,000 atoms (<u>MONAMI</u>).

Defect diffusion will be studied without an external field either using classical force fields or fully abinitio Car-Parrinello methods (<u>IFOX</u>).

Car-Parrinello-like molecular dynamics simulations based on density functional theory will be performed to model the atomistic structure of the amorphous and crystalline phases of chalcogenide alloys (<u>SYNAPSE</u>).

2.2.3 Quantum mechanics/molecular mechanics (QM/MM)

For systems in which full consideration of electrons is not feasible, it may still be possible to perform calculations that retain some quantum mechanical details. Quantum Mechanical/Molecular Mechanics methods (QM/MM) consist in finding a working subdivision of the system into a part that needs to be calculated at quantum mechanical level and a (larger) part that can be calculated using classical force fields. They are used to model atoms for energy optimization calculations, calculation of reaction paths and other explorations of the potential energy landscape, and molecular dynamics simulations. For example, a QM/MM scheme can be used to calculate the reactions occurring between a drug and the target protein binding site atoms, while the rest of the protein is simulated with classical molecular dynamics. The challenge is to define the forces at the interface between the region treated with QM and the region treated with MM.

QM/MM has been used to calculate the adhesion of proteins at the interface between a glassy SiO2 phase and a water solution, relevant to pharmaceutical applications and the cohesion between a glassy SiO2 phase and crystalline TiO2 phases, relevant to thin-layer-based conditioning of glass materials for applications in architectural glass and photovoltaic cells (<u>ADGLASS</u>). ONIOM-like scheme (DFT/MM) have been used to simulate the formation energy of inclusion complexes in layered magnesium oxides, relevant for the synthesis of quasi-solid electrolytes to be used in solar cells and binding energy of the different crystallographic phases to organic passivants (<u>INNOVASOL</u>).

DFT/MM gives reaction paths and relative energies of stationary points on the reaction paths for large systems of metal organic frameworks (<u>MACADEMIA</u>) and in organic-based electronic devices (<u>MINOTOR</u>).

2.3. Statistical Mechanics models: Monte Carlo molecular models

In the mathematical framework of statistical mechanics, it is not necessary to follow the dynamics of the systems to calculate macroscopic observables. These are in fact derived from an accurate sampling of all equivalent microscopic configurations of the system.

Monte Carlo (MC) molecular simulations first require a model of the potential energy of the system, like in Molecular Dynamics. The Monte Carlo technique is then used for sampling all possible configurations of the

system. This technique consists in generating configurations of the system The new configuration is then accepted or rejected on the basis of the energy change that the results for the move, in general. Although Monte Carlo is a well-known technique used for sampling in a variety of different fields in the context of molecular simulations, the fact that it does not describe the dynamics of a system influences the physics and chemistry that can be included in the simulation and leads to definitions of the energy potential that would not be possible in Molecular Dynamics.

Statistical thermodynamics equations are subsequently used to derive the macroscopic observables (e.g. temperature, pressure, work, heat, free energy, and entropy) from the positions of the atoms in all configurations sampled, even if each subsequent configurations are not connected with each other in time.

With MC technique the sampling efficiency can be increased, which is particularly important where the potential surface contains many local minima (as in close to state transitions, in large proteins etc). Note also that the random sampling of Monte Carlo based methods fulfills the ergodic condition intrinsically.

The success of this technique in statistical mechanics has led to various generalisations, such as the method of simulated annealing for energy optimisation of a system, in which a fictitious high temperature is introduced to obtain a fully random sample and then gradually lowered to obtain a configuration close to the ground state. Hybrid Monte Carlo methods introduce an acceptance criterion into molecular dynamics simulations, allowing the use of large time steps. <u>Kinetic Monte Carlo</u> methods apply the same statistical principles to simulate the time evolution of the processes under consideration. Typically these are processes that occur with a given known rate and the rates with which these processes evolve are inputs to the KMC algorithm, the method itself cannot predict them.

Monte Carlo based methods have been used to predict the CO2 sorption isotherms in the investigated materials: zeolitic imidazolate frameworks, hyperbranched aminosilicas, and functionalised polymers (AMCOS), to study the aggregation of C-S-H particles growth of microstructure using macroscale parameters (CODICE), to calculate diffusivities of charge carriers and band structure for up to 10000 atoms (*HIPERSOL*), to describe adsorption phenomena when specific interactions occur that can't be treated using generic force field (MACADEMIA), to calculate charge carrier propagation and density in the doped layer (MINOTOR), to calculate statistical variability of electrical impact of defects (<u>MORDRED</u>). Atomistic Monte Carlo simulations have also been used to determine adsorption sites of Phase Change Materials (PCMs) molecules inside the pigment at different pressures and temperatures and to calculate interactions energies between nanoparticles/pigment surfaces, in order to select the more suitable conditions for adsorption, predict the kind of molecules that can be adsorbed (type of functional groups and sizes of the molecules) and preferred adsorption sites (NANOPIGMY). Kinetic Monte Carlo models have been used to calculate charge propagation and charge carrier mobility, to quantify the impact of different dielectrics on the charge carrier mobility and the exciton diffusion length (<u>ONE-P</u>); and to follow the evolution of individual defects in order to calculate irreversible processes at atomic scale under irradiation conditions (RADINTERFACES).

Monte Carlo method was also used to solve the Boltzmann transport equation for the description of gas flow and plasma to calculate particle motion, interaction between phases, and transport proprieties in oxide based electronic materials (<u>ORAMA</u>).

2.4. Atomistic spin models

Spin models are used to describe magnetic material properties. A spin here normally represents the magnetic moment of an atom, the energy of which is typically parameterized within a Heisenberg formalism, though even relativistic interactions, like Dzyaloshinskii-Moriyam interactions or anisotropies can be taken into account. The fact that magnetic structures are described on an atomic level allows for an investigation of ferromagnets as well as ferrimagnets and antiferromagnets or even heterostructures composed of different materials.

In the classical limit the equation of motion is the Landau-Lifshitz-Gilbert (LLG) equation. The LLG equation describes the spin precession that follows from Heisenberg's equation of motion and its relaxation into an equilibrium direction via a damping term (either after Landau and Lifshitz or after Gilbert) with a corresponding damping parameter. Though the LLG equation is partly phenomenological this approach turns out to be very successful.

<u>FEMTOSPIN</u> developed a model which currently can treat up to 10⁸ spins for 2-D structures corresponding to up to 1000 nm length scale, and up to some nano seconds time scale. This model has been used to calculate dissipation channels and energy transfer in order to identify optimal materials for ultrafast optically induced magnetic switching and the relevance of the specific spin ordering in ferro-, ferri-, antiferro-magnetic and magnetic semiconductors.

2.5 Statistical Mechanics for atomistic systems

Statistical mechanics (see introduction of Chapter 2) provides a framework for relating the properties of individual atoms and molecules to the continuum properties of materials that can be observed in everyday life. In physics, specifically non-equilibrium statistical mechanics, the Boltzmann equation (or Boltzmann transport equation) describes the statistical behaviour of a fluid not in thermodynamic equilibrium, i.e. when there are temperature gradients in space causing heat to flow from hotter regions to colder ones, by the random (and biased) transport of particles. The equation expresses the probability that a number of particles all occupy a very small region of space centered at the tip of the position vector, and have very nearly equal small changes in momenta from a momentum vector, at an instant of time. The set of all possible positions and momenta is called the phase space of the system. In the equation there is a collision term. It is a statistical term representing the particle collisions, and requires knowledge of the statistics the particles obey, like the Maxwell-Boltzmann, Fermi-Dirac or Bose-Einstein distributions.

The probabilistic Boltzmann equation can be used to derive the fluid dynamic conservation laws for mass, charge, momentum and energy. In Chapter <u>4</u> the continuum equivalent (Navier–Stokes, Nernst-Planck and there approximations diffusion, diffusion and convection (advection) equations for scalar tansport will be discussed.

The Langevin equation describes advection, diffusion, and other phenomena in an explicitly stochastic way. One of the simplest forms of the Langevin equation is when its "noise term" is Gaussian; in this case, the Langevin equation is exactly equivalent to the convection–diffusion equation. Its use at atomistic level will be discussed in Chapter 2.5.
2.5.1 Langevin Dynamic method for magnetic spin systems

The Landau-Lifshitz-Gilbert equation is an equation used to solve time-dependent micromagnetic problems. When augmented by a stochastic term describing thermal fluctuations as random fields, the LLG equation is converted into the Langevin equation of the problem. Langevin Dynamics (LD) is the principal method for dynamic models of atomistic and mesoscopic spin systems at non-zero temperature. It allows for the calculation of thermal equilibrium and non-equilibrium properties of magnetic systems where the heatbath can be described by phononic or electronic degrees of freedom. With that approach equilibrium properties like magnetic phase transitions can be described and investigated as well as ultra fast phenomena like optically induced switching events. The properties of the random field are determined via the fluctuation-dissipation theorem. Following this approach the random field values are determined by a correlator dependent on the damping constant representing the coupling of the spin system to the heat bath, and also the magnitude of the spin. LD is used on two lengthscales. It was first introduced to model temperature dependent properties in the mesoscopic formalism (micromagnetics see Chapter 3.3) and later to atomistic spin models. In using LD it is necessary to ensure that the time integration follows Stratonovich calculus, which is generally achieved using the Heun integration scheme, although normalization of the spin after each timestep fulfills this basic requirement.

LD calculations at atomistic scale were used in <u>ULTRAMAGNETRON</u> to study ultrafast spin dynamic processes driven by femtosecond lasers, particularly foscussing on the opt-magnetic reversal phenomenon. The simulations demonstrated an entirely new (linear) reversal mode which is governed by the longitudinal relaxation time and which gives rise to the ultrafast reversal. It was also shown that heating with an ultrafast laser pulse was a sufficient stimulus for magnetisation switching. <u>FEMTOSPIN</u> is further developing these ideas and strengthening the link between abinitio and atomistic simulations with calculations of the opto-magnetic field and ab-initio simulation of the intrinsic magnetic properties and studies of the energy transfer channels linking the spin system to the heat bath.

2.5.2 Semi-classical non-equilibrium spin transport model

Irradiation of a ferromagnetic metal layer with a femtosecond laser pulse causes a sudden demagnetization within a few hundred femtoseconds. The non-equilibrium spin transport model describes the laser-induced non-equilibrium transport occurring on the nanoscale using statistical principles. It treats explicitly the laser-created distribution of highly energetic, spin-polarized electrons, which immediately start to move randomly through the material (typical velocities of several nm/fs). These hot non-equilibrium electrons undergo random scattering with other electrons or with phonons and thereby they loose energy, i.e., the process of electron thermalization

<u>FEMTOSPIN</u> developed this non-equilibrium spin transport model to uncover the underlying physical mechanism of ultrafast laser-induced demagnetization. Computational modelling is needed to unravel the various possible contributions to the demagnetization processes.

Solving numerically the derived transport equation, using spin-lifetimes taken from ab-initio calculations, revealed that laser-excited hot electron transport occurs neither in the diffusive nor ballistic regime, it is superdiffusive. Moreover, as spin-majority and minority electrons have distinct lifetimes, fast spin-dynamics on the femtosecond time scale is generated. <u>FEMTOSPIN</u> is using the

non-equilibrium spin transport model to simulate the laser-induced hot electron transport on the femtosecond time-scale, treating magnetic layered heterostructures with a total layer thickness of about 100 nm.

2.5.3 Statistical transport model at atomistic level

The same statistical methodology that can be used to simulate electronic transport (Chapter<u>1.4</u>) can be adapted to simulate transport of molecules (transport at atomistic level). This can again be used for diffusion or percolation phenomena.

In <u>CODICE</u>, a statistical growth model is used to simulate aggregation of C-S-H particle.

<u>HYMEC</u> used a statistical mechanics model for percolation of nanoparticles based on random walk over a network of nodes to simulate creation, transport and recombination of charges (including charging and de-charging of metal nanoparticle). Each node represents a metal nanoparticle NP and so a possible site for charges and it is connected to a certain number of other nodes. The problem is solved using a Monte Carlo method and solving a Pauli Master Equation.

In <u>IMS & CPS</u>, ion transport is simulated with percolations models, which emphasize the importance of the interfacial interactions at the boundary between the individual filler particles and the polymeric host for the network formation.

In <u>NAMASTE</u> modelling of the transport anisotropies in tunnelling or ohmic regime employed the Boltzmann or Kubo transport theories for uniform systems, whereas Landauer-Buttiker and Green's function formalisms were employed for spatially non-uniform nanogeometries and non-equilibrium conditions.

Chapter 3 Mesoscopic models

Mesoscopic models describe the behaviour of entities like nanoparticles, grains, agglomerates, large biomolecules or macrospins. The models are applied to 10⁶ up to unlimited number of atoms, length scales of 100nm-mm and timescales of ms-s. Molecular models belong to this class, if they group more than one atom together in an entity, whose behaviour is described by an equation (model) in order to allow simulation of larger systems and for longer times, although in so doing the models loose some of the atomistic details. Also micro-magnetics is classified in this group as it describes a group of coupled spins as one macrospin. Even if the physics of many models may be similar to the ones already discussed and doesn't need to be repeated here, some implications and unique aspects of meso-scopic models will be highlighted in this Chapter.

Mesoscopic and mesoscale

Mesoscopic models are categorised into one class based on the type of entity they describe. This is not necessarily directly related to the size of the application domain the model can simulate. When the application domain is of nm size, we say that the model is applied to the meso-scale. We strictly classify models according to the entity described, not according to the size of the application and thus warn the reader for the different way in which words can be used.

Note that in micromechanics and in materials engineering in general the term "mesoscale modelling" is used for a continuum model applied to an application domain of nm-mm lengthscale. We want to stress that this use of the word relates to the size of the application domain, while the model remains continuum.

The first two models are deterministic (Coarse Grained Molecular Dynamics Ch 3.1 and Discrete lattice Dynamics (Ch 3.2) while the third model is based on Statistical Mechanics (Ch 3.3). All these models describe the forces between the mesoscopic entities and calculate the position and velocity of the entities. The macroscopic bulk observable properties of materials are given by conformational sampling relating the calculated positions and velocities with pressure, temperature, density and free energies. The fourth model (Ch 3.4) is a phase field modeling microstructures.

The fifth model (Ch 3.5) is describing magnetism.



Fig.3.1 Number of projects that used one of the five main types of mesoscopic models treated here.

3.1. Coarse-grained Molecular Dynamics

Coarse-grained Molecular Dynamics is a particular kind of classical (deterministic) molecular dynamics where the entity whose behaviour is described is a group of atoms forming a large single unit, also called pseudo-atom (the entity). The behaviour is decribed by a particular force field (the model). The simplest form of coarse-graining is the "united atom" (sometimes called "extended atom") and was used in most early MD simulations of proteins, lipids and nucleic acids. For example, instead of treating all four atoms of a CH₃ methyl group explicitly (or all three atoms of CH₂ methylene group), one represents the whole group with a single pseudo-atom. This pseudo-atom must, of course, be properly parameterized so that its van der Waals interactions with other groups have the proper distance-dependence. Similar considerations apply to the bonds, angles, and torsions in which the pseudo-atom participates. In this kind of united atom representation, one typically eliminates all explicit hydrogen atoms except those that have the capability to participate in hydrogen bonds ("polar hydrogens"). This approximation can provide substantial savings in computer time as coarse-grained models can provide a simpler representation of nucleotides and acids which are large molecular units for the simulation of larger systems: DNA/RNA strands, long chain polymer, membrane lipids and proteins.

The modelling challenge is in the calculation of the forces, in the determination of the pseudo-atoms charge distribution and in the parametrisation of these coarser-grained potentials.

Coarse grained MD models are used to describe the competition between cohesive and adhesive failure and cross-linked models of epoxy networks (<u>NANOINTERFACE</u>) and to study the structure and dynamics of silica-polystyrene nanocomposite systems (<u>NANOMODEL</u>). Coarse-grained MD models have also been used to calculate the flow of latex particles to obtain semi-quantitative predictions of linear and non-linear rheology (<u>MODIFY</u>) and the formation of layers of nanoparticles on cellulose surfaces (<u>SURFUNCELL</u>).

3.2 Discrete lattice dynamics model

The discrete lattice dynamics model describes the (deterministic) behaviour of discrete units like bars or trusses (the entity). The behaviour of the bar is described by an inter-entity potential (the model). The simulation is then done with an "atomic" finite element method, where the units like bars, or trusses, function just like the elements in a standard finite element analysis. This enables an atomic lattice to be modelled by an assemblage of units that deform according to a prescribed interatomic potential, which governs their relative separations under applied loading. A key feature of the atomic finite element method is that it results in a finite element equation with displacement degrees of freedom. An atomic finite element mesh can be directly coupled to other element types and to find element models at larger scales. Note that this resembles the Finite Element approach in micromechanics, but there the elements describe a continuum.

The discrete lattice dynamics model has been used to calculate breaking of atomic bonds between the discrete elements for the prediction of dislocation generation, crack nucleation and growth in coating materials (<u>M3-2S</u>).

3.3. Statistical Mechanics mesoscopic models

Statistical Mechanics models based the theory discussed before (see Chapter <u>1.4</u> <u>2.3</u>, and <u>2.5</u>) can also be used to describe entities like nanoparticles and grains. It describes the motions of the entities as stochastic (not deterministic) and this can be used to describe diffusion and percolation at the mesoscale and using conformational sampling also thermodynamic properties are derived.

In <u>CODICE</u> a mesoscopic statistical model is used to simulate grain based flow in cement and together with an agglomeration description this gives the growth of the cement. <u>MONAMI</u> used mesoscopic coarse-grained models with effective soft potentials with stochastic terms to simulate essential motions.

A kinetic mesoscopic Monte Carlo model has been used to evaluate effective H diffusivities under different strain conditions and trap densities and temperature (<u>MULTIHY</u>).

Monte Carlo models describing the behaviour of mesoscopic entities have been used to calculate thermodynamic properties such as the Curie temperature, and non-equilibrium properties such as kinetic growth in oxide heterostructures, on the mesoscale (IFOX).

Exploiting the polymer mean field approximation, Monte Carlo based particle simulations were performed on micrometer-sized domains of the nanocomposite system, wherein the nanofillers are represented as solid spheres (interacting via Hamaker integrated potentials) and the polymer chains as freely jointed sequences of Kuhn segments (<u>NANOMODEL</u>).

3.3.1 Lattice gas automata

Lattice gas automata (LGA) or lattice gas cellular automata (LGCA) models are Statistical Mechanics models used to simulate diffusion. It was the precursor to the lattice Boltzmann models. From the LGCA, it is possible to derive the macroscopic Navier-Stokes equations (Chapter <u>4.2)</u>. These Eularian models comprise of a lattice, where the sites on the lattice can take a certain number of different states. The various states are 'particles' with certain velocities (entities). Evolution of the simulation is done in discrete time steps. After each time step, the state at a given site can be determined by the state of the site itself and neighboring sites, before the time step. The state at each site is purely Boolean. At a given site, there either is or is not a particle that is moving up. At each time step, two processes are carried out, propagation and collision (model). In the propagation step, each particle will move to a neighboring site determined by the velocity that particle had. Barring any collisions, a particle with an upwards velocity will after the time step maintain that velocity, but be moved to the neighboring site above the original site. The so-called exclusion principle prevents two or more particles from travelling on the same link in the same direction. In the collision step, collision rules are used to determine what happens if multiple particles reach the same site. These collision rules are required to maintain mass conservation, and conserve the total momentum; the block cellular automaton model can be used to achieve these conservation laws. Note that the exclusion principle does not prevent two particles from travelling on the same link in opposite directions. When this happens, the two particles pass each other without colliding.

Macroscopic quantities like the density at a site can be found by counting the number of particles at each site. If the particles are multiplied with the unit velocity before being summed, one can obtain the momentum at the site. However, calculating density, momentum, and velocity for individual sites is subject

to a large amount of noise, and in practice, one would average over a larger region to obtain more reasonable results. Ensemble averaging is often used to reduce the statistical noise further.

Kinetic Monte Carlo and lattice gas automata have been used to calculate diffusive transport and sorption of carbon dioxide (<u>AMCOS</u>). Lattice gas models have also been used to simulate the release of the healing agent from micro-containers and its propagation during self-healing action (<u>MUST</u>) and to calculate charge and mass transfer (<u>SUPERLION</u>).

3.3.2 Dissipative Particle Dynamics (DPD)

Another Statistical Mechanics model is Dissipative Particle Dynamics (DPD. It is a stochastic Lagrangian technique describing a set of beads (entity) moving in continuous space and discrete time. In the DPD model, a bead may represent many atoms, whole molecules or even fluid regions. The forces between the beads consists of simplified pairwise dissipative and random forces, so as to conserve momentum locally and ensure correct hydrodynamic behaviour (model). The model is used to simulate the dynamic and rheological properties of fluids at the mesoscale.

DPD was used (in addition to the lattice gas model) to simulate the propagation of inhibitor/healing agent upon the mechanical impact during formation of mechanical defects (<u>MUST</u>); DPD was used to generate cross-linked epoxy structure by simulating the dynamics of beads representing the repeating unit of the epoxy (<u>NANOINTERFACE</u>) and to study the structure and dynamics of silica-polystyrene nanocomposite systems where each "superatom" or bead represented a monomeric unit or a meso or racemo diad of styrene monomers (<u>NANOMODEL</u>).

3.4 Discrete Phase field models

Phase field models are a recent approach to address discrete phenomena (mesoscopic modelling) at small scales, like the description of individual particles moving in a continuum (gas/liquid) and microstructure formation. Phase field models are constructed to predict the microstructure formation in time and space. Note that <u>thermodynamics</u> does NOT comprise any information about structures as thermodynamics do not comprise time/length scales.

The properties of materials follow from their crystal structures on an atomic (or Å) length scale and from their microstructure (i.e. "the arrangement of phases and defects") on the nm-cm length scale. In a microstructure interfaces appear between phases. Phenomena related to the microstructure can be modeled by mesoscopic models describing the behaviour of e.g. grains. The equilibrium nature of microstructures can be interpreted by considering the phase diagram, which itself can be predicted by computational thermodynamics.

Phase Field models describe the state of the entire microstructure by representing structural and/or chemical spatial homogenous assemblies (mesoassemblies), such as domains or grains, with constant phase field(s) or order parameter(s) while allowing diffuse interface across thin boundary layer between the mesoassemblies by continuously interpolating its bulk values of order parameter(s).

Phase field models derive the potential "driving force" usually from the difference in Gibbs energy across the interface. The dynamics of one or more order parameter (s), that is the evolution of the microstructure with time, are governed by set of non-linear partial differential equations (i.e. Cahn-Hilliard, timedependent Ginzburg-Landau, and other Newtonian based dynamics) through a minimization of phenomenological free energy functional (or potential or driving force). This functional (potential) is expressingthe influence of the Gibbs free energy (where thermodynamics plays its role), interfacial energy, elastic energy and other contributions executed by external fields including electrical, magnetic and applied stress fields, etc). In order to do so, the free energy functional is written in terms of the order parameters including composition and other fields (temperature, pressure, strain, electrical, magnetic, etc).

Microstructure formation in time and space during phase transitions can be calculated with these models if complemented by a diffusion equation.

Phase Field models were originally developed to predict fundamental properties of extended defects, such as interface and critical nucleus, and the associated energy and nucleation and migration, whose chemical and structural inhomogeneity occurs at length scale usually between 1 and 100 nm. The coarse-grained phase field, subsequently developed to describe collective behaviors of "large" mesoscale assemblies, covers length scales up to mm for the heterogeneity during dendritic solidification, grain growth, domain coarsening and coalescence, and various phase transformations events.

Note that Mesoscale refers to a scale "in between" the nanoscale and the microscale, typically distances of 10–100 nanometres, however can go up to mm in coarse-grained models, where the quantum physics meets the classical physics, or where systems are on the boundary between interacting and isolated systems

<u>HIPERSOL</u> does phase field modelling of Ag, combined with diffusion and firing described with COMSOL to calculate the dissolution and transport of Ag.

<u>MINTWELD</u> is using phase field models (nm and μ m scale) to describe grain boundary and interface chemistry and structure.

3.5. Micromagnetic models

The underlying assumption in micromagnetics is that the spins at electronic and atomic level are coupled to one "macro-spin" (entity). The interactions between the macrospins are described by several competing energy terms (model). Exchange interaction (responsible for the very existence of ferro- and antiferromagnetic materials) 'attempts' to align adjacent magnetic moments (in ferromagnetic materials) or antiparallel (in antiferromagnetic materials). Magnetodipolar contribution accounts for the energy of a magnetic moment in the (dipolar) field created by all other moments of a magnetic body. Anisotropy energy is mainly due to the spin-orbit interaction and the anisotropy of the crystal lattice: it is low when the magnetic moments are aligned along a particular crystallographic direction. Zeeman energy describes the interaction between magnetic moments and external magnetic field and is at its lowest when the moments lie parallel to this external field. The competition of these interactions under different conditions is responsible for the overall behavior of a magnet.

Since the equilibrium arrangement of magnetic moments ("magnetisation configuration") is usually (but not always!)the one in which the total magnetic energy is lowest, the sum of these four energy terms will 'attempt' to become as small as possible (with some energy terms decreasing at the expense of the others), yielding complex physical interactions.

A form of the Landau-Lifshitz-Gilbert equation is used to solve time-dependent micromagnetic problems. An essential merit of the micromagnetic theory concerns the answer to the question, how the effective magnetic field depends on the relevant interactions, namely, (i), on the exchange interaction; (ii), on the socalled anisotropy interaction; (iii), on the magnetic dipole-dipole interaction creating the internal field; and, (iv), on the external field (the so-called "Zeeman field").

Usually the exchange interaction and the magnetic dipole-dipole interaction term play the dominating role, usually a *competing* one. In particular: due to the last term the effective field is a *nonlocal* function of the magnetisation, i.e. although the Landau-Lifshitz-Gilbert equation looks relatively harmless, one is actually dealing with a complicated nonlinear set of integro-differential equations.

The necessary material constants can either come from measurements or from electron-spin and atomistic ab-initio models (10⁻¹⁰m). These electronic models can e.g. give the lattice distortions near interfaces and compute the anisotropy as function of lattice constant. They also give the reversal curves.

The micromagnetic models are used to describe the magnetics at the nanoscale in domains (which have an magnitude of the order of 10⁻⁶m) nucleation of domains, pinning and expansion behavior of magnetic domains and wall motion. Input to the model can be grain size, shape, boundary type and boundary phases. Outcome will be the macroscopic properties coorcivity, remanence, max energy product and thermal stability (thermal dependance of coercivity).

<u>**DYNAMAG</u>** is using micromagnetics models OOMF and NMAG for spin dynamics including spin transfer and anti-ferromagnetic and ferromagnetic sub-lattices interactions.</u>

<u>FEMTOSPIN</u> is using micromagnetics model called 'Madrid/Konstanz code' to predict the behaviour of ferrimagnetic and anti-ferromagnetic materials and magnetic semiconductors for heat assisted recording.

<u>MAGNONICS</u> uses several micromagnetic codes (finite-difference codes MicroMagus and OOMMF and a finite-element package Nmag) to compute magnetization reversal processes and pico- and nanosecond magnetization dynamics in structured arrays of magnetic nanoelements.

<u>MASTER</u> is using a micromagnetics model based on the Landau-Lifshitz-Gilbert equation called SPINPM to predict magnetisation dynamics in an array of hetero-structures.

<u>NAMASTE</u> is using an in-house micromagnetics code to calculate magnetisation, relativistic magneto-crystalline anisotropy constants, gilbert damping coefficients and magneto-resistance coefficients of metals and magneto-transport properties of ferromagnetic semiconductor nanostructures.

<u>NANOPYME</u> is using a micromagnetic model to evaluate which magnetisation processes take place in thin polycrystalline magnetic films, which structural and magnetic parameters (characteristics) determine the hysteretic behaviour of such materials and to study how the exchange coupling through the interphase boundary affects magnetisation processes. <u>ROMEO</u> is using micromagnetic to compute the influence of the local change of intrinsic magnetic properties near grain-boundaries in grain-boundary engineered magnets. They will compute the minimum required thickness of the layer that contains heavy-rare-earths. Using numerical optimisation techniques combined with micromagnetic simulations. They will apply the non-zero temperature micromagnetics based on the elastic band method.

<u>REFREEPERMAG</u> is using micromagnetics dynamic models based on Landau-Lifshitz-Glibert equation called FEMME and MAGPAR to calculate the shape anisotropy and hysteresis properties of meso-scopic magnetic structures including coercive field and switching times. Also the thermal stability depending on geometry and the size of the magnetic volumes is calculated.

<u>SSEEC</u> is using a micromagnetics model to provide the exchange coupling at nano-scale between "particles" in a composite (meta-) material.

<u>ULTRAMAGNETRON</u> has used a micromagnetics code based on the LLBloch equation at nm scale taking the exchange coupling as well as the dipolar interaction into account to calculate magnetisation at elevated temperatures and the dynamics of ferrimagnetic materials.

Chapter 4 Continuum modelling of materials

Parts of this text have been taken from Wikipedia

This chapter is concerned with the designing of materials with desired continuum scale properties. Modeling for materials design is about investigation of relations between chemical composition, microstructure and effective properties.

Materials, such as solids, liquids and gases, are composed of molecules separated by empty space. Physical and chemical processes at the smallest scale are modeled by electronic and atomistic models as addressed in Chapter <u>1</u> & <u>2</u>. However, certain physical phenomena can be modeled assuming the materials exist as a continuum, meaning the matter in the body is continuously distributed and fills the entire region of space it occupies. Many physical phenomena are multi-scale in nature and researchers must look to multi-scale methods that couple electronic, atomistic and continuum simulations. This linking will be addressed in Chapter <u>5</u>. In this Chapter continuum models describing the behaviour of continuum unit cells will be presented.

The length scale for the entity (unit cell) modelled in continuum models has two limits: the lower limit is related to the notion "continuum" and this lower limit is so big that even heterogeneous materials can be considered to vary in a continuous fashion; the upper limit is related to the requirement that the model adequately describes reality and this upper limit is thus smaller than any spatial variation in material properties. When the spatial variation length scales are not much greater than that of inter-atomic distances or when a continuum of a finer resolution is to be established statistical mechanics is used (see Chapter <u>3</u>) and modellers employ statistical volume elements and random continuum fields linking continuum mechanics to statistical mechanics. Specifically for fluids, the Knudsen number is used to assess to what extent the approximation of continuity can be made.

In continuum modeling it is possible to apply a chain of modelling that uses the same physics and chemistry equations applied to different scales. Often the modeling at a smaller scale is called "micro-modeling" and the results of these models are, after being homogenised, fed into "macro-models" in the form of new macroscopic constitutive equations (a concept that will be elaborated below).

This chapter will deal with

- 4.1 Solid Mechanics
- 4.2 Fluid Mechanics
- 4.3 Heat flow and thermo-mechanics
- 4.4 Continuum Thermodynamics
- 4.5 Chemistry reaction (kinetic) models (meso and continuum)
- 4.6 Electromagnetism (including optics, magnetics, electrical)
- 4.7 Process and device modelling

The text has been rigorously organised along the concepts

- 1. Fundamental physics and chemistry laws (conservation equations) forming the model
- 2. Material specification in constitutive equations and constraints



Fig.4.1 Number of projects that used one of the seven main types of continuum models treated here.

Chapter 4.1-4.4 covers:	<i>Continuum mechanics</i> The study of the physics of continuous materials	<i>Solid mechanics</i> The study of the physics of continuous materials with a defined rest shape.	<i>Elasticity and visco-elasticity</i> Describes materials that return to their rest shape after an applied stress.		
			<i>Plasticity</i> Describes materials that permanently deform after a sufficient applied stress.	<i>Rheology</i> The study of materials with both solid and fluid characteristics	
		Fluid mechanics The study of the physics of continuous materials which take the shape of their container.	Non-Newtonian fluids	lewtonian fluids	
			Newtonian fluids		
		<i>Continuum Thermodynamics</i> The study of energy conversion			

In Chapter <u>4.5</u> chemistry reaction (kinetic) models (meso and continuum) will be described and in Chapter <u>4.6</u> Electromagnetism (including optics, magnetics, electrical). In the last Chapter <u>4.7</u> we shortly discuss Process and Device modelling but often these rely on models already discussed.

Conservation equations

Fundamental physical laws such as the conservation of mass, the conservation of momentum, and the conservation of energy are including the physical principles that govern the mechanical response of a continuous medium. These laws allow us to write mathematical relationships of physical quantities like displacements, velocities, temperature, stresses and strains in mechanical systems. The solution to the equations represents the response of the system. The equations of motion and equilibrium e.g. are derived from the fundamental principle of conservation of linear momentum. Heat flow is derived from the energy conservation law.

Constitutive equations

Information about the particular material studied (e.g. material constants) and its response to external agents (e.g. forces or fields) is added through a constitutive relation, expressing that the material is homogeneous or inhomogeneous, isotropic or anisotropic, linear or nonlinear or thermo-elastic or that the material shows plasticity, visco-elasticity, or visco-plasticity. In more general terms the constitutive equations relate the primary field variables (like density, temperature, displacement and velocity) to secondary field variables (energy, heat and stress). The detail employed may be macroscopic or microscopic, depending upon the level necessary to the problem under scrutiny.

These relations might be derived from theory, models at finer scale, experimentally or they might be "phenomenological".

The theoretical derivation of a material's constitutive equations is a common, important, and sometimes difficult task in theoretical materials science. Here, the constitutive equations are determined by calculating how a molecule responds to the local fields. This might e.g. be the Lorentz force or lattice vibrations in crystals or bond forces. This requires finer scale models like the ones discussed in Chapter $\underline{1}$, $\underline{2}$ and $\underline{3}$.

Phenomenology goes beyond purely empirical data as it involves a certain concept. A phenomenological constitutive equation is not completely based on physical mechanisms responsible for the behaviour. As a rule, phenomenological relations take the form of a system of equations (of algebraic, differential or integral type) with a number of parameters (or functions) to be identified from experiments.

Kinematic constraints

The model equations are the conservation equations. Material information enters the system via constitutive equations and material information can also enter via constraints on the solution. Such constraints are e.g. used in simplified Molecular Dynamics and in Material Mechanics. In Material Mechanics kinematic constraints express the limits on the movement. This can be due to the properties of the material like incompressibility, but more frequently kinematic constraints reflect the requirement of internal kinematic compatibility of motion of the continuum (e.g. across boundaries between

different constituents of a heterogeneous material) or compatibility with external boundary conditions of kinematic type (e.g. including periodic boundary conditions). The latter (and more frequent internal or external) constraints are independent of the physical properties of the material and constitute a part of the formulation of a micromechanical model of the material. In Mechanics of Materials kinematic constraints are additional restrictions on the motion of a system under investigation. They are usually separate from physical properties of the material.

Geometric changes in a continuous medium (in static or dynamic equilibrium under mechanical and/or thermal forces) are expressed by the conservation laws, constitutive equations and kinematic constraints considered jointly. The solution describes how each little part of a material moves and where it will go and how large a space will be occupied in a certain place and time.

(People involved in continuum mechanics call this solution "the kinematic equations".)

Kinematic behavior as expressed in the solution is often a necessary basis for the formulation of constitutive equations for larger scale models. Also the temperature gradient can be part of this description.

Governing equations

The conservation equations together with the constitutive equations and constraints are called the governing equations.

4.1 Solid Mechanics

Solid mechanics is the branch of mechanics, that is concerned with properties and behavior of solid matter under external actions like external forces, temperature changes, applied displacements. Contact mechanics is the study of deformation and behaviour of bodies that touch each other and may undergo relative motion and contact phenomena such as friction, lubrication, wear, heat transfer. Modeling of materials behavior under service conditions is about predicting materials behavior under e.g. mechanical (static or dynamic) loading, thermo-mechanical loading, chemically aggressive environment (e.g. all types of corrosion) and combinations thereof.

In continuum modeling also a chain of modeling can be applied that uses the same physics and chemistry equations applied to different scales. When continuum mechanics is applied to the smaller (nm and μ m) scale it is called "continuum micro-mechanics" (note this name refers to the dimensions of the sample only) and the larger scale case is called "macro-mechanics".

Micromechanics

Heterogeneous materials, such as composites, solid foams, poly-crystals and human intervertebral discs, consist of clearly distinguishable constituents (or phases) that show different mechanical and physical material properties. Micromechanics of materials predict the response of the heterogeneous material on the basis of the geometries and properties of the individual phases. The results are then "homogenised" to describe the properties and behaviour of a heterogeneous material. Such properties and behaviour are often difficult to measure experimentally, and micromechanics models can avoid expensive tests that would involve a large number of permutations of constituent material combinations; fibre and particle volume fractions; fibre and particle arrangements and processing histories.

Micromechanics of materials can also evaluate the local (stress and strain) fields in the phases for given macroscopic load states, phase properties, and phase geometries. Such knowledge is especially important in understanding and describing material damage and failure.

<u>LISSEN</u> does 3D microstructural modeling of battery cells for an assessment of the role of electrode structure. The morphological parameters of cathode and anode, needed for single-cell reactive-transport models are e.g. volume fractions of the components, volume-specific surface areas and phase boundaries and these will be obtained by interpreting micromechanical models which calculate the changes in the porous electrodes (geometrical considerations of structural changes of individual pores, particles, or particle agglomerates)) during the chemical reactions.

<u>PMJOIN</u> uses a micromechanical model to predict the most appropriate micro-structured pattern geometry in the metallic part of polymer-metal joined structures, which facilitates anchorage of the melted polymer during the joining operation.

Macro-mechanics

The same continuum mechanics governing equations (conservation and constitutive equations of the same form) can be applied to larger (macro) scales and this is called "continuum macro-mechanics". The constitutive equations can either be calculated by micromechanics or experimental or phenomenological constitutive equations can be used.

Examples of micro and macro-mechanics modelling

Heterogeneous materials, such as composites, solid foams and poly-crystals have been modelled a.o. by <u>MATRANS</u>, <u>IMS & CPS</u> and <u>NANOINTERFACE</u>.

<u>CODICE</u> developed micro and macro models to predict the structural evolution of cement.

<u>DISC REGENERATION</u> is modelling the biphasic properties of soft tissues of the intervertebral disc to calculate hydrostatic stresses and deformation of the disc using poro-hyper-elastic constitutive equations.

<u>IMS & CPS</u> is modeling materials consisting of composites or fibers which move during fabrication or during in-service operations.

<u>MODIFY</u> developed a model for the response of polymer acrylics to elongational deformation fields.

<u>NPMIMETIC</u> developed a hybrid model, using the multi body system tool to predict the motion and deformation of intervertebral discs. The kinematics, stress distribution and its effects can be analysed simultaneously, allowing a more precise definition of the loading state of the different parts.

<u>PMJOIN</u> uses micromechanical modelling to model the constitutive behaviour and the nature of breaking of the joint interface of polymer-metal joined structures.

<u>SIMUGLASS</u> is modelling glass behaviour including thermal transport phenomena and large scale deformation in a thermo-moulding process to predict the index drop inside glass material.

Stress-Strain constitutive equations for solid mechanics

A material has a rest shape and its shape departs away from the rest shape due to stress (force per unit area). The amount of departure from rest shape is called deformation; the proportion of deformation to original size is called strain. The strain induces stresses in the material (and vice versa) and how they exactly do this in a particular material is expressed in the constitutive equations for solid mechanics relating the strain to the stress.

Macromechanical models will be used to calculate the mechanical stress at the interface of thermoplastics and thermoplastic based composites joint with dissimilar materials, especially metals (<u>YBRIDIO</u>).

There are four major models that describe how a solid responds to an applied stress:

 <u>Elastically</u> – If the applied stress is sufficiently low (or the imposed strain is small enough), almost all solid materials behave in such a way that the strain is directly proportional to the stress; the coefficient of the proportion is called the modulus of elasticity. This region of deformation is known as the linearly elastic region. When an applied stress is removed, the material returns to its un-deformed state, i.e. no permanent strain remains after unloading. Linearly elastic materials, those that deform proportionally to the applied load, can be described by the linear elasticity constitutive equations such as Hooke's law. When the strain becomes larger the material might react non-linearly and this is called hyper-elasticity.

<u>DISC REGENERATION</u> is using poro-hyper-elastic constitutive equations in their model for biphasic properties of soft tissues of the intervertebral disc. With this they calculate hydrostatic stresses and deformation of the disc.

<u>MATRANS</u> is using standard linear thermo-elasticity constitutive equations in their macro-scale thermo-mechanics model. Material parameters in the constitutive equations for composites are obtained from micromechanics.

<u>SIMUGLASS</u> is using elastic and viscoelastic constitutive equations in their macro-mechanics models and combined with the ideal gas equation they model glass behaviour including thermal transport phenomena and large scale deformation in a thermo-moulding process and to predict the index drop inside glass material.

<u>SMASH</u> is using linear elasticity constitutive equations in the model for strain in hetero-structures and with this they predict structure parameters for optimised LED performance.

<u>ROLICER</u> is using elastic and thermo-elastic constitutive equations in ANSYS and ABAQUS to obtain material stresses as a function of material properties and realistic working conditions.

2. <u>Viscoelastically</u> – These are materials that behave elastically, but also have damping: when the stress is applied and removed, work has to be done against the damping effects and is converted in heat within the material resulting in a hysteresis loop in the stress–strain curve. This implies that the material response is time dependent or rate sensitive. This is modeled by constitutive equations resulting from

the superposition of the elastic (spring) and viscous (dashpot) models, which can be joined in series (Maxwell solid) or in parallel (Kelvin solid) or as various combinations of spring-dashpot assemblies.

<u>NPMIMETIC</u> is using an in-house hyper-visco-elastic constitutive equation in their model for bulk material. With this they simulate the mechanical properties of the native nucleus pulposus within the intervertebral disc.

<u>ROLICER</u> is using an elasto-hydro-dynamics constitutive equation to calculate loading limits.

<u>SIMUGLASS</u> is using elastic and viscoelastic constitutive equations in their macro-mechanics models and combined with the ideal gas equation they model glass behaviour including thermal transport phenomena and large scale deformation in a thermo-moulding process and to predict the index drop inside glass material.

3. <u>Plastically</u> – Materials that behave elastically generally do so when the applied stress is less than a yield value. When the stress is greater than the yield stress, the material behaves plastically and does not return to its previous state. That is, deformation that occurs after yield is permanent. This is modeled by constitutive equations in which the total strain is decomposed into elastic and plastic part. The onset of plastic flow is characterised by a yield condition and the elastic strains are related to the stresses by Hooke's law, whereas the constitutive equation for the plastic strain increment (flow rule) is obtained from the plastic potential, often assumed the same as the yield function. The plastic potential specifies the components (to within a multiplier) and the direction of the vector of plastic strain increment (exterior normal of the flow surface) through the system of partial differential equations.

<u>NANOINTERFACE</u> is using a semi-analytical plasticity constitutive equation for Cu/polymer interfaces to establish cohesive/adhesive interfacial delamination criteria under external loading and to quantify the effect of roughness on adhesive properties.

<u>M3-25</u> is using discrete dislocation plasticity modelling to link the crystal plasticity scale and the atomic finite element scale.

<u>MATRANS</u> is using elasto-plastic constitutive equations to model residual stresses after sintering of composites and FGMs.

4. <u>Rheologically</u> - Rheology is the study of the flow of "soft solids' or solids which respond plastically rather than deforming elastically in response to an applied force (see also Chapter <u>4.2</u>). It applies to substances which have a complex molecular structure, such as muds, sludges, suspensions, polymers and other glass formers (e.g. silicates), as well as many foods and additives, bodily fluids (e.g. blood) and other biological materials. This is modeled by constitutive equations of non-Newtonian fluid mechanics or linear or nonlinear viscoelasticity and plasticity.

Here speaking of a linear elastic material, plastic material, viscoelastic material, means that their behavior under external loading follows that of the corresponding constitutive equation.

<u>GRENADA</u> is modeling the morphological structure (a.o. number of layers, defects and roughness) of graphene using a rheology code.

The above classification does not cover possible non-mechanical effects. Among them, heat conduction and temperature effects play an important role in a number of applications. The Chapter <u>4.3</u> treats briefly this issue.

Case studies: Governing equations describing behavior of solid materials

Under the action of thermo-mechanical loadings the materials may undergo such processes as fatigue, fracture, creep, wear and oxidation etc. Wear, fatigue and fracture are processes that start at a fine scale and a detailed geometry is necessary to capture these processes otherwise lost in homogenisation. These processes are thus described by a multi-scale approach.

Fatigue/damage

In materials science, fatigue is the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. If the loads are above a certain threshold, microscopic cracks will begin to form. In homogeneous materials, like metals, eventually a crack will reach a critical size, and the structure will suddenly fracture. In heterogeneous materials fatigue damage can be distributed and material can still bear load notwithstanding excessive micro-cracking.

The shape of the structure will significantly affect the fatigue life; square holes or sharp corners will lead to elevated local stresses where fatigue cracks can initiate. Round holes and smooth transitions or fillets are therefore important to increase the fatigue strength of the structure.

Fatigue is modeled with the solid mechanics equations closed by constitutive damage equations like Miner's, Paris's or Goodman's rule. This system describes how so-called damage variables change under applied stress-strain state and give the change of the load-carrying ability (for example, material stiffness) with the changing damage variables.

For multi-scale modeling at the micro- and macro-scales the same physics (physical principles) for both scales can be used. To model fatigue the energy equations are formulated to describe the energy balance with account for the stress transfer at a fine scale with different possible scenarios of damage localisation. The results are then fed into a macro-scale mechanics model.

<u>IMS & CPS</u> has developed simple in-house solid mechanics analytical & FEM models to describe damage initiation on the macro-scale. The constitutive equation is of the static linear mechanics type. This model predicts transverse damage initiation in carbon fabric/polymer composites with and without carbon nanotubes.

<u>MATRANS</u> is modelling fatigue using the elastic strain energy balance and the particle-matrix interactions. They also use damage theory to model micro-cracking due to residual stresses after sintering. The same physics is used at the micro and macro scale considering the stress transfer between the brittle particles, interphase and ductile-matrix. The constitutive equation is that of linear thermo-elasticity with damage for the ceramic reinforcement and the elasto-plastic for the metal matrix.

<u>RADINTERFACES</u> is using a new hybrid kinetic Monte Carlo-Molecular Dynamics model to describe damage accumulation and with this they generate damage constitutive equations

<u>Fracture mechanics</u> is the field of mechanics concerned with the study of the propagation of cracks in materials. In modern materials science, fracture mechanics is an important tool in improving the mechanical performance of materials and components.

Fracture mechanics is a typical multi-scale problem: the initial crack starts at a very small scale (having a very small process zone). It uses methods of solid mechanics to calculate the driving force on a crack and those of experimental solid mechanics to characterize the material's resistance to fracture. With the knowledge of the crack driving force and the crack resistance Griffith's or Irwin's criterion is then used to assess the criticality of a crack.

Macroscopically speaking, the crack propagates if the driving force is larger than the fracture toughness (i.e., Griffith's energy balance). Now, the driving force and the fracture toughness are both defined by multi-scale processes:

-the driving force is dependent on the mechanics at molecular-meso-micro-macro-scale (i.e., different dissipation mechanisms at different scales such as creation of new surfaces and micro-scale plasticity)

-the fracture toughness is dependent on the physical properties of the material(s) at molecularmeso-micro-macro-scales.

On the macro-scale, the integrity of structural members, such as beams, columns and shafts is also an important issue, which is not only addressed by strength of materials or fracture mechanics methods. The methods employed to predict the response of a structure under loading and its susceptibility to various failure modes may take into account various properties of the materials other than material yield strength and ultimate strength; for example, failure by buckling is dependent on material stiffness and thus Young's Modulus.

<u>CODICE</u> is using constitutive equations in a lattice fracture model in which the continuum is replaced by a lattice beam elements. The constitutive equations are derived from results of a atomistic and analytical micromechanical models calculating the microstructure(linear-brittle behaviour of the phases) which is mapped on the lattice beams by assigning them different properties (elastic modulus and tensile strength of porous cement), depending on where the beams lie (cement grain, inner C-S-H variety, overlapping C-S-H variety).

<u>IMS & CPS</u> has developed simple in-house solid mechanics analytical & FEM models to describe delamination propagation on the macro-scale. This model predicts transverse delamination propagation in carbon fabric/polymer composites with and without carbon nanotubes.

<u>MATRANS</u> is using finite element method to compute configurational forces. The method is capable of treating inhomogeneous (functionally graded) materials under static and dynamic loadings. The crack driving force is computed as function of the loading, the crack length and the elastic properties, which can vary in space. On micro-level a damage mechanics approach was used (i.e. in the thermo-mechnical homogenisation) while in the macro mechanical approach the focus is on fracture mechanical concepts (energy release rate). The damage mechanics approach was rather simple using a maximal principal stress criterion in the brittle ceramics, while a plastic strain criterion was used in the metallic phase. If the damage indicator reached a critical value the element was "killed" from the FEM calculation. <u>ROLICER</u> is using a solid mechanics model to describe crack nucleation based on traction separation laws. Then they use a macro-scale structural model to study crack formation, crack propagation, and fracture behaviour in ceramic materials. They also examine the fracture properties of silicon nitride. They are testing the assumption of anisotropic fracture of the βgrains with a micromechanical finite elements simulation.

<u>Creep</u>

In materials science, creep is the tendency of a solid material to move slowly or deform permanently under the influence of stresses. It occurs as a result of long term exposure to high levels of stress that are below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods, and near melting point. Creep always increases with temperature. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function. But moderate creep in concrete is sometimes welcomed because it relieves tensile stresses that might otherwise lead to cracking.

The rate of this deformation is a function of the material properties, exposure time, exposure temperature and the applied structural load. Unlike brittle fracture, creep deformation does not occur suddenly upon the application of stress. Instead, strain accumulates as a result of long-term stress. Creep is a "time-dependent" deformation. The constitutive equations for creep are those of the plastic flow (cf. above) with the concept of yield condition and associated flow rule or a creep potential function different than the yield function.

<u>DISC REGENERATION</u> is modeling the effect of creep on the relaxation of soft tissues under sustained compression simulating the standing of a person during daily activities.

Wear

In materials science, wear is erosion or sideways displacement of material from its "derivative" and original position on a solid surface performed by the action of another surface. Wear is related to interactions between surfaces and more specifically the removal and deformation of material on a surface as a result of mechanical action of the opposite surface (see also chemical diffusion under CFD in Chapter <u>4.2</u>)

Impulse wear e.g. can be described by a constitutive equations based on a synthesized average on the energy transport between two travelling solids in opposite converging contact.

The micro-scale calculations are performed to obtain the averaged activation parameter for the oxidation process. The macro-scale calculations are done to explicitly model wear and oxidation. But the time dependent parameters needed to do that are obtained from micro-scale calculation. The temperature distribution around a single asperity can reach very high values. This might be lost in homogenisation as on the macro level, the averaged temperature in the unit cell containing the asperity, can be well below the oxidation threshold. Thus micro scale calculations are needed to obtain the exact temperature distribution around the asperity. To do that standard heat conduction models can be applied with the heat flux acting on the upper surface of the conical asperity. Having this micro-scale temperature, an averaged activation factor for oxidation can be calculated, which allows the oxidation to take place for relatively low temperatures on the macro scale.

In short: on the micro-scale only heat conduction and temperature distribution need to be calculated. But on the micro-level, a completely different geometry is used, a conical asperity, whereas on the macro scale the contact zone could e.g. be flat. On the macro scale other mechanical processes can be simulated, not part of micro-level simulations.

<u>CODICE</u> has developed models for the development of wear and fracture and predicted the degradation by ammonium nitrata of porous cement structures. It is a finite element model, which solves the Nernst-Plank equations over a voxeled cementitious structure (composed of cement grains, C-S-H varieties and pore space) in which ammonium nitrate solutions flow through the porous network. The phenomenological constitutive equations for the wear model import information about the micro-structural changes which take place when the ammonium nitrate ions react with the solid phases and calcium ions are released into the solution. Upon this reaction the diffusion constants are readjusted. The model can simulate the effect of accelerated calcium leaching (an intrinsic osteoporosis-like degradation process) for cementitious structures.

<u>MATRANS</u> is modelling progressive wear. The constitutive equation is of the Archard type, i.e. wear volume is proportional to energy dissipated at the contact interface (equivalently, the wear volume is proportional to normal force and sliding distance). For the description of material deformation, heat transfer, and temperature distribution the same constitutive relation in macro and micro scale are used but calculations are performed assuming different geometries. On the micro-scale the real surface topography is considered, and Finite Element Analysis with thermomechanical coupling was used for the calculation of averaged wear-oxidation parameters. In macro scale flat surface was assumed.

<u>Corrosion (oxidation)</u> is to be included in wear phenomena, when the damage is amplified and performed by chemical reactions rather than mechanical action. The constitutive equations can be chemical, but can also be purely phenomenological without any account of the underlying chemical process. In such models the rate of change of mass of the corrosion product (oxide) is related to temperature and time based on experimentally observed relations from thermo-gravimetric analysis (TGA). Chemical properties of the oxide layer are considered through parameters in the phenomenological function approximating results of the TGA.

Other chemical reactions

<u>MATRANS</u> is using a coupled heat conduction model for oxidation and wear to predict oxide masses. On the micro-scale a conical geometry of the asperity is used, whereas on the macro-scale the contact zone is modeled as flat.

New constitutive equations for solid mechanics

Note that the conservation equations are not often subject to new modelling and it is thus rather rare that mechanical models discover new physics. However modelling does take place on the constitutive equations modelling the material properties.

<u>MODIFY</u> developed new macroscopic constitutive equations capable of describing quite reliably the deformation equations (e.g., the shear and elongational behaviour) of the synthesized PSA materials. The new equation utilizes generalized expressions for the strain energy density as a

function of the three invariants of the conformation or deformation gradient tensor. In limiting cases, it reduces to known laws widely used to describe hyper-elastic materials, such as the Rivlin-Saunders and Hart-Smith theories.

<u>MULTIHY</u> has developed macroscopic models based on novel set of constitutive equations for H diffusion capable of exploiting the information being derived from the atomistic calculations. The equations are more generalised than those commonly used in the literature, enabling the description of hydrogen diffusion under a broader range of conditions (e.g. temperature variations, trap occupancies) as before.

<u>POCO</u> developed an electro-dynamics constitutive equation relating the polarisability of the CNTs, the electric field applied and the viscosity of the polymer with the torque.

4.2 Fluid Mechanics

Fluid mechanics is the study of the motion of fluids due to forces. (Fluids include liquids, gases, and plasmas if sufficiently dense to be a continuum)

The foundational axioms of fluid dynamics are the conservation laws, specifically, conservation of mass, conservation of linear momentum (also known as Newton's Second Law of Motion), and conservation of energy (also known as First Law of Thermodynamics). These can be reworked to give the Navier–Stokes equations, named after Claude-Louis Navier and George Gabriel Stokes, which are a non-linear set of differential equations that describes the flow of a fluid whose stress depends linearly on velocity gradients and pressure. The solution to a fluid dynamics problem typically involves solving these equations calculating speed, pressure, density and temperature.

Flow of electrically conducting fluids (e.g. fluids including plasmas, liquid metals, and salt water) in electromagnetic fields need to be described by coupled Navier-Stokes equations and Maxwell's equations of electromagnetism, which need to be solved simultaneously. This part of fluid dynamics is called magneto-hydrodynamics.

<u>SIMBA</u> is doing plasma modeling for reaction chambers.

Flow models

Modelling efforts simplify the principle physical equations in a number of ways, and set of approximations will be discussed.

<u>GRENADA</u> is using computational fluid dynamics to model fluid dynamics inside the Chemical Vapour Deposition (CVD) reactor used to grow graphene.

Diffusion

The simplest model is for diffusive mass transport and this is the differential equation describing the phenomena at continuum scale.

<u>AMON_RA</u> models diffusion in semi-conductors with diffusion equation (CFD) using a non-linear Poisson equation for the electrostatic potential.

<u>ARTIVASC-3D</u> used an advection-diffusion equation for transport of nutritients and O2 (microscale)

<u>DISC_GENERATION</u> used advection-diffusion equation for transport of nutritients and O2 (microscale)

<u>LISSEN</u> models transport of mass and charge in sulfur-based battery cells.

<u>M3-25</u> modeled diffusion model to simulate plasma nitriding, plasma carburising and plasma nitrocarburising which are lading to surface modification.

<u>MULTIHY</u> models hydrogen diffusion to study microstructure and mechanical properties of materials under the effect of hydrogen embrittlement

<u>MUST</u> used a multi-phase diffusion equations for water, ions, corrosion products and inhibitor particles in a multilayer anticorrosive film

<u>SOLAR DESIGN</u> modelled carrier transport model in solar cells with electronic drift-diffusion, atomistic Monte Carlo or continuum diffusion model.

Compressible vs incompressible flow

All fluids are compressible to some extent, that is, changes in pressure or temperature will result in changes in density. However, in many situations the changes in pressure and temperature are sufficiently small that the changes in density are negligible. In this case the flow can be modeled as an incompressible flow. Otherwise the more general compressible flow equations must be used. Mathematically, incompressibility is expressed by saying that the density ρ of a fluid parcel does not change as it moves in the flow field.

This additional constraint simplifies the governing equations, especially in the case when the fluid has a uniform density.

Viscous vs inviscid flow

Viscous problems are those in which fluid friction has significant effects on the fluid motion. The Reynolds number, which is a ratio between inertial and viscous forces, can be used to evaluate whether viscous or inviscid equations are appropriate to the problem.

Stokes flow is flow at very low Reynolds numbers, *Re*<<1, such that inertial forces can be neglected compared to viscous forces.

On the contrary, high Reynolds numbers indicate that the inertial forces are more significant than the viscous (friction) forces. Therefore, one may assume the flow to be an inviscid flow, an approximation in which viscosity is neglected completely, compared to inertial terms.

This idea can work fairly well when the Reynolds number is high. However, certain problems such as those involving solid boundaries, may require that the viscosity be included. Viscosity often cannot be neglected near solid boundaries because the no-slip condition can generate a thin region of large strain rate (known as boundary layer) which enhances the effect of even a small amount of viscosity, and thus generating vorticity. The standard equations of inviscid flow are the Euler equations. Another often used model, especially in computational fluid dynamics, is to use the Euler equations away from the body and the boundary layer equations, which incorporates viscosity, in a region close to the body. The Euler equations can be integrated along a streamline to get Bernoulli's equation. When the flow is everywhere irrotational and inviscid, Bernoulli's equation can be used throughout the flow field. Such flows are called potential flows.

Laminar vs turbulent flow

Turbulence is flow with a high Reynolds number and is characterized by recirculation, eddies, and apparent randomness. Flow in which turbulence is not exhibited is called laminar. It should be noted, however, that the presence of eddies or recirculation alone does not necessarily indicate turbulent flow—these phenomena may be present in laminar flow as well. Mathematically, turbulent flow is often represented via a Reynolds decomposition, in which the flow is broken down into the sum of an average component and a perturbation component.

Equations for the perturbation component are subject to different models (k-eps, second order models etc).

<u>SIMUGLASS</u> is using an incompressible viscous fluid dynamics model to describe the behaviour of the laminar flow of protection gasses.

Newtonian vs non-Newtonian fluids and Rheology

If fluids can be characterized by a single coefficient of viscosity for a specific temperature they are called Newtonian fluids. Although this viscosity will change with temperature, it does not change with the flow rate or strain rate. Only a small group of fluids exhibit such constant viscosity.

For a large class of fluids, the viscosity change with the strain rate (or relative velocity of flow) and are called non-Newtonian fluids. The behaviour of non-Newtonian fluids is described by rheology. These materials include sticky liquids such as latex, honey, and lubricants.

For example, ketchup can have its viscosity reduced by shaking (or other forms of mechanical agitation, where the relative movement of different layers in the material actually causes the reduction in viscosity) but water cannot. Ketchup is a shear thinning material, as an increase in relative velocity caused a reduction in viscosity, while some other non-Newtonian materials show the opposite behaviour: viscosity going up with relative deformation, which is called shear thickening or dilatant materials.

Rheology is the study non Newtonian-fluids or otherwise describes as the flow of matter, primarily in the liquid state, but also as 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. It applies to substances which have a complex molecular structure, such as muds, sludges, suspensions, polymers and other glass formers (e.g.

silicates), as well as many foods and additives, bodily fluids (e.g. blood) and other biological materials. Theoretical aspects of rheology are the relation of the flow/deformation behaviour of material and its internal structure (e.g., the orientation and elongation of polymer molecules), and the flow/deformation behaviour of materials that cannot be described by classical fluid mechanics or elasticity.

<u>MODIFY</u> is studying rheology with the POM-POM tube constitutive equation to study flow and deformation of acrylic polymers.

<u>MUST</u> is using an in-house diffusion model and phenomenological model of formation of liquid emulsion cores by membrane emulsification (balance of hydrodynamic, capillary and buoyancy forces) to calculate the optimal composition and structure of the coating to deal with corrosion of metallic and polymeric substrates and structures.

<u>ORAMA</u> is using a CFD code for droplet formation and optimization of Ink-Jet and Sol-Gel processes.

Two phase flows

Without the wish to be complete it should be stated that many flows need their own models like e.g. two-phase flows where interactions between the phases have to be modeled.

Constitutive equations for flows

Besides modeling of the fundamental physics equations, there are also different constitutive equations in use and some projects have developed new ones.

Fick's law

Fick's first law relates the diffusive flux to the concentration under the assumption of steady state. It postulates that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative). This constitutive equation is used to close the conservation of mass (flow) equations reduced to diffusion only.

Constitutive equation for the diffusion of chemical species

Diffusion of interstitial atoms due to chemical potential gradients can be described by an extended Fick's diffusion equation with added terms due to chemical potential gradients (stress and temperature). The Nernst–Planck equation is a constitutive equation used to close the conservation of mass equations to describe the diffusion of charged chemical species in a fluid in an electric field. It relates the flux of ions under the influence of both an ionic concentration gradient and an electric field. It extends Fick's law of diffusion for the case where the diffusing particles are also moved with respect to the fluid by electrostatic forces. If the diffusing particles are themselves charged they influence the electric field on moving. Hence the Nernst–Planck equation is applied in describing the ion-exchange kinetics. Please see also the diffusion equation described at atomistic level.

<u>ARTIVASC-3D</u> used a constitutive equation of the Nernst-Planck type in the advection-diffusiondeposition model for the permeation-times of nutrients and O2.

<u>MULTIHY</u> is using Fick's diffusion equation as constitutive equation extended with terms due to chemical potential gradient and trapping. This is used with codes to obtain a description of

hydrogen diffusion under broader range of conditions (temperature variations, trap occupancy) at the specimen and component level.

<u>CODICE</u> used the Nernst-Planck constitutive equations simulating grain-based flow and hydrogen diffusion with their continuum model.

Poro-elastic flow

When fluids are streaming through a porous medium a combination of solid mechanics and fluid mechanics is to be applied. Two mechanisms play a key role in this interaction (i) an increase of pore pressure induces a dilation of the porous solid, and (ii) compression of the solid causes a rise of pore pressure, if the fluid is prevented from escaping the pore network.

The fluid transport in the interstitial space can be described by the well-known Darcy's law, which is an empirical (phenomenologically) derived constitutive equation that describes the flow of a fluid through a porous medium (see also Chapter <u>4.2</u>). Darcy's law works with variables averaged over several porewidths. It can also be derived from Navier-Stokes equations by dropping the inertial terms, so this is an example of a constitutive equation being derived from the physics equations. Darcy's law is a simple proportional relationship between the instantaneous discharge rate through a porous medium, the viscosity of the fluid and the pressure drop over a given distance.

<u>DISC REGENERATION</u> coupled poro-hyper-elastic constitutive equations and vascular transport models to predict the movement of solutes within the intervertebral disc. They simulated the disc mechanical response to external compressive loads which affect diffusion of oxygen and lactate and thus their content within the disc. They also simulated fluid-solid interaction within high porous polymer implants as well as interaction between implants itself and surrounding intact biological structures and test different disc replacement configurations.

Scales

Also in this part of continuum mechanics models can be created for the behaviour at different scales and also in this discipline a chain of flow models at different scales might be used.

State-of-the-art models for flow at the smallest scale are e.g. the so called "atomistic" finite elements which can be applied to length scales of 100 nm – mm and timescale of ms to s. (This scale is called meso by electronic modellers and micro by continuum modelers, here the first name is adopted.)

<u>M3-25</u> is using atomistic finite element flow models (discrete lattice model) to model the breaking of atomic bonds between the discrete elements.

The calculated properties can be used as constitutive equations in the flow models at higher scales.

4.3 Heat Flow and Thermo-mechanical behaviour

On the crossing point of micromechanics and fluid dynamics there is the domain of heat flow and its influence on mechanical properties. Thermomechanics studies the properties of materials as they change with temperature. The materials might show a change of dimension (expressed in the calculated macroscopic thermal expansion coefficients) or of a mechanical property. The bonding in the material

determines this response. Crystallinity and fillers introduce physical constraints to motion. Cross-linking between molecules will restrict the molecular response to temperature change since the degree of freedom for segmental motions is reduced as molecules become irreversibly linked.

Principle physical equation describing heat flow

The conservation of energy equation contains the energy change due to heat flow. This term can be modeled by different assumptions and this is expressed in different constitutive equations. Heat transfer may take place due to conduction (also called diffusion), convection (energy taken away by the surroundings solids or fluids) or radiation.

Constitutive equations

The thermo-elastic constitutive equation defines a relationship between stress, strain and temperature, and thermal conductivity equation relates the heat flux density to temperature gradient. For anisotropic solids, both have to be written in a tensor form. Coefficients of these equations depend themselves of the temperature and represent thus material functions rather than constant parameters for a specified material. Other material functions determine temperature dependence of parameters in constitutive equations of plasticity, visco-plasticity and rheology. Such material functions are usually determined empirically.

A constitutive equation for conductive heat flow is the Fourier's law that states that the heat flow is proportional to the temperature gradient.

A constitutive equation for convective heat flow can be Newton's law of cooling.

A constitutive equation for radiative heat flow is the Stefan Boltmann's law.

<u>MATRANS</u> modelled the effective linear thermo-elastic properties of the functionally graded materials with micromechanical (incl. heat conduction) approaches and the optimal content of the ceramic phase was searched for meeting the required thermo-mechanical properties of the composite for the target applications.

A multi-scale model of thermal residual stresses in graded metal-ceramic composites, generated during the cooling phase of the sintering process, was developed. The constitutive equations used in the finite element computations of thermal stresses were those of linear elasticity for the ceramic and elasto-plasticity for the metal phase.

MATRANS is using parameters of thermal conductivity and thermal expansion as well as mechanical properties at elevated temperatures to characterize quality of composite materials.

<u>MACADEMIA</u> uses multi-scale mass transfer model (IAST, Heterogeneous Ideal Adsorbed Solution Theory (HIAST) and VST) and heat transfer model to calculate the equilibrium adsorption of mixtures from single component isotherms and thus their selectivity for a series of gas mixtures.

<u>PMJOIN</u> uses continuum thermal modelling to provide thermal gradients, weld seam geometry and thermal distortions of polymer-metal joined structures, based on laser parameters, material properties and clamping conditions.

<u>SYNAPSE</u> will use Fourier's heat law to understand, or predict, the thermal behaviour of nanoscaled devices.

<u>YBRIDIO</u> will use continuum modeling of heat transfer in solid to calculate induction heating of composite laminates and metal composite hybrids.

4.4 Continuum thermodynamics

The first law of thermodynamics states, that energy is conserved.

The energy related to the atomic and molecular structure of the material and the degree of their activity is independent of outside reference frames and is called internal energy. The macroscopic energy is the kinetic energy and potential energy of the material sample. The only two forms of energy interactions are heat transfer and work

For each application it has to be decided which forms of energy have to be taken into account in the model. The portion of the internal energy associated with the kinetic energies of the atoms/molecules (rotation and vibration of the atoms about the center of mass) is called sensible energy. The internal energy associated with the atomic bonds in a molecule is called chemical energy. Mutual potential energy of the atoms as they change their distance inside the molecules is part of the internal energy. Stresses in the material can be regarded as part of the internal energy.

The energy associated with the phase –change process related to the binding between molecules is called latent heat. Nuclear energy is not considered in NMP projects.

Internal energy and temperature:

Temperature is a measure of the average kinetic energy of the center-of-mass motion of individual molecules. In daily life sensible and latent energy are called "heat", while in thermodynamics it is called thermal energy to distinguish it from heat transfer. Energy can be put into a material in many ways (friction, radiation, conduction, kinetic impacts etc.). Some part of the energy goes into vibrations and rotations about the center of mass (if not a mono-atomic gas) and only a part of it ends up as increasing the temperature.

The second law relates kinetic energy and internal energy to the power exerted on/by the system and the heat transfer. The second law is often considered to fall outside the domain of continuum mechanics. This additional law determines the direction into which this energy flows via the concept entropy.

All mechanical energy can be changed into internal energy, but one can change only a fraction of the internal energy into work.

Thermodynamic models consist in a description of the Gibbs energy as a function of external and initial system conditions (p, V, T, relative composition). They describe the equilibrium of the system under given conditions and are used to study materials being processed. There are several types of models available to describe how the Gibbs Energy of a phase changes as function of (T,p,V,relative composition). These models are in the form of polynomials and other functional dependancies (e.g. sublattice model, ideal mixtures, Redlich-Kister polynomials). The parameters occurring in these equations are derived from other sources of knowledge (experimental, empirical or electronic and atomistic models).

From the Gibbs energy all thermodynamic values can be derived applying their definition (usually involving partial derivatives).

In the model and in the definition of thermodynamic variables constants appear. These can be calculated by electronic or atomistic models, but the computational effort would simply not be acceptable to industry. Therefore databases collect and assess the results obtained from theoretical calculations using molecular simulations and from measurements of empirical data (measuments of Gibbs energy). The assessment of the measured data and the subsequent decision on exclusion or inclusion is a very difficult task requiring a lot of understanding of the phenomena involved. This classification and evaluation of empirical data is based on models and on reasonable, physically motivated approximations.

But thermodynamic databases are limited to equilibrium data and can thus be used to predict equilibria, while the main challenge for the modelling is describing the relaxation process from non-equilibrium to equilibrium. The models for the relaxation processes are derived from the principles of physics and involve theoretical approximations.

<u>IMS&CPS</u> does thermodynamics models of percolation at nm scale to predict percolation thresholds of composites.

<u>MONAMI</u> does continuous thermo-dynamical and kinetic modelling of local mass density and energy density.

<u>Phase field models</u> are constructed to predict the stability of phases and phase diagrams. These models are based on interfacial dynamics. For phase field models the reader is referred to Chapter <u>3.4</u> where mesoscopic models are decribed.

4.5 Chemistry reaction (kinetic) models (meso and continuum)

Chemical reaction (kinetics) models are mathematical models that describe the characteristics of a chemical reaction, for example to study the effect of a catalyst. Normally, all the different chemical intermediate molecular species are represented explicitly. These models are based on thermodynamics and the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Although some of the parameters in the kinetic reaction models may need to be determined experimentally, such models can still be re-used for a wide range of operating conditions and are more versatile than purely empirical phenomenological methods ("operational" kinetics).

Chemical reaction kinetics models are used to determine the rates of chemical processes and how different experimental conditions (e.g. the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction) can influence the speed of a chemical reaction. They yield information about the reaction's mechanism and transition states and can be used in combination with other continuum models to take into account the changing relative concentration of the chemical species.

Electrochemistry reactions are chemical reactions which take place in a solution at the interface of an electron conductor and an ionic conductor (the electrolyte) e.g in batteries. These reactions involve electron transfer between the electrode and the electrolyte or species in solution where oxidation and

reduction reactions are separated in space or time, and may be connected by an external electric circuit. To model such reactions the forward reaction rate coefficient for each reaction is usually calculated by a modified Arrhenius formulation incorporating also the influence of the electric potential difference. All reactions are considered surface reactions and are modelled to happen on defined interfaces between solid species and/or the liquid electrolyte.

<u>FREECATS</u> is using a reaction kinetic model combined with hydrodynamics at nm scale to detail surface reactions and adsorption processes of the new catalysts.

<u>LISSEN</u> models chemical reactions in a battery cell based on a 1D continuum approach. The multi-species redox chemistry of sulphur to lithium sulphide via polysulfides (and vice versa) will be modelled at the cathode. At the anode, lithium deposition/intercalation into an anode material will be described. Parasitic side reactions (e.g. polysulfide reduction at the anode) will be implemented as appropriate. When useful and feasible, the intercalation induced volume changes of electrodes as well as pore size changes resulting from dissolution and precipitation of solids will be modelled.

<u>NANOINTERFACE</u> is using an exponential continuum cohesive-zone model to quantify metaloxide-polymer adhesion properties at the macro-scale level.

<u>NEXT-GEN-CAT</u> is using catalytic reaction kinetic models (CO oxidation, CxHy oxidation and NOx reduction) for the simulation of species concentration in gas near and far from catalytic surfaces along the flow direction.

<u>SUPERLION</u> is doing electrochemical modelling to simulate current-voltage relationships for the porous electrodes.

4.6 Electromagnetism (including optics, magnetics and electrical)

Electromagnetism is the branch of science concerned with the forces that occur between electrically charged particles. In electromagnetic theory these forces are explained using electromagnetic fields. Electromagnetic force is one of the four fundamental interactions in nature, the other three being the strong interaction, the weak interaction and gravitation.

The electromagnetic force is the one responsible for practically all the phenomena one encounters in daily life above the nuclear scale, with the exception of gravity. Roughly speaking, all the forces involved in interactions between atoms can be explained by the electromagnetic force acting on the electrically charged atomic nuclei and electrons inside and around the atoms, together with how these particles carry momentum by their movement. This includes the forces experienced in "pushing" or "pulling" ordinary material objects, which come from the intermolecular forces between the individual molecules in our bodies and those in the objects. It also includes all forms of chemical phenomena.

In classical electromagnetism, the electromagnetic field obeys a set of equations known as Maxwell's equations, and the electromagnetic force is given by the Lorentz force law.

The dynamics of free charges and currents are described by Maxwell's equations directly, but the dynamics of bound charges and currents enter Maxwell's equations through the constitutive relations.

The constitutive equations link the electrical and magnetic field to the electrical flux density (displacement) and the magnetic flux density. Each type of material (magnets, conductors etc.) has their own relation.

An often used technique is the plan wave method which is a computational technique in electromagnetics to solve the Maxwell's equations by formulating an eigenvalue problem out of the equation. This method is popular among the photonic crystal community as a method of solving for the band structure (dispersion relation) of specific photonic crystal geometries.

Most projects solve the EM equations via FE techniques but also ray tracing methods with Monte Carlo algorithms for the scattering are employed.

The projects <u>AMON-RA</u> used the Maxwell equations and semi-classical drift-diffusion model for the calculation of electro-optical properties for nanostructured solar cells.

<u>LIGHT.TOUCH.MATTER</u> uses electromagnetic models to predict the effective dielectric constant (i.e. piezo-electric sensitivity) of the piezoelectric composite material in relationship to the composites, composition and the electromagnetic field applied during composite formation.

<u>MAGNONICS</u> makes electromagnetic and spin dynamics models using the dynamical matrix method and Ewald-FFT method to calculate the magnetic behaviour of dipole-coupled and arrays of anti-dots and the magneto-dipole interaction field, to characterise the nature and spatial structure of magnons in magnonics array.

<u>METACHEM</u> uses the Maxwell equations (nm scale) and generalised Mie model (mm scale) to calculate individual polarizabilities of complex scatterer (electric and magnetic), surface susceptibilites of metasurfaces (electric, magnetic and magnetoelectric), refractive index, thickness and bi-anisotropy of metamaterials and to calculate scattering by cluster of simple and core-shell spheres in order to determine optical devices performance with metamaterials.

<u>MONAMI</u> used a coarse grained model with effective soft potentials for calculation of spin dynamics in small magnetic clusters.

<u>NANOMAGMA</u> solved Maxwell's equations in presence of magneto-optical effects in magnetoplasmonic nanostructures

<u>NIM-NIL</u> did characterisation based on electromagnetic wave theory (Maxwell solver) to describe the dissipative loss in resonant electromagnetic metamaterials. The model takes into account the radiation damping of the resonant currents.

<u>PMJOIN</u> used ray tracing software to model the behaviour of the laser beam through the polymer. The laser beam is used to heat materials to be joined.

<u>POCO</u> developed constitutive equations for electro-dynamics. These are used for the alignment of CarbonNanoT ubes under electric fields. They used these to describe crystallisation of thermoplastics with and without CNT and for the determination of alignment of CNT in viscous media under electric fields.

<u>SMASH</u> uses electromagnetic models for the calculation of optical properties of nanorods, optical extraction efficiency, emission directionality and polarization and to calculate the radiation characteristics as input to processing technologies.

<u>YBRIDIO</u> will use Maxwell equations in the Eddy current (induction-diffusion) approximation to calculate the electromagnetic behaviour.

Magnetics, Elect(ron)ics and Optics.

Electromagnetics at electronic level is discussed in Chapter 1

The continuum level is not discussed here and the reader is referred to the literature. It is only noted that electric fields and magnetic fields are different aspects of electromagnetism, and hence are intrinsically related. A changing electric field generates a magnetic field and via versa.

<u>AMON-RA</u> calculates the electrical properties of nanowire arrays using the software CELS/QUATRA and DESSIS for electronic transport and Esaki interband tunneling diode simulation in large diameter hetero-junction nanowires with tunnel junctions.

<u>IMS&CPS</u>models electrical conductivity and percolation at nm scale to predict electrical conductivity and percolation thresholds of composites

<u>IRONSEA</u> models resistively and capacitively shunted junctions with electrical device modelling to calculate the characteristic of junctions based on Fe-based superconducting films.

<u>NANOPYME</u> is using a continuum macromagnetic model to predict magnetic performance of of macroscopic magnetic components in operation conditions and possible performance decay.

<u>MINOTOR</u> uses classical micro-electrostatic model (at nm scale) to calculate energetic profile of the charge carriers around the interface to optimize mechanism of chemical doping in organic layers providing energetic disorder

<u>SYNAPSE</u> will use Poisson's equation for electrical conductivity to understand, or predict, the electrical effects occurring in nanoscaled devices.

Optics is the branch of physics which involves the behaviour and properties of light, including its interactions with matter. Because light is an electromagnetic wave, most optical phenomena can be accounted for using the classical electromagnetic description of light.

Some phenomena depend on the fact that light has both wave-like and particle-like properties. Explanation of these effects requires quantum mechanics and this is discussed in Chapter <u>1</u>.

<u>ORAMA</u> uses electromagnetic codes to calculate magnetic and optical properties of their devices.

4.7 Process and Device Modelling

Manufacturing process models

Once the material has been designed it has to be produced. The manufacturing processes too can be designed and optimised via modelling. Manufacturing processes that can be modelled are a.o.

- deposition (isotropic (sputtering) or anisotropic),
- etching (basic etching is treated as the opposite of deposition and is modeled as a pure geometric process, which is e.g. (an-)isotropic, of fourier-type, directional, crystallographic), oxidation (basic oxidation models only calculates a velocity however, the influence of mechanical stress can also be considered for oxidation and etching),
- dopant diffusion during growth,
- all sorts of thermal induced reactions during annealing steps,
- interface movements or
- epitaxy (also reactions based on gas flows).

Note that the relation of the micromechanical models for oxidation (see Chapter <u>4.1</u>) strongly depends on the used transport equation and other reaction terms like clustering.

The diffusion, transport and reaction models can include thermal induced stress, clustering and amorphization models for dopants. The simulation tool will allow the researcher to select parameters to be investigated and visualize the influence of each parameter, as well as to compute the influence of mechanical stresses in devices etc.

<u>MACADEMIA</u> have used macroscopic models like the Simulated Moving Bed and Pressure Swing Adsorption for different separation processes (propane/propene, acid gas....) to evaluate the materials on the process scale and to predict material behaviour and ageing in real applications.

<u>NEXT-GEN-CAT</u> is doing process modelling with mass, energy and momentum balances to predict the performance of catalytic converters and to predict the concentration distribution of the chemical species.

<u>ORAMA</u> is doing PVD and process control for deposition in a PVD chamber.

<u>SIMBA</u> is using CFD models for plasma behaviour in of a lab-scale reactor. The models include electro-magnetism, thermodynamics and chemistry processes. With these they can calculate non-equilibrium plasma and nanopowder nucleation out of the gas phase.

<u>SOLARDESIGN</u> is using process simulation TCAD SENTAURUS PROCESS will deal with modelling (2Dor 3D-) of the fabrication steps of solar cells/modules, like e.g. different types of depositions, etching, oxidation, diffusion, and implementation of models for custom solar cell processes in different process conditions like the ambient chemical composition, pressure, temperature etc.

Device modelling

And, last but not least, the material will be used in applications and integrated in devices, and also this can be optimised via modelling.

<u>MORDRED</u> uses RANDOMSPICE to predict reliability of electronic devices. RANDOM SPICE is a Monte Carlo circuit simulation engine for ICT devices, which enables simulations of statistical and process variability, data harvesting and statistical analysis of the simulation results. RandomSpice provides the facilities necessary for accurate statistical circuit and standard cell characterisation, and supports power–performance–yield (PPY) analysis. Input includes bias, temperature, materials etc., but also a lot of non-physical fitting parameters and output is current/voltage behaviour. <u>SOLARDESIGN</u> will use an advanced multidimensional device (TCAD) simulator capable of simulating electrical, thermal, and optical characteristics of CIGS solar cells/modules, for development and optimization of their performance.

<u>SUPERLION</u> is doing nano-scale battery architecture models to calculate the efficiency of the battery.

Chapter 5 Linking of models and Numerics

5.1 Linking different models (multi-scaling and multi-modelling)

Depending on the timescale of the phenomena and the accuracy needed, models at describing different entities can be applied and the results need to be transferred from one model to another. This is here called multi-scale modelling.

It might also happen that different physics and chemistry need to be coupled at the same scale like solid and fluid mechanics with thermodynamics or reaction kinetics. This is called here multi-modelling as the models are applied to the same length- and time- scales and the word multi-scaling does not really apply.

A few examples, out of many:

Developing composites for aircraft is a multiscale problem, where first the fiber-matrix system is modelled at electronic and atomistic level, then the composite ply at mesoscopic level, and finally the laminate and structural part for the airplane at macroscale level. (<u>IMS & CPS</u>)

MINTWELD will use the multiscale framework shown in Fig. 1. Ab-initio molecular dynamics simulations were used to calculate multi-component force fields and to provide an extensive configurational database for the energetics and dynamics of alloys in complex environments. These data will be used as input in molecular dynamics modelling. Molecular dynamics modelling was then performed to explore the process of grain boundary formation under various conditions using results from micro-scale phase-field modelling as input data. The atomic-scale grain boundary structure and chemistry will be determined and this information will then be used in ab-initio simulations and mesoscale phase-field modelling. Phase Field modelling is used obtain a complete picture of microstructure and defect (e.g. cracking) formation in the welding process. The input (structure of the interface and its thermodynamics properties) is provided by atomistic molecular dynamics simulations. The predicted results on transformation kinetics and interface morphology are fed to grain-scale models; the calculated chemistry and crystal orientation and stress can be feed back as input for molecular dynamics modelling. At the continuum level, CFD modelling is taking into account a wide range of predicted thermal and grain structure information of welded interfaces to relate the process variables to the properties of the weld pool. The dynamics of welding interface evolution is solved to give the local chemistry and the flow of molten liquid in the weld pool, through linking the continuum models with the mesoscopic solidification model. Grain scale (at the mesoscale, from cm to tens of μ m) models are being used to model grain structure evolution, such as grain size and distribution, and local solidification profile (e.g. mushy zone) for continuum computational fluid dynamics (CFD) modelling of weld flow; predicted thermal and grain structure information is used as input for micro-scale continuum modelling, as shown in Figure 1.

The multi-scale framework developed in <u>NANOINTERFACE</u> starts with Molecular Dynamics simulations to describe the thermo-mechanical and failure behaviour of epoxies, copper, copper oxides and the respective interfaces. At the mesoscopic level, coarse grained models are used to transfer structural and force information from molecular simulations to continuum and vice versa. At the continuum scale, metal-oxide-polymer adhesion properties are determined by describing the relevant dissipative mechanisms that affect adhesion, including the underlying microstructural mechanisms obtained through a sequential coupling. The project <u>NEXT-GEN-CAT</u> calculated reaction kinetics of catalysts reactivity with ab initio modelling. This will be used in fluid flow simulations for the prediction automotive catalytic converter performance.

In <u>ORAMA</u> (see Fig.2) first principle modelling is used to calculate the electronic structure and doping mechanisms of oxide materials foreseen for electronic application as n- or p-type oxide semiconductor. Self-interaction correction is performed to calculate realistic band structures. Grain boundary effects are also taken into account. ORAMA used parametrised electron density distribution obtained through ab initio quantum mechanical models to develop semi-empirical potentials. These were used in molecular dynamics simulation at the atomistic scale. In ORAMA the multifunctional oxides structures resulting from molecular dynamics simulations at the atomistic scale have been fed into mesoscopic models that solve the Boltzmann transport equation for the description of gas flow phenomena by means of Direct Simulation Monte-Carlo (DSMC) techniques. With self-consistent electric field computation that approach is extended to Particle-in-Cell Monte-Carlo Techniques (PIC-MC) for plasma phenomena. ORAMA used the Statistical Mechanics (Boltzmann) transport equation for the description of gas flow phenometic flow phenometic flow flow phenometic flow flow models.



Fig 5.1. Data flow in multiscale modelling in *MINTWELD* (Hongbiao Dong, Leicester University, UK)





5.1.1 Linking between different electronic models

<u>GOFAST</u> uses LDA-DFT to calculate realistic Hamiltonian parameters from ab-initio LDA-DFT to be used in DMFT models.

<u>HYMEC</u> uses the time-dependent mean-field theory to calculate transport properties and the electronic drift-diffusion model for the jump rate and the coordination numbers (substantially related to the density of nanoparticles). The output is used in a statistical mechanics model for percolation.

<u>INNOVASOL</u> used DFT to calculate the formation energy of some inclusion complexes in layered magnesium oxides (HTLC) which is relevant for the synthesis of quasi-solid electrolytes to be used in solar cells. When necessary, the solvent effects were included in the calculations through the Polarizable Continuum Model, where the solvent reaction field is simulated by a set of apparent charges self-consistently determined on the basis of the electric potential generated by the solvated molecule(s).

In <u>IRON-SEA</u> modelling is used to calculate transport properties in superconductors (mainly Josephson Junctions). The multiband Eliashberg model requires input from band structure calculations (normal DOSs at the Fermi levels) provided by the Blonder-Tinkham-Klapwijk model. The connection between the models is schematized below:

1. the Fermi surface is an input to the 3D-BTK model, with which we can fit the experimental PCAR spectrum and obtain the number, amplitude and symmetry of the gaps Δi . Note that, in this step: i) the gap amplitudes Δi are constant (do not depend on energy), ii) it is NOT possible to fit the electron-boson spectral features often present in the spectra, but only the gaps.

2. Eliashberg calculations require as an input the partial DOSs from DFT calculations (see above) and the typical boson energy. The latter can be obtained from neutron scattering experiments (in literature) or, if these lack, can be inferred from the PCAR spectra themselves, by analyzing the second derivative of the current with respect to the voltage (this is a standard procedure for tunnel and point-contact spectroscopy to determine the electron-boson features). Within the Eliashberg theory we can determine the coupling strengths that allow reproducing the gap amplitudes Δi provided by the BTK fit of the experimental PCAR spectra and the critical temperature. The model however has also various other outputs: it allows calculating many physical observables that can be
compared to experiments. It finally provides also the full $\Delta i(E)$ functions (in Eliashberg theory, unlike in BCS theory, the order parameter is not a constant but a function of energy). These functions contain all the information about the electron-boson coupling.

3. The $\Delta i(E)$ functions can be in turn used to calculate, within an extended BTK model, the PCAR spectrum that however now shows not only the gap features but also the structures connected to the electron-boson coupling. The resulting spectrum can be finally compared to the experimental one.

In <u>ORAMA</u> first principles modelling is used to calculate the electronic structure and doping mechanisms of oxide materials foreseen for electronic application as n- or p-type oxide semiconductor. Self-interaction correction is performed to calculate realistic band structures. Grain boundary effects are also taken into account.



Fig 5.3 Linking of electronic models in IRON-SEA (Kazumasa lida, Institute for Metalic Materials, DE)

5.1.2 Linking of electronic and atomistic models

Note that we have not included QM/MM in this chapter as this is using two models side by side; part of the atom coordindates are calculated using QM and part using MM. there is no transfer of information, the two models act on the basis of all atomic coordinates of all parts.

<u>AMCOS</u> uses DFT calculation to produce a force field for Molecular Dynamics and grand canonical Monte Carlo atomistic simulation.

<u>ATHENA</u> combines electronic structure calculations at the level of DFT with model Hamiltonian schemes for simulating the thermodynamical properties of complex oxides and oxides interfaces. The electronic structure is then mapped onto model Hamiltonian via the rigorous Wannier function scheme. Then the model Hamiltonian is solved at the Monte Carlo level for extracting finite temperature properties of oxides and their interfaces. These properties include magnetic order, critical temperature for magnetism, conductivity, ferroelectric distortion. <u>FEMTOSPIN</u> uses ab-initio information (spin, exchange integrals, anisotropy) to parameterise atomistic and heat bath model calculations. A multiband Hubbard model is under development and will be used to improve the calculation of the exchange field in disordered systems and the introduction of longitudinal spin fluctuations.

<u>GRENADA</u> used the electrical and structural properties of graphene (electronic interaction between graphene and its surroundings and in between graphene layers in multilayers) calculated with DFT in ab-initio molecular dynamics calculations to model mechanical, magnetic and electrical properties of materials

<u>HIPERSOL</u> is connecting DFT and molecular dynamics with a finite element model of the current transport from the silver finger to the silicon in a standard Si-based solar cell. The interfacial resistivities are obtained from Schottky barriers calculated with DFT based on atomic interface models optimised using empirical molecular dynamics.

<u>HYPOMAP</u> is using DFT and higher level ab –initio electronic calculationsto to develop force fields to assess adsorption at atomistic level (Quantum Liquid DFT or Grand Canonical Monte Carlo) and calculate proton conductance in polymeric proton exchange membranes.

<u>IFOX</u> uses electronic structure and transport characteristics of transition metal oxide heterostructures and their interfaces calculated with DFT in Molecular Dynamics calculations for defects diffusion in oxides.

<u>IMS & CPS</u> models the ion transport percolation with statistical mechanics based codes that take the structure into account and calculate thermodynamic properties with data calculated from electron tunnelling quantum mechanical percolation models which assume the charge transport between carbon nanotubes are partly through physical contacts and partly through electron tunneling between carbon nanotubes.

<u>LEMSUPER</u> used Gutzwiller and Dynamical Mean Field Theory to generate input for the ab initio molecular dynamics models whichwere used to simulate pressure induced metallization of potential high pressure superconductors and to study interactions, vibron properties and Jahn Teller effects.

<u>MACADEMIA</u> uses classical simulations Grand Canonical Monte Carlo and Molecular Dynamics to characterize the selectivity and transport properties of different MOF materials with respect to the different liquid and gas mixtures. Both Molecular Dynamics and Grand Canonical Monte Carlo are conducted using rigid or flexible force fields generated by quantum calculations (DFT-CC) describing the adsorption phenomena when specific interactions occur at open metal sites that cannot be treated using generic force field.

<u>MINOTOR</u> linked DFT and MD to compute the interface dipole at organic/organic interfaces; since this dipole is highly sensitive to the molecular packing at the interface, we have first generated realistic morphologies with MD simulations before computing the interface dipole at the DFT level on clusters extracted from the MD snapshots.

The <u>MONAMI</u> project has done simulations of magnetisation dynamics. First the electronic structure is modelled with density functional theory and this is used as input for atomistic length-scale models for spin-dynamics.

<u>MORDRED</u> used parameters calculated with DFT and electronic drift diffusion models expressed as force fields fro dynamic charge transfer in atomistic MD models.

<u>MUST</u> uses the ab-initio quantum chemical calculation to determine some of the force field parameters for the molecular dynamic simulations of adsorption of polyelectrolytes during the layer-by-layer formation of thin film coatings and capsule shells.

<u>NAMASTE</u> has performed density-functional and microscopic tight-binding Anderson calculations of the band structure of ferromagnetic semiconductors. Results of these calculations served as a justification for the choice of an effective Kondo spin Hamiltonian and provided the values of the Kondo Hamiltonian parameters. The effective model Hamiltonian description served then as a basis for calculating a wide range of thermodynamic magnetic properties and magneto-transport properties with a special focus on spin-orbit coupling induced effects.

<u>ONE-P</u> used electronic quantum-chemical models for the evaluation of the molecular parameters defining the rate of charge transfer between molecules in organic conjugated compounds for applications in organic electronics. These were used in atomistic Molecular Dynamics simulations for the prediction of the bulk organization and in kinetic Monte Carlo models for the propagation of the charge and the evaluation of the charge carrier mobility.

<u>ORAMA</u> used parametrised electron density distribution obtained through ab initio quantum mechanical models to develop semi-empirical potentials. These were used in molecular dynamics simulation at the atomistic scale.

<u>OXIDES</u> is interfacing electronic and atomistic calculations through DFT calculations which will set the basis for the derivation of the appropriate effective Hamiltonians describing how the ferro-electric and anti-ferroelectric domain distortions couple to each other at the interface and what the relevant an-harmonic interactions are. The effective Hamiltonian should be able to capture the physical effects which dominate the behaviour of super-lattices.

<u>**RADINTERFACES</u>** used DFT and fitted many body potentials the project will quantify the energies required to activate diffusion (diffusion barriers). These were used in molecular dynamics models.</u>

<u>ROLICER</u> uses DFT to calculate adhesion energy bonding and structure of interfaces and grain boundaries and uses this in MD calculations.

<u>SMASH</u> is using amulti-scale model where atomistic band structure calculation on a sub region is linked to a continuum drift-diffusion type electronic transport model.

<u>SYNAPSE</u> is developing interatomic potentials from a DFT database by fitting the data with the help of a Neural Network. The potentials will be used in the molecular dynamics simulations. The molecular dynamics simulations will calculate thermal conductivity and crystallization speed of chalcogenides.

<u>SUPER-IRON</u> calculated effective tight-binding Hamiltonians starting from first-principles to describe the electronic properties of defects, superlattices and grain boundaries and simulate the superconducting properties (Jc, Hc, Tc) This provided fundamental information on the superconducting transition, and its dependance on the critical temperature. This information is

used in molecular dynamics models to calculate the the stability and energetics of thin film geometry and superlattices formed by different layers of various FeAs superconductors.

<u>SURFUNCELL</u> calculated forc fields for water-cellulose interaction in bulk water with DFT and used them in molecular dynamics simulations.

<u>ULTRAMAGNETRON</u> used electronic modelling to calculate the ultrafast laser-induced magnetization reversal based on the use of the Heisenberg formalism for the exchange interaction between atomic spins. This was then used in atomistic modelling of a ferrimagnetic material with magnetic compensation pointsLandau-Lifshitz-Bloch (LLB) equation.

5.1.3 Linking between electronic and mesoscopic models

<u>DYNAMAG</u> and <u>MAGNONICS</u> used ab-initio calculations are used to calculate the saturation magnetisation, the exchange stiffness and the anisotropy constants of magnetic materials and the strength of the exchange interaction and surface anisotropy at interfaces in composite magnetic materials. The parameters are then used in micro-magnetic simulations e.g. on the basis of the Landau-Lifshitz equations.

<u>MULTIHY</u> used electronic models for the energetics of hydrogen in bulk phases and around point defects hydrogen interactions with extended defects and used this as input to mesoscopic kinetic montecarlo simulations for hydrogen diffusion as function of defect distribution.

<u>NANOPYME</u> uses DFT to calculate electronic properties: critical temperatures (Curie temperature for magnetic systems and Verwey temperature for Co-ferrites systems) and magnetic anisotropy.

<u>REFREEPERMAG</u> used DFT models to calculate the magneto-crystalline anisotropy both fullpotential and pseudopotentials methods and used this in micromagnetic simulations.

<u>ROMEO</u> calculates intrinsic magnetic properties with spin polarised DFT and these serve as input for mesoscopemodel simulations with micromagnetics codes. The electronic models give the lattice distortions near interfaces and compute the anisotropy as function of lattice constant. These models also give the magnetic reversal curves. Micromagntics models use these data to describe the magnetics at the nanoscale in domains and the outcome will be the macroscopic properties coercivity, remanence, max energy product and thermal stability (thermal dependance of coercivity). Elastic band method finds the optimal path where the gradient of energy points is everywhere parallel to the path.

<u>SSEEC</u> calculated exchange couplings with DFT which were then used in mesoscopic micromagnetics.

5.1.4 Linking between electronic and continuum models

<u>AMON-RA</u> uses diffusivities calculated with electronic drift diffusion models in electrical continuum models. Also the bandgap calculated with electronic k.p models was used in optical continuum models.

<u>IMS & CPS</u> has developed electrical models of carbon nanotubes at nano-scale to study electron displacements between nanotubes. In parallel, macro-scale models of solid continuum mechanics are performed to predict the mechanical behaviour of a composite part (a landing gear door of civil aircraft). When the optimal location of nanotubes in the composite is determined at nano-scale, the mechanic model at macro-scale is modified to add the carbon nanotubes in the analysis of the mechanical behaviour of the composite part.

<u>IRON-SEA</u> calculated characteristics of Josephson junctions fabricated from Fe-based superconducting films by the electrical circuit resistively and capacitively shunted junction (RSCJ) model using parameters calculated by the Eliashberg theory.

<u>NEXT-GEN-CAT</u> aims at linking DFT calculations with full scale catalytic converters simulation. Adsorption energies and reaction barriers obtained through DFT methods provide the basis to develop a surface reaction mechanism. This has to be included in continuum models of the nonisothermal, reacting flow bounded by catalytic surfaces, to simulate experimental activity measurements of different PGM-free catalysts.

<u>ROLICER</u> uses DFT to calculate constitutive eqs for micromechanics describing the relation between interface structure, point defects and adhesion. They also derived a fracture constitutive equation from DFT results and used this in micromechanics models.

<u>SMASH</u> used a multi-physics model where linear elasticity theory is coupled to electronic band structure calculation which itself is coupled to a drift-diffusion system. Within the drift-diffusion electron transport system, a k.p-method is coupled to take care of the regions where quantisation processes of carriers take place. The result of this model is then taken as input to calculate the electromagnetic problem for the extraction efficiency.

<u>SOLARDESIGN</u> calculated electronic charge transport within the solar cell with drift diffusion models and used these results to extract a diffusivit in the continuum models fro charge transport.

<u>SSEEC</u> calculates exchange couplings with DFT which were used in continuum models for magnetic cooling containing modules for thermal, fluid and magnetic switching behaviour.

<u>SYNAPSE</u> will use molecular dynamics simulations to calculate thermal conductivity and crystallization speed of chalcogenide and these will be employed as input in the finite-elements electro-thermal modelling of actual devices.

5.1.5 Linking between different atomistic models

<u>AMCOS</u> performed ab initio molecular dynamics (Car–Parrinello and Born–Oppenheimer) to develop force fields for the sub category of metal-organic frameworks, the ZIFs, to be used as input in the classical molecular dynamics computer experiments.

<u>MINTWELD</u> carried out ab-initio simulations molecular dynamics calculations to predict multicomponent force fields and to provide an extensive configurational database for the energetics and dynamics of alloys in complex environments. These data will be used as input in Molecular dynamics modelling. Molecular dynamics modelling was then performed to explore the process of grain boundary formation under various conditions using results from micro-scale phase-field modelling as input data. The atomic-scale grain boundary structure and chemistry will be determined and this information will then be used in Ab-initio simulations and micro-scale phase-field modelling.

In <u>NANOINTERFACE</u>, the interaction parameters for Coarse Graining (CGMD) and Discrete Particle Dynamics (DPD) simulation of cross-linked epoxy structures are obtained from molecular simulations (MD).

5.1.6 Linking of atomistic and mesocopic models

<u>AMCOS</u> carried out atomistic molecular dynamics and kinetic Monte Carlo calculations providing sorption isothermes and diffusivities for the lattice gas cellular automata flow models, bridging atomistic to mesoscopic models.

<u>ARTIVASC-3D</u> uses atomistic MD models to calculate pore-size-dependant ion transport to input the optimal morphology into mesoscopic ion infiltration models.

<u>CODICE</u> used atomistic Molecular Dynamic simulations to identify the smallest bricks of cementious structures. Afterwards, these segmental pieces have been approximated by 4-5 nm-sized spherical particles which served as coarse grained particles in a home-made kinetic Monte Carlo scheme. This KMC scheme has enabled to describe larger structures of C-S-H gel and establish a linkage with a new continuous chemical model which provided microstructural information.

<u>FEMTOSPIN</u> used atomistic models to calculate temperature dependence of magnetisation, anisotropy and longitudinal and transverse susceptibilities for use by mesoscopic (micro-magnetic) models.

<u>IFOX</u> uses defects diffusioncoefficients calculated with Molecular Dynamics in corase grained Monte Carlo codes to evaluate thermodynamical properties for example critical temperatures.

<u>M3-2S</u> used coating deposition parameters calculated with MD in atomic lattice models to calculate dislocation generation and crack nucleation and growth in the coating materials.

<u>MODIFY</u> calculated flow characteristics by using information from the atomistic simulations to parameterize a statistical mechanics model based on a particle- coarse-grained picture of the latex particles.

<u>MORDRED</u> used first principles simulations describing the atomic and electronic structure of the sources of fluctuations (discrete dopants, localised defects, interface roughness, body thickness,

composition, strain, structure variation) in oxide interfaces to parameterise hierarchical device simulations in order to predict realistically intrinsic fluctuations in CMOS devices.

<u>NAMASTE</u> used some of the results of the atomistic calculations, including the magnetization, magnetic anisotropy constants, spin stiffness, and Gilbert damping parameter as inputs into the phenomenological Landau-Lifshitz-Gilbert micro-magnetic simulations of various magnetization dynamics phenomena of relevance to the devices studied in the project.

<u>ONE-P</u> modelled the charge mobility in the bulk of organic semiconductors. On the basis of a generated morphology, first the rate of charge hopping between two molecules is computed by evaluating at the quantum-chemical level the relevant parameters (transfer integral, reorganization energy, energetic disorder). In a next step, the rates are injected into Kinetic Monte Carlo simulations to propagate the charge carrier(s) and estimate the mobility from the total distance travelled during the time of the simulation.

In <u>ORAMA</u> the multifunctional oxides structures resulting from molecular dynamics simulations at the atomistic scale have been fed into mesoscopic models that solve the Boltzmann transport equation for the description of gas flow phenomena by means of Direct Simulation Monte-Carlo (DSMC) techniques. With self-consistent electric field computation that approach is extended to Particle-in-Cell Monte-Carlo Techniques (PIC-MC) for plasma phenomena.

5.1.7 Linking of atomistic models and continuum mechanics

<u>AUTOSUPERCAP</u> applied classical molecular dynamics model to calculate geometrical parameters (ion size and limiting pore size) of different ions, solvated and unsolvated in various solvents. These were used in continuum flow models for the infiltration of ions and electrons into the porous carbon structure during the operation of the energy storage device.

<u>CODICE</u> used the knowledge of the structure generated with atomistic MD models in micromechanics fracture model predicting the elastic modulus and tensile strength of cementitious skeletons.

<u>GRENADA</u> use mechanical, magnetic and electrical properties of materials calculated with abinitio molecular dynamics in continuum mechanical modelling to find the morphological properties of graphene based flakes and to study the transport in multilayer graphene (with and without defects) in media of variable polarisability.

<u>HIPERSOL</u> has calculated diffusivities of Ag and other elements in different silver pastes (glasses) with first principles molecular dynamics and used this as input to a phase-field model (with Gibbs free energies taken from a thermodynamic database) of transport of silver through a glass layer.

<u>HYMEC</u> uses diffusivities calculated with atomistic statistical mechanics models in a continuum model simulating electrical characteristics of steady-state transport in the two different conduction states.

<u>MACADEMIA</u> used the selectivity and transport properties of different MOF materials with respect to the different liquid and gas mixtures calculated by the GCMD and MD in thermodynamic and flow models.

<u>MINOTOR</u> used outputs from quantum-chemical calculations to feed into electromagnetic models applied at very small scale (micro-electrostatic models) to determine the energy landscape of the charge transport levels in molecularly doped organic semiconductors.

In <u>MINTWELD</u> micro-scale Phase Field modelling is used obtain a complete picture of microstructure and defect (e.g. cracking) formation in the welding process, as illustrated in Fig 1. Atomistic molecular dynamics simulations provide the structure of the interface and its thermodynamics properties as input. The predicted results on transformation kinetics and interface morphology are fed to grain-scale models; the calculated chemistry and crystal orientation and stress can be used as input for molecular dynamics modelling.

<u>MODIFY</u> calculated flow characteristics with information from the atomistic simulations used to parameterize a continuum rheology model using the Pom-Pom tube constitutive equation. Furthermore non-equilibrium thermodynamics (phase fields) were applied to mixed systems consisting of bulk regions and interfaces where atomistic displacements of the interface calculated with atomistic models were taken into account which calculates molecular structural changes upon stretching, which computes the entanglement network. The outcome of this effort has been a new type of boundary condition for elastic polymers strongly adhered on hard substrates.

<u>MULTIHY</u> will employ novel constitutive equations for hydrogen diffusion and trapping that are informed by atomistic descriptions of the occupancy of different trap sites with respect to lattice concentration and their effect on the overall diffusion rate, there by enabling use of atomistic results at the continuum level.

<u>MUST</u> used molecular mechanics for modelling of the limiting adsorption of organic anticorrosive or hydrophobizing agents. This information is then used as the boundary condition for the transport(diffusion) equation to determine the critical concentration of agents in capsules and of capsules in multifunctional coating necessary to achieve protection of the damaged surface. Similar methodology was used to predict surface activity (i.e. determine the hydrophilichydrophobic ratio) of selected compounds with silanol groups, which can be used to built the silica shell around the capsule core. In addition the MD simulations of the L-b-L formation of polyelectrolyte shells allow determination of its porosity, which enters as a parameter for prediction of the release rate of anti-corrosives from capsules.

<u>NANOINTERFACE</u> bridged length scales between atomistic and continuum by re-casting the data obtained from MD simulations within the framework of continuum cohesive zone model (CZM) to quantify the cohesive zone law. Atomistic simulations on the epoxy resin were conducted to compute its material properties, and interfacial interaction energy on its interfaces with copper and cuprous oxid and roughness. These were input to micromechanics models to establish cohesive/adhesive interfacial delamination criteria under external loading. The molecular dynamics model also gave material properties, including densities, glass transition temperature, volumetric coefficient of thermal expansion and isotropic mechanical properties and constitutive equations for interfaces between a 2D polymer network and copper as well as cuprous oxide.

<u>NANOMODEL</u> linked Molecular Dynamics and Continuum Mechanics models. They are closely connected, via forward and reverse mapping schemes.

<u>ORAMA</u> used the Statistical mechanics (Boltzmann) transport equation for the description of gas flow phenomena as atomistic level and used the diffusivities extracted in the continuum fluid flow models.

<u>POCO</u> used MD to calculate constititutive eqs for elastic properties and interface energy and used this in continuum mechanical models

<u>SIMBA</u> is using the atomistic statistical mechanics Boltzmann kinetic gas equation to calculate plasma thermodynamic and transport properties needed in CFD simulations.

<u>SMASH</u> is linking micro solid mechanics, continuum drift-diffusion, kp band structure and electromagnetics for nanorod LED simulation. The data transfer mechanism between solid mechanics and kp band calculation is displacement data on a mesh. Kp calculation and drift diffusion is iterated self-consistently. Drift-diffusion hands over optical generation data to electromagnetics.

<u>SYNAPSE</u> uses thermal conductivity and crystallisation rates calculated with atomistic Molecular Dynamics models in continuum for coupled electrical and thermal behaviour.

5.1.8 Linking of mesoscopic and continuum mechanics

<u>DYNAMAG</u> used the output of micromagnetics models (the spin wave spectra and dispersion in multilayer structures andf relative dynamics of different sublattices in antiferromagnetic and ferrimagnetic materials) in models of electromagnetic absorption and emission in magnetic nanomaterials.

<u>MAGNONICS</u> micromagnetic simulations results describing the behaviour of thermally excited spin waves in planar one- and two-dimensional magnonic crystals have been used in the electromagnetics plane wave method (PWM) for the calculation of magnonic band structure and the calculation of magnonic spectra of thin slabs of 1D and 2D magnonic crystals consisting of arrays of dense magnetic elements (dots and stripes) and antidots (periodic arrangement of holes embedded into a continuous magnetic film).

In <u>MINTWELD</u> macro-scale CFD modelling is taking into account a wide range of predicted thermal and grain structure information of welded interfaces to relate the process variables to the properties of the weld pool. The dynamics of welding interface evolution is being solved to give the local chemistry and the flow of molten liquid in the weld pool, through linking the macro-scale models with the mesoscopic solidification model. Grain scale (Mesoscale from cm to tens of μ m) models are being used to model grain structure evolution, such as grain size and distribution, and local solidification profile (e.g. mushy zone) for macro-scale computational fluid dynamics (CFD) modelling of weld flow; predicted thermal and grain structure information is used as input for micro-scale continuum modelling, as shown in Figure 1.

<u>MUST</u> uses the DPD modelling in parallel with the continuum modelling of transport of anticorrosive or protective agents in the cracked coatings to determine the values of effective parameters used in continuum approach. The solution of diffusion equation in inhomogeneous media, based on the lattice gas model and finite differences were elaborated. Finally the one dimensional diffusion equation describing water (or ions transport) in the effective medium was derived using the values of the effective parameters devised basing on the discrete 2D and 3D approach. In the model various triggering mechanisms of the release of inhibitor from containers as concentration thresholds of corrosive ions or corrosion products were considered. Single and multilayer coatings were simulated with the arbitrary distribution of water, ion traps and inhibitor containers. <u>NANOMODEL</u> starts with coarse-grained Molecular Dynamics models and transfer s structural (thermo-mechanical and failure) information to continuum scale. These CGMD models also provide metal-oxide-polymer adhesion properties describing the relevant dissipative mechanisms that affect adhesion, including the underlying microstructural mechanisms and these are use in continuum micromechanics and flow models. Also the mesoscopic transport equations Dissipative Particle Dynamics are used to provide input for these continuum models.

<u>NANOPYME</u> used micromagnetic modeling of thin films, bilayers and two-phase nanocomposites to study magnetisation processes like hysteretic behaviour. These are used in finite element simulations of devices (e.g., electric motors) to predict magnetic performance of NANOPYME magnets in operation conditions.

5.1.9 Linking between different continuum models

<u>ARTIVASC-3D</u> uses micro CFD to generate deposition rules to be used in macro CFD.

<u>DISC-REGENERATION</u> modelled vascular transport models using a poromechanical model coupled to a diffusive transport model to study the effect of mechanical and nutritional factors on the diffusion of two fundamental cell solutes, oxygen and lactate, strongly related with disc cell metabolism.

Within <u>DYNAMAG</u> and <u>MAGNONICS</u>, micro-magnetic simulations are run to determine magnetic response of nanostructured materials (mainly resulting from magnonic responses). The output is used to calculate magnetic susceptibility of the magnonic meta-atoms. Using appropriate homogenisation procedures, the susceptibility is then used to calculate the magnetic permeability of corresponding magnonic metamaterials, which is then used with Maxwell equations to explore how electromagnetic waves propagate in such metamaterials.

<u>HIVOCOMP</u> uses micromechanics models for mechanical deformation and shrinkage to get the description of resistance of the hybrid (carbon/self reinforced PP or PA) preform to deformation and shrinkage during thermoforming. The models will produce material constitutive equations to be used in the macro-modelling of forming.

<u>LIGHT.TOUCH.MATTERS</u> uses a hybrid of continuum mechanics (either solid or fluid) and electromagnetic models. The effective dielectric constant of a composite material is calculated and its dependence on different deformation modes of the composite (e.g. bending versus torsion, or bending versus compression) and the model will calculate which material shows this anisotropy.

<u>LISSEN</u> couples chemical and microstructural models to simulate battery cells. The morphological parameters of cathode and anode, needed for single-cell reactive-transport models (e.g. volume fractions of the components, volume-specific surface areas and phase boundaries) will be obtained by interpreting results from 3D microstructural modeling of the porous electrodes and by geometrical considerations of structural changes of individual pores, particles, or particle agglomerates.

<u>MATRANS</u> used effective thermomechanical properties calculated with continuum micromechanical models (modelling of wear, including shape evolution and coupling with oxidation) in continuum macromechanics models. These were transported as phenomenological constitutive equations for materials behaviour (processing induced thermal residual stresses and material damage; static and dynamic fracture; thermomechanical fatigue).

<u>METACHEM</u> is linking the response of structured media with equivalent parameters of homogeneous media. They link equivalent permittivity representations at bulk material level with full-wave continuous-domain simulations. Those in turn are linked with equivalent-parameter representations for structured media.

<u>MUST</u> uses the large scale modelling of transport of anticorrosive or hydrophobizing agent to the damaged area in the protective coating together with statistical analysis to determine probability of achieving satisfactory corrosion protection at a given concentrations of capsules and agents in capsules (i.e. the technical risk analysis of "not performing").

<u>NANOINTERFACE</u> is linking solid mechanics with chemistry models to describe the thermomechanical and failure behaviour of epoxies, copper, copper oxides, and the respective interfaces. The data transfer mechanism involves thermo-mechanical and failure properties by means of sequential coupling.

<u>NEXT-GEN-CAT</u> is coupling fluid flow characteristics of exhaust gases within a real catalytic converter with the equations derived from the mass and energy balances.

<u>SYNAPSE</u> uses coupled electro-thermal models based on Poisson's equation for electrical conductivity and Fourier's heat law, which can be tailored to fit different materials (In-Sb/In-Te, In-Sb-Te) and architectures (confined cell PCM, free-standing NWs, confined NWs).

<u>RADINTERFACES</u> calculated micromechanics damage and hardening constitutive eq and used them in macromechanics models.

<u>YBRIDIO</u> will link electromagnetic, thermal, mechanical models at continuum level to predict Joule heating temperatures, thermal fields, cooling behaviour, pressure requirements for consolidation, magnetic fields, electric fields, Lorentz forces, thermal expansion/deflection of joined dissimilar materials. All physics equations are solved in a coupled model within each completely independent FEA code. There is no need for data transfer between the two codes.

5.1.10 Linking of flow models with thermo-mechanics

<u>DISC REGENERATION</u> coupled mechanical deformation of the disc with diffusion and convection of small solutes within the disc and vertebra.

<u>FREECATS</u> used a CFD code with kinetic equation results as boundary conditions and micro-model for heat conduction (mm scale) to resolve macroscopic heat, mass, momentum transport in boundary layers near catalytic surfaces.

5.2 Numerics

In the fiches (Annex 1) hints are given of the specific numerical features of the simulations done. We would like to highlight a few of them, but for the details the reader is referred to the specialised literature.

5.2.1 Discretisation

Discretisation methods are used to allow numerical solving of the governing equations and these include

- Finite difference methods
- Finite volume methods
- Finite element methods or analysis (FEM or FEA)
- Spectral element methods
- Boundary element methods

In all of these approaches the same basic procedure is followed:

- 1. During preprocessing
 - a. The geometry (physical bounds) of the problem is defined.
 - b. The volume occupied by the material sample is divided into discrete points or cells (the mesh). The mesh may be uniform or non uniform.
 - c. The physical modeling is defined for example, the equations of motions + enthalpy + radiation + species conservation
 - d. Boundary conditions are defined. This involves specifying the fluid behaviour and properties at the boundaries of the problem. For transient problems, the initial conditions are also defined.
- 2. The simulation is started and the equations are solved iteratively to converge to as a steadystate or to describe transient situations.
- 3. Finally a postprocessor is used for the analysis and visualisation of the resulting solution. Extraction of data for further model can be done.

<u>CODICE</u> developed a novel digitalization model that generates a 3D voxel structure of the virtual microstructure and can be used for information exchange within the run of each time step. This new model employs as input macroscopical processing variables, such as the cement grain size, the water/cement ratio, etc. and gives for each voxel relevant information like density, relative humidity, saturation, chemistry, etc.

<u>MODIFY</u> developed a powerful finite-element code for the full three-dimensional (3-d) simulation of the deformation of acrylic adhesives. It is based on a consistent coupling of an elliptic-mesh generation methodology with domain decomposition and local mesh refinement around deforming and moving interfaces. The transport code can follow the large adhesive and bubble deformations inside the material (which lead to fibrillation); it can also trace the elastic boundary layers that form at the moving interfaces. It can therefore reliably simulate the force-deformation history of the material under industrially relevant conditions.

<u>NANOINTERFACE</u> has obtained interchange between Molecular Dynamics and continuum mechanics by creating a finite element "boundary" around the Molecular Dynamics boxes and defining so-called "anchor atoms" reaching into the "boundary". The anchor atoms are part of the polymer chains within the MD domain. In the continuum domain, they are coupled to the finite elements and moved along with their displacements.

<u>NANOMODEL</u> has developed numerical techniques for Molecular Dynamics models to do a coarse graining of the nanocomposit. . They impose stochastic boundary conditions with a dissipative particle dynamics thermostat on the grains. I information on forces and positions is then transfreed via fixed anchor points.

<u>Smoothed-particle hydrodynamic (SPH) calculations</u> are a computational method used for simulating fluid flows. The smoothed-particle hydrodynamics (SPH) method works by dividing the fluid into a set of discrete elements, referred to as particles. These particles have a spatial distance (known as the "smoothing length"), over which their properties are "smoothed" by a *kernel function*. It is a mesh-free Lagrangian method (where the coordinates move with the fluid), and the resolution of the method can easily be adjusted with respect to variables such as the density.

Smoothed-particle hydrodynamic model has been used to predict wall shear stresses at the vascular graft walls (<u>ARTIVASC-3D</u>).

5.2.2 Statistical methods to solve differential equations

Statistical methods, like the Monte Carlo method, can be used to solve efficiently equations with very large sparse matrices.

The Monte Carlo method was used in many body quantum mechanical models to evaluate the governing matrices by sampling the, then evaluating the energy expectation value and minimising it. The Quantum Monte Carlo method starts with a direct representation of the many-body wave function. The Hartree-Fock approximation can be used as starting point of the many-body wavefunction and then be multiplied by any symmetric function designed to represent the correlations (GOFAST, MONAMI).

Quantum Monte Carlo methods have been used to derive a DFT exchange-correlation functional which was used in molecular dynamics to calculate adsorption of light-weight hydrogen (<u>HYPOMAP</u>) and to calculate thermodynamic properties of single and double perovskites many body Hamilton problem at finite-temperature problem (<u>ATHENA</u>).

5.2.3 Accelerated simulations in molecular dynamics

The main problem of standard molecular simulations is that the time of the simulation sampling is often not long enough to ensure complete statistical sampling (ergodic theorem not valid, see Chapter <u>2</u>). For example, "centuries" on their available supercomputer would be needed to simulate 1s of "a day in the life" of a polymer. For this reason, calculating free energy, reaction pathways and rare events may be not possible using standard molecular simulations. Advanced methods have thus been developed to increase the efficiency of the sampling and to obtain a more accurate answer in a limited amount of time, e.g. temperature accelerated molecular dynamics, metadynamics and kinetic Monte Carlo.

<u>Accelerated Molecular Dynamics (AMD)</u> and <u>Metadynamics</u> are methods to increase the sampling in Molecular Dynamics simulations. Accelerated molecular dynamics (AMD) tricks MD into reducing the separation of timescales between fast and slow components of the dynamics and renormalizes the MDtime accordingly. Metadynamics is an artificial molecular dynamics method performed in the space defined by a few collective variables, which are assumed to provide a coarse-grained description of the system.

<u>Kinetic Monte Carlo (KMC)</u> is a stochastic computational procedure that generates statistically correct state-to-state trajectories. It is based on the assumption that **all** transition pathways are known (input) and then generates a correct state-to-state trajectory (output) by randomly selecting pathways with a probability proportional to their rate.

Accelerated simulation methods and kinetic Monte Carlo have been used to calculate diffusivities of charge carriers, band structure calculations for up to 10000 atoms (<u>HIPERSOL</u>) and to calculate adsorption including quantum effects of light-weight hydrogen (<u>HYPOMAP</u>). Metadynamics will be employed to study slow migration processes or migration involving a large and complex energy surface in conducting oxides and oxide-based junctions (<u>IFOX</u>).

5.2.4 Post-processing and extraction of parameters

Models will produce values at many points in space and time and these results might have to be reduced into values representing a larger area. Post-processing is concerned with homogenisation for further use of the data in coarser models and in visualising the results or in the generation of constitutive equations.

<u>DYNAMAG</u> and <u>MAGNONICS</u> are using SEMARGL for post processing and data transfer, notably for covering the results of simulations performed in the time and real space domain to the frequency and reciprocal space domain.

<u>FEMTOSPIN</u> Is developing interfaces to transfer ab-initio information from various packages into atomistic codes and to transfer atomistic information into mesoscopic codes

<u>METACHEM</u> and <u>NIM-NIL</u> are calculating the EM field at many points in space and from these scattering, transmission and reflection parameters have to be extracted. Further processing is done into negative refractive indexes but the value of this notion is currently subject to debate.

<u>ROMEO</u> creates a database with spin-polarised DFT results and will use high-throughput descriptors which will allow rapid screening of the database. The descriptors will help identify promising materials. Convex Hill diagrams will be used against the ICST database, which will establish whether or not a material is thermodynamically stable.

<u>SIMBA</u> has developed software with which to describe nanopowder nucleation out of the gas phase. This is an aerosol model tracking the particle size-distribution and particle population in the reactor region and gives the precursor particle thermal history and trajectory prediction. The software then calculates the process yield.

<u>SYNAPSE</u> is developing interatomic potentials from a DFT database by fitting with the help of a Neural Network approach.

ThyssenKrupp in <u>MULTIHY</u> uses statistical models (mainly based on multilinear regression) to process data from the production process and relate the process parameters to the mechanical properties of the produced coil. The statistical models help to optimize the steel production processes and the properties of the produced strips.

5.2.5 Databases

Models that are not worked up from quantum mechanical (ab-initio) principles need values for the parameters used in the model. Huge databases are created for each class of compounds in any medium (environment). These contain e.g. potentials parameters (e.g. for classic force fields) to use in electronic and atomistic models, polymer properties and thermodynamic phase diagrams for micromechanical modelling.

The creation and use of these databases is often a commercially sensitive topic and is not the subject of this document.

Chapter 6 Model Development

6.1 Modelling of fundamental equations

In the introduction chapter the definition of models and of model development was given. The following projects added physics and/or chemistry to existing models.

ARTIVASC-3D

This project developed of a new equation to describe clogging and deposition of blood platelets.

<u>ATHENA</u>

This project developed first-principle models for complex oxides: DFT extended with variational formulation of the pseudo-self-interaction correction scheme (pSIC) new version of DFT exact exchange model new hybrid Hartree-Fock DFT method combining DFT with dynamical mean-field theory (DMFT)< describing what?>

AUTOSUPERCAP

Fast charge and discharge behaviour in a new model for the behaviour of battery-super-capacitor (or battery only) power systems.

CODICE

This project developed a new micro-level model for individual hydration of cement grains (HYMOSTRUC-3D). Also a novel Monte Carlo growth scheme to calculate aggregation of dried C-S-H particles was created, which provides a better insight than the existing phenomenological models. The degradation model (CODICE_DEG) is a novel toolkit which solves the Nerst-Planck set of equations over a voxelized microstructal piece of cementitious material. By selecting sufficiently large voxels (but still within the nano-range) the code exploits the fact that the decoupling of the transport and chemical reaction equations is feasible. It enables to monitor the microstructural changes that take place along the degradation process.

A new fracture model enables virtual mechanical testing (e.g. tensile strength evaluations). It is based on a lattice beam formalism specifically adapted to the case of cement structures.

<u>CRONOS</u>

The project will make new descriptions of photo-energy conversion (combined electron-ion dynamics) and laser-induced ultrafast magnetisation dynamics. CRONOS will contribute to the development of TDDFT along four directions:

- o development of new DFT and TDDFT meta-GGA exchange and correlation functionals
- development of new spin non-collinear DFT and TDDFT exchange and correlation functionals
- $\circ~$ development of method to combine non-adiabatic ionic dynamics with time-dependent $\ensuremath{\mathsf{DFT}}$
- o development of optimal quantum control theory for TDDFT

<u>DYNAMAG</u>

Spintronic and thermodynamic aspects were added to an existing micro-magnetic model. Also the relative dynamics of different sub-lattices in ferri-magnets and antiferro-magnets and new spin-transfer torque mechanisms have been added to this existing model.

FEMTOSPIN

Optical spin manipulation and light induced magnetisation processes involving interactions between spin, conduction electrons and laser light have been developed in a new femto-scale model for exchange, spin-orbit coupling and spin-flip scattering, that can describe non-equilibrium spin-scattering (energy and spin transfer). The project developed a LLB equation for ferrimagnetic materials and parameterisation using atomistic models the new version has two sublattices to represent ferrimagnets and antiferromagnets. The two sublattices give very different dynamics and allow exchange modes which we believe explain the thermally driven magnetisation reversal. Development of an entirely new 'heat bath' approach, in which the thermally excited heat bath (for example, the conduction electron population) is simulated and coupled directly to the spin system. A model based on the multiband Hubbard Hamiltonian to calculate exchange in disordered systems is also developed.

<u>GOFAST</u>

The project will develop a model to describe the temporal evolution after being driven out of equilibrium by high-energy excitations (photo-injection by ultrafast laser pulses) in correlated materials (conduction in Mott insulators and superconductivity in cuprates.

<u>HIPERSOL</u>

HiperSol developed two completely novel schemes for the calculation of recombination rates. The first approach is based on Fermi's golden rule. Envelope functions are fitted to band structures obtained from first principles calculations of structures containing different kind of traps (e.g. strongly localised K-centres in the silicon nitride with Si atoms bounded to three N atoms instead of four). Also a model will be developed to obtain Auger recombination rates (the most important non-radiative process in semiconductors) from k-point interpolation of orbitals and eigen-energies using Gutzwiller techniques.

<u>HYPOMAP</u>

QLDFT (Quantum Liquid Density Functional Theory) was developed because there was no adequate modelling method for the adsorption calculations on the market that included the quantum effects of light-weight hydrogen. QLDFT is an atomistic model that can be used to describe physisorption and loading/unloading of physisorbed hydrogen including quantum effects and hence is a fundamentally higher-level treatment. It uses the same formalism than electronic DFT, but instead of electrons it describes H2 molecules which obey a Boltzmann statistics (rather than a Fermi statistics that holds for electrons).

<u>LEMSUPER</u>

Many-body techniques for metal-insulator interfacesexist (e.g. Dynamical Mean Field Theory (DMFT) but generally assume spatial uniformity. The project will develop models able to describe inhomogeneous situations and will apply these to surface doping.

This may be done by assuming that the electron self-energy depends, besides on the frequency, also on the layer depth below the surface plane. Dividing the space below the surface into layers the self-energy will be calculated by solving an auxiliary impurity model for each layer in which the conducting bath depends self-consistently on the fully interacting impurity Green's functions not only of that given layer, but also of the nearby ones. The effect of many body interactions beyond mean-field levels in picene and similar molecular systems will be added to the models. Improvements to the modeling of new superconducting materials will include Gutzwiller correlations, applying a method recently developed (before Dynamical Mean Field Theory).

<u>MONAMI</u>

The project developed a theoretical technique for calculating the effect of electron-electron correlations. The developed models are an elaboration of existing models to make the theory general to treat complex crystal structures like that of V2O3.

Non–Newtonian dynamics (temporal evolution of a system of classical objects) are incorporated in UppASD package for spin-dynamics in order to describe the behaviour of nano-sized magnetic systems of particular symmetries.

Also an extension was made to allow accurate and fast calculations of ground state properties of solids by incorporating tail cancellation of orbitals. This is base on physical insight in how electrons move around in solids, and how to best describe their quantum mechanical equation of motion. In the model developed in *MONAMI*, several conceptual steps and mathematical derivations have been made to come to a set of equations which enable a numerical implementation.

<u>MORDRED</u>

Models have been developed for statistical impact of bias temperature instabilities and hot carriers on the electrical characteristics of CMOS transistors. Also a model for the impact of local defect generation on dielectric gate leakage current is developed.

<u>NAMASTE</u>

The project has implemented relativistic corrections (i.e. spin orbit coupling) to the band structure calculations of diluted ferromagnetic semi-conductors (DMS). (no codes to do so existed yet). They have subsequently used these tools to: a) describe the magnetic anisotropy of DMS, b) explore how magnetization and anisotropy change either varying the total electron carrier density or strain acting on the films/nanostructures; c) predict a new batch of antiferromagnetic metals with strong spin orbit coupling (antiferromagnetic materials for spintronics) and d) to describe single electron transistors.

NIM NIL

A EM model was developed to describe the dissipative loss in resonant electromagnetic metamaterials. The model takes into account the radiation damping of the resonant currents, which is necessary to model metamaterials made from low-loss conducting materials. This model led to an identification of which conducting materials are useful for metamaterials. Silver was found to be the best conducting material at optical wavelength. Graphene was ruled out.

<u>ONE-P</u>

The project developed a methodology to model the triplet energy transfer at the molecular scale from quantum-chemical calculations to end up with exciton diffusion length using Kinetic Monte Carlo.

<u>OXIDES</u>

This project has developed models using pSIC and B1-PW wave functions.

RADINTERFACES

Irreversible processes leading to material damage taking place under irradiation described by a new hybrid kinetic Monte Carlo-Molecular Dynamics model. This Object Oriented kinetic Monte Carlo (OKMC) method allows to follow the evolution of individual defects (i.e. vacancies, interstitials, He and their clusters) by listing all possible reactions and paths that a given defect could follow and choose the most probable one based on a statistical method (allowing the use of longer time step). All possible events are quantified using migration energies, formation energies (leading to binding energies). These energies are quantified using Nudged Elastic Band method in Molecular Dynamics.

A damage accumulation model is also developed based on differential equations to describe the thermodynamic and kinetic response of the synthesized materials to microstructural features. This

is a 3 Dimensional Cluster dynamics model -where transport and reactions in the form of absorption and emission of defects are taken into account. In this model, rather than following individual defects within the nanloayered system, defect quantities are followed as densities. This leads to a great decrease in the amount of information (i.e. defects) to be followed which then allows to simulate the evolution of defect for long time scales.

<u>SIMBA</u>

An existing model for plasma fluid-dynamics for nanoparticles production has been extended to simulate non-equilibrium plasma allowing low pressure operating conditions and strong temperature gradients due to the quenching system.

ULTRAMAGNETRON

Basic physics for opto-magnetic reversal process have been added to an atomistic Heisenberg model. These describe the thermal processes involved.

The single-macro spin Landau-Lifshitz-Bloch model was extended into a multi-macro spin model taking the exchange coupling as well as the dipolar interaction into account.

6.2 Modelling of constitutive equations

<u>MATRANS</u> developed a new constitutive model defining the relationship between tensile strength of functionally graded materials (FGMs) and volume fraction of ceramic phase has been developed to simplify complicated mechanical behaviour of FGMs.

In oxidation modelling a new constitutive relation has been proposed between the oxide growth rate and the surface temperature. Since the calculated macro temperatures are too low to allow for the oxidation, only closer look at surface asperities can provide the mathematical model for the experimentally observed oxidation phenomena. A user-defined FORTRAN code for the developed constitutive relation has been added to a commercial FE software.

<u>MODIFY</u> developed new macroscopic constitutive equations capable of describing quite reliably the deformation equations (e.g. the shear and elongational behaviour) of the synthesized PSA materials. The new equation utilizes generalized expressions for the strain energy density as a function of the three invariants of the conformation or deformation gradient tensor. In limiting cases, it reduces to known laws widely used to describe hyper-elastic materials, such as the Rivlin-Saunders and Hart-Smith theories.

<u>MULTIHY</u> has developed macroscopic models based on novel set of constitutive equations for H diffusion capable of exploiting the information being derived from the atomistic calculations. The equations are more generalised than those commonly used in the literature, enabling the description of hydrogen diffusion under a broader range of conditions (e.g. temperature variations, trap occupancies) as before.

<u>POCO</u> developed an electro-dynamics constitutive equation relating the polarisability of the CNTs, the electric field applied and the viscosity of the polymer with the torque.

<u>ROLICER</u> extended existing models that treat damage and fracture in silicon nitride to include under cyclic contact loading based on the behaviour of the solid phases and boundaries phases.

Chapter 7 Modelling applications

Modelling in the projects considered cover 7 main areas of application: Energy, Information and Communication Technologies (ICT), Health, Environment, Construction, Manufacturing, and Transport. Projects have been defined cross-cutting if they can be applied to more than one sector. The variety and frequency of models have been applied in each of the sector are illustrated inFig. 7.1.



Fig. 7.1 Bar chart of the models used in the different application sectors.

Each fragment corresponds to a model type and the color code is in the legend. The size of the fragments is proportional to the number of projects in that sector using that model type.



Fig.7.2 shows the number of projects per sector that are using the different models.



Fig 7.3 The number of projects developing linking of models describing the same entity (multiphysics) and for different entities (multiscale) per sector.

Chapter 8

Impressions of Industrial modelling

The NMP Programme has as objective to support the industry. This chapter presents how companies involved in NMP Materials projects are using models.

Please note that these are impressions and <u>not</u> necessarily a complete account of what these companies do.

8.1 Industrial areas

The responding industries are operational in the following industry sectors: chemical, materials research (BASF) transport (BMW) energy efficient, gas-free refrigeration and cooling technology (CAMFRIDGE) near net shape composite technologies for aeronautics (COEXPAIR) polymer manufacturing (DOW) aeronautic and space industry (EADS) magnetic material (IMA) magnetic and optical systems, crystal growth (INNOVENT, magnetic and optical systems) Chemicals, energy, catalysis, environment, manufacturing, health (JOHNSON-MATTHEY) chemicals and polymer manufacturing (LYONDELL-BASELL) chemistry (MERCK) automotive transmission systems (OERLIKON DRIVE SYSTEMS) manufacturing of ICT devices (OXFORD INSTRUMENTS) manufacturing of ICT devices (PHILIPS) risk technologies (RISK-TECHNOLOGIES) cutting tools for grinding, milling and drilling (SANDVIK COROMANT) data storage (SEAGATE) chemicals, processes, materials research (SOLVAY/RHODIA) solar energy (SOLARONIX) steel manufacturing (TATA STEEL) steel manufacturing (THYSSEN KRUPP) manufacturing of oxide nanoparticles for catalysts (TECNAN) energy, security (explosion), manufacturing (TOTAL) materials technology / chemistry / material sciences (UMICORE) car manufacturing (VOLKSWAGEN)

8.2 Type of models used

The models used span all classes of modelling (electronic to continuum modelling)

8.3 The reason why industry uses modelling

BASF uses modelling as it offers unique insight and modelling is considered to allow for faster development cycles (guide to experiments, interpretation of experiments).

BMW wants to reduce development time, development cost and hardware for testing.

CAMFRIDGE states that modelling helps them design their products more quickly.

COEXPAIR is using modelling to design composite parts for aeronautics applications by analytical and numerical calculations and models. They so ensure that the composite part can withstand the loads occurring during flight of the aircraft.

DOW uses modelling as it speeds up development of new products and provides insights into application properties of materials.

EADS wants to gain process knowledge, shorten lead time, replace time and cost expensive trials.

IMA uses magnetic simulations to help them design prototypes for magnets and choose the optimum dimensions, materials.

INNOVENT uses modelling as it is often the only available mean to understand intrinsic properties and behaviour of magnetic, optical and semiconducting materials and it saves time and money when designing new device prototypes.

JOHNSON-MATTHEY uses modelling to aid understanding and guide experimental work. Simulation offers a faster and cheaper method of designing systems, than an experimental "traial and error" approach.

LYONDELL-BASELL predicts final product properties and performance with modelling. They also limit experimental cost and minimize time to develop new products, understand and control industrial processes.

MERCK predicts specific material properties as a form of pre-screening.

OERLIKON predicts the effect of the transmission system design on vehicle performance and energy efficiency with modelling.

PHILIPS uses models to understand the underlying physics of devices and processes; to optimize product designs and processes, to shorten development and qualification time and to decrease the time-to-market.

RISK-TECHNOLOGIES use multi-scale modelling of corrosion protection for new materials, testing and optimisation of new materials and new devices.

SANDVIK COROMANT uses models to gain deeper understanding of the materials properties of i.e. hard cutting tools and to enable faster development of new products. FEM modelling of the cutting tool process is used to save time in machining tests and to better understand the wear behaviour of the cutting tool. One common method is the prediction of phase diagrams (ThermoCalc), but also, the energetics and geometry of metastable compounds or compounds where no/little experimental data exists can be calculated by first principles software such as VASP, Phonopy etc. CFD and other methods are used to simulate synthesis processes in order to save time and improve understanding of these processes.

SEAGATE uses modelling as it reduces time to learning and allow them to determine if a design concept works without having to build it.

SOLARONIX states that modelling helps to optimize solar equipment. Modelling helps screening new materials by discarding the ones that are not compatible seen their energetic levels.

SOLVAY/RHODIA uses modelling to catalyse and support all stages of its innovation processes and to continuously improve the operational performance of its production technologies. Modelling is a key part in SOLVAY/RHODIA to understand, predict, design, optimize and control, which highly complements experiments.

TATASTEEL have been using modelling through the years in various R&D activities, such as materials design, processing route selection and optimisation. Recently, they have benefited from their weld modelling and simulation exercises in terms of understanding and control of weld induced residual stresses and distortion, as well as avoidance of formation of unfavourable microstructures in critical areas such as heat affected zone. They also use modelling to complement our physical experiments and generate inputs for engineering critical assessment work of structures in service.

TECNAN uses models to anticipate the properties of the materials to be created and reduce the time and materials spent on trials.

THYSSENKRUPP uses modelling as it improves the understanding of physical mechanisms and effects determining the materials' properties, for the optimisation of production processes and in order to provide improved material models describing the properties of new steels in industrial applications (i.e. forming, crash, etc.).

TOTAL uses modelling to understand the behaviour of certain materials under well-controlled conditions and to study physic-chemical properties of compounds, thermodynamics, CO2 storage, new active compounds (polymers and lubricants, etc.) for interface activities.

UMICORE uses modelling as it can speed up considerably the design time for new processes (faster screening of alternative designs). It helps to optimize the efficiency and performance of processes by giving a more thorough insight in the physics involved, which will facilitate the debottlenecking. The use of modelling can also help to reduce the number of required experimental tests, thereby reducing the overall costs.

VOLKSWAGEN is using modelling to get a deeper insight into the battery cell behaviour.

8.4 Industrial use of models for new materials

BASF uses these models for rapid screening and simulated tests of quantum chemistry (reaction mechanisms, kinetics, photo-physics, new chemistries), complex liquid mixtures (formulations) and organic semiconductor properties (e.g. exciton or charge carrier mobilities). They are working on homogeneous and heterogeneous catalysis (mainly quantum chemistry) quite extensively! Also theoretical thermochemistry is an important topic (including high level methods like CCSD(T)). We are also using Hybrid-QM/MM-approaches for catalysis (mainly enzymatic reactions) from time to time and there is now some revival of these methods with respect to organic semiconductors. Besides that theoretical photochemistry/photo-physics is an important topic.

DOW uses materials modelling going from molecular structure to processing and end-use properties, and back. They do fundamental modelling of reaction mechanisms, rheology, interfacial behaviour and self-assembly; rational design of formulations.

EADS: newly developed alloys lack a proper description in terms of constitutive laws necessary for FE simulation studies. EADS uses new and self developed models to validate such new materials and get more insight into its behaviour during manufacturing operations.

INNOVENT does simulations of static and dynamic behaviour of patterned magnetic films and magnetic nano-composites in order to understand the results of corresponding measurements and predict the properties of new magnetic materials. They also use (home-made) software for simulating dislocation dynamics in crystals.

JOHNSON-MATTHEY does simulations of new alloys for fuel cell and electronic applications. They also do modelling of chemical reactions to predict the reactivity of their catalysts. These models can locate molecules within porous materials and provide understanding of diffusion and adsorption. This is used for automotive emissions after treatment systems and emission control catalysts.

LYONDELL-BASELL calculates material parameters from rheological and other physical tests, predict rheological properties from chemical structure, compare theoretical predictions to experimental results.

MERCK uses materials models for the estimations of electronic energy levels (e.g. HOMO / LUMO) in molecules / polymers.

RISK-TECH uses dedicated Molecular Dynamics, Dissipative Particle Dynamics, Computational Fluid Dynamics, continuum mechanics, fluid-structure interaction software for simulated test of new materials and as the software allows optimising of the fitting parameters they can determine the optimal material characteristics. They e.g. analyse the effect of varying the nanocontainers fillings, particle-particle interactions, diffusivity parameter and the localization of the particles into the scratch. These findings provide guidelines for formulating nanocomposite coatings that effectively heal the surfaces through the self-assembly of the particles into the defects.

SANDVIK COROMANT uses electronic structure methods like VASP/VASP+phonopy to calculate thermodynamic properties, geometry and electronic structure of compounds used in the bulk and coating

of the cutting tools. Empirical models based on large sets of measured data are used to predict mechanical properties of the cutting tool.

SEAGATE screens new device and material designs for perpendicular writers. New material properties and advanced geometries are entered into the simulation to and output magnetic fields are measured to determine the likely performance and reliability of the prototype structure. If successful in simulation, the new device design or material is processed in a real prototype to determine electrical performance.

SOLARONIX calculates the energy levels in new solar cell material.

SOLVAY/RHODIA is oriented toward a computer-aided rational design and optimisation of new highly functional materials and formulations for sustainable solutions in the fields of energy, consumer chemicals, electronics, automotive, ... Molecular modelling (ranging from electronic to meso-scopic scale) and empirical modelling are used to perform a virtual and high throughput experiment screening of new materials as well as to pinpoint the most important microscopic material properties which (qualitatively or quantitatively) determine the macroscopic performance and application properties. Also, they are a valuable tool to establish new design concepts that can enlarge the discovery process and help experimentalists in their daily work. End application behaviours are simulated (e.g. with Finite Elements) in order to optimise the solutions that are delivered. Process technologies used to produce these materials are also simulated (e.g. reaction kinetics, computational fluid dynamics, heat integration, dynamic process modelling) to design eco-efficient processes which minimize the environmental footprint and reduce associated CAPEX and OPEX.

TATASTEEL uses materials modelling for thermodynamic and phase diagram calculations (during solidification and heat treatment) and microstructure prediction during thermo-mechanical processing of steels.

THYSSENKRUPP uses modelling to simulate phase transformations and recrystallization processes in the hot strip material and to predict the microstructural properties as well as the mechanical properties. They use modeling to establish phase diagrams of the steels.

TOTAL study materials properties and absorption capacity, enhanced oil recovery, polymers development, additives for lubricants or fuels, friction studies and corrosion.

UMICORE simulate the mechanical strength/service life of new materials in specific customer applications.

8.5 Industrial use of models for manufacturing

COEXPAIR is using visualisation models to generate and visualise the finite element model before and after calculation. They use analytical modelling and continuum mechanics models to calculate stress, deformations, displacements of composite parts such as T shape junctions or I shape beams up to the complete final part e.g. the landing gear door of an aircraft.

With these they do analysis of deformation and stress in the material loaded with a static or dynamic mechanic load, thermal load, thermo-mechanic load, vibration load for resonance and instability.

EADS uses Finite Element based software for process development to optimize part accuracy or process parameters during metal forming or machining.

INNOVENT uses (home-made) software for simulating crystal growth and dynamics of point defects in crystals.

LYONDELL-BASELL: uses modelling for reactor engineering and process engineering, checking proper functioning of the reactor and predicting final product structure and material performance at customer-applications.

OXFORD-INSTRUMENTS models processes in order to optimise their design of new plasma etch and deposition hardware.

RISK-TECHNOLOGIES use two different modelling approaches for self-healing materials consisting of nanocontainers. Simulation determines nano-containers fillings, particle-particle interactions, diffusivity parameter and the localization of the particles into the scratch.

The models are Dissipative Particle Dynamics, Finite Element Method and continuum mechanics.

SANDVIK COROMANT uses CFD-modelling as well as other internally developed methods to simulate manufacturing processes.

SOLVAY/RHODIA uses modelling for the sustainable improvement of the operational performance of its manufacturing units, looking for optimizing capital and operational expenditures. Computational fluid dynamics is used to troubleshoot, debottleneck, re-vamp process equipment and to optimize their overall efficiency. Heat integration is performed to make efficient use of energy. Advanced process control solutions are used to operate processes as close as possible to the optimum limits while satisfying safety constraints and ensuring that quality requirements are met. Statistical data mining is used to value plant historical production data coming from manufacturing execution systems so as to identify and optimize key process variables. Dynamic process modelling allows building Operator Training Systems to develop skills of manufacturing teams. Polymer processing technologies that are used by our customers are also simulated to bring them our knowledge of our materials.

TATA STEEL uses manufacturing models for loading and deformation prediction in rolling and pipe forming, characterisation of residual stress and distortion due to welding, prediction of microstructure and properties in thermo-mechanical processing of steels and assessment of in-service performance of steel products and Computational Fluid Dynamics.

THYSSEN KRUPP use continuum mechanics, thermo-mechanical models, CFD and statistical models to simulate casting and hot rolling processes. They also use welding models to simulate weldings for crash relevant parts including the description of the microstructure evolution and the residual stresses. The simulations are validated by comparison to experimental results. They also simulate precipitation forming which plays a crucial role during the development of new steels and the optimization of steel concepts.

TOTAL uses models for polymers compounds manufacturing processes.

UMICORE is simulating metallurgical and chemical processes ranging from a single operation to entire plants. It is used to debottleneck and troubleshoot manufacturing processes. The models are often used to reduce the number of measurements and to design efficient experiments. They also do verification of new designs of processes (i.e. ovens, gas treatment plants).

8.6 Industrial use of models for products and devices design

BMW uses computational fluid dynamics and crash, fatigue and stamping simulation to predict the behaviour of their cars.

CAMFRIDGE use software to optimise device architectures by optimising geometries for heat transfer, fluid flow, magnetic force maximisation, magnet design. The code is integrated with CAD design tools – "really it is our SWISS army knife".

COEXPAIR is using the same approach for product design as they do for material design (visualisation models and continuum mechanics models to analyse deformation and stress in a composite part loaded with a static or dynamic mechanic load, thermal load, thermo-mechanic load, vibration load for resonance of the part and instability).

INNOVENT uses models based on electromagnetic field theory and mesoscopic theory of ferromagnetic materials to optimise permanent magnets and current circuit configuration in order to achieve the desired magnetic field configuration.

OERLIKON uses Finite Element Analysis, CFD, general computing software and multi-physics modelling software for the design of the mechanical parts, the optimisation of the transmission internals (churning losses) and the evaluation of the impact of the transmission system design on the overall vehicle performance.

SANDVIK COROMANT uses FEM modelling to simulate the cutting tool process and predict wear behaviour at different process conditions. The utilization of first principles modelling to simulate the chemical interaction between the cutting tool and a work-piece material is at an early stage development.

SEAGATE uses models for simulation of writers for perpendicular magnetic recording. This writer technology forms the basis of all current hard drive products and is expected to do so for the next four years at least. Modelling involves creating new geometries with complex shapes and critical dimensions

typically less than 100nm. Output magnetic fields are measured with geometric and material parameters varied to determine optimal writer designs.

They use models for plasmonic nanostructures for Heat Assisted Magnetic Recording (HAMR). Simulation experiments are carried out with various geometries and

Also thermomechanical modelling for coupled mechanical modelling of a recording head under various temperature conditions is done. This is critical for recording head designs which works at a given fly height and meet certain reliability conditions in the final drive product.

SOLARONIX uses solar illumination simulation software and device design software for the design of microwave wave guides and antenna's.

SOLVAY.RHODIA uses modelling tools to predict and validate relationship between parameters to prepare and synthesize product versus final properties.

PHILIPS applies new and existing models to predict the physical behaviour of current and future devices thereby taking into account the processing history. After experimental validation, the models are applied to achieve optimized product and process design with respect to several failure mechanisms such as interface cracking and fatigue. The models deal with thermo-mechanics, fracture mechanics, multi-scale mechanics, heat transfer and multi-physics phenomena.

TATA STEEL carries out system design, optimisation and performance evaluation of a novel (mechanical) device (machine) for weld (hot) cracking susceptibility testing with the models. RISK-TECHNOLOGIES develop the computational procedures and software for modelling of blood flow in micro-vessels and particle margination and endocytosis. A general scheme of the physical process involving blood microcirculation, nanoparticle motion, attachment and endocytosis is modelled using continuum-based methods

TOTAL uses chemical engineering models for simulation of reactors and processes and apply this a.o. to multiphase-multi-fluid flows, flows in porous media and combustion.

UMICORE does design optimisation of new devices with respect to efficiency and /or mechanical strength/service life.

VOLKSWAGEN is using device modelling for battery pack optimisation.

8.7 Industrial research into modelling

BASF is doing development of multiscale modelling, both vertical (parameter estimation from chemistry to coarse graining) and horizontal (coupling of continuum mechanical modeling and particle based MD). Related to organic semiconductor research quantum chemical parameters for intermolecular interactions relevant to charge and exciton transport as well as drift diffusion models are focus of research. They participated in an EU-project QUASI, where they were co-developing the software Chemshell.

DOW does research into a large variety of simulation routines in polymer science.

LYONDELL-BASELL is developing reaction engineering and polymerization kinetics for their own processes in order to achieve process optimization

INNOVENT participates in research into numerical methods in micro-magnetics, in order to increase the efficiency of existing packages and to develop new packages for simulations of those classes of magnetic material which can not be simulated with the state-of-the-art software. They also do development of the software for simulations of the dislocation dynamics in crystals in order to understand the formation of equilibrium and non-equilibrium dislocation patterns in semi-conductors.

OERLIKON is doing simulations based on newly developed vehicle models and energy management system models, actuation system models, churning and windage losses models.

OXFORD INSTRUMENTS is developing new atomic and molecular chemical reactions sets to be added to their plasma modelling code.

PHILIPS is doing research into fracture and damage mechanics, multi-scale mechanics and thin film mechanics.

RISK-TECHNOLOGIES develop computational procedures and software for modelling of blood flow in microvessels and particle margination and endocytosis. They developed two different modeling approaches, DPD and FEM for self-healing materials, based on the nanocontainers healing concept.

SANDVIK COROMANT develops empirical/semi-empirical models of mechanical properties of hard materials and performs thermo-dynamical assessments of new materials ´systems. Models for manufacturing processes are continuously developed and improved.

SEAGATE does model development in micromagnetic and plasmonics. Micromagnetic modelling development takes place to improve modelling times and accuracy for reader and writer modelling in perpendicular recording heads. Modifications are made to a freely available modelling platform. This development is aimed towards products being developed for the next 4 years. Plasmonics modelling is carried out to compliment modelling capability. This is carried out to improve modelling capability for very small nanophotonic elements. This is targeted towards the Heat Assisted Magnetic Recording (HAMR) application which should be in product hard drives in around 2017.

SOLVAY/RHODIA has internal R&D activities and external partnerships in the modelling of catalytic reactions, reactive and multiphasic flows, multi-physics and multi-scale simulation of advanced materials, development of quantitative laws for predicting materials and blends properties.

TATA STEEL is developing industrial scale modelling of welding for weld induced residual stress and distortion characterisation, incorporating the capabilities of defect prediction such as cracking using multi-scale modelling techniques.

TOTAL develops models for multiphase flows in risers (avoid Hydrates), and derives closure equations of "slug flows".

Chapter 9 Achievements of the models

Of course the results of all the models are very impressive and useful for industry. In this chapter a subset of these results is presented, listing those achievements that <u>can NOT be achieved</u> <u>experimentally</u>. It is hoped that this can convince experimentalists of the value of modelling!

ADGLASS

The modelling revealed previously unknown details of an important process (hydrogen embrittlement of silicon crystals) widely employed for the fabrication of Silicon-On-Insulators (SOI) nanoelectronic devices. It also unveiled undiscovered mechanisms of brittle fracture in solid materials, including the precise chemomechanical role of defects (impurities, reconstructions, dislocations) and dynamical instabilities during the propagation of cracks in brittle materials. Moreover, the simulations explained the reasons for the previously observed, yet so far very poorly understood, binding specificity of certain peptide sequences to inorganic materials surfaces. They revealed an unknown adhesion driving force modulated by the local variations of water density at the solid/liquid interface.

AMCOS

Simulations can predict the sorption isotherms of pure and mixed gases in recently synthesized nanoporous materials (zeolites, metal-organic frameworks, polymers), or in hypothetical materials considered for synthesis. They can also predict the rates of diffusive transport through these materials.

AMON-RA

The model guides nanorod solar cell devices device development and clarifies the specific underlying physics by

Definition of suitable bandgap energies for single- and dual-junction nanowire solar cells Definition of suitable device structure including doping levels and barrier layers Definition of optimum configuration for wire length, distance and diameter in nanowire array Understanding of optical and electrical loss mechanism in single- and dual-junction nanowire solar cells

Contribution to roadmap for assessment of III-V nanowire photovoltaics

ARTIVASC-3D

The hydrodynamic modelling will be able to predict wall shear stresses at the vascular graft walls. These stresses have to be within a certain range in order to stimulate the endothelial cells to perform e.g. neo-angiogenesis.. These wall shear stresses would be extremely difficult to measure for any possible graft geometry. Therefore, a modelling-based design approach is crucial for tissue engineering.

ATHENA

Identification of candidate materials and materials interfaces for future nano-electronics based on complex oxides. These included hetero-junctions, superlattices and multilayers consisting of doped magnetic perovskites (e.g. LaxSr1-xMnO3, PrxCa1-xMnO3), double perovskites (e.g. LaNi1-xMnxO3) and diluted magnetic ferroelectrics designed to exploit and manipulate the coupling of different order parameters at the two sides of the interface. Prediction of the phase diagram of complex magnetic oxides MnO and NiO under pressure, Explanation of the extremely high antiferromagnetic ordering temperature in SrTcO3 and BaTcO3.

AUTOSUPERCAP

The battery-supercapacitor modelling and simulations allow selection of the best materials/supercapacitor for scaling up reducing experimental costs. The molecular ion simulations guided the research for a pore size, maximising the specific capacitance for carbonaceous electrode materials and thereby increasing energy and power density.

CODICE

The developed toolkits revealed that there is a synergy in the hydration of alite and belite phases of cement clinker, which opens the door to new eco-cements.

While a priori one would expect that the larger the content of C_3S the better the resulting mechanical properties, the simulations have revealed that there is synergy in the hydration of C_3S and C_2S blends, and that there is an optimum C_3S/C_2S ratio around 70/30.

DISC-GENERATION

The modelling contributions are twofold:

The coupled transport-mechano model is able to predict the movement of solutes within the intervertebral disc and predicts the interactions between mechanical properties, fluid and solute transport, and cell viability. This is essential for a proper understanding of the mechanisms of disc degeneration and disc regeneration with the use of biomaterials as disc substitute.

Simulations of the effect of partial and complete disc nuleotomy on load transfer as a function of the biomaterial substitute used can be used to determine the surgical variability during nucleus removal.

Both contributions cannot be obtained experimentally and therefore are complementary to the experimental evaluation of the biomaterial performance.

DYNAMAG

The calculations pointed out samples that were until then simply not considered. A novel magnonic logic architecture has been developed based on physics discovered by the models. The, until then unexplained, origin of the response experimentally observed in optical pump-probe studies of magnetic multilayers with strong perpendicular magnetic anisotropy, has been revealed via calculations in the discrete lattice model.Mechanisms behind unusually low magnetic domain wall depinning currents within spintronic devices have been revealed via full 3D finite element simulations.

FEMTOSPIN

Prediction efficiency of ultrafast spin dynamics in multiferroics excited by THz laser pulses Prediction of the smallest stable domain structure in magnetic thin films Prediction of the time and spatial scales of magnetic pattern formation Identification of optimal materials for ultrafast optically induced magnetic switching

FREECATS

Heat transfer modelling guides the design of the foam materials and predicts the deposition of carbons during operation, (a phenomenon critical in oxidative dehydrogenation) and so reduce costs of trial and error developments.

Multi-scale modelling of reaction, surface-fluid interactions, heat transfer and hydrodynamics allow to predict from first principles the behaviour of the overall reactor system and to screen a large space of operating conditions prior to experimentation. This leads to better understanding of physical phenomena involved and dynamics of processes within the system, thus reducing the number of experimental trials required.

GOFAST

The model identified optimal correlated materials (composition, size, direction of the laser pulse versus surfaces, etc...) and excitation pathways (photon energy, intensity, polarization and temporal profile) for the production of controllable and reversible photo-induced transition between very distinct phases, e.g. metallic and insulating, or normal and superconducting.

HIPERSOL

The methods can predict contacting and recombination properties of nanostructured materials and complicated interfaces.

The model gave fundamental insight into nitrogen diffusion in silicon, into the nature of different recombination traps, into dissolution and transport of Ag during the firing process, and insight in how the current flows through the contacting region. Based on this optimal Ag crystallites geometries were gained.

HIVOCOMP

Prediction of structural properties to avoid unfeasible or expensive experimental tests. The models also enabled screening of possible choices for the resins. The flow modeling shortened part of the design by predicting permeability and impregnation time of the different resins.

The model predicted structural behavior in function of the above properties and damage initiation by calculating the threshold and damage development parameters in the composite during different loading types

HYMEC

The electric field distribution of charged metal nanoparticles in organic matrices can be predicted, which allows identifying the switching mechanisms of memory cells. This, in turn, allows optimizing the morphology of devices.

HYPOMAP

Computational modelling, in particular on the electron or atomistic scale, allows the investigation of processes beyond the experimental scale. People often speak of the "computer microscope" that allows to monitor the motion of a single atom. It also provides understanding of an individual vibrational mode, or of the contributions of material fragments to an individual property. In this project modeling provide insight in the adsorption energy of hydrogen as function of the composition of the individual building blocks of a molecular framework. With this data it is possible to improve the performance of the target materials.

IMS & CPS

The "electrical conductivity" model predicts the electrical percolation and conductivity of CNT/polymer composites close to the experimental observations. The achievements beyond experiments include the positive effect of agglomeration and the transverse conductivity of the CNT/polymer composite with the CNTs only sprayed on the surface. In fact, nobody believed that there will be conductivity in the transverse direction when the CNTs are sprayed on the surface alone. In addition, this model correctly predicted that the addition of compatibilizers and copolymers has a significant effect on electrical percolation threshold and conductivity. These characteristics are experimentally proved and this is the only model which can predict this behaviour.

The toughness model will predict the effect of carbon nanotubes and their agglomerates on redistribution of stresses and strains inside the composite and the threshold strain for the onset of damage on the micro-scale.

The model utilized for validation elements can predict the initial failure of the T junctions and of the I beams for the different used materials (with and without CNT). This will help to design the test jigs to be used in the project.

INNOVASOL

Trial and error synthesis costs were avoided by computing the energetics of inclusion of some anions (iodide and tri-iodide) in a layered solid analogous to hydrotalcite before the actual systems were synthesized. The calculations showed the limit concentration expected for anions in this environment.

The models could provide understanding of phenomena occurring, e.g. the excess of lead observed in certain conditions.

The calculations allowed to predict which surface passivant would help obtain particles of octahedral shape exposing (111) crystallographic faces, and this will guide the experiments.

IRON-SEA

The model determined the pairing symmetry and its evolution with doping, which is impossible to determine experimentally.

The model determined the characteristic energy of the boson that mediates superconductivity (examples: Co-doped Ba-122, Sm-1111) and of the coupling strength.

The model determined the effects of disorder, doping, lattice strain, etc on the superconducting properties.

The model determined the effects that are optimal or detrimental for device fabrication and optimization.
LEMSUPER

New correlation-driven mechanisms for superconductivity in light element systems were predicted long before they were validated. A superconductivity mechanism for fullerides was predicted, where electron-vibron coupling, orbital degeneracy, and strong electron correlations implying a nearby Mott transition all play a crucial role. Cesium fullerides validated this theory.

Identification of new electronic ground states in light element systems leading to superconductivity, potentially unveiling new light element molecule-based superconductors, something that cannot be done experimentally.

MAGNONICS

Numerical simulation of quasistatic magnetization processes explain measurements by MOKE and of spin-wave excitations observed by FMR, BLS, and TRSKM techniques in 2D arrays of nanoscale magnetic dots and antidots. These simulations facilitate explaining the nature and spatial structure of magnons in the magnonic arrays.

MASTER

The model can predict the magnetization dynamics in an array of hetero-structures. These dynamics cannot be computed analytically. These simulations are used to optimize the design of spin devices as optimization by experimental means would be too costly.

MATRANS

Most of the modelling in the project is done to replace the experiments, which are usually complex and costly or, in other words, the modelling predicts the materials' properties/behaviour which will be observed in experiments and thus shortens the development process.

METACHEM

The model predicts whether the metamaterial can be described within effective media theory. The model extracts parameters not directly measurable.

The model can determine individual polarizabilities of a complex scatterer (electric and magnetic), surface susceptibilities of metasurfaces (electric, magnetic and magnetoelectric), efractive index of the wave in a lattice and wave impedance of the wave in a lattice.

MINOTOR

Modelling allows material design of multilayer devices with optimized proprieties as follows:

- The model has predicted the contributions to the discontinuity between the electronic structure at the interface and the bulk material
- The model explained the origin of the electronic level alignments at organic/organic interfaces as measured in short-circuit current and the open circuit voltage of solar cell devices, two key quantities that directly dictate the efficiency of those cells.
- The model has shown that modifying the surface of electrodes, can tune the charge or spin injection barriers in devices such as OLEDs.
- The model predicted the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties.

MINTWELD

Manufacturing industry, metal alloys, welding, EAM (electric active materials) modeling

MODIFY

Modelling has explained the interplay between the chemical composition of the synthesized PSA samples and the degree, strength and life-time of the specific hydrogen forces developing in the polymer, which in turn governs the unique cohesive properties and strong elasticity of these materials. Models also explained the big role played by particle-to-particle transient forces on the elasticity-to-viscosity ratio which seems to be at the heart of the design task for new adhesives. Modelling explained the connection between bulk rheological properties in extension and shear and the debonding mechanisms during stretching of PSAs.

MONAMI

Modelling of materials properties allows the search for new materials or to make accurate interpretations of observed materials phenomena. An example can be found for magnetic materials where two properties are most important from an application point of view, namely the size of the saturation moment at room temperature and a large magnetic hardness (or synonymously, a large magnetic anisotropy energy – MAE). These two properties can be predicted for any material, with an accuracy that is needed to make the search for novel permanent magnetic materials much more efficient.

MORDRED

Predict defect character and density that causes device breakdown in realistic environments and over realistic performance times.

Characterize this for a variety of new, industrially untested materials.

Suggest routes for device design that should eliminate or reduce reliability problems

MULTIHY

Optimisation of the pulse-plating process used in the fabrication of the combustion chamber of the Ariane satellite delivery vehicle

Mechanistic understanding of the susceptibility of advanced high strength steels to HE by absorbed H

Prediction of the influence of H on the fatigue lifetime of wind turbine bearings.

<u>MUST</u>

The model can be used do give recommendation concerning optimal composition and structure of the coating to delay corrosion of metallic and polymeric substrates and structures, thus reducing development costs.

The model predicts service-life time via the probability of the scratch healing or inhibition based on the physico-chemical properties of the materials and realistic scratch geometries.

NAMASTE

Reproduction of the valence band nature of Fermi level states the archetypical ferromagnetic semiconductor (Ga,Mn)As. Prediction and explanation of the observed magnetic and magneto-

transport properties in ferromagnetic semiconductors.Understanding of the observed spin-torque effects which lead to the discovery of new ferromagnetic resonance (FMR) effects. Based on the developed capabilities to model spin-orbit in metals, it was shown that appropriate antiferromagnetic materials could be employed as active layers in spintronic devices (GMR, etc), thus opening up the possibility of the new field of antiferromagnetic spintronics.

NANOINTERFACE

A set of design and reliability guidelines guidelines for microelectronic packages for microelectronic packages with respect to delamination risk has been elaborated, which can only be generated in a systematic way by accurate models.

A better, quantitative understanding of adhesion mechanisms at the very small to macroscopic scale and of the effect of surface roughening on adhesion properties has been provided. This was only possible via mesoscopic semi-analytical and numerical fracture mechanics models.

NANOMAGMA

The model predicted that the optical and magneto-optical response of complex structures where metals and magneto-optical materials are simultaneously present is proportional to the electromagnetic field in the magnetic material. This guided the design and now the whole structure is grown to try to maximize the field in that material.

NANOMODEL

The role of the interphase (structure and dynamics) is difficult to investigate experimentally. Only modelling can give access to the structure of matrix, nanoparticles and their interphases. Modelling revealed details how the interface is influenced by the chemistry.

NIM_NIL

Modelling allowed the optical properties to be calculated before the sample is fabricated, being essential for design and leaving room for optimization. Once a sample is fabricated and characterized, modelling gave results usually in excellent agreement with measured data, allowing to understand the underlaying physics and proving the sample high quality. It helped identify the EM properties of fishnets in the wedge configuration demonstrating the operation of a metamaterial in the visible regime.

NPMIMETIC

The study of the intervertebral disc (IVD) mechanical behaviour presents a high level of difficulty, due to intrinsic uncertainty on the quantification of real working loads (coupling compression forces, flections and torsion moments). Post-mortem analysis doesn't allow a full understanding of these phenomena, mainly due to the highly hydrated nature and the fact that the osmotic role of nucleus function is not achieved in those conditions. Modelling can overcome these restrictions and predict two fundamental situations:

i) degenerated IVD – stress/strain conditions due to nucleus degeneration (geometry, stress conditions, prediction of overstretched annulus' fibres)

ii) restored IVD – prediction of restoration conditions, annulus rupture state and/or failure risks on the nucleus 'refilling' process, influence of nucleus prosthetic materials characteristics on overall mechanical stability

OXIDES

Theoretical predictions to be further validated experimentally:

The unexpected possibility to induce multiferroism in epitaxially strained CaMnO₃

The unexpected possibility to achieve exploitable Tunnel Electro-Resistance (TER) in symmetric Ferroelectric Tunnel Junction (FTJ); for memory applications

The prediction of the unexpected appearance of a half-metallic ferromagnetic highly-confined 2-dimensional electron gas (2DEG) in $SrTiO_3/SrRuO_3$ superlattices

The unexpected role of oxygen rotation in shifting by 300 K the ferroelectric phase transition of $PbTiO_3$;

Joined theoretical-experimental breakthroughs

Improper ferroelectricity in oxide superlattices in which modelling identified a new microscopic mechanism (the so-called trilinear coupling of structural instabilites) as observed in parallel experimentally

Exchange bias in $LaNiO_3/LaMnO_3$ superlattices; modelling allowed the proper understanding of the unusual spin order giving rise to the experimental results

Compelling evidence of the intrinsic nature of the 2DEG at polar oxide interfaces; modelling of ideal interfaces was required to unambiguously distinguish between intrinsic and extrinsic effects

Confinement properties of the 2DEG at the LaAlO₃/SrTiO₃ interface; modelling provides key information on the electronic band structure, mandatory to interprete measured properties

POCO

Molecular models of functionalized CNTs and polymer matrices could predict the influence of the functional groups on the mechanical properties of the CNT and the interfacial shear strength (IFSS) of the nanocomposites. The influence of the functionalization of CNTs on the IFSS of the nanocomposite was demonstrated, something that would otherwise have cost many experiments.

The pull-out of CNTs from molecular matrices is difficult to analyze by experimental methods due to the scales involved. In this case, the process modelling of the pull-out was necessary to analyze the interfacial shear strength of the nanocomposites.

RADINTERFACES

The modelling is going to guide the appropriate tuning of interfaces within multi-laminate composite materials to obtain defect absorption materials with a self-healing mechanism.

REFREEPERMAG

The theory can pre-identify interesting materials prior to the actual synthesis and experiments and thus save time and resources.

ROLICER

The FEM simulations provide solutions for material stresses, which cannot be obtained experimentally. The fracture models describe crack nucleation based on traction-separation laws which provide a phenomenological lifetime prediction tool without the need for extensive experiments.

The microscale models achieve homogenisation of thermoelastic properties and thermomechanical homogenisation of strengthening effects in ceramics. Such simulations provide information that cannot be obtained experimentally.

The ab initio models provide reliable properties of the bulk material and solid-solid interfaces as criteria for crack initiation, which are very difficult to obtain by experiments.

Molecular dynamics models are used in modelling hybrid steel-ceramic contact to study the interaction between additives in lubricants and bearing surfaces. Experiments that provide such information are not possible.

SIMBA

The modelling of the plasma flow dynamics and particle trajectories permitted to define the process at different scales and to predict the influences of the main process parameters (e.g. effects on nanopowder production yield when changing the reactor geometry and operating conditions). The model enabled the design of an optimum reactor chamber with increased flow of particles for collection thus avoiding an expensive try-and-fail approach, and saving time and effort in optimising the lab scale process and in transferring main results to an industrial ICP installation.

SIMUGLAS

Shape of moulds can be now predicted with the help of modelling of the glass shrinkages, which had to be done previously by expensive try-out experiments. Index drop inside glass lens can be now predicted with the help of modelling of the structure relaxation behaviour of glass material, which was unknown only by pure experiments. Material flow and temperature during forming process can be predicted, which cannot be observed and measured in the real moulding process.

SMASH

The modelling and simulation of GaN-based LEDs is able to guide the device design, by optimizing strain, polarization and quantum effects in order to improve the performance of the devices. Atomistic simulations can shed light on the effect of clustering in the alloy active regions.

SSEEC

The materials modelling of the overall system gave us invaluable feedback on experimental development, reducing the time that would otherwise be required to make multiple measurements or a full phase space of physical samples. The 2D model of an active magnetic regenerator (AMR) enabled accurate optimisation of geometry (packing density, absolute length scales), system operating parameters (frequency, flow rate) and identification of optimal (or ideal) refrigerant material properties (magnetocaloric effect and heat capacity) against overall efficiency and power requirements.

SUPER-IRON

Prediction of high-pressure phase transitions in $Ba(Ca)Fe_2As_2$ and of non-hydrostatic effect, confirmed by high-pressure XRD measurements.

Prediction of the peculiar structural and electronic modification upon doping with rare-earth metals in CaFe₂As₂.

Understanding of disorder, surface and interface effects.

Model calculations, joined with DFT calculations, were able to predict a tri-critical point in the phase diagram of iron-pnictides, now a hot subject for experimental confirmation.

SUPERLION

The model allowed shortened and better-informed selection of the most efficient cell architectures and geometries, and the optimal cell materials. Modelling can avoid excessive and often futile efforts to create more impressive micro-architectured electrodes, since these will often not result in improved battery performance.

SURFUNCELL

Modelling reproduced and predicted the strength and structured build-up of hydrogen bonds of water to the cellulose surface and inside the water layer as a function of the water layer thickness. This lead to suggestions for the design of the surface structure and charge distribution at cellulose surfaces.

ULTRAMAGNETRON

Materials with a compensation point are shown to be very promising media for magnetic recording. The magnetization reversal by a single circularly polarized laser pulse has been successfully simulated A phase diagram for opto-magnetic reversal was obtained, demonstrating a window of peak electron temperature and effective magnetic field pulse duration for opto-magnetic switching. A new mechanism of linear magnetization reversal was discovered. Experimentally the two sublattices of a ferrimagnetic alloy (GdFeCo) were found to demagnetise at different rates which was then confirmed by the model. The model predicted that the ferrimagnet transitioned into a transient ferromagnetic phase stable for only around 300femtoseconds which was found experimentally. The theoretical model predicted that the magnetisation of the ferrimagnet reversed spontaneously on application of a heat pulse, which was then experimentally verified.

Chapter 10 Conclusions

According to the stakeholders, the future of the European industry is associated with a strong modelling capacity. Their opinion is that an efficient modelling approach is needed to shorten the development process of materials-enabled products.

Industries identify the specifications for material properties and the modelling then work backwards to find which material composition can meet the specs and how production can be done. This **Materials by Design** approach has been supported during the last decade in the EU Framework Programmes.

To predict properties of final products several models covering a wide range of physics and chemistry phenomena are used. This requires strong interaction between the different modelling communities and industry. Because of the complexity and long timescale of the code development and validation processes, the support of programmes such as NMP makes an important contribution.

This brochure provides insight and helps the reader to see the models as more than mere "black boxes". It shows that:

- Industry is a very active player both in modelling for production and in modelling research areas
- Application areas of modelling span all industrial sectors. In each industrial sector all types of models are used except for Health where electronic modelling is underrepresented and except for mesoscopic models which are predominantly used in ICT and Energy and Transport.
- The majority of the projects performed modelling at the continuum scale, corroborating the idea that modelling has reached a level of maturity that enables realistic simulation of macroscopic behaviour that can be used in industrial applications.
- Electronic and atomistic models have a much respected position in industrial use and they are a traditionally a stronghold of the Europe.
- Mesoscopic models are the least represented in this survey. This is probably due to lower level of maturity of these models which have to bridge the gap between the established concepts of "electrons" and "continuum".
- Winners in frequency of use are: ab intio quantum mechanics, molecular dynamics and continuum mechanics (solid and fluid).
- The bulk of the projects are applying existing models to new materials, which shows that the current state of the art of modelling can be characterised as "mature".
- Model validation against a chain of experimental data of increasing complexity is an ongoing activity.
- Development of the physics and chemistry models seems to progress steadily and there is a significant number of research groups that is constantly pushing the boundaries by developing models based on theoretical physics and chemistry.
- Linking between models at different scales, especially through newly developed force fields and constitutive equations is extensive.

Industrial impact of modelling

The modelling discussed has lead to progress in many industrial sectors, such as energy, chemistry, ICT, healthcare and transport. Models can provide insights that experiments can not provide. Predictive design of novel materials optimised for specified applications is heavily used by industry e.g. to add properties and functionality to new materials. The **material by design** approach has generated improved control of materials development and an improved control of concerned industrial products and processes, minimising the environmental impact, reducing risk of product failure and increasing service life-time.



Fig 10.1 Industrial feedback on modelling use and benefits (see Ch. 8)

Future research needs

The community, contributing to this brochure, highlighted that future research could target linking of models to extending the width and breadth of the models.

In parallel, it could be targeted to elaborate the physics and chemistry involved in existing codes to extend their application scales, especially an elaboration of mesoscopic would be welcome.

Interface design to facilitate the future implementation in larger and extendable framework architectures would be of added value.

Conclusions

We hope that the analysis in this brochure of results of NMP projects in materials modelling bring insights. We hope that, with this insight, material behaviour and manufacturing processes across length and time scales can be better understood. This understanding of materials should then enlarge the application area and shorten the development process of materials-enabled products, which is key to increased global competitiveness of our industries.

Annex I Projects fiches

The modelling done in some 70 materials projects in the NMP Programme is described in individual project fiches. The past tense is used for projects that have finished at the time of writing (January 2013) and the present tense for projects still on-going.

To show the value of modelling, the achievements of the models beyond experiments have been listed.



in ADGLASS 229205

Subject of the modelling

Protein adhesion, interface cohesion and crack propagation in glasses

Models used

Atomistic: <u>QM/MM</u>

Simulation software and type of numerics used

QUIP, CP2K, Amber, with ad-hoc modifications Plug-ins for other academic/industrial codes (e.g. LAMMPS, OpenKIM, VASP, Castep) extended buffer zone in QM/MM to mitigate the effects of its artificial surface

Achievements of the model beyond experiments

The modelling revealed previously unknown details of an important process (hydrogen embrittlement of silicon crystals) widely employed for the fabrication of Silicon-On-Insulators (SOI) nanoelectronic devices. It also unveiled undiscovered mechanisms of brittle fracture in solid materials, including the precise chemomechanical role of defects (impurities, reconstructions, dislocations) and dynamical instabilities during the propagation of cracks in brittle materials. Moreover, the simulations explained the reasons for the previously observed, yet so far very poorly understood, binding specificity of certain peptide sequences to inorganic materials surfaces. They revealed an unknown adhesion driving force modulated by the local variations of water density at the solid/liquid interface.

Application

Pharmaceutical and biomedical products Optical and photovoltaic devices Architectural panels

Relevant review articles

J. Schneider, L. Colombi Ciacchi, "Specific material recognition by small peptides is mediated by the interfacial solvent structure", Journal of the American Chemical Society 134, 2407-2413 (2012)

N. Bernstein, et al "QM/MM simulation of liquid water with an adaptive quantum region", Physical Chemistry Chemical Physics 14, 646-656 (2012)

F. Atrash and D. Sherman, "Dynamic Fracture Instabilities Generated by Phonon Emission: Experiments and Atomistic Simulations", Journal of the Mechanics and Physics of Solids 60, 844-856 (2012)

G. Moras, et al "Atomically smooth stress-corrosion cleavage of a hydrogen-implanted crystal", Physical Review Letters 105, 075502 (2010) (Featured in Physical Review Focus, vol. 26, 13th August 2010)

Summary of the project

The project target detailed knowledge of chemical and physical processes taking place at glassy interface systems and is devoted to improving the efficiency, functionality and reliability of glass products for pharmaceutical and photovoltaic applications.

Summary of the modelling

The project applied multi-scale a hybrid quantum-mechanical molecular mechanics (QM/MM), atomistic modelling method. Large length scales (many tens of thousands of atoms) are required to describe the systems of interest, and key physics have been added in quantum mechanical models, combining the highly accurate QM models with the fast MM dynamics. The QM calculations are performed on a limited portion of the system which includes an extended buffer zone to mitigate the effects of its artificial surface. The QM calculations are only carried out when the dynamic evolution of the system leads it out of the range of configurations which can be accurately simulated by the classical potential alone (e.g. during chemical reactions involving bond breaking or forming).

To aid the above applications, the electronic degrees of freedom of an explicit quantum mechanical model have been removed without sacrificing the accuracy of the atomistic potential, formally derived from quantum mechanical models. We gain speeds of many orders of magnitude. Novel quantum-accurate classical potentials have been created for carbon, silicon, water, tungsten, and various oxides.

This method is applied for example to the simulation of fracture experiments where the mismatch between the thermal expansion coefficients of frame and specimen generate normal and tangential strain fields at the specimen's boundaries that serve as the driving force for crack initiation and propagation.

We have extended the method so that it can handle liquids, which enables us to study solid/liquid interfaces.

The novel method has been applied to two scientific problems which require at the same time quantum precision and very large model system sizes. Namely, we have investigated (i) the adhesion of proteins at the interface between a glassy SiO_2 phase and a water solution, relevant to pharmaceutical applications and (ii) the cohesion between heterogeneous glassy interfaces (e.g. containing SiO_2 and TiO_2 phases) relevant to thin-layer-based conditioning of glass materials for applications in architectural glass and photovoltaic cells.

www.adglass.eu

Project Acronym and Number: ADGLASS 229205 Project Title: Adhesion and Cohesion at Interfaces in High Performance Glassy Systems Start and End Dates: 01/01/09/2009 till 28/02/2013 EU Contribution: 2.999.622 € Coordinator: Lucio Colombi Ciacchi, University of Bremen and Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Bremen, Germany,<u>colombi@hmi.uni-bremen.de</u>



in AMCOS 233502

Subject of the modelling

Advanced materials for selective sorption of carbon dioxide from gaseous mixtures (zeolitic imidazolate frameworks, hyperbranched aminosilicas, functionalised polymers)

Models used

Electronic: <u>Density Functional Theory (DFT)</u> for electronic structure calculations Atomistic: <u>Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM)</u> approaches <u>Metropolis Monte Carlo</u> in the grand canonical ensemble Ab-initio and classical <u>Molecular Dynamics</u>

Mesoscopic: Statistical flow simulation methods (Lattice Gas Cellular Automata)

Simulation software and type of numerics used

In house codes CPMD and CP2 for QM/MM

Numerical solution of initial value problems in ~105 unknown functions of time. Stochastic sampling of rare events (activated processes) by Transition State Theory which includes multidimensional spaces spanned by ~105 coordinates according to prescribed probability density functions. This entails computation of minima and saddle points on complex potential energy hypersurfaces of the high dimensionality.

Achievements of the model beyond experiments

Simulations can predict the sorption isotherms of pure and mixed gases in recently synthesized nanoporous materials (zeolites, metal-organic frameworks, polymers), or in hypothetical materials considered for synthesis. They can also predict the rates of diffusive transport through these materials.

Application

Capture of CO_2 and CH_4 by novel classes of MOF materials for applications in Carbon Negative technology and storage of H_2 in the above materials.

Relevant review articles

Pantatosaki, E.; Pazzona, F.G.; Megariotis, G.; Papadopoulos, G.K. "Atomistic Simulation Studies on the Dynamics and Thermodynamics of Nonpolar Molecules within the Zeolite Imidazolate Framework-8", J. Phys. Chem. B 2010, 114, 2493-2503.

E. Pantatosaki, H. Jobic, D. Kolokolov, S. Karmakar, R. Biniwale and G. K. Papadopoulos J. Chem. Phys. 2013, 138, "Probing the Hydrogen Equilibrium and Kinetics in Zeolite Imidazolate Frameworks via Molecular Dynamics and Quasi-elastic Neutron Scattering Experiments

The objective of the EU-India collaborative research project AMCOS is to investigate newly synthesized and/or modified classes of advanced sorbents, such as the zeolitic imidazolate frameworks (ZIF), functionalized polymers (FP), and the new category of inorganic-organic hybrid sorbents known as hyperbranched aminosilicas (HAS). Thanks to their exceptional physicochemical properties and enhanced ability for adsorbing specific groups of molecules, these advanced materials have been used for environmental and energy-related applications, such as the selective separation of carbon dioxide from flue gases and natural gas.

Summary of the modelling

Computer modelling has been utilized mainly for the study of CO_2 -sorbent interactions along with the mobility of a wider class of guest molecules in the various advanced materials host systems, such as hyperbranched aminosilica (HAS), zeolitic imidazolate frameworks (ZIFs), and functionalised polymers. A focus of the project is the selective separation of CO_2 from CO_2/CH_4 and CO_2/N_2 mixtures, which is important for CO_2 capture and CH_4 enrichment, respectively, for environmental and energy resource related applications.

The ZIF-8 crystal was modelled using rigid and flexible models, starting from conventional generalpurpose force fields (Dreiding) and proceeding to more refined energy expressions that better represent specific interactions with the metal atoms. <u>Quantum mechanical calculations</u> have provided a new, more reliable input for the values of the partial charges of the ZIF framework atoms. DFT calculations on periodic structures were performed using BLYP and PBE functionals. We have found that the fluctuations of the atomic charges are almost negligible, hinting that using a simple point charge approximation for <u>classical Molecular Dynamics</u> simulations of ZIF-8 is sensible. Car-Parrinello and Born-Oppenheimer first principle Molecular Dynamics simulations were conducted for the calculation of the charge distribution in metal-organic frameworks. We have also applied an ab initio quantum mechanical model to calculate the force field of the ZIF-8. QM/MM models have been used with methods enabling the enhancement of the sampling of rare events (activated processes), such as the newly developed Transition State Theory. The QM/MM model was used for the computation of the Force Field of the novel MOF materials employed in the project, by calculating the charge distribution on the atoms of the frameworks, the bond and angle force coefficients, which eventually were used as input in the atomistic modeling. Using these improved tools for describing interactions, we have designed and implemented efficient Grand Canonical Monte Carlo stochastic scheme and Molecular Dynamics simulations for the prediction of the sorption thermodynamics, the distribution of guest molecules over the adsorption sites (singlet probability density), isotherms (equilibrium amount of gas sorbed per unit mass of nanoporous material at given temperature and pressure) and finally the diffusivities of hydrogen (H2), methane (CH4), and carbon dioxide (CO2) within the project materials.

Lattice Gas Cellular Automata has been used for the study of diffusive mass transport processes in zeolites occurring on very long time scales. The main input for the model comes from data: (i) local density dependent mean-field potentials and transition probabilities obtained from atomistic simulations that will be used as the starting point to derive adsorption and diffusion properties. (ii) Thermodynamic and kinetic data obtained from experiments and/or other simulation methods, used as the starting point of a fit procedure to trace which local behaviour causes the system to produce these

Predictions are generally in very good agreement with the measurements conducted by the experimental partners of the project, validating our predictive computational approach.

http://comse.chemeng.ntua.gr/amcos/

Project Acronym and Number: AMCOS 233502

Project Title: Advanced Materials as CO2 Removers: A Computational Study of CO2 Sorption Thermodynamics and Kinetics

Start and End Dates: 01/05/2009 till 30/04/2012

EC Contribution: 520.000 €

Coordinator: George K Papadopoulos, National Technical University of Athens, GR gkpap@chemeng.ntua.gr



in AMON-RA 214814

Subject of the modelling

III-V Semiconductor materials, devices and systems

Models used

Electronic models: <u>k.p theory</u> for band structure calculation, <u>drift-diffusion</u> Continuum modeling: electrical and optical modelling (continuity equation and diffusion equation (<u>CFD</u>) non-linear Poisson equation for the <u>electrostatic</u> potential)

Simulation software and type of numerics used

Electronic models

QUATRA/CELS (used and developed): three-dimensional drift-diffusion model Continuum modelling

FDMAX (formerly lumi3) (used and developed)

Finite Element solver for vectorial Maxwell equations in three dimensions;

EtaOpt (used)

Scattering Matrix Method for electromagnetics (used and developed) Sentaurus device (DESSIS) for electrical circuit modelling

Achievements of the model beyond experiments

The model guides solar cell development by

Definition of suitable bandgap energies for single- and dual-junction nanowire solar cells Definition of suitable device structure including doping levels and barrier layers Definition of optimum configuration for wire length, distance and diameter in nanowire array Understanding of optical and electrical loss mechanism in single- and dual-junction nanowire solar cells

Contribution to roadmap for assessment of III-V nanowire photovoltaics

Application

IIIrd Generation Photovoltaics Solar Cells Nanowire Optoelectronics

Relevant review articles

J. Kupec, B. Witzigmann, 'Computational electromagnetics for nanostructured solar cells', J. Comp. El., 2012, invited review

B. Witzigmann, R. Veprek, S. Steiger, and J. Kupec, 'Comprehensive Modeling of Optoelectronic Nanostructures', J. Comp. El., No. 4, Vol. 4, pp. 389-397, 2009, invited

Summary of the project

The project AMON-RA targeted photovoltaic cells made from arrays of light-harvesting nanowires on silicon substrates made with hetero-epitaxy of III–V semiconductors. Two main architectures were investigated: The first, called "Light Guiding made from core-shell nanowires, in which the sunlight will be guided through materials with decreasing band gap. The second architecture, called "Effective Medium", consists of denser arrays of much thinner wires, where the light waves will experience an effectively averaged medium as they propagate downwards. The high degree of self-assembly and insensitivity to lattice parameters and the use of inexpensive silicon substrates made the production cheap.

Summary of the modelling

The optical and electronic properties of nanowire photovoltaic cells are modeled using a combination of existing and custom developed multi-scale simulation methods. Models combining optoelectronic and quantization effects in a heterojunction nanowire were developed within AMON-RA.

The optical generation in nano-wires is calculated by spectrally integrating the local optical power density times the material absorption (excitonic and phonon loss effects). The optical power density is calculated from the numerical solution of the vectorial Helmholtz equation (which is derived from <u>Maxwells equations</u>) with the electronic model CELS/QUATRA using as input the resulting EM field of the three-dimensional Maxwells equation calculated with FDMAX. (FDMAX is a model originally for eigenproblems, but is extended to model scattering problems within AMON-RA.) Optical generation is then used as source term in the continuity equation for the electronic system. The project numerically solves the electronic system of equations consisting of a continuity equation for electrons and holes, with diffusion currents for bulk regions (CFD) and thermionic emission currents for hetero interfaces, coupled to the nonlinear Poisson equation for the electrostatic potential. The electrical simulation of carrier transport in large diameter hetero-junction nanowires with tunnel junctions is described. A continuum model <u>EtaOpt</u> calculates the efficiency of a solar cell dependent on the band gap. Band gap is an input parameter. Thus the optimum bandgap combination for multi-junction solar cells with two or more junctions is evaluated depending on the spectral conditions and calculates the thermodynamic efficiency limit for a given bandgap combination. The optical properties absorptivity of nanowire arrays are modelled with a transfer matrix method within EtaOpt.

The <u>continuum electrical modelling</u> of the Esaki interband tunneling diode the most critical part of the solar cell, is done by the commercial DESSIS software. The resulting current flow and resistance of different device architectures is calculated and analysed and the optimum wire configuration is determined.

www.amonra.eu

Project Acronym and Number: AMON-RA 214814 Project Title: Architectures, Materials, and One-dimensional Nanowires for Photovoltaics - Research and Applications Start and End Dates: 01/10/2008 till 30/09/2012 EC Contribution: 3.199.987 € Coordinator: Prof. Knut Deppert, Lund University, <u>knut.deppert@ftf.lth.se</u>



in ARTIVASC_3D 263416

Subject of the modelling

Blood and nutrient transport in vascularised biomaterials

Models used

Continuum: computational fluid dynamics (<u>CFD</u>): advection-diffusion equation for transport of nutritients and O2 (microscale) hydrodynamics model based on Navier-Stokes equations (macroscale)

Simulation software and type of numerics used

FEM code "Elmer" to simulate the transport of nutrients and O2 Smoothed particle hydrodynamics code "SimPARTIX" to simulate blood flow

Achievements of the model beyond experiments

The hydrodynamic modelling will be able to predict wall shear stresses at the vascular graft walls. These stresses have to be within a certain range in order to stimulate the endothelial cells to perform e.g. neo-angiogenesis. These wall shear stresses would be extremely difficult to measure for any possible graft geometry. Therefore, a modelling-based design approach is crucial for tissue engineering.

Application

Regenerative medicine, additive manufacturing of tissues

ArtiVasc 3D aims at developing a bioartificial vascularised skin which will, for the first time, allow tissue replacement with optimum properties in a fully automated and standardised manufacturing approach. This will be achieved through an innovative combination of hi-tech engineering such as micro-scale printing, nano-scale multiphoton polymerisation and electro-spinning with biological research on biochemical surface modification and complex cell culture and using a multidisciplinary approach which involves experts in biomaterial development, cell-matrix interaction, angiogenesis, tissue engineering, simulation, design and fabrication methods work.

This new bioartificial vascularised skin will be of great value in a vast array of clinical treatments, e.g. as a transplant in trauma treatment. In addition, it will be used as an innovative in vitro skin equivalent for pharmaceutical, cosmetics or chemical substance testing, which represents a promising method to reduce expensive, ethically disputed animal testing.

Summary of the modelling

The project develops and applies modelling techniques for the design a vascular system that effectively delivers O_2 and other nutrients from the circulating blood flow to the surrounding tissue. Experiments and simulations will be employed in order to develop design rules and 3D models of the artificial vascular system. The modelling in this project aims at providing the link between biological demands and the scaffold manufacturing and development.

An (microscale) <u>advection-diffusion model</u> is applied to predict permeation times of nutrients and O_2 depending on material type (e.g. polymer, hydrogel, fat), and vascular system parameters like porosity and wall thickness. The simulation model explicitly considers the local porosity structure and, thus, gives far more detailed results than simple calculations using Darcy's Law. Model parameters will be adjusted by reference to the experimental data. The model is used to calculate permeation times which are necessary for the nutrients/ O_2 to reach the cells in the surrounding hydrogel matrix.

The avoidance of clogging of the vascular grafts is of paramount importance to the long-term functionality of the system. In order to account for this aspect, the smoothed particle hydrodynamics solver will be extended by a deposition model. This allows for the analysis of deposition of platelets on the vessel walls depending on systematically varied flow conditions. Based on these microscopic simulations deposition/clogging rules will be derived to be incorporate into the finite element modelling on the length-scale of the complete vascular system.

<u>Fluid dynamics simulations</u> (at larger scale) of pulsatile blood flow through elastic blood vessels will be conducted and compared with pressure-controlled experiments. For this purpose a fluid-structure-interaction scheme will be used within the hydrodynamics code.

The blood flow simulations will provide information on the local geometry. Design rules for the local geometry (e.g. bifurcations, diminutions) will be derived. These rules will ensure the avoidance of flow anomalies (recirculating flows) and the compliance with a reasonable range of wall shear stresses to provide an endothelium-friendly flow environment. Thereby, neo-angiogenesis will be stimulated and clogging of the vascular grafts will be avoided.

The numerical results will be used for the 3D design of the complete artificial vascular system. The modelling-based design will ensure biomimetic conditions for the endothelial cell layer which is the key to a functional vascularised system.

http://www.artivasc.eu/

Project Acronym and Number: ARTIVASC_3D 263416 Project Title: Artificial vascularised scaffolds for 3D-tissue-regeneration Start and End Dates: 01/11/2011 till 31/10/2015 EU Contribution: 7.800.000 € Coordinator: Arnold Gillner, FhG, DE <u>Arnold.Gillner@ilt.fraunhofer.de</u>



in ATHENA 233553

Subject of the modelling

Transition metal oxides (magnetic perovskites, double perovskites, diluted magnetic ferroelectrics, piezoelectrics, magneto resistivity heterojunctions, superlattices and multilayers)

Models used

Electronic: First-principles density-functional theory (<u>DFT</u>) based methods <u>Tight binding model</u>

Simulation software and type of numerics used

High performance electronic structure codes based on density functional theory: highly parallelised versions of the LCAO-based SIESTA code, the PWSIC code, the developer version of VASP. Model Hamiltonian solved with a range on Monte Carlo technique, including the travelling cluster scheme for large-scale simulations.

Maximally localized Wannier function suit WanT, interfaced with the DFT codes to give parameters for the model Hamiltonian

Achievements of the model beyond experiments

The integrated multi-scale approach (DFT WanT MH) allows a full parameter-free description of thermodynamics properties of complex oxides and oxides interfaces ahead of experiments, or where experimental information are difficult/impossible to extract.

Identification of candidate materials and materials interfaces for future nano-electronics based on complex oxides. These included hetero-junctions, superlattices and multilayers consisting of doped magnetic perovskites (e.g. LaxSr1-xMnO3, PrxCa1-xMnO3), double perovskites (e.g. LaNi1-xMnxO3) and diluted magnetic ferroelectrics designed to exploit and manipulate the coupling of different order parameters at the two sides of the interface.

Prediction of the phase diagram of complex magnetic oxides MnO and NiO under pressure, Explanation of the extremely high antiferromagnetic ordering temperature in SrTcO3 and BaTcO3,

Application

Multiferroic devices (both single-phased multi-functional materials and heterostructures), non-volatile memories based on multiferroic materials

Relevant review articles

A. Filippetti, et al Variational pseudo-self-interaction-corrected density functional approach to the ab initio description of correlated solids and molecules, Phys. Rev. B 84, 195127 (2011).
T. Archer, et.al Exchange interactions and magnetic phases of transition metal oxides: Benchmarking advanced ab initio methods, Phys. Rev. B 84, 115114 (2011).

C. Franchini, et al. Exceptionally strong magnetism in the 4d perovskites RTcO3 (R=Ca, Sr, Ba), Phys. Rev. B 83, 220402(R) (2011).

The overall aim of the project is the investigation of the properties and functionalities of transition metal oxides and their heterostructure, as these may be viable candidates as building blocks of future micro- and nanoelectronic devices. The project investigates the physics of strong-correlated materials, which includes charge and orbital ordering, polaronic formation, spin-charge separation, non-Fermi liquid behaviour, just to name a few.

Summary of the modelling

The modelling consists of a multi-scale approach merging parameter-free first-principles methods based on density-functional theory (DFT) with many-body model Hamiltonian calculations suited for exploring the temperature dependant properties of strong-correlated systems. On the one hand, first principles techniques allow one to describe at a quantitative level the electronic structure of perfectly crystalline materials at zero-temperature. In this case the description does not necessitate parameters as the underlying quantum mechanical problem is solved exactly, within well-controlled approximations. On the other hand, the model Hamiltonian approach is suitable for exploring effects connected to finite temperature and disorder. This however requires parameters, which usually are extracted from experiments, whenever possible, or simply inferred from chemical/physical intuition. Our research strategy combines the benefits of the two approaches as the parameters for the model Hamiltonians are rigorously extracted from our first principles calculations.

The project developed several methodologies for first principles calculations tailored to the specific class of materials comprising complex oxides and their interfaces and heterojunctions. This is a class of materials critical to standard electronic structure methods, which usually fail in describing even the most elementary properties as the electronic band-gap or are too expensive to use for interfaces. Our newly developed methods are based on DFT and include a completely novel variational formulation of the pseudo-self-interaction correction scheme (pSIC), a new version of the DFT exact exchange method, the hybrid <u>Hartree-Fock DFT</u> approach and a hybrid method combining DFT with the dynamical mean-field scheme.

The project formulated novel model Hamiltonians for describing the finite-temperature thermodynamic properties of single and double perovskites, with the possibility of including both A- and B-site doping/disorder. The parameters for the models are rigorously derived by a procedure in which the DFT-calculated electronic band-structure is mapped onto a <u>tight-binding Hamiltonian</u> model. Such a mapping is carried out by constructing the system's maximally localized Wannier function, which is a universal procedure applicable to any material, no matter its complexity. New interfaces between the consortium available first principles codes (SIESTA, VASP and PWSIC) and the maximally localized Wannier function suit (WanT) have been constructed and will be soon distributed.

Achievements of the project include 1) the description of the phase diagram of both MnO and NiO under pressure, 2) the explanation of the spectacularly high antiferromagnetic ordering temperature in SrTcO3 and BaTcO3, currently the two materials with the highest Neel temperature among the 4d series, 3) the demonstration of the possibility of the coexistence of a tunnelling magneto-resistance and tunnelling electro-resistance in a complex oxides heterojunction, SrRuO3/BaTiO3/SrRuO3, and the tuning of the effect by intercalating a think SrTiO3 layers at one of the junction interfaces. 4)The project designed a new heterojunction stack, SrRuO3/BaTiO3/SrTiO3/SrRuO3, displaying both tunnelling magnetoresistance (TMR) and tunnelling electroresistance (TER). Furthermore we demonstrated that the TER is fully tuneable by changing the SrTiO3 layer thickness. This may have significant application as a 4-state non-volatile multifunctional random access memory element. Predictions on new devices functionalities are now possible.

www.athenacomp.eu

Project Acronym and Number: ATHENA 233553 Project Title: Advanced theories for functional oxides: new routes to handle the devices of the future Start and End Dates: 01/06/2009 till 31/05/2012 EU Contribution: 849.998 € Coordinator: Stefano Sanvito, Trinity College Dublin, Ireland, <u>sanvitos@tcd.ie</u>



in AUTOSUPERCAP 266097

Subject of the modelling

Battery-supercapacitor power system for an electric vehicle application Ion transport in supercapacitors made of carbonaceous materials, e.g. activated carbon, carbon nanotubes, graphene

Models used

Atomistic: <u>Classical MD</u> code for ion and electrolyte transport to calculate ion size and limiting pore size Continuum: <u>flow model</u> for ion and electron transport <u>Device model</u> for optimal control of a battery-supercapacitors system

Simulation software and type of numerics used

Matlab Simulink for power system Materials Studio v5.0 for molecular dynamics simulations In house code for continuum flow modelling

Achievements of the model beyond experiments

The battery-supercapacitor modelling and simulations allow selection of the best materials/supercapacitor for scaling up reducing experimental costs. The molecular ion simulations guided the research for a pore size, maximising the specific capacitance for carbonaceous electrode materials and thereby increasing energy and power density.

Application

Supercapacitors for energy storage units

Relevant review articles:

A. Santucci, F. Markoulidis, M.K. Abbas, C. Lekakou, B. Martorana, M. Gosso and J. Perry "A Model of a Battery-Supercapacitor Power and Energy Storage System for Electric Vehicle Applications", submitted to International Journal of Powertrains, May 2012 C.Lekakou, F.Markoulidis, C.Lei, A.Sorniotti, J.Perry, C.Hoy, B.Martorana, I.Cannavaro, M.Gosso "Meso-nano and micro-nano ion transport in porous carbon composite electrodes for energy storage applications", Proceedings ECCM15 - 15TH European Conference on composite materials, Venice, Italy, 24-28 June 2012

The project is aiming at developing supercapacitors which are essential in electric vehicles for supplying power during acceleration and recovering braking energy. High power and high energy density are required in the automotive industry for both an effective power system but also to reduce weight.

Summary of the modelling

The project works with computer simulations at <u>device level</u> to optimise the power system and the design of supercapacitor banks. An existing generic power system and electric vehicle computer model have been elaborated with a model for a battery-supercapacitor energy storage unit (ESU) or a battery only ESU. Input to the model is imposed driving time schedule, in terms of speed and requested power as functions of time, imposes power requirements to a dc bus and associated control system. charge cycles will also be incorporated in the model as a control sub-loop, including charging of supercapacitor and battery from combined energy sources, e.g. fuel cell, electricity sub-stations, braking energy during the deceleration phases of the driving schedule. The fast discharge and charge phases impose a requirement for reliable and optimum operation, especially in urban driving schedules. The computer code to simulate these processes will be produced in MATLAB Simulink environment.

This power system computer model has been incorporated in the test rig computer model and in a generic electric-hybrid vehicle model (for parametric studies) to decide on the specifications of a generic electric-hybrid vehicle model. With this model, parametric and optimisation studies will be carried out for different scenarios in automotive applications and different battery-supercapacitor load combinations in order to establish supercapacitor specifications for the different types of supercapacitors to be developed in this project.

The work will aim to establish the 'real world' working envelope of typical supercapacitor energy storage systems. This will lead to minimisation of system mass, a very important consideration for an electrical vehicle, and also the cost of the system.

The project designed and tailored optimum electrode material morphologies for the ion transport of certain electrolytes to achieve maximum power and energy densities.

In energy storage devices carbonaceous composite electrodes are a popular choice, consisting of activated carbon (ac), conductive additives and a polymeric binder matrix. The active electrode components are in the form of ac particles, ac fibres, or ac monolith combined with conductive additives such as carbon black. Activated carbon plays the most important role for storing a large amount of energy in the form of ions contained in the carbon nanopores.

The project applied classical molecular dynamics model to calculate ion size and limiting pore size. <u>Molecular dynamics</u> simulations (Materials Studio v5.0) have been performed to determine the values of the geometrical parameters of different ions, solvated and unsolvated in various solvents. This project used continuum <u>flow models</u> for the infiltration of ions and electrons into the porous carbon structure during the operation of the energy storage device. Depending on the pore size, ion size and solvent molecule size, ions may be solvated or unsolvated as they move, where ions are solvated in meso-pores for most cases. The ion infiltration model can calculate both steady state and dynamic conditions. The model is implemented into a computer code and it can run for various input parameters to optimise speed, extent of ion transport and capacitance in a porous material.

Linking between the models was achieved by using the pore-size diffusion coefficients determined by the MD models in the continuum ion transport model. There was no linking between the ion transport model and the device model.

http://autosupercap.eps.surrey.ac.uk/

Project Acronym and Number: AUTOSUPERCAP 266097 Project Title: development of high energy/power density supercapacitors for automotive applications Start and End Dates: 01/1/2011 till 31/12/2013 EU Contribution: 3.974.595€ Coordinator: Dr Constantina Lekakou, University of Surrey, UK, <u>C.Lekakou@surrey.ac.uk</u>



in CODICE 214030

Subject of the modelling

Cement, cement hydration

Models used

Atomistic: <u>Molecular Dynamics</u> (Garofalini force field) for hydration Atomistic and Mesoscopic: Hierarchical <u>Statistical Mechanics growth model</u> for aggregation of C-S-H particles and <u>grain based flow</u>. Continuum: <u>mechanical</u> (wear and fracture model) and <u>transport model for hydration</u> (extended Nerst-Planck equations)

Simulation software and type of numerics used

HYMOSTRUC-3D for hydration CODICE_HYD Monte Carlo growth model (based on C4) CODICE_DEG and CODICE_MEC for wear and fracture (Finite Elements)

Achievements of the model beyond experiments

The developed toolkits revealed that there is a synergy in the hydration of alite and belite phases of cement clinker, which opens the door to new eco-cements. While a priori one would expect that the larger the content of C_3S the better the resulting mechanical properties, the simulations have revealed that there is synergy in the hydration of C_3S and C_2S blends, and that there is an optimum C_3S/C_2S ratio around 70/30.

Application

Eco cement for construction

Relevant review articles

Puertas F et al. A model for the C-A-S-H gel formed in alkali-activated slag cements; JOURNAL OF THE EUROPEAN CERAMIC SOCIETY Volume: 31 Issue: 12 Pages: 2043-2056 DOI:10.1016/j.jeurceramsoc.2011.04.036 Published: OCT 15 2011 – Dolado Jorge S.; van Breugel Klaas; Recent advances in modeling for cementitious materials; CEMENT AND CONCRETE RESEARCH Volume: 41 Issue: 7 Special Issue: SI Pages: 711-726 DOI: 10.1016/j.cemconres.2011.03.014 Published: JUL 2011

CODICE brought producers and suppliers of cement-based materials together with universities and research institutes for the development of new and radically improved computational toolkits that monitor the formation and properties of cementitious materiales by starting from macroscopic processing variables: size of cement grains, water-cement ratio, temperature, grain composition.

Summary of the modelling

CODICE project has developed a serial parameter-passing multi-scale modelling scheme to predict the structural evolution and the mechanical performance of non-degraded and degraded cementitious matrices as a function of macroscopical processing variables to guide the design of cementitious materials

A1) Coarse macrolevel description in CODICE_HYD TOOLKIT

The coarser description of the cementitious skeletons is provided by a new and modified version of HYMOSTRUC-3D which is <u>mesoscopic statistical model</u> based on a mass balance concept for individual hydrating cement grains and distinguishes three independent phases, i.e. C3S, C2S and CH (E. A. B. Koenders et al.; A Density Model for Micro- to Nano-structures; under review). Moreover a novel digitalization mode has been implemented that generates a 3D voxel structure of the virtual microstructure and can be used for information exchange within the run of each time step. This new HYMOSTRUC-3D model employs as input macroscopical processing variables, such as the cement grain size, the water/cement ratio, etc and gives for each voxel relevant information like density, relative humidity, saturation, chemistry, etc.

A2) Refined nano-level description in CODICE_HYD TOOLKIT

The refinement of the coarse microstructure is performed by a Monte Carlo based algorithm named C4 (CODICE_Colloidal_CSH_Code) model. With the data flushed from the micro level simulations, each voxel can be refined. To this end, current implementation of C4 receives as input the density of the C-S-H voxel, and its water content (saturation index). Then the structure at the submicro level is conceived as a resulting from aggregation of dried C-S-H particles using an <u>atomistic statistical</u> <u>model</u>. The information about the size, density or water content of these basic dried-C-S-H units is based on the knowledge gained from intensive atomistic simulations. Afterwards the voxel structure is generated through Monte Carlo growth scheme which mimics the textural details provided by Jenning's model. This is possible by adjusting the growth parameters so as to reproduce the right density of the voxel, and the saturation index.

The atomistic <u>MD</u> with garolini force field model identified the smallest bricks of cementious structures. By employing Molecular Dynamic simulations CODICE has revealed that the main constituent of cement hydration (C-S-H) is nano-branched, with segmental pieces of 3x3x6 nm-sized. Afterwards, these segmental pieces have been approximated by 4-5 nm-sized spherical particles which served as coarse grained particles in a home-made <u>kinetic Monte Carlo</u> scheme used for aggregation. This KMC scheme has enabled to describe larger structures of C-S-H gel and establish a linkage.

B) CODICE_DEG TOOLKIT simulates the accelerated <u>micromechanics</u> degradation processes that occur when ammonium nitrate (NH4NO3) solutions pass into the cementitious pore network. In essence, it solves by standard Finite Element Model (FEM) <u>CFD</u> (the extended Nerst-Plank set of equations) by decoupling the transport and chemical reaction equations. Remarkably, CODICE_DEG is well suited to trace the degradation processes at the C-S-H level, and to the best of our knowledge, it is the first time that the calcium leaching can be visualized in 3D. This new tools will contribute not only to a better understanding of the phenomenon of calcium leaching but they will also help engineers to the design of safer structures with smaller amount of material. C) CODICE_MEC TOOLKIT, a 3D lattice <u>micromechanics</u> fracture model, completes the "structure-performance" linkage by predicting the elastic modulus and tensile strength of cementitious skeletons starting from the knowledge of their structure. Finally, the outputs of the fracture process simulation are the load-displacement diagram and micro-crack propagation. The load-displacement diagram reveals the tensile behaviour of cement paste at micro-scale, from which the elastic modulus and tensile strength can be obtained.

www.codice-project.eu

Project Acronym and Number: CODICE 214030 Project Title: COmputationally Driven design of Innovative CEment-based materials Start and End Dates: 01/09/2008 till 31/08/2011 EU Contribution: 2.700.000€ Coordinator: Jorge Sánchez Dolado, TECNALIA , jorge.dolado@tecnalia.com



in CRONOS 280879

Subject of the modelling

Energy photo-conversion and laser-induced ultrafast magnetization dynamics

Models used

Full first principles method: time-dependent density functional theory (TDDFT)

Simulation software and type of numerics used

Open-source OCTOPUS code

OCTOPUS has a modular structure with a real-space grid as basis set. Extreme parallelization with sparse matrix linear algebra

Achievements of the model beyond experiments

Prediction of full time-evolution of ultrafast pump-probe dynamics and their spectroscopy measurements for new materials. Prediction of charge oscillations in the electron transfer process in supra-molecular light harvesting organic triads. Prediction of demagnetization and spin-dynamics in bulk Ni in the first few fs subsequent an intense laser irradiation.

Application

Solar cell, magnetic recording

Relevant review articles

Time dependent DFT (the main theoretical tool of the project) Miguel A. L. Marques and E. K. U. Gross, Time-dependent Density Functional Theory, Annual Review of Physical Chemistry 55, 427 (2004)

Dye sensitized solar cells Anders Hagfeldt, Gerrit Boschloo, Licheng Sun, Lars Kloo and Henrik Pettersson, Dye-Sensitized Solar Cells, Chem. Rev. 110, 6595 (2010)

Ultrafast spin dynamics Andrei Kirilyuk, Alexey V. Kimel and Theo Rasing, Ultrafast optical manipulation of magnetic order, Rev. Mod. Phys. 82, 2731 (2010)

The CRONOS project will go beyond the "static total-energy and mapping" scheme for materials modelling and develop a full time-dependent, fully atomistic theory of ultrafast dynamics in materials. The processes addressed are energy photo-conversion and laser-induced ultrafast magnetization dynamics.

Summary of the modelling

Photo-energy conversion and laser-induced ultrafast magnetisation dynamics both consist of describing how an electronic system reaches equilibrium after an initial perturbation pumps energy into it. This is governed by dynamics of materials at the femtosecond (fs, 1 fs=10-15 seconds) timescale and at the microscopic level. The modelling will address how the relaxation to the equilibrium can be driven towards a particular "useful" final state (for instance the separation of an electron-hole pair in a solar cell or the magnetisation reversal in magnetic recording).

Such dynamics are the result of the interplay between all the degrees of freedom involved, namely electronic, ionic and spin. Each one of them is characterised by a different timescale and by a characteristic interaction with the others. Furthermore the same degrees of freedom may evolve rather differently in different materials, so that fully atomistic modelling in the time-domain is necessary.

Time-dependent Density Functional Theory (<u>TDDFT</u>) will be the common theoretical/computational framework of the project. CRONOS will contribute to the development of TDDFT along four directions:

- 1) Development of new DFT and TDDFT meta-GGA exchange and correlation functionals
- 2) Development of new spin non-collinear DFT and TDDFT exchange and correlation functionals
- 3) Development of method to combine non-adiabatic ionic dynamics with time-dependent DFT
- 4) Development of optimal quantum control theory for TDDFT

The model will be parallelised so to ensure efficient scaling with system size.

www.cronostheory.eu

Project Acronym and Number: CRONOS 280879 Project Title: Time dynamics and control in nanostructures for magnetic recording and energy applications Start and End Dates: 01/06/2012 till 30/06/2015 EC Contribution: 3.380.058 € Coordinator: Stefano Sanvito, TCD, Ireland, <u>sanvitos@tcd.ie</u>



in DISC REGENERATION 213904

Subject of the modelling

Biomaterials, scaffolds, intervertebral disc, angiogenesis

Models used

Continuum: <u>Poroelastic model</u> <u>Diffusive transport model</u>

Simulation software and type of numerics used

Commercial software (Abaqus) with specific Fortran subroutines for non-linear material properties and coupling between diffusion, convection and structural analyses Finite Element method with an implicit scheme Parallelization for such non-linear model and such coupling between structural equations and thermodynamic equations

Achievements of the model beyond experiments

The modelling contributions are twofold:

The coupled transport-mechano model is able to predict the movement of solutes within the intervertebral disc and predicts the interactions between mechanical properties, fluid and solute transport, and cell viability. This is essential for a proper understanding of the mechanisms of disc degeneration and disc regeneration with the use of biomaterials as disc substitute.

Simulations of the effect of partial and complete disc nuleotomy on load transfer as a function of the biomaterial substitute used can be used to determine the surgical variability during nucleus removal.

Both contributions cannot be obtained experimentally and therefore are complementary to the experimental evaluation of the biomaterial performance.

Application

Biomedical implants

Summary of the project

The project seeks to provide a cure for lower back pain by developing injectable a-cellular and cell-loaded bioactive polymer-based scaffolds and technology which will repair a damaged intervertebral disc (IVD) by enabling its regeneration to a natural healthy state or better.

Summary of the modelling

This new generation of replacement devices are designed with a biomimetic approach which will confer the appropriate mechanical and biological properties and enable the inclusion of the requisite cell signalling factors to produce a bio-hybrid structure which closely resembles the human tissue in all its essential attributes.

This requires comprehensive numerical studies to predict their behavior under stress in the post-implantation period. Particular attention needs also to be paid to angiogenesis because in IVD tissue, vascularization must be carefully controlled, due to the unique anatomy and physiology of the intervertebral disc. Modelling studies within this project identified the key physical and mechanical properties of the natural IVD and the substitute materials, and provided an understanding of the physical aspects of the regeneration process.

1) Mechanical model

Complex computational models are required for explorative preclinical biomechanical investigations, as they can potentially account for the complex physics of the intervertebral disc environment, such as the fluid-solid interactions within the implant as well as the interaction between the implant itself and the surrounding intact biological structures, which involve the contact between nonlinear and nonhomogeneous multi-phasic materials. For that purpose different disc replacement configurations were evaluated on how they affect the response of a poroelastic finite element model of the intervertebral disc under complex physiological loads.

2) Vascular transport model (mechanics and fluid dynamics)

Using a poromechanical finite element (FE) model coupled to a diffusive transport model we studied the effect of mechanical and nutritional factors on the diffusion of two fundamental cell solutes, oxygen and lactate, strongly related with disc cell metabolism1. In our model crucial disc properties such as fluid content, osmotic pressure of the nuclear region, disc height, permeability, cell density, pH, were parameterized and their effect was studied on both the mechanical and solute transport response. Importantly, disc mechanical response to external compressive loads was simulated at the same time. External compressive loads affected oxygen and lactate contents within the disc. Sustained compression had its greatest influence on nutrient transport by decreasing diffusion distances diffusivity of solutes. We found that the more the disc was deformable, the larger was the effect. By comparing with in vivo literature data the model predicted similar oxygen and lactate patterns. A parametric study showed that the most important factors affecting the solutes' transport were: cell density, fluid content, disc height and nucleus osmotic pressure while other parameters had no effect. It is also important that a model should be able to account for the detrimental effect of acidic pH (due to lactate accumulation) which is the most relevant nutrient affecting cell viability.

http://www.disc-regeneration.eu

Project Acronym and Number: Disc Regeneration—213904 Project Title: Novel biofunctional high porous polymer scaffolds and techniques controlling angiogenesis for the regeneration and repair of the degenerated intervertebral disc Start and End Dates: 01/11/2008 till 31/10/2012 EU Contribution: 6.977.150€ Coordinator: LUIGI AMBROSIO, <u>ambrosio@unina.it</u>



in DYNAMAG 233552

Subject of the modelling

Dynamics in magnetic nano-materials and devices

Models used

Electronic: <u>Ab-initio models</u> for the exchange interaction, magnetic anisotropy and magnetization.

Mesoscopic: <u>Micromagnetic models</u> based upon the Landau-Lifshitz equation with ab initio parameters to calculate the spin wave spectra and dispersion in multilayer structures. Models of relative dynamics of different sublattices in antiferromagnetic and ferrimagnetic materials Continuum: <u>Models of electromagnetism</u>: absorption and emission in magnetic nanomaterials

Simulation software and type of numerics used

Electronic: VASP and WIEN2k (DFT)

Mesoscopic: NMAG: Finite difference micromagnetic packages and parallel version of OOMMF A code based on the Dynamical Guiding Centre approximation (GCA)

Dynamical matrix method (DMM) calculations

Micromagnetic data processing software SEMARGL

Utilities for data transfer between Nmag and OOMMF (SEMARGL);

Continuum ElectroMagnetism: Plane wave method (PWM) calculations

Parallel versions, in particular for multicore desktop PCs

Achievements of the model beyond experiments

The calculations pointed out samples that were until then simply not considered. A novel magnonic logic architecture has been developed based on physics discovered by the models.

The, until then unexplained, origin of the response experimentally observed in optical pumpprobe studies of magnetic multilayers with strong perpendicular magnetic anisotropy, has been revealed via calculations in the discrete lattice model.

Mechanisms behind unusually low magnetic domain wall depinning currents within spintronic devices have been revealed via full 3D finite element simulations.

Application

Spintronics and magnonics, including magnonic crystals, spintronic and magnonic devices interconnected with more conventional photonic, plasmonic, and electronic devices.

Relevant review articles

S. - K. Kim, "Micromagnetic computer simulations of spin waves in nanometre-scale patterned magnetic elements", J. Phys. D – Appl. Phys. 43, 264004 (2010).

Dynamag is a modelling project that focusses on magnonic crystals, a sub-field of a wider field of research called magnonics, and also deals with nanomagnetism and more specifically spin dynamics in magnetic nanomaterials and nanodevices. The ability to accurately predict fundamental and functional properties of fabricated magnetic nanostructures and complete devices by theoretical means is based on a thorough understanding of the relation between their chemical and physical fine structures and the desired useful magnetic functionalities.

Summary of the modelling

Competition between long and short range magnetic interactions leads to inherent complexity of phenomena observed in magnetic structures with nanoscale features, and hence to dramatic difficulties in their analytical treatment.

<u>DFT</u> models have been used to calculate the exchange interaction, magnetic anisotropy and magnetization.

DYNAMAG has extended the mathematical formalism of numerical <u>micromagnetic</u> solvers beyond the classical Landau-Lifshitz equation by a rigorous account of spintronic and temperature dependant aspects of modelled phenomena occurring in multi-sub-lattice magnetic materials. DYNAMAG also developed new software applications to process and analyse large amounts of data produced by micromagnetic simulations, in particular those run using supercomputers.

The finite element <u>micromagnetic</u> package Nmag has been extended to explicitly simulate relative dynamics of different sub-lattices in ferrimagnets and antiferromagnets and to facilitate inclusion of various spin transfer torque terms within models of magnonic devices interconnected with those of magneto-electronics (spintronics). This inclusion has provided deeper insights into the dynamical performance of magnetic sensors and recording heads.

On the numerical side the dynamical matrix method (DMM) code has been further developed, in particular to facilitate the calculation of the Brillouin Light Scattering (BLS) cross-section from the DMM results. The complete 2D magnonic band structure (and the resulting magnonic dispersions) has been successfully reproduced and interpreted Also a new dynamic simulation code based on the guiding centre approximation (GCA) has been developed, which deals withslow-variable micromagnetism.

A <u>micromagnetic</u> code particularly for studying static magnetic configuration and time domain dynamics of magnetic vortices in arrays of magnetic discs has been developed.

For the data processing a new software tool called SEMARGL as been developed to facilitate comprehensive analyses of large volumes of data produced by micromagnetic calculations. A new methodology has been developed to use the tool for calculating the scattering parameters of spin waves from magnetic non-uniformities, the magnetic susceptibility and permeability of magnonic metamaterials, as well as the magneto-optical signal measured in optical pump-probe experiments. Also a new software utility for Nmag that allows one to convert its output into the OVF format of OOMMF.

For the continuous <u>electromagnetic</u> calculations the plane wave method (PWM) has been developed to calculate magnonic dispersion relations in samples that are currently in focus of experimental studies.

http://www.dynamag.eu/

Project Acronym and Number: DYNAMAG 233552 Project Title: Advanced Computational Studies of Dynamic Phenomena in Magnetic Nanomaterials Start and End Dates: 01/06/2009 till 31/05/2012 EU Contribution: 899.936 € Coordinator: Volodymyr Kruglyak, University of Exeter, UK, <u>V.V.Kruglyak@exeter.ac.uk</u>



in FEMTOSPIN 3281043

Subject of the modelling

Heat-assisted or optically induced ultrafast reversal of magnetism

Models used

Electronic first principles method:

<u>Time-dependent spin density functional theory (TDSDFT)</u> with spin scattering effects <u>Tight Binding</u> model with Hubbard Hamiltonian

Atomistic models: <u>Atomistic spin model</u> based on_LLG model using Heisenberg formalism and <u>Langevin dynamics</u> which include thermodynamics with improved dissipation and energy transfer mechanisms for non-zero temperatures.

Mesoscopic models: <u>Micromagnetic (macrospin) model</u> including quantum effects based on the generalised Landau-Lifshitz-Bloch equation for ferrimagnets, antiferromagnets and magnetic semiconductors

Simulation software and type of numerics used

Budapest code based on the kkr code using spin-cluster expansion technique to calculate abinitio parameters (spin, exchange integrals, anisotropy).

Uppsala code for TDDFT calculations to understand the origin of the optomagnetic field. VAMPIRE (Visual Atomistic Massively Parallel Integrator Engine) for atomistic calculations of dynamic response to ultrafast laser pulses.

York code for heat bath models, used to understand the underlying processes of energy transfer between the excited conduction electrons and the spins.

Madrid/Konstanz code for micromagnetics with finite-difference discretisation for large-scale calculations for comparison with experimental data, especially imaging.

Achievements of the model beyond experiments

Prediction efficiency of ultrafast spin dynamics in multiferroics excited by THz laser pulses Prediction of the smallest stable domain structure in magnetic thin films Prediction of the time and spatial scales of magnetic pattern formation Identification of optimal materials for ultrafast optically induced magnetic switching

Application

Magnetic recording with increased speed of logic and data storage devices with increased storage density, Novel ICT-devices based on spin manipulation

Relevant review articles

I Radu et al, Ultrafast magnetism as seen by x-rays, Proc. SPIE 8260, 82601M (2012); http://dx.doi.org/10.1117/12.907433

The project addresses spin dynamics for magnetic information storage technology, which is based on nanostructured magnetic materials, and for spin electronics in which the manipulation of the spin forms the basis of the device operation. Magnetic spins can be manipulated on the femtosecond timescale, while the actual switching by precessional motion lasts hundreds of picoseconds. The project investigates the physics of these multi-scale processes.

Summary of the modelling

The standard formalism used for materials and device simulations (<u>micromagnetics</u>) is a continuum formalism dealing with the spin precession timescale of 10ps upward. However, optical spin manipulation and magnetisation processes are intrinsically much faster than that of precessional switching e.g. complete demagnetisation happens on the timescale of hundreds of fs. Thus multi-scale models are required dealing with the timescales associated with exchange, spin-orbit coupling and spin-flip scattering. The project will investigate processes at the light-spin interaction level, electronic structure level, atomistic level and mesoscopic level.

The fundamental interactions between spin, conduction electrons and the laser light (excitation and demagnetization processes) that occur on very short time scales (atto- to femto-seconds) will be described and the beyond- linear-response real-time formulations shall be combined with ab-initio code on the basis of the time-dependent spin-density functional theory (<u>TSDFT</u>) to compute ultrafast magneto-optical response.

The inverse Faraday effect is at the origin of the laser-induced "optomagnetic" field and this mechanism is further investigated so that it can be implemented in the <u>atomistic spin Hamiltonians</u> used in electronic simulations calculating atomic properties. A model of non-equilibrium spin-scattering (energy and spin transfer) channels will be built that can predict ultrafast demagnetization. The aim is to develop a suitably parameterized form of demagnetization caused through hot electron transport that can be used and incorporated in the spin Hamiltonians used for atomic simulations. The temperature dependent ab-initio parameters of spin Hamiltonians can be used in the atomistic spin-dynamics simulations. The first-principle electronic structure will be mapped to a multiband <u>Hubbard model</u>, with realistic <u>tight-binding</u> and interaction parameters. Within the framework of the multiband Hubbard model, the effects of exchange interactions being different from those in equilibrium (non-adiabatic effects) will be studied.

The project will introduce the above mentioned physics into the atomistic lengthscale <u>heat bath</u> <u>models</u> which rest on fixed spin length and fixed model parameters. They will develop equations of motion beyond current Langevin dynamics to arrive at a better treatment of the coupling of the spin system to electronic and phononic degrees of freedom and hence a better modelling of the dissipation channels. Also a more realistic model for the energy transfer on the fs timescale will be included. The coupling between the atomic spins and the heat bath will be based on the ab-initio models developed. To identify optimal materials for ultrafast optically induced magnetic switching the relevance of the specific spin ordering in ferro-, ferri-, antiferro-magnetic and magnetic semiconductors will be studied.

The project will include quantum effects in <u>macrospin models</u> of ferrimagnetic and antiferromagnetic materials. These macrospin models are based on the micromagnetic approach with finite-differences discretization and use the input of the electronic structure and atomic models. The codes will be used for (granular and polycrystalline) materials design exercises for heat assisted magnetic recording. The atomistic and multiscale spin models, developed within <u>ULTRAMAGNETRON</u> and FEMTOSPIN are providing important insight into the physics of Heat Assisted Magnetic Recording (HAMR), and the testing and validation carried out within those projects are leading to the point at which the computer models are ready to become predictive design tools.

www.femtospin.eu

Project Acronym and Number: FEMTOSPIN NMP3281043 Project Title: Multiscale modelling of femtosecond spin dynamics Start and End Dates: 1/6/2012 till 30/6/2015 EU Contribution: 3.999.500 € Coordinator: Roy Chantrell, University of York, UK, <u>roy.chantrell@york.ac.uk</u>



in FREECATS 280658

Subject of the modelling

Catalysis reactions and processes in foam structures

Models used

Continuum: Multi-scale model for mass (CFD) and <u>heat transfer</u>, <u>reaction kinetics</u> and <u>hydrodynamics</u> in foam structures

Simulation software and type of numerics used

MODELICA, MATLAB custom systems of partial differential equations with commercial PDE solvers; ANSYS CFD based code with custom reaction code written in C++

Achievements of the model beyond experiments

Heat transfer modelling guides the design of the foam materials and predicts the deposition of carbons during operation, (a phenomenon critical in oxidative dehydrogenation) and so reduce costs of trial and error developments.

Multi-scale modelling of reaction, surface-fluid interactions, heat transfer and hydrodynamics allow to predict from first principles the behaviour of the overall reactor system and to screen a large space of operating conditions prior to experimentation. This leads to better understanding of physical phenomena involved and dynamics of processes within the system, thus reducing the number of experimental trials required.

Application

Catalysts, reactor design

Relevant review articles

Kambiz Chizari, et al Nitrogen-Doped Carbon Nanotubes as a Highly Active Metal-Free Catalyst for Selective Oxidation: ChemSusChem (2012) DOI: 10.1002/cssc.201100276

Summary of the project

This project is addressing catalysis for the sustainable production of chemicals and commodities. The FREECATS project deals with the development of new metal-free catalysts, either in the form of bulk nanomaterials or in hierarchically organized structures both capable to replace traditional noble metal-based catalysts in catalytic transformations of strategic importance. Metal-based catalytic processes are considered in the light of new tailored metal-free catalytic architectures designed and fabricated starting from appropriate nanoscale building blocks.

Summary of the modelling

The models to be developed will address the chemical reactions, heat and mass transfer, and hydrodynamics with the foam structure as a parameter.

Based on the data on catalysts characterisation and kinetic measurements an analytical mechanistic <u>reaction kinetic model</u> will be developed and validated against the available data. The code solving the equation will be developed in MODELICA, which is an open-code modelling environment. The code will later be transferred (as custom-routines coded in C++) into commercial software (ANSYS). The model will be used to detail surface reactions and adsorption processes of the new catalysts.

A micro-model of <u>heat conduction</u> through a foam material based on the solid mechanics package within ANSYS and using finite elements methods will be applied. For this the actual structure of the foam, obtained through electron tomography, and geometrical models of the foam structure, will be used.

Two process models will be applied:

In the first approach, the above described reaction kinetic MODELICA model will be coupled to MODELICA gas-solid, gas-liquid and gas-liquid-solid <u>mass transfer models</u>, <u>heat transfer</u> and <u>hydrodynamics</u>. These continuum models will ignore inertia effects. The MODELICA code will be used for process optimisation. The model will explore a wide range of operating conditions. The key part of the model will be the part of the code relating foam structure to heat and mass transfer characteristics. This will be a semi-empirical model, as ab-initio model is unnecessarily complex for the desired outcome.

In another approach to describe the total process a <u>CFD</u> code describing the foam geometry at a coarser level to represent the continuous fluid domain will be run. Information from the MODELICA reaction kinetics model will be fed in via boundary conditions detailing surface reactions and adsorption processes. The CFD model will take into account complex physical processes, resolving heat, mass and momentum transport in boundary layers and accounting for inertia. The purpose will be to resolve macroscopic heat, mass, momentum transport everywhere in the foam.

www.freecats.eu

Project Acronym and Number: FREECATS 280658 Project Title: Doped carbon nanostructures as metal-free catalysts Start and End Dates: 01/04/2012 till 31/03/2015 EU Contribution: 3.955.619 € Coordinator: Professor Magnus Rønning, NTNU, <u>magnus.ronning@chemeng.ntnu.no</u>



in GOFAST 280555

Subject of the modelling

Optical control by intense ultra-fast laser pulses of metallic phases in the prototypical Mott insulator V2O3 and of the superconductive phase in the high-temperature superconductor family BSCCO.

Models used

Electronic: <u>DFT</u> Models for correlated systems: Multi-orbital lattice models of the <u>Hubbard</u> type <u>Time-dependent Dynamic Mean Field Theory (DMFT)</u> for out-of-equilibrium evolution <u>Time-dependent Gutzwiller variational approach</u>

Simulation software and type of numerics used

LDA-DFT calculations with Quantum Espresso for realistic Hamiltonian parameters DMFT model solved with continuous-Time Quantum Monte Carlo (CTQMC) and Exact Diagonalization (ED) and Iterated Perturbation Theory (IPT) Gutzwiller model (time-dependent) with multi-dimensional optimization

Achievements of the model beyond experiments

The model identified optimal correlated materials (composition, size, direction of the laser pulse versus surfaces, etc) and excitation pathways (photon energy, intensity, polarization and temporal profile) for the production of controllable and reversible photo-induced transitions between distinct phases, e.g. metallic and insulating, or normal and superconducting.

Application

Switching devices based on the optical switching between phases with very different conducting properties.

Relevant review articles

Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions, Antoine Georges, et al Mod. Phys. 68, 13 (1996)

The Out-of-Equilibrium Time-Dependent Gutzwiller Approximation, M. Fabrizio, arXiv: 1204:2175 (2012).

Non-equilibrium dynamics of the driven Hubbard model, A. Amaricci, et al, arXiv:1106:3483 (2011). Time-Dependent Mean Field Theory for Quench Dynamics in Correlated Electron Systems, Marco Schiró and Michele Fabrizio, Phys. Rev. Lett. 105, 076401 (2010)

The aim of this research project is to develop femtoscale-modelling schemes to study electronic, optical and structural properties of correlated materials driven out of equilibrium. The possibility to optically switch on and off the metallic phase in a model Mott insulator (vanadium sesquioxide) and the superconducting phase in model high-temperature superconductors (cuprates) will be investigated and tested. The photo-excited phases are investigated experimentally by different time-resolved spectroscopic tools, like reflectivity or photoemission.

Summary of the modelling

GOFAST will extend techniques for correlated systems, i.e. Dynamical Mean Field Theory (DMFT) and the <u>Gutzwiller variational approach</u>, to model the temporal evolution after high-energy excitations are impulsively photo-injected by ultrafast laser pulses. DMFT is a quite accurate technique, although numerically very demanding. The Gutzwiller approach is less rigorous but very flexible, relatively easy to implement and to push towards long simulation times. An important step to be undertaken is finding the minimal models able to provide a reliable description of the materials under investigation, where minimal means the minimum amount of complexity.

These models aim at describing the properties of a subset of electrons that participate to conduction and where correlation effects are predominant. In transition metal oxides these electrons are commonly those that reside on the partially filled d-shell of the transition metal ions (as opposed to light elements where the p-shell electrons control the properties). If one assumes that all the other occupied shells, both of the transition metal ions and of the oxygen's, just provide an effective potential for the d-electrons that adds to the ionic one, then the effective Hamiltonian projected onto the d-like Wannier orbitals has generally the form of a tight-binding model of interacting conduction electrons. Besides a long-range part, the electron-electron interaction comprises also a short-range contribution that includes a charge-repulsion, so-called Hubbard U, and an exchange splitting responsible for the Hund's rules. In vanadium sesquioxide, each V donates three electrons to the oxygen's; hence there remain two electrons to accommodate into the t2g-orbitals that derive from the original five d-orbitals split by a cubic field. In this situation, Hund's rules play an important role. In addition, a trigonal field further splits the t2g-orbitals into a doublet and a singlet, e_{ng} and a_{1g} , respectively, and the phonon mode that controls such a splitting is known to play an important role in all physical properties. In BSSCO cuprates only one among the crystal field split d-orbitals is involved in the physics, which is a simplification with respect to V2O3. However, antiferromagnetic fluctuations are known to play an important role in these materials, hence these have to be taken into account either explicitly or via an effective bosonic mode. When needed, realistic Hamiltonian parameters will be extracted from ab-initio LDA-DFT calculations through the Quantum Espresso Density Functional package

The other crucial task is to extend DMFT and the Gutzwiller variation approach for studying out-ofequilibrium conditions provoked by an intense ultrafast laser pulse. The simplest models will be studied both at equilibrium and out-of-equilibrium and the results compared with experiments. If the agreement is not satisfactory, additional ingredients suggested by the experiments will be included in the models, which will be once again analysed at equilibrium and out of it. The procedure will continue till the modeling will compare well with experiments.

www.gofastproject.eu

Project Acronym and Number: GOFAST 280555 Project Title: Governing ultrafast the conductivity of correlated materials Start and End Dates: 01/04/2012 till 31/03/2015 EC Contribution: 1.673.200 € Coordinator: Michele Fabrizio, University of Trieste, Italy; <u>fabrizio@sissa.it</u>


in GRENADA 246073

Subject of the modelling

Optical, electronic and structural mechanical properties of graphene and its growth

Models used

Electronic: Density Functional Theory (<u>DFT</u>) and ab-initio Molecular Dynamics (<u>MD</u>) Continuum: <u>Solid mechanics model</u> <u>Computational Fluid Dynamics</u> (CFD) of Chemical Vapor Deposition processes

Simulation software and type of numerics used

VASP, Abinit and Quantum Espresso (DFT as well as ABMD) for electrical and structural properties of graphene

COMSOL (morphology) to simulate the structural, thermal and mechanical properties of graphene inside the local environment of batteries and ultracapacitors (i.e. graphene inside ionic and non-ionic liquids)

FLUENT (CFD) to model fluid dynamics inside the CVD reactor used to grow graphene.

Achievements of the model beyond experiments

CFD modelling of the chemical vapour deposition reactor provides accurate temperatures, gas flow, heat and mass transfer - information that could not possibly be obtained empirically. The choice of optimum graphene growth conditions are guided by modelling of the CVD processes.

Application

Energy storage (batteries and ultra-capacitors).

Transparent conductive electrodes (OLED displays).

Relevant review articles

"Role of the gas phase in graphene formation by Chemical Vapor Deposition on copper". P. Trinsoutrot, C. Rabot, H. Vergnes, A. Delamoreanu, A. Zenasni, B. Caussat. Submitted to Carbon

"Multi-scale modeling of silicon nanocrystals synthesis by low pressure chemical vapor deposition" I. Zahi, P. Mur, Ph. Blaise, A. Esteve, M. Djafari Rouhani, H. Vergnes, B. Caussat. Thin Solid Films, Vol. 519, 7650-7658 (2011).

The objective of GRENADA is to optimize the material synthesis techniques which provide high quality graphene with optimal properties and morphologies for target applications. Reduced graphene oxide is expected to provide a larger storage of energy than usual carbon based materials and graphene is a good candidate for the replacement of ITO electrodes as its intrinsic properties outperform those of ITO. Graphene materials are tested in-situ in configurations and environments typically found in energy storage and display applications. Formation and evolution of defects and their impact on integrated graphene properties will be studied.

Summary of the modelling

The morphology and physical properties of as-grown and modified graphene material will be modelled to understand dependence of properties on types of graphene defects. Especially interaction with local environment and in nanostructures multi-phase systems will be studied. Modelling will address unexplored area of graphene properties and mechanisms.

Density functional theory (<u>DFT</u>) calculations with the planewave code ABINIT, VASP and Quantum Espresso will be done in order to simulate the electrical and structural properties of graphene in its local environment. Especially, the electronic interaction between graphene and its surroundings and in between graphene layers in multilayers will be investigated.

We will use also <u>ab-initio molecular dynamics</u> (MD) calculations to model mechanical, magnetic and electrical properties of materials.

Continuum COMSOL <u>mechanical modelling</u> will be performed for understanding of morphological properties of graphene based flakes. The model will also be used to study the transport in multilayer graphene (with and without defects) in media of variable polarisability.

Modelling of the growth of graphene by Chemical Vapour Deposition has been performed with Computational Fluid Dynamics (<u>CFD</u>). This modelling provided insights into the growth kinetics and the flow of gases into the CVD reactor. The simulation revealed the precise influence of gas flow, temperature of gases, types of gases, and concentration profiles on the structural properties of graphene. These insights have been used to adjust the experimental conditions finally resulting in high quality monolayer graphene.

www.fp7grenada.eu

Project Acronym and Number: GRENADA 246073 Project Title: GRaphenE for NAnoscaleD Applications Start and End Dates: 01/01/2011 till 31/12/2013 EU Contribution: 3.445.370 € Coordinator: David Holden, CEA, FR, <u>david.holden@cea.fr</u>



in HIPERSOL 228513

Subject of the modelling

Resistance and recombination of charges at interfaces in solar cells

Models used

Electronic:

First principle (<u>DFT</u>) method to construct inter-atomic potentials (up to 2000 atoms) Atomistic:

<u>Classical Molecular Dynamics</u> using DFT-constructed inter-atomic potentials Mesoscopic:

<u>Phase field modeling</u> of dissolution of Ag particles and transport of Ag through the amorphous glass layer to the bulk Si

Simulation software and type of numerics used

VASP and extensions for DFT based on matrix diagonalisation procedures for plane wave based Hamiltonians

DL-POLY used for classical molecular dynamics based on velocity and leapfrog Verlet integration schemes

LAMMPS used for classical molecular dynamics and energy minimization applying specialdecomposition techniques

FactSage used for estimation of Gibbs free energies

COMSOL for transport model (conductivity) of current flow through the interface region and phase field model of the firing process based on solution of large sparce systems

Achievements of the model beyond experiments

The methods can predict contacting and recombination properties of nanostructured materials and complicated interfaces.

The model gave fundamental insight into nitrogen diffusion in silicon, into the nature of different recombination traps, into dissolution and transport of Ag during the firing process, and insight in how the current flows through the contacting region. Based on this optimal Ag crystallites geometries were gained.

Application

Optimisation of contacting and passivation schemes for solar cells

Relevant review articles

K.T. Butler, et al. Structural and electronic properties of silver/silicon interfaces and implications for solar cell performance. Phys. Rev. B 83, 235307, 2011

Keith T. Butler, et al. Molecular dynamics studies of the bonding properties of amorphous silicon nitride coatings on crystalline silicon. J. Appl. Phys. 110, 124905, 2011

G. Kresse et al. Optical and electronic properties of Si3N4 and a-SiO2. Phys. rev. B 85, 45205, 2012 M. Marsman, G. Jordan, L.-E. Hintzsche, Y.-S. Kim, and G. Kresse. Gaussian charge-transfer charge distributions for non-self-consistent electronic structure calculations. Phys. rev. B 85, 115122, 2012

Summary of project

The HIPERSOL project will address the improvement of solar cells (beyond bulk calculations of band gaps) via modelling reflecting the complexity of the real surfaces and want to include impurities and defects which determine the performance in practice. Included will be the effects of recombination (at the interface between base (passivation layer) and emitter (semiconductor) and resistive losses (at this interface and at the metal contact-emittor interface) as they are the major loss mechanisms for the light generated carriers (electrons and holes).

Summary of the modelling

HIPERSOL is to develop an integrated multi-scale modelling environment that is applicable to properties of real materials on length scales not accessible by ab initio modelling; and to use this environment to accurately describe and predict important parameters and properties of interfaces of contacting and passivation layers with silicon. HIPERSOL targeted to do fully self-consistent DFT band structure calculations for systems containing up to 10.000 atoms, as the typical extension of such interfaces easily stretches to hundreds of nanometres. This is done integrating ab initio calculations with empirical atomistic modelling and finite-element methods.

First the construction of inter-atomic potentials was derived from first principles <u>DFT</u> calculations (0.1-1 nm). These inter-atomic potentials were used in <u>classical molecular dynamics</u> performed on the most relevant and interesting interfacial regions of the contacting and passivation interfaces, accounting for strain and for misfit dislocations. The MD simulations provided input for DFT calculations of the contacting interface. The Si/Ag and Si/Ni interfaces have been generated using MD and based upon derived inter-atomic potentials. These structures have been used to calculate Schottky barriers from DFT. The passivation (Si/SiNx) interface has also been modelled with inter-atomic potentials developed. These simulations were used to investigate the influence of N content and gradients on the trap density at the interface.

To apply DFT at a much larger scale than done until now, semi-empirical pseudo-potentials (SEPP) (10-100nm) were created based on first-principles calculations on a smaller scale (density functional theory, hybrid functionals and the GW approximation). These screened potentials can be used within the framework of DFT to calculate the accurate electronic structure of large structures with up to millions of non-equivalent atoms and calculate life times of charge carriers

The atomic coordinates at quasi-equilibrium were transferred to, and formed the basis for the rest of the first principle modelling in this project. Diffusivities and surface energies were also extracted as input to the modelling of the metallisation process. Statistical temperature <u>accelerated molecular dynamics</u> and <u>kinetic Monte-Carlo</u> was needed to calculate diffusivities of charge carriers, band structure calculations for up to 10000 atoms.

In a following stage, results from classical MD and first principles calculations (such diffusion parameters and surface energies) were used as input to finite element method calculations for <u>phase</u> <u>fields</u>, reaching the size and time scales of real devices.

To support the above, numerical techniques were developed for accurate calculation of electronic band structures in sub-systems large enough to include macroscopically relevant features. This involved the integration of realistic band structures and first principles wave functions in the envelope function approach, which were used to calculate life times of excited charge carriers.

Calculations have been performed on novel stacked Si/SiNx structures and new model paste compositions for metallisation under different firing conditions to improve contacting and passivation schemes. The applicability of new pastes was assessed to industrial production. The transport of Ag from the finger through the glass layer to the bulk silicon was modelled with a <u>phase-field model</u>, based on Gibbs free energies obtained from FactSage (using a database developed for solar grade silicon) and diffusivities obtained from first principles molecular dynamics.

www.sintef.no/Projectweb/HiperSol

Project Acronym and Number: HIPERSOL 228513 Project Title: Modelling of interfaces for high performance solar cell materials Start and End Dates: 01/12/2009 till 31/11/2012 EU Contribution: 3.399.990 € Coordinator: Jesper Friis, SINTEF, Norway, <u>jesper.friis@sintef.no</u>



in HIVOCOMP 246389

Subject of the modelling

Composites consisting of a matrix and textile fibrous reinforcement (woven carbon fabric). Self-reinforced composites consisting of a matrix and the reinforcement of the same chemical nature (polypropylene or polyamide).

Models used

Continuum:

Microscale model for Newtonian <u>fluid flow</u> in porous medium (formed by fibres inside the yarns) Mesoscopic (unit cell of the textile reinforcement) model for uncompressible <u>fluid flow</u> (resin) through the textile reinforcement (Navier-Stokes/Stokes and Brinkmann equations) resulting in calculation of the homogenized permeability

<u>Micro-mechanics models</u> (elasticity and plasticity and fracture) to calculate the deformation resistance (compression, shear, tension, bending) of dry preform and stiffness and strength of the impregnated composite.

The results of the micromechanics modeling are used in <u>macro-level models</u> for simulation of forming and impregnation and finally the structural behavior of the part.

Geometrical description of the reinforcement is the starting point of all the models.

Simulation software and type of numerics used

PAM-RTM a Darcy solver to simulate flow of Newtonian liquid through a porous medium (impregnation of a composite part)

FlowTex for micro scale Stokes, Navier-Stokes and Brinkmann flow

WiseTex micromechanics software to compute the internal structure and deformability of textiles PAM-family of ESI for macroscale forming

All flow models use finite difference and mechanical models use FE technology

Achievements of the model beyond experiments

Prediction of structural properties to avoid unfeasible or expensive experimental tests. The models also enabled screening of possible choices for the resins. The flow modeling shortened part of the design by predicting permeability and impregnation time of the different

resins. The model predicted structural behavior in function of the above properties and damage initiation by calculating the threshold and damage development parameters in the composite during different loading types

Application

Composite parts for the transport industry

HIVOCOMP focuses on improving two materials systems for high performance carbon fibre reinforced parts and their production. The materials systems are: 1) advanced polyurethane (PU) thermoset matrix materials (resin) reinforced with textile (carbon) fibres and 2) composites consisting of self-reinforced thermoplastic polypropylene and polyamide composites, incorporating carbon fibre reinforcements.

Summary of the modelling

HIVOCOMP uses <u>CFD models</u> for the flow of the novel low-viscosity resin impregnating the network of textile reinforcements at meso and macro scale which is performed with an existing finite difference model for Newtonian flows in porous media and Stokes, Navier-Stokes and Brinkmann flow in the network of fibrous reinforcements.

The modelling starts with a geometrical description of the textile. <u>Micromechanics models</u> for mechanical deformation and shrinkage will lead to the description of resistance of the hybrid (carbon/self reinforced PP or PA) preform to deformation and shrinkage during thermoforming. The models will produce material constitutive equations to be used in the macro-modelling of forming.

Novel, predictive micro-mechanics models of elasticity are used to model damage and toughness of the materials following two routes:

1. Micro-level mechanics/elasticity model of textile reinforced PU composite and self-reinforced PP/PA. To account for the specific adhesion behaviour of carbon fibres in PP/PA, special finite elements will be introduced in the calculations. Novel theory of distributed damage, based on Ladeveze-type damage parameters and Puck-type damage initiation criterion is implemented in the model. An alternative predictive approach suitable to crack initiation and growth and based on the existing nonlocal damage EWK (ESI-Wilkins-Kamoulakos) model will also be used and coupled to the MultiModel Coupling capability of PAM-codes to achieve immediately simulation capabilities of industrial dimension.

2. Fast simulation using method of inclusions (Eschelby and Mori-Tanaka) of strength and damageinduced deterioration of the stiffness of composite including strength analysis of the equivalent inclusions and degradation of the stiffness of the inclusions. The method of inclusions is based on Eshelby's transformation concepts, and uses a short fibre analogy to describe the mechanical behaviour of curved yarn segments, combined with a Mori-Tanaka or self-consistent scheme to account for interaction effects. The geometrical input from WiseTex consists of the yarn mid-line representations and cross-sectional dimensions. Yarns are split up into segments and replaced by a short fibre equivalent using the yarn orientation and the local curvature. The output of the model is full stiffness matrix of the homogenised unit cell. In the elasticity model the orientation and length distribution of the fibres are used to generate instances of the random placement of the inclusions. Monte-Carlo scheme is then used to calculate homogenised stiffness matrix

Deterioration of stiffness of the composite with increased loading is calculated in the form of non-linear stress-strain diagrams. This approach lacks the thoroughness of meso-FEA, but will allow integration into the macro-level structural analysis of the composite part.

Finally the developed micro-meso level results are implemented in <u>macro-mechanics</u> tools (PAM- family of ESI) to simulate forming.

http://hivocomp.eu/

Project Acronym and Number: HIVOCOMP 246389 Project Title: Advanced materials enabling HIgh-Volume road transport applications of lightweight structural COMPosite parts Start and End Dates: 01/10/2010 30/09/2014 EU Contribution: 4.775.278€ Coordinator: Ignaas Verpoest, KU Leuven, BE, (+32 16 321306) <u>ignaas.verpoest@mtm.kuleuven.be</u>



in HYMEC 263073

Subject of the modelling

Organic semiconductors

Models used

Electronic: <u>drift-diffusion models</u>, (<u>T</u>)DMFT , <u>Hubbard model</u> Atomistic: <u>percolation model</u> Continuum: <u>electrical model</u>

Simulation Software and type of numerics used

TIBERCAD (commercial, but developed in part by partner of HYMEC) Statistical mechanics (Monte Carlo algorithm) to calculate percolation

Achievements of the model beyond experiments

The electric field distribution of charged metal nanoparticles in organic matrices can be predicted, which allows identifying the switching mechanisms of memory cells. This, in turn, allows optimizing the morphology of devices.

Application

Photonics and electronics

Summary of project

The goal of the project is to investigate all relevant properties of systems comprising inorganic metal nanoparticles embedded in matrices of conjugated organic materials (organic semiconductors) and demonstrate the potential of such material hybrids as non-volatile memory elements (NVME) that can be addressed electrically and optically. This will allow interconnection of future hybrid electronic and photonic circuitry. Moreover, we target implementing cost-efficient production routes, such as printing, as well as exploring the ultimate miniaturization of such memory elements by novel sublimation- and imprinting-based nanostructuring processes.

Summary of the modelling

The theoretical work consist in developing computational tools for the structure-property-function relationships for NVMEs based on metal nanoparticles embedded in organic matrices, with the view of expanding the functionality of NV-MEs towards optical addressing capability and allow cost-efficient fabrication methods (printing and nanostructure formation).

A continuum model will be used to simulate <u>electrical</u> characteristics of steady-state transport in the two different conduction states. The effect of optical addressing the device to induce charging and de-charging of the metal nanoparticles in the macroscopic device is included in the modelling tool. Improving an existing multiscale code called TiberCAD we will study recombination mechanisms. An electronic <u>drift-diffusion model</u> has been already implemented with several submodels for recombination and charge mobility (in particular a field dependent mobility). It includes also a module to include a fixed charge background and is currently going on the development of a module to include trapping and de-trapping models, both for energy localized traps or for more extended band-tails (like in amorphous materials). This computational tool will be used to model the device in steady state conduction when it is in high conductivity state or low conductivity state, respectively. Experiments will provide information on adequate rate equations for trapping mechanisms and charge mobility. Experimental results on the electrode/organic matrix interface energetics will be used to model the boundary conditions as Schottky-barriers at the contacts.

A statistical mechanics model for <u>percolation</u> uses a random walk over a network of nodes, which each represent a metal nanoparticle and so a possible site for charges, connected to a certain number of other nodes. The problem is solved using a Monte Carlo method and solving a Pauli Master Equation.The main parameters for this model are related to the jump rate and the coordination numbers (substantially related to the density of nanoparticles) and can be determined phenomenologically with well-known methods of quantum field theory and the support of experimental measurements.

The most demanding part of the theoretical work is the inclusion of exciton creation, transport and recombination (including charging and de-charging of metal nanoparticles) to grasp optical addressing in the drift-diffusion model and the Statistical Mechanics random walk model. The time-dependent mean-field theory (TDMFT) is used to caluclate transport properties. The Hamiltonian of the system is described by a <u>Hubbard model</u> but with a strong correlation term between particles. We will solve the equations by density matrix renormalization group (DMRG) for the ground state properties.

A software package is developed to model transport through NV-MEs including the main physical processes which affect conduction, such as charge effects, trap and de-trapping processes. When the simulation tool is well tested and established as being reliable, it will be used as a support for the further engineering of devices, and it will be instrumental for the development of array and integration efforts in order to find the best selections of materials and device architectures.

http://hymec2.physik.hu-berlin.de

Project Acronym and Number: HYMEC 263073 Project Title: Hybrid organic/inorganic memory elements for integration of electronic and photonic circuitry Start and End Dates: 1 October 2011 till 31 September 2014 EU Contribution: 3.132.475 € Coordinator: Norbert Koch, Humboldt-Universität zu Berlin, Institut f. Physik, Germany; <u>norbert.koch@physik.hu-berlin.de</u>



in HYPOMAP 233482

Subject of the modelling

Hydrogen storage materials (physisorption and chemisorption), ad- and desorption processes, and proton exchange membranes.

Models used

Electronic:

Density-Functional Theory (<u>DFT</u>) Higher level quantum mechanical methods (<u>MP2, CCSD(T)</u>) Atomistic: <u>QM/MM</u> model for proton conductance Statistical Mechanics (<u>Monte Carlo</u>) simulations

Simulation software and type of numerics used

Electronic: Gaussian09, VASP, deMon2k, GPAW, TurboMOLE

Various Order-N techniques are used, including (i) diagonalization methods, (ii) Fast Fourier Transform, (iii) Matrix-matrix linear algebra operations, (iv) solvers for systems of linear equations

Atomistic: in-house codes for newly developed model called Quantized Liquid Density-Functional Theory (QLDFT)

Achievements of the model beyond experiments

Computational modelling, in particular on the electron or atomistic scale, allows the investigation of processes beyond the experimental scale. People often speak of the "computer microscope" that allows to monitor the motion of a single atom. It also provides understanding of an individual vibrational mode, or of the contributions of material fragments to an individual property. In this project modeling provide insight in the adsorption energy of hydrogen as function of the composition of the individual building blocks of a molecular framework. With this data it is possible to improve the performance of the target materials.

Application

Hydrogen storage and fuel cells

Relevant review articles

R. B. Getman, Y. S. Bae, C. E. Wilmer, R. Q. Snurr, Chem. Rev. 112 (2012) 703-723, DOI: 10.1021/cr200217c.
S. S. Han, J. L. Mendoza-Cortes, W. A. Goddard III, Chem. Soc. Rev. 38 (2009) 1460-1476, DOI: 10.1039/b802430h.
S. A. Shevlin, Z. X. Guo, Chem. Soc. Rev. 38 (2009) 211-225, DOI: 10.1039/b815553b.

Effective hydrogen storage and fuel cell systems are required for the implementation of a hydrogen economy. HYPOMAP uses computational approaches to predict hydrogen adsorption and proton transfer in new candidate materials for technological application.

Summary of the modelling

For hydrogen storage by physisorption, the weak interaction between the H2 molecules and the host structures need to be modelled in order to understand the thermodynamics of the system. For chemisorption, the critical steps are the loading and unloading, so the mechanism of catalysts on the storage systems needs to be modelled. For fuel cells, the proton conductance in the proton exchange membranes needs to be studied. In all cases, dependence on temperature and pressure are to be included.

Physisorption was modelled linking different models:

- 1. Band structure comes from experiment or from a <u>DFT</u> calculation (VASP, deMonNano) the Kohn-Sham equations of a bosonic system of hydrogen molecules are applied
- a force field describing the host-guest interaction usually from high-level ab initio electronic calculations (<u>MP2, CCSD(T)</u>) or literature.
- 3. atomistic statistical mechanics many body method to calculate adsorption (QLDFT and <u>Grand</u> <u>Canonical Monte Carlo</u>)

Chemisorption has been modeled using electronic <u>DFT</u> calculations (for ammoniaboranes and protonated nanotubes), software: VASP or GPAW. Sometimes a hierarchical approach has been used (the interaction energy is refined with a <u>higher-level electronic method</u>). Molecular storage, such as functionalized linkers in MOFs and transition metal complexes have been modeled with a variety of electronic models (Gaussian09 and Turbomole).

For proton conductance a <u>QM/MM</u> hierarchical protocol, combining Born-Oppenheimer techniques in conjunction with transition state theory and molecular dynamics, is applied:

- 1. a DFT functional for proton hopping is calculated with the QM part of QM/MM
- 2. this functions is refined witht high-level ab initio model (CCSD(T))
- 3. development of a force field with the new functional
- 4. MD simulations (the MM part of QM/MM) using this force fields of proton transfer in the polymeric proton exchange membranes.

QLDFT (Quantum Liquid Density Functional Theory) is an atomistic Statistical Mechanics model that describes physisorption and loading/unloading of physisorbed hydrogen. Also Grand Canonical <u>Monte Carlo atomistic</u> simulations can be used for this purpose, but QLDFT includes the quantum effects and hence is a fundamentally higher-level treatment. Formally, it is similar to electronic DFT, but instead of electrons it describes H2 molecules, and those obey a Boltzmann statistics (rather than a Fermi statistics that holds for electrons). QLDFT was developed because there was no adequate modelling method for the adsorption calculations on the market that included the quantum effects of light-weight hydrogen. This was a considerable development effort, as (i) a physical method needed to be developed, implemented and validated; and (ii) a series of numerical techniques, treating very large sparse matrices (dimension of ~100,000) efficiently had to be implemented. Moreover, we implemented an efficient technique to account for London Dispersion (a weak interaction governing the interaction of hydrogen with host materials) within DFT and implemented it into deMon2k.

https://www.jacobs-university.de/ses/theine/projects/HYPOMAP

Project Acronym and Number HYPOMAP 233482 Project Title: New materials for hydrogen powered mobile applications Start and End Dates: 01/06/2009 till 30/05/2012 EU Contribution: 899.958 € Coordinator: Thomas Heine, Jacobs University, DE, <u>t.heine@jacobs-university.de</u>



in IFOX 246102

Subject of the modelling

Transition metal oxide hetero-structures and their interfaces

Models used

Electronic scale: <u>Density functional theory (DFT)</u> for electronic structure and transport Atomistic scale: <u>Molecular Dynamics</u> for defects diffusion in oxides <u>Coarse-grained Monte Carlo</u> codes to evaluate thermodynamical properties for example critical temperatures

Simulation software and type of numerics used

Various DFT codes:

FLEUR: Full-potential linearized augmented plane wave (FLAPW) method, linear scaling algorithms for the treatment of nanometer-thick heterostructures, Green-functions for the calculation of semi-infinite solids and of electronic transport under finite bias KKRnano: Korringa-Kohn-Rostoker Green-function code for large scale parallel calculations SMEAGOL: code for transport calculations SIESTA: Molecular Dynamics MC code (inhouse)

Achievements of the model beyond experiments

Ab-initio calculations based on Density Functional Theory provide the necessary link between simple models used to interpret materials properties and the complex interplay between electronics, the atomistic structure and magnetism found in experiments. These calculations enable the correct interpretation of experiments and can lead to guide research. An example for this process relevant to our field was the prediction and interpretation of huge tunneling magnetoresistance in tunneljunctions with magnesiumoxide barriers which predated the experimental findings for several years.

Application

Memory, programmable logic and sensors

Relevant review articles

Computational Nanoscience: Do It Yourself! edited by J. Grotendorst, S. Blügel, D. Marx, NIC Series Volume 31, ISBN 3-00-017350-1, URL: www.fz-juelich.de/nic

IFOX is to explore electronic and magnetic functionalities that result from the rich interplay of charge, spin and orbital degrees of freedom in transition metal oxide heterostructures and their interfaces. The project will grow oxide films on commercial substrates and establish oxide patterning and processing conditions to deliver novel device concepts for memory, programmable logic and sensors.

Summary of the modelling

IFOX addresses three major classes of oxide heterostructures:

- Ferromagnetic oxide heterostructures controlled by charge or spin-polarized
- Ferroelectric oxide heterostructures controlled by charge and electric fields
- Multifunctional multiferroic oxide heterostructures controlled either by charge or by spin and ultimately by ultrashort light pulses

The models will be applied to understand electronic reconstructions at the interfaces; spin tunnelling and transport across oxide interfaces; fundamental properties of nanoscale oxide elements with respect to the ionic and electronic contributions to the screening of polarization charges at the electrode -oxide interfaces; the interaction of redox-centers and extended defects with ferroelectric polarization charges and interface coupling between ferromagnetic and ferroelectric oxides in artificial multiferroics.

Density functional theory (DFT) will be applied using the earlier developed full-potential linearized augmented plane wave (FLAPW) method FLEUR. It can model non-collinear magnetism, electric fields applied to surfaces, electric polarization and the mapping of the electronic structure to <u>tight-binding</u> Hamiltonians. SPEX is a recent addition to the FLEUR model that will be used to determine quasiparticle properties including band structures and band gaps to much higher accuracy than is currently possible with DFT.The DFT-based methods available within IFOX are based on a pseudopotential and local orbital implementation of DFT, which allows for more rapid and larger scale simulations than those possible with all-electron plane wave codes.

Moving beyond perfect interfaces, a realistic interface model must include large and extended defects and needs modelling of thousands of inequivalent atoms. The massively parallelized Korringa-Kohn-Rostoker Green-function code will be used to solve the DFT models. The electronic structure of point-like defects in oxides is affected by the interplay between strong electron correlation and polaronic coupling with the lattice distortions. Accurate description requires both the correct determination of the electronic structure of the host oxides, including the band gap and an extremely accurate estimate of the defect total energy. To this goal, a range of orbital-dependent exchange and correlation functionals, such as DFT exact exchange, self-interaction correction and hybrid functionals will be applied.

Bias dependent electronic transport calculations for oxide heterojunctions can be performed with the SMEAGOL code. At present only the ballistic limit is accessible, although inelastic effects can be included at a phenomenological level and an algorithm has been recently finalized within SMEAGOL.

Molecular Dynamics (MD) methods will be applied to model the electrical hysteresis of conducting oxides and oxide-based junctions. Initially, defect diffusion will be studied without an external field either using classical force fields or fully ab-initio <u>Car-Parrinello</u> methods. <u>Metadynamics</u> will be employed in the case of slow migration processes or migration involving a large and complex energy surface. Similar MD schemes will be employed for defect diffusion at the interface between heterogeneous materials.

The Heisenberg spin-Hamiltonianare employed in <u>DFT</u> models and parameters like hopping parameters or exchange couplings are extracted. These are input to <u>coarse grained Monte Carlo models</u> to calculate thermodynamic properties such as the Curie temperature, or non-equilibrium properties such as kinetic growth, on the mesoscale.

www.ifox-project.eu

Project Acronym and Number: IFOX 246102 Project Title: Interfacing Oxides Start and End Dates: 01/12/2010 till 31/11/2014 EU Contribution: 11.302.718 € Coordinator: Theo Rasing, Radbout University Nijmegen, NL <u>th.rasing@science.ru.nl</u>



in IMS & CPS 246243

Subject of the modelling

Textile carbon fibre/epoxy composites reinforced with carbon nanotubes (CNTs), damage resistance, electrical conductivity and lightning strike protection

Models used

Microscale <u>damage</u> initiation model in textile fiber/reinforced composites Electron tunneling <u>percolation models</u> and <u>ion transport</u> statistical mecahnics models

Simulation software and type of numerics used

WiseTex, TexComp for the calculation of stress and strain fields numerically in the representative volume using geometrical modeller WiseTex and commercial FE packages (such as ANSYS and ABAQUS).

Random Microstructure Generation (RMG) algorithm e.g. for buckling of the I beam with classic eigenvalue analysis.

Achievements of the model beyond experiments

The "electrical conductivity" model predicts the electrical percolation and conductivity of CNT/polymer composites close to the experimental observations. The achievements beyond experiments include the positive effect of agglomeration and the transverse conductivity of the CNT/polymer composite with the CNTs only sprayed on the surface. In fact, nobody believed that there will be conductivity in the transverse direction when the CNTs are sprayed on the surface alone. In addition, this model correctly predicted that the addition of compatibilizers and copolymers has a significant effect on electrical percolation threshold and conductivity. These characteristics are experimentally proved and this is the only model which can predict this behaviour.

The toughness model will predict the effect of carbon nanotubes and their agglomerates on redistribution of stresses and strains inside the composite and the threshold strain for the onset of damage on the micro-scale.

The model utilized for validation elements can predict the initial failure of the T junctions and of the I beams for the different used materials (with and without CNT). This will help to design the test jigs to be used in the project.

Application

Textile reinforced composites, transport, aviation, railway

Relevant review articles

Verpoest I and Lomov SV, Composites Science and Technology 65 (2005) 2563–2574. Lomov, S.V., et.al. Meso-FE modelling of textile composites: Road map, data flow and algorithms. Composites Science and Technology, 67, 2007, 1870-1891

Weibang Lu, et.al. A three-dimensional model of electrical percolation thresholds in carbon nanotube-based composites. Applied Physics Letters, 96(22):223106, 2010.

Andriy V Kyrylyuk, Marie Claire Hermant, Tanja Schilling, Bert Klumperman, Cor E Koning, and Paul van der Schoot. Controlling electrical percolation in multicomponent carbon nanotube dispersions. Nature nanotechnology, 6(6):364 – 9, January 2011.

IMS&CPS intends to gather innovations linked to carbon nanotubes based innovative materials and innovative composite processings for transport applications (aeronautics and railway applications).

Summary of the modelling

In order to achieve higher mechanical properties and higher electrical conductivities in multi-scale carbon fiber/epoxy composites, an important part of the IMS&CPS project is dedicated to the development of modeling methodologies and predictive tools. The goal of these tools is to help understand how to maximize the benefit of carbon nanotubes in the structural composites for the improvement of such properties as damage resistance, electrical conductivity and lightning strike protection. The success of this modelling lies in the geometric modeling of the CNTs, polymer chains and their interactions because the geometrical distribution of the CNTs in the representative volume has a significant impact on the electrical conductivity and the percolation threshold.

Representation of the sample

The software package WiseTex implements a generalised description of internal structure of textile reinforcements on the unit cell level, integrated with mechanical models of the relaxed and deformed state of fabrics. TexComp uses the geometrical input from WiseTex, which consists of the yarn mid-line representations and cross-sectional dimensions. Yarns are then split up into segments and replaced by a short fibre equivalent using the yarn orientation and the local curvature. The output of the model is full stiffness matrix of the homogenised unit cell. The representation is further refined using the random microstructure generation (RMG) algorithm to simulate a fiber distribution in the representative volume element. In the framework of the IMS&CPS it is proven this algorithm generates microstructures that are statistically equivalent to real microstructures (from the point of view of geometrical characteristics and mechanical performance). The modified version of this model is currently in the development, which goal is to simulate fibers and nanotubes in a single model without transferring parameters from simulations on one scale to another. This is mainly explained by numerical challenges that come from modeling objects that differ in dimensions by 1000 times (microscopic fibers and nanoscopic tubes).

Physics and chemistry

The above internal geometry and stiffness prediction is a necessary input for physics and chemistry modelling.

The <u>damage initiation model</u> is developed on the micro-scale. This model predicts transverse damage initiation in unidirectional fiber/polymer composites with and without carbon nanotubes. The conductivity model for polymer/CNT composites predicts electrical percolation thresholds and electrical conductivity of polymers reinforced with CNTs. It can be applied to different kinds of CNT/polymer nano-composites. The model accounts for the two types of charge transport mechanisms with and without chemical bonding between CNTs and the polymer. In the first case creation of ions and charge transport through CNTs and polymer chain networks play a role, while in the second case charge transport through the physical contact between CNTs, through the electron tunneling between CNTs and through the electron tunneling between CNTs and through the electron tunneling between CNTs and through the electron tunneling between CNTs.

To model the <u>ion transport percolation models</u> are used (statistical mechanics based codes that take the structure into account and calculate thermodynamic properties), which emphasize the importance of the interfacial interactions at the boundary between the individual filler particles and the polymeric host for the network formation. As a consequence, these models interpret the percolation phenomena as a phase separation process.

Electron tunnelling is described with <u>quantum mechanical percolation models</u> which assume the charge transport between carbon nanotubes are partly through physical contacts and partly through electron tunneling between carbon nanotubes.

Representation of the sample

Different calculations are done to find a representation of where the fibers are after the physics and chemistry have evolved. Statistical calculations of random placement during dispersion and further agglomeration of carbon nanotubes give networks of physically connected paths. This is further refined in geometrical calculations to obtain a representation of the fibres in different dry premixed and subsequently sintered mixtures of conductive and insulating powders. Structure oriented models based on the parameters that have to be determined from the micro level structure of the mixture after final processing step. A detailed substitution of the real material structure by a theoretical model structure is needed for the determination of such parameters.

www.imscps.eu Project Acronym and Number: IMS&CPS 246243

Project Title: Innovative material synergies and composite processing strategies Start and End Dates: 01/10/2010 till 31/09/2013 EU Contribution: 4.925.711 € Coordinator: André Bertin, COEXPAIR S.A., BE <u>coordimscps@coexpair.com</u>



in INNOVASOL 227057

Subject of the modelling

Excitonic solar cell materials (QuantumDots, Transparant Conductive Oxides and solid electrolyte)

Models used

Elcetronic:

<u>Ab initio Hartree-Fock</u> and <u>Density Functional Theory</u> for calculations of structures, electronic distribution and properties;

<u>Polarizable Continuum Model (PCM)</u> for the simulation of solvent effects on molecular structures and energies

Simulation software and type of numerics used

Computational packages:

Gaussian03, Turbomole 6.0 for DFT Crystal06 (for DFT with periodic boundary conditions) Gaussian03(for PCM) SCF Self-consistent differential equations for solvent effects with PCM MSINW07 solution of Schroedinger equation in the mean-field approximation, with atomic expansion of molecular orbitals and periodic boundary conditions

Achievements of the model beyond experiments

Trial and error synthesis costs were avoided by computing the energetics of inclusion of some anions (iodide and tri-iodide) in a layered solid analogous to hydrotalcite before the actual systems were synthesized. The calculations showed the limit concentration expected for anions in this environment.

The models could provide understanding of phenomena occurring, e.g. the excess of lead observed in certain conditions.

The calculations allowed to predict which surface passivant would help obtain particles of octahedral shape exposing (111) crystallographic faces, and this will guide the experiments.

Application

Solar cells

Relevant review articles

Simona Fantacci, Filippo De Angelis "A computational approach to the electronic and optical properties of Ru(II) and Ir(III) polypyridyl complexes: Applications to DSC, OLED and NLO", Coordination Chemistry Reviews 255 (2011) 2704–2726

Walter R. Duncan and Oleg V. Prezhdo "Theoretical Studies of Photoinduced Electron Transfer in Dye-Sensitized TiO2", Annu. Rev. Phys. Chem. 58 (2007) 143–184

INNOVASOL aims at developing nanostructured and molecular materials for photovoltaic (PV) excitonic solar cells. The first step is the substitution of the liquid electrolytes, currently used in dyesensitised solar cells, with solid-state hole conductors. In parallel, semiconductor quantum dots (QDs) with tuned band gap, designed to enhance the photon capture efficiency, will replace the organic dyes as light absorbers.

Summary of the modelling

Most modelling results have been obtained with <u>DFT</u> with hybrid GGA functionals, though also <u>Hartree-Fock</u> and post-Hartree-Fock calculations have been performed. In some cases, periodic boundary conditions have been used; both finite cluster and infinite periodic models made use of Gaussian-type atomic orbitals to expand the molecular orbitals. The packages adopted were Gaussian03 and Turbomole 6.0 for finite cluster models and Crystal06 for periodic systems. When necessary, the solvent effects were included in the calculations through the Polarizable Continuum Model <u>PCM</u>, where the solvent reaction field is simulated by a set of apparent charges self-consistently determined on the basis of the electric potential generated by the solvated molecule(s). This approach, partially developed in the past by some participants to the project is presently implemented in several codes: during INNOVASOL the implementation in Gaussian03 was used. In addition to ab initio and DFT methods, also semi-empirical were used to describe at a lower level the effect of surrounding micro-systems, weakly interacting with the molecules. The adopted semi-empirical method was MSINDO7, with some adjustment of the parameters to fit model post-HF calculations.

Suitable meta-procedures were developed to link DFT and semi-empirical calculations in an ONIOMlike scheme (in which the more expensive DFT calculations are limited to the central molecules, whose properties are to be determined accurately, while the cheaper semi-empirical approach is used to include at a lower level the interactions with the surroundings). Routines to link MSINDO7 and Gaussian03 codes were written.

This way, the formation energy of some inclusion complexes in layered magnesium oxides (HTLC) which is relevant for the synthesis of quasi-solid electrolytes to be used in solar cells was simulated. Also PbSe nanoparticles were modeled, with particular attention to the binding energy of the different crystallographic faces to organic passivants, and the simulation of organic dyes/PbSe nanoparticles adducts.

In summary, computational tools proved to be efficient and useful in the following project achievements.

- Limit concentration and best choice of reaction partners were predicted for the synthesis of quasisolid electrolytes by means of ab initio periodic calculations.

- Structural properties of PbSe nanoclusters and best affinities of clusters for different organic ligands used in syntheses were computed with ab initio finite cluster approach.

- Light absorption spectra of squaraine molecules in different conditions (isolated, dissolved in liquid media, attached on top of nanoparticles) were computed with time-dependent DFT methods

including solvent effects via PCM, indicating which anchoring groups are more promising for adding the dye to the nanoparticles, and how the absorption spectra can change upon addition.

- The structure of dye monolayers on TiO2 surfaces has been described with mixed ab initio – semiempirical calculations, to estimate the binding energy as a function of anchoring groups and degree of surface coverage, i. e. the limit concentration of adsorbed dye.

http:// www.innovasol.eu

Project Acronym and Number: INNOVASOL 227057 Project Title: Innovative Materials for Future Generation Excitonic Solar Cells Start and End Dates: 01/04/2009 till 31/03/2012 EC Contribution: 2.899.510 € Coordinator: Prof. Leonardo Marchese, Dipartimento di Scienze e Innovazione Tecnologica, Università degli Studi del Piemonte Orientale "A. Avogadro", Italy, <u>leonardo.marchese@mfn.unipm.it</u>



in IRON-SEA 283141

Subject of the modelling

Fe-based superconductors

Characteristics of Josephson junctions (junctions where a supercurrent can flow through a non superconducting medium between two superconductors)

Models used

Electronic: <u>DFT</u> electronic structure calculations <u>Multiband Eliashberg models</u> (development and application) <u>Blonder-Tinkham-Klapwijk model</u> (application and extensions) Continuum: <u>Electrical circuit model</u>: (resistively and capacitively shunted junction model) (application)

Simulation software and type of numerics used

DFT calculations using the FP-LAPW Code

Systems of non linear singular integral equations solved numerically by using in-house developed code.

Systems of second-order differential equations where standard solvers are used (i.e. Runge-Kutta)

Elk code for the calculation of band-structure and Fermi surface.

Achievements of the model beyond experiments

The model determined the pairing symmetry and its evolution with doping, which is impossible to determine experimentally.

The model determined the characteristic energy of the boson that mediates superconductivity (examples: Co-doped Ba-122, Sm-1111) and of the coupling strength.

The model determined the effects of disorder, doping, lattice strain, etc on the superconducting properties.

The model determined the effects that are optimal or detrimental for device fabrication and optimization.

Application

Superconductors

Relevant review articles

P. Seidel, Supercond. Sci. Technol. 24, 043001 (2011)

D. Daghero and R.S. Gonnelli, Supercond. Sci. Technol. 23, 043001 (2010)

D. Daghero, M. Tortello, G.A. Ummarino, R.S. Gonnelli, Rep. Prog. Phys. 74, 124509 (2011)

G.A. Ummarino, Physical Review B 83, 092508 (2011).

P. Popovich, A.V. Boris, O.V. Dolgov, A.A. Golubov, D.L. Sun, C.T. Lin, R.K. Kremer, and B. Keimer, Phys. Rev. Lett. 105, 027003 (2010)

The project will study iron-based superconductors in the form of thin films, which have been prepared by molecular beam epitaxy and by pulsed laser deposition. The goal is to find unique physical properties, which lead to exploring new kinds of devices and applications. Since the iron-based superconductors have a multi-band nature, comparative studies to MgB2, which is a two-band superconductor, are also carried out.

Summary of the modelling

Intrinsic physical parameters (e.g. the superconducting transition temperature, the penetration depth, the upper critical field, and etc.) of Fe-based superconductors can be calculated by solving the three or four band Eliashberg equation, once the relevant Eliashberg parameters for a given materials are fixed. The Eliashberg theory allows calculating many different observables related to the superconducting state. In Fe-based superconductors, the solution of multiband Eliashberg equations requires some input parameters that can be either determined experimentally or provided by DFT electronic structure calculations. DFT electronic calculations have been carried out for calculations of the bandstructure and of the Fermi surface for the compounds under study. The shape of the Fermi surface is needed as input for the 3D- Blonder-Tinkam Klapwijk model for the fitting of the experimental point-contact spectra. Eliashberg calculations require as an input the density of states projected on the different bands from DFT calculations. Some very basic parameters related to the superconducting state can be adjusted to reproduce given experimental results. After that, it is possible to calculate with the same parameters and no further assumptions many different observables that can then be compared to experimental results or trigger new experiments to test the predictions. The analysis of a given material within the multiband Eliashberg models, especially when it is possible to explore the phase diagram can help discriminating between the effects of disorder, lattice parameters, changes in the density of states in determining the critical temperature or other superconducting properties. This can help optimizing the quality of the samples or even suggest some alternative chemical compositions or substrates (in the case of films).

Conductance-Voltage characteristics of Fe-based superconducting films obtained from point contact Andreev reflection spectroscopy measurements will be fitted to extract the superconducting energy gaps by means of the Blonder-Tinkam Klapwijk model and its generalizations, for example to account for the real shape of the Fermi surface.

Characteristics of Josephson junctions fabricated from Fe-based superconducting films can be described by the electrical circuit resistively and capacitively shunted junction (<u>RSCJ</u>) model. These models (BTK and its generalizations and RSCJ) are explained and can fit experimental data. Some of the parameters that can be extracted from the fit are specific of the single junction or point contact. Others can be compared to the outcomes of other measurements (specific heat, superfluid density, ARPES and so on). In most cases, the results for a specific material turn out to be in good agreement with those provided by these other techniques.

Theoretical aspects of the tunnelling and Andreev reflection in unconventional superconductors will be studied. In particular, they shall concentrate on:

- the Josephson effect and its dependence on the pairing symmetry

- the possibilities to use the Josephson effect to gain insight into deviations from the standard BCS -like behaviour.

- the analysis of the results of the different spectroscopy measurements in the framework of multiband Eliashberg theory with the main purpose of shedding light on the pairing mechanism and the nature of the mediating boson in Fe-based superconductors.

http://www.IronSea.eu

Project Acronym and Number: IRON-SEA 283141 Project Title: Establishing the basic science and technology for Iron-based superconducting electronics applications Start and End Dates: 01/10/2011 till 30/09/2014 EU Contribution: 1.665.611 € Coordinator: Kazumasa Iida, IFW, Dresden, Germany <u>k.iida@ifw-dresden.de</u>



in LEMSUPER 283214

Subject of the modelling

Light element superconductivity

Models used

Electronic: <u>DFT</u> for electronic structure of relevant materials

<u>Tight binding (TB)</u> and <u>Hubbard models</u> built by direct inspection or by downfolding DFT electronic structure as relevant for actual or potential superconductors <u>Gutzwiller</u> and <u>DMFT</u>

Atomistic: <u>Ab initio Molecular Dynamics</u> models for pressure induced metallization of potential high pressure superconductors, and interactions, vibron properties, Jahn Teller effects

Simulation software and type of numerics used

Kohn-Sham and related equations for standard DFT calculations and simulations with a variety of hybrid functionals (HSE, B3LYP) and LDA+U Gutzwiller projector technique calculations for the ab-initio codes Single site cellular DMFT calculations of appropriately built Hubbard models, using Anderson model methods as an ingredient

Existing Car-Parrinello-Rahman codes for MD

Achievements of the model beyond experiments

New correlation-driven mechanisms for superconductivity in light element systems were predicted long before they were validated. A superconductivity mechanism for fullerides was predicted, where electron-vibron coupling, orbital degeneracy, and strong electron correlations implying a nearby Mott transition all play a crucial role. Cesium fullerides validated this theory.

Identification of new electronic ground states in light element systems leading to superconductivity, potentially unveiling new light element molecule-based superconductors, something that cannot be done experimentally.

Application

Light element molecules superconductors

Relevant review articles

Capone et al. Modeling the unconventional superconducting properties of expanded A(3)C(60) fullerides 10.1103/RevModPhys.81.943 Apr-Jun 2009 Kubozono, Yoshihiro et al Metal-intercalated aromatic hydrocarbons: a new class of carbon-based superconductors PhysChemChemPhys 13/17 2011 pp: 16476-16493 DOI: 10.1039/c1cp20961b

Summary of project

This project addresses the design and understanding of light (and cheap, abundant, benign) element (B, C, O) cluster/molecule-based superconducting systems with higher transition temperatures. The project aims to develop new understanding of the electronic and crystal structures required for high Tc superconductivity in light element systems. Competing electronic ground states and pairing mechanisms are at the basis of superconductivity. In light element materials a fine balance exists between electron-phonon coupling and the electron correlations. This was recently identified as the potential of light elements as superconductors.In light elements superconductivity is controlled by p orbitals and the n-orbitals of C contribute to the LUMO (lowest unoccupied molecular orbital, filled by the electrons donated by the alkali dopants). Furthermore the Coulomb exchange interaction plays a role, and the C-C phonon modes bring about the molecular vibrations relevant for superconductivity. Alkali doped fullerenes, fullerides and polycyclic aromatic hydrocarbons near metal-insulator transitions, where they are likely to develop superconductivity, will be studied. Also the influence of external actions, such as doping, pressure, electric fields will be investigated. The simultaneous role of correlations, screening and disorder will be considered, with special attention to the role that disorder may play in enhancing the critical temperature at the transition.

Summary of the modelling

The electronic structure, magnetism, phonon structure will be obtained by density functional theory (DFT) calculations, even in strongly correlated systems. Insulating or metallic tendencies and the Fermi surfaces of candidate light element and molecular superconductors can be addressed with an initial DFT study. The DFT total energies and enthalpies generally provide a good indication of the relative stability of different crystal structures. Relativistic effects, including Rashba at interfaces, can automatically be included by means of DFT codes including spin orbit. The electron phonon couplings, key ingredients to BCS (Bardeen, Cooper, Schrieffer) superconductivity (standard theory of superconductivity, based on electron-phonon interactions driving ordinary metals unstable against electron pairing) in regular metals and also in Jahn Teller systems, can be reasonably obtained by DFT. In addition correlations can be built-in at the mean-field level through approximations such as LDA+U or equivalent. DFT with a variety of hybrid functionals (HSE, B3LYP) and LDA+U models will be applied to identify aromatic superconductor materials that show a conduction band which comprises multibands and a Fermi surface which is an interesting composite of surfaces having different spatial dimensionalities. We use a Gutzwiller projector technique to introduce approximately electron-electron correlations in the ab-initio density functional theory (DFT) based codes. In this approximation, the Kohn Sham equations of ordinary DFT are modified into new ones, where the electron hoppings are reduced by factors reflecting the renormalization caused by repulsive correlations.

Full many-body models such as Dynamical Mean Field Theory (<u>DMFT</u>) with the "downfolding" description of the Mott-Hubbard insulator will also be applied.

Many body techniques for metal-insulator interfaces able to describe inhomogeneous situations will be developed for application to surface doping. The effect of many body interactions beyond meanfield levels in picene and similar molecular systems will be added to the models. The models will then be available for materials exploration of the rich variety in molecular species (various aromatic molecules in the present project), orbitals and crystal structures in order to find materials with longranged electron-electron interaction, expected to substantially affect the mechanism of superconductivity.

The superconductor- insulator transition in lattice expanded alkali fullerides has properties not yet experimentally explored. Insulator-superconductor transitions obtainable under pressure and/or in other organic doped systems will be investigated to identify materials that are possible candidates.

http://www.lemsuper.eu

Project Acronym and Number: LEMSUPER 283214 Project Title: Light element molecular superconductivity and interdisciplinary approach Start and End Dates: 01/10/2011 till 31/03/2015 EU Contribution: 1.606.660 € Coordinator: E. Tosatti, SISSA, Trieste, Italy; tosatti@sissa.it



Modelling in LIGHT.TOUCH.MATTERS 310311

Subject of the modelling

Piezoelectric composites and OLEDs

Models used

Continuum: mechanics (either <u>solid</u> or <u>liquid</u>) <u>electromagnetics</u>

Simulation software and type of numerics used

Micromechanics and EM models: conventional software packages such as Matlab, Abaqus or Comsol

Achievements of the model beyond experiments

The model will greatly facilitate making trade-offs between e.g. cost and sensitivity, as well as streamline tests of material stacks;

Application

Touch sensitive luminous user-product interfaces for creative industries, electronic health care and consumer goods, but also the chemical, automotive and printing industries, as well as mechanical-, electrical-, packaging- and systems engineering.

Relevant review articles

Y. Benveniste 1987 Mech. Mater. 6, 147-157
M.L. Dunn, M. Taya 1993 Proc. R. Soc. A. 443, 265-287
C.Andrews, Y. Lin, H.A. Sodano 2010 Smart Mater. Struct. 19, 025018
C.P. Bowen, R.E. Newnham, C.A. Randall 1998 J. Mater. Res. 13, 205

Summary of project

In Light.Touch.Matters polymeric piezo materials (piezo-active particles in a polymeric matrix) and flexible OLEDs will be designed that combine touch sensitivity with luminosity. Manufactured on plastic substrates, these novel 'light touch materials' will be thin, flexible and formable.They will expand design freedom and allow new modes of product-user interaction, using touch sensitivity and luminosity to produce simple, affordable and intuitive user interfaces.

Summary of the modelling

<u>Micromechanical models</u> will be applied to piezoelectric composites to predict performance in a wide variety of load cases, e.g. under tension, compression, bending or torsion, either directly loaded or indirectly loaded. The composite will be part of a 'stack' of materials with other materials placed between the load and the composite.

Electromagnetic models will predict the effective dielectric constant (i.e. piezo-electric sensitivity) of the piezoelectric composite material in relationship to the composite's,

composition and the electromagnetic field applied during composite formation.

The modelling work involved is a hybrid of continuum mechanics (either <u>solid</u> or <u>fluid</u>)

and electromagnetic models, i.e. multi-physics. With this materials can be designed that meet the properties desired by designers to enable certain modes of product-user interaction. These specifications might include that this constant will be different for different deformation modes of the composite (e.g. bending versus torsion, or bending versus compression), and the model will calculate which material shows this anisotropy.

http://www.light-touch-matters-project.eu/

Project Acronym and Number: Light.Touch.Matters 310311 Project Title: Design driven development of touch sensitive luminous flexible plastics for applications in care & well-being Start and End Dates: 1/2/2013 till 31/7/2016 EU Contribution: 3,984,150 € Coordinator: E. Tempelman, Delft University of Technology, e.tempelman@tudelft.nl



in LISSEN 314282

Subject of the modeling

Sulfur-based battery cells

Models used

<u>Continuum</u>: A single-battery-cell reactive-transport models (1D continuum-based <u>transport</u> of mass and charge, elementary <u>kinetic description</u> of electrochemistry and heterogeneous chemistry)

3D <u>microstructural models</u> for cathode and anode (geometrical representation of experimentally obtained structures, simulation of material properties based on structure)

Modeling and simulation software and type of numerics used

DENIS, a C-based DLR modeling framework for single-cell reactive-transport calculations GeoDict, a 3D microstructural modeling Matlab

Achievements of the models

The models will be used to simulate the influence of physical parameters on key performance metrics and cell lifetime, therefore generating a deeper understanding of functional principles of the studied system. Based on the resulting findings, experimentalists can be advised and guided, speeding up the actual development of the envisioned "Lissen Battery".

Application

Lithium-Sulfur battery cells

Relevant articles covering the topic:

- K. Kumaresan, Y. Mikhaylik, R. White; A mathematical model for Lithium-Sulfur Cell, J. Electrochem. Soc., 155 (8) A576-B582 (2008)
- S. Gewies, W. Bessler; Physically based impedance modeling of Ni/YSZ Cermet, J. Electrochem. Soc., 155 (9) B937-B952 (2008)
- J. P. Neidhardt, D. N. Fronczek, T. Jahnke, T. Danner, B. Horstmann, W. G. Bessler; A Flexible framework for Modeling Multiple Solid, Liquid and Gaseous Phases in Batteries and Fuel Cells, J. Electrochem. Soc., 159 (9), A1528-A1542 (2012)

Summary of project

This project aims for the identification and development of nanostructured electrode and electrolyte materials as well as appropriate cell designs to promote the practical implementation of the very high-energy lithium-sulfur battery. In particular, the project will be directed to the definition and test of a new lithium metal-free battery configuration based on the use of lithiated silicon as the anode and a nanostructured sulfur-carbon composite as the cathode.

Summary of the modelling

3D microstructural models will be coupled to single-cell <u>reactive-transport</u> models in a unidirectional "offline" fashion: electrode properties will be calculated for a range of parameters with microstructural models, and results are used as input for reactive-transport models. A bi-directional online coupling of different numerical codes or the integration of analytical results obtained from microstructural models in cell-level models might be established where useful and feasible.

The models developed within the LISSEN project will improve the conceptual understanding of mechanisms governing the functioning and degradation of Lithium-Sulfur battery cells. To this end, the role of three main aspects of Lithium-Sulfur cells for key performance metrics and longevity will be investigated: 1) the involved multi-step redox chemistry, 2) the surface and internal structure of electrodes used, and 3) the overall cell design (type and composition of active materials in the electrodes, used electrolytes, etc.)

Single-cell reactive-transport models based on a 1D continuum approach will be used to investigate the role of involved chemical reactions. The model couples <u>chemical reactions</u> and continuum mass and charge <u>transport equations</u> and solves them simultaneously. The multi-species redox chemistry of sulfur to lithium sulfide via polysulfides (and vice versa) will be modelled at the cathode. At the anode, lithium deposition/intercalation into an anode material will be described. Parasitic side reactions (e.g. polysulfide reduction at the anode) will be implemented as appropriate. When useful and feasible, the intercalation induced volume changes of electrodes as well as pore size changes resulting from dissolution and precipitation of solids will be modeled. The <u>transport equation</u> will describe the transport in the liquid electrolyte. Experimental data (as e.g. polarization behavior, electrochemical impedance, and other kinds of in-situ measurement results available from the partners or appropriate literature data) will be used to validate the model. Interpretation of simulation results then provides insights into the role and influence of the involved electrochemical reaction network and the results will also form the basis for describing the cross talk between the two electrodes (e.g., shuttle mechanism).

For an assessment of the role of electrode structures, the morphological parameters of cathode and anode, needed for single-cell reactive-transport models (e.g. volume fractions of the components, volume-specific surface areas and phase boundaries) will be obtained by interpreting results from 3D <u>microstructural modelling</u> of the porous electrodes and by geometrical considerations of structural changes of individual pores, particles, or particle agglomerates. Simulation results based on various electrode-microstructures will be compared. Existing or newly developed single-cell reactive-transport models and morphological models will be applied to various cell designs. Simulated cell performance and longevity will be compared.

Experimentally determined parameters that can aid in the development of the single-cell reactive transport models include the diffusion coefficients, the ion transference numbers, the conductivity and the initial concentration of participating components (electrolyte, conducting salt, polysulfides), as well as kinetic reaction parameters derived from, e.g., impedance measurements and the analysis of discharge/charge curves. Information about the morphology of solid components (sulfur, carbon, Li-Sn, Li-Si), like density, volume fraction, specific surface area, and particle size, will help in the development of the microstructural models. Here, input from ex-situ characterization from experimental work packages (SEM, TEM, BET) is required.

http://www.lissen.eu/

Project Acronym and Number: LISSEN 314282 Project Title: Lithium Sulfur Super battery Exploiting Nanotechnology Start and End Dates: 01/09/2012 – 31/08/2015 EU Contribution: 2,579,940€ Coordinator: Riccardo Carelli; Consorzio Sapienza Innovazione, Italy, <u>riccardo.carelli@sapienzainnovazione.it</u>



in M3-2S 213600

Subject of the modelling

Load bearing capacity of nano/micro-scale multi-layered films (TiN, CrN and NbN) for improving the wear resistance of tools (e.g. for cutting)

Models used

Atomistic: <u>Molecular Dynamics</u> for coating deposition

Mesoscopic: <u>(called "Atomic") lattice</u> modelling for the breaking and forming of atomic bonds for the prediction of dislocation generation and crack nucleation and growth in the coating materials

Continuum: Discrete dislocation plasticity modelling to link the crystal plasticity scale and the atomic finite element scale

diffusion model at the component scale

Simulation software and type of numerics used

The combined system linking the scales was implemented in a novel surface load-bearing expert software system integrated with DEFORM FE software to predict the load bearing capacity of the multilayer coatings.

virtual grain structure generation by controlled Poisson Voronoi tessellation

Achievements of the model beyond experiments

The multiscale modelling system for multilayers can predict crack initiation based on nano- and micro-mechanics, in particular so-called ring cracking, consistent with what is observed in experiments under load bearing scenarios. These predictions can then be used to evaluate the load bearing capacity of a coatings system, allowing virtual design of multilayers. This is not feasible using experiments as it would require a very costly and time consuming trial and error design approach.

Application

Coatings, manufacturing, surface engineering

Relevant review articles

Z. Xu, Y. Li, D. Shan and B. Guo, Computational Materials Science, 20(2011), 1432-1436. R.Neuge-bauer, R.Wertheim, U.Semmler, Journal of Multiscale Modelling, 3(2011), 91-107. J. Feng, Y. Qin, Q. Zeng, E. Almandoz, G. Fuente, H. Dong, Raghavan and J. Michler, Journal of Multiscale Modelling, 3(2011), 1-22.

Currently, the design of multilayered surfaces (MSSs) in engineering components is normally based on experience and surface modelling techniques are needed to explain and avoid surface related failures in engineering components. The aim of this project is to address an urgent scientific, technological and market need for consistently reliable high performance MSSs, by developing generic, robust multiscale materials and process modelling techniques for the design, optimisation and performance prediction of MSSs.

Summary of the modelling

The goal is to develop an integrated multiscale modelling approach to link molecular dynamics crystal plasticity and continuum mechanics modelling activities for the applications. <u>Molecular Dynamics</u> techniques have been applied to model atom deposition processes and the atomic structure and interfaces to achieve optimal coating microstructures. The MD method was used to simulate the formation of lattice structures of coatings and layer interfaces in thermo-chemical processes and the results was used as input for nano- and micro-mechanics modelling for defining material structures.

Continuum <u>diffusion models</u> are used to simulate such processes as plasma nitriding, plasma carburising and plasma nitrocarburising. These surface modification processes have been widely used in the design of multilayered surface systems to improve their load supporting capacity. The outcomes have been used to define material structures as inputs for mechanics analysis. New physically based constitutive equations based on evolving microstructural state variables (e.g. dislocation density) were developed to predict damage, hence load bearing, in MSSs. These incorporated with the newly developed controlled Poisson Voronoi tessellation technique for generating virtual grain structures allows load bearing capacity of polycrystalline films and multilayers to be predicted.

In parallel, we have applied mesoscopic(called atomic) and crystal plasticity FE modelling capabilities and facilities for predicting deformation and failure of individual layers of nano-/micro-coatings. The "atomic" lattice model is solved by finite element methods. Elements are used like bars or trusses. The behavior of the bar is described by an interatomic potential. This enables an atomic lattice to be modelled by a truss-like assemblage of members that deform according to a prescribed interatomic potential, which governs their relative separations under applied loading. A key feature of the atomic finite element method is that it results in a finite element equation with displacement degrees of freedom, hence an atomic finite element mesh can be directly coupled to other element types and larger scales. Discrete dislocation models were also used to model at scales between the atomic and crystal scales, with concurrent coupling.The lattice structure of coatings, atomic mismatch and dislocations at layer interfaces modelled at the atomistic level is used for the FE models.

Therefore, an integrated technique to determine mechanical properties of nano- and micro-scale coatings has been developed. Application software packages will be developed and attached to commercial FE codes for the analyses.

www.m3-2s.bham.ac.uk

Project Acronym and Number: M3-2S 213600 Project Title: Multiscale Modelling for Multilayered Surface Systems Start and End Dates: 01/11/2008 till 31/10/2011 EU Contribution: 3.447.883 € Coordinator: Hanshan Dong, University of Birmingham, UK, <u>h.dong.20@bham.ac.uk</u>



in MACADEMIA 228862

Subject of the modelling

Metal organic frameworks (MOFs) for separation of gases and liquids Catalysis

Models used

Electronic: <u>Density Functional Theory</u> (Kohn-Sham method) and <u>post Hartree-Fock models</u> Atomistic: <u>Molecular Dynamics</u>, <u>QM/MM</u> and <u>Grand Canonical Monte Carlo (GCMC)</u> Continuum: Thermodynamic models: multi-scale mass transfer models (bed/pellet/crystal scale) and

heat transfer models (bed scale) for adsorption.

<u>process model</u>: Simulated Moving Bed and Pressure Swing Adsorption

Simulation software and type of numerics used

VASP & TurboMol softwares for DFT

DL_POLY software for molecular dynamics

In-house & MUSIC software codes for Monte Carlo simulations (statistical techniques)

In-house numerical simulation packages with Matlab software:

Ideal Adsorbed Solution Theory (IAST), Real Adsorbed Solution Theory (RAST), Heterogeneous Ideal Adsorbed Solution Theory HIAST and the Vacancy Solution Theory with different models of activity coefficients: Flory-Huggins (VST-FH) and Wilson (VST-Wilson)

COMSOL and Matlab softwares for transfer models

PC-based clusters used for parallel computing under Linux Operating System

In-house numerical process simulation tools including the Linear Driving Force strategy.

Achievements of the model beyond experiments

The modeling avoided time consuming and costly experiments characterizing the adsorption performances of a large set of MOFs and thus allowed the fast identification of promising novel MOFs for a given application. For example, the simulations led to the discovery of a simple rule that allows quick assessment if a MOF is suitable for xylene separations. This reduces the number of time consuming experiments. Furthermore, a screening strategy was developed to predict the separation properties of a large number of MOFs for N_2/CO_2 and CO_2/CH_4 mixtures.

Application

Industrial separation processes for gases, vapours and liquids as well as catalysis

Relevant review articles

Tina Düren, Youn-Sang Bae, Randall Q. Snurr "Using molecular simulation to characterise metal-organic frameworks for adsorption applications", Chemical Society Reviews, 1237-1247, 2009

G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P.L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi & J. S. Chang, "*Why hybrid porous solids capture greenhouse gases?"* Chemical Society Reviews 40, 550, 2011

The project MACADEMIA addresses the development of specific, energy saving processes for separation of gas and liquids, and catalysis with reduced environmental impact. These processes are to be optimised via the use of improved Metal Organic Frameworks (MOFs).

Summary of the modelling

The material/process properties modelled in MACADEMIA are:

- Thermodynamic and kinetic selectivity of the materials for gas/liquid mixtures
- Catalytic activity of the materials for a series of reactions and the resulting mechanisms.

<u>Density functional theory</u> (DFT) is used to characterise the chemisorption processes occurring at the surface of open metal centres. Chemisorption is an adsorption process where at least one partially covalent bond is formed between the adsorbate and adsorbent. The particular functional to be used most will be described with the PBE exchange-correlation density functional corrected within the DFT/CC correction scheme.

The catalytic activity of MOFs is explored regarding reactions catalysed by Lewis acid sites, using either traditional <u>post-Hartree-Fock methods</u> (e.g. MP2 or CCSD(T) methods) on cluster models or periodic <u>DFT</u> calculations. For larger systems, a combined quantum mechanical/molecular mechanical (<u>QM/MM</u>) model will be also employed to give the reaction path and relative energies of stationary points on the reaction path.

Classical simulations including <u>Grand Canonical Monte Carlo</u> (GCMC) and <u>Molecular Dynamics</u> (MD) are used to fully characterize the selectivity and transport properties of different MOF materials with respect to the different liquid and gas mixtures. Both MD and GCMC are conducted using rigid or flexible force fields. Output generated from quantum calculations (DFT-CC) are implemented in the classical Grand Canonical Monte Carlo simulations to more accurately describe the adsorption phenomena when specific interactions occur at open metal sites that cannot be treated using generic force field. Furthermore, equilibrium and non-equilibrium MD simulations provide additional information on the molecular diffusion mechanisms of the separation processes in both liquid and gas phases. To support the experimental high throughput screening complementary Monte Carlo computational screening tools were developed that allow to get a realistic, first assessment if a MOF is promising once its structure is determined and therefore whether the synthesis should be scaled up for further experimental tests.

<u>Thermodynamic models</u> such as ideal adsorbed solution theory (IAST), heterogenous ideal absorbed solution theory (HIAST) or Vacancy Solution Theory (VST) are employed to predict the equilibrium adsorption of mixtures from single component isotherms and thus their selectivity for a series of gas mixtures.

Continuum modelling are used to evaluate the materials on the process scale and to predict material behaviour and ageing in real applications. Macroscopic modelling includes the <u>Simulated Moving Bed and</u> <u>Pressure Swing Adsorption</u> for different separation processes (propane/propene, acid gas....). It is possible to:

1) predict the performance parameters of the process: productivity, product purity/recovery, energy consumption;

- 2) size the pilot/industrial scale process for a preliminary technical evaluation;
- 3) compare the experimental results provided by industrial tests with simulated data.

www.macademia-project.eu

Project Acronym and Number: MACADEMIA 228862 Project Title: MOFs as catalysts and adsorbents: Discovery and engineering of materials for industrial applications Start and End Dates: 01/07/2009 till 30/06/2013 EU Contribution: 7.600.000 € Coordinator: Francis Luck, TOTAL S.A., FR, <u>francis.luck@total.com</u>



in MAGNONICS 228673

Subject of the modelling

Nanostructured magnetic (magnonic) metamaterials with GHz and THz dynamics and/or with unusual electromagnetic properties (negative permeability in certain frequency ranges, band gaps in magnonic dispersion etc).

Models used

Mesoscopic: Spin dynamics: <u>micromagnetic simulations</u> based on the Landau-Lifshitz equation for computing magnetization dynamics in the time-domain and band gap gap and effectively continuous properties describing excitations in magnonic metamaterials consisting of patterned magnetic nanoelements

Continuum: <u>electromagnetics</u> Plane wave method (PWM) for the calculation of magnonic Spectra for full Maxwell equations with account of ferromagnetic resonance phenomena

Simulation software and type of numerics used

Finite-difference (MicroMagus, OOMMF) and finite-element (Nmag) Dynamical matrix method for dipole-coupled magnetic nanoelements and arrays of antidots Simulations of ordered and disordered systems of <u>single-domain</u> fine magnetic particles taking into account the magnetodipolar interparticle interaction MatLab based solution of Maxwell equations Matrix diagonalization

Achievements of the model beyond experiments

Numerical simulation of quasistatic magnetization processes explain measurements by MOKE and of spin-wave excitations observed by FMR, BLS, and TRSKM techniques in 2D arrays of nanoscale magnetic dots and antidots. These simulations facilitate explaining the nature and spatial structure of magnons in the magnonic arrays.

Application

Electromagnetic antennas (e.g. patch antennas), and signal conditioning devices (e.g. microwave filters); magnonic devices and logic architectures, including magnonic filters, logic gates, programmable gate arrays.

Relevant review articles

V. V. Kruglyak, S. O. Demokritov, and D. Grundler, "Magnonics", J. Phys. D – Appl. Phys. 43, 264001 (2010); S. - K. Kim, "Micromagnetic computer simulations of spin waves in nanometre-scale patterned magnetic elements", J. Phys. D – Appl. Phys. 43, 264004 (2010).

The project aims at creation of materials with artificial structures - so called metamaterials – having the GHz and THz excitation spectra with prescribed features (peaks and band gaps in given frequency regions). With respect to long wavelength spin waves, the artificial nanostructures will behave as effectively uniform and have effectively continuous magnetic properties not seen in nature. For short wavelengths the material will show band gaps.

Summary of the modelling

MAGNONICS focussed on the comprehensive theoretical understanding of the band gap and effectively continuous properties of the created magnonic metamaterials.

The <u>electromagnetics plane wave method</u> (PWM) has been used for the calculation of magnonic band structure of thin slabs of 1D and 2D magnonic crystals and validated via comparison with experimental results. The PWM has been applied to the calculation of magnonic spectra of antidot lattices and used to interpret experimental data acquired using broadband microwave spectroscopy and BLS.

Thermally excited spin waves in planar one- and two-dimensional magnonic crystals have been studied using both conventional (k-vector resolved) and micro-focused (spatial resolved) BLS measurements in arrays of dense magnetic elements (dots and stripes) and antidots (periodic arrangement of holes embedded into a continuous magnetic film), and the results have been compared with calculations performed by <u>micromagnetic simulations</u>.

The 3-dimensional (3D) version of the Fast Fourier technique (FFT) for calculating the magneto-dipolar interaction field in continuous ferromagnetic structures has been implemented, so that large-scale simulations of 3D micromagnetic problems have become possible.

A numerical technique, the dynamical matrix method has been used to deal with dipolecoupled nanoelements and arrays of antidots and to evaluate the BLS cross section. It has been applied to systems experimentally investigated within the project: chains and 2D arrays of magnetic dots, square arrays of antidots.

The combined Ewald-FFT method for the calculation of the magneto-dipole interaction field in ordered and disordered systems of fine magnetic particles has been applied. In particular, this method enables highly efficient numerical simulations of magnetization processes in magneto-ferritin-based crystals.

Numerical simulation of quasi-static magnetization processes measured by MOKE and of spinwave excitations observed by FMR, BLS, and TRSKM techniques in 2D arrays of magnetic nanodots have been performed. These simulations allow to explain the nature and to find out the spatial structure of corresponding magnons in the nanodot arrays under study.

www.magnonics.org

Project Acronym and Number: MAGNONICS 228673 Project Title: MAGNONICS: Mastering Magnons in Magnetic Meta-Materials Start and End Dates: 15/09/2009 till 14/09/2012 EU Contribution: 3.499.820 € Coordinator: Volodymyr Kruglyak, University of Exeter, UK, <u>V.V.Kruglyak@exeter.ac.uk</u>



in MASTER 212257

Subject of the modelling

Spin wave excitation by spin-polarized current and spin-diffusion effect in normal metal near a junction

Models used

Mesoscopic: Micromagnetic model

Simulation software and type of numerics used

Micromagnetic package SpinPM, a generalized Landau Lifshitz Gilbert solver based on 4th order Runge-Kutta scheme with INTEL MKL FFT acceleration. It integrates:

Plug&Play user-friendly GUI FFT-accelerated magnetostatics time integration using 4th order Runge-Kutta solver time step auto-adaptation very flexible system definition Spin Transfer Torque with both Slonczewski and Field-like torques

Achievements of the model beyond experiments

The model can predict the magnetization dynamics in an array of hetero-structures. These dynamics cannot be computed analytically. These simulations are used to optimize the design of spin devices as optimization by experimental means would be too costly.

Application

Mobile and wireless telecommunication technology Spin torque devices

Relevant review articles

A.V. Khvalkovskiy, KAZ, et al Phys. Rev. B. 80, 140401(R), (2009)
A. Chanthbouala, AVKh, KAZ, et al., Nature Physics 7, 626 (2011)
A. Dussaux, AVKh, KAZ et al., Nature Com. 1, 1 (2010)
A.D.Belanovsky, KAZ, et al, Phys. Rev. B 85, 100409(R), (2012)

MASTER is to explore microwave signal generation for integrated microwave components and wireless communications systems. The so-called Spin Transfer Nano-Oscillator (or STNO), can provide solutions to miniturization and broad-range microwave detection due to their specific spin polarized transport properties. This project aims at exploiting the coherent coupling within and between devices developed in large array to improve the microwave performances in terms of phase noise, emission power and to operate in different frequency ranges.

Summary of the modelling

The application of existing <u>micromagnetic</u> packages allowed us to reveal the influence of geometry and structural defects upon the STO phase diagram, phase-locking performance, and line width, and to create a virtual prototype of the STO array with optimized properties. The role of the thermal fluctuations in the phase-locking mechanism has also been investigated within the framework of a full scale 3D micromagnetic model, allowing the optimization of the array. Magnetization dynamics have been investigated in polycrystalline films, with the parameters of magnetic materials being distributed randomly over the crystallites. The model has been elaborated with the Berger / Slonczewski transport term. The code SpinPM simulates spin current-related effects and an extension that includes spin transfer-induced torque has been developed.

The project also developed a simple theoretical framework for transport in magnetic multilayers, based on the Landauer-Büttiker scattering formalism and random matrix theory. A simple transformation allows one to go from the scattering point of view to theories expressed in terms of local currents and the electromagnetic potential. In particular, the theory can be mapped onto the well-established classical Valet-Fert theory for collinear systems. The scattering formalism as our starting point and develop a theory which fully captures Valet-Fert and (generalized) circuit theory. The theory, referred to as C-RMT (for Continuous Random Matrix Theory), can be tabulated by the same set of (experimentally accessible) parameters as Valet-Fert. C-RMT will be included in the micromagnetic solver.

The projects also enhanced the micromagnetic numerical solver. The code has been elaborated to be able to deal with high simulation volume (up to few micrometer big lateral sizes), non-regular structure (multilayered structures), non-regular dynamics (very short-wavelength modes are excited), and huge computational times (> 50 ns). Features to define the structures and to help the analysis of the magnetization dynamics of the system have been added. The most important improvements in the software SpinPM are:

New time integration algorithm based on an integration procedure that includes an adaptive time-step control with a 4th order Runge-Kutta method

New exchange energy calculation algorithm: a new, energy-conserving, numerical algorithm has been developed and implemented allowing very simulations on very long time range Fine system specification allowing much better flexibility in object specification Spectra calculations: This tool provides us with a possibility to calculate these spectra for a batch of projects

http://iramis.cea.fr/spec/Phocea/Page/index.php?id=23

Project Acronym and Number: MASTER 212257 Project Title: Microwave Amplification by Spin Transfer Emission Radiation Start and End Dates: 01/09/2008 till 29/02/2012EU Contribution: $2,044,210 \in$ Coordinator: Olivier Klein, CEA, FR <u>olivier.klein@cea.fr</u>



in MATRANS 228869

Subject of the modelling

Properties and behaviour of metal-ceramic functionally graded materials (FGM) (alumina ceramics and copper or Ni-Al intermetallics) at the stage of processing and under service conditions

Models used

Continuum:

- <u>macromechanics models</u> with phenomenological constitutive equations for materials behaviour (processing induced thermal residual stresses and material damage; static and dynamic fracture; thermomechanical fatigue)
- <u>micromechanical models</u> (modelling of wear, including shape evolution and coupling with oxidation) for effective thermomechanical properties

Simulation software and type of numerics used

Abaqus, ANSYS AceFEM and FEAP for micro and macro-mechanics

FE² for multi-scale thermomechanics modeling

Numerics

Finite elements with three dimensional automatic mesh generation (e.g. SCAN/IP SCAN/FE) coupled with micro-tomography digital images of real material microstructures

Automation of finite element computations using symbolic algebra software (e.g. AceFEM)

self-consistent method or the Mori-Tanaka method

Multi-objective optimisation method to find the optimal composition

Achievements of the model beyond experiments

Most of the modelling in the project is done to replace the experiments, which are usually complex and costly or, in other words, the modelling predicts the materials' properties/behaviour which will be observed in experiments and thus shortens the development process.

Application

- Transport (aerospace and automotive), Energy

Relevant review articles

Y.C. Fung and Pin Tong. Classical and Computational Solid Mechanics, World Scientific, 2001.

P. Wriggers. Computational Contact Mechanics, Springer-Verlag, Berlin Heidelberg 2006.

G.W. Stachowiak (ed.). Wear - Materials, Mechanisms and Practice, John Wiley and Sons 2006.

R.M. Christensen. Mechanics of Composite Materials. Dover Publications, Mineola, New York 2005.

M.F. Ashby. Material selection in mechanical design, 4-th edition. Butterworth-Heinemann, Amsterdam 2011.

J. LLorca. Fatigue of particle-and whisker-reinforced metal-matrix composites. *Progress in Materials Science*, 2002 (47), 283 P.N. Bogdanovich, D.V. Tkachuk. Thermal and Thermomechanical Phenomena in Sliding Contact. Journal of Friction and

Wear, 2009 (30), 153–163. G.A. Maugin, Configurational Forces: Thermomechanics, physics, mathematics, and numerics. Taylor & Francis, NY, 2011.

S. Murakami, Continuum Damage Mechanics: A Continuum Mechanics Approach to the Analysis of Damage and Fracture. Springer, 2012.

L. Mishnaevsky Jr., Computational Mesomechanics of Composites, Wiley, England, 2007.

MATRANS aims at developing novel metal-ceramic functionally graded materials (FGMs) for aerospace and automotive applications in exhaust and propulsion systems (e.g. thruster), power transmission systems (e.g. valves), and braking systems. The main objective is to enhance the mechanical properties of these materials through spatial variations of material composition and microstructure.

Summary of the modelling

Modelling of graded profile of FGMs (i.e. number of layers, their arrangement and volume fraction of metal and ceramic phases in individual layers) was approached as a transient thermo-mechanical problem of <u>continuum mechanics</u> with account of deformation and damage evolution depending on structural parameters variation.

Physical quantities involved in this analysis include temperature, stress, strain, yield and crack resistivity. The sample is subjected to different temperatures and mechanical loadings. As the outcome we obtain stress, strain and optimal ceramic phase distribution in the sample. The software used for numerical solution was AceFEM - a general finite element system for Mathematica, combining symbolic and numeric approaches.

The effective linear thermoelastic properties of the FGM constituent layers were modeled using the full set of conservation principles along with the constitutive equations that relate the mechanical and thermal properties of the individual (metal and ceramic) solid phases. Macroscopic properties of the heterogeneous material were derived from the phase and morphology data either analytically or numerically by using homogenisation techniques such as the self-consistent method or the Mori-Tanaka method.

To model nonlinear overall properties, the above micromechanical approaches were extended to a sequence of incremental problems, linearized using either tangent or secant stiffness moduli, and implemented numerically within the Mathematica package.

Calculated macroscopic properties depend strongly on the material composition. An optimal content of the ceramic phase was searched for, which would meet the required thermomechanical properties of the composite for the target applications. For this purpose, a multiobjective optimization problem of continuum thermomechanics was formulated and solved numerically. The relevant objective function expresses the distance between required effective properties and their micromechanical estimates.

Several existing constitutive models have been coupled in such a way as to assist in revealing the influence of various micro defects (pores, matrix cracks, debonding cracks at interfaces between matrix and inclusions) introduced during the manufacture of metal-ceramic functionally graded materials on their macroscopic properties. These models have been validated on Cu- Al_2O_3 metal-matrix composites and implemented as an external module in the commercial finite element code Abaqus.

A continuum model to calculate thermal residual stresses and damage in graded metal-ceramic composites, generated during the cooling phase of the sintering process, was developed and implemented numerically with FEM, making use of microstructural material data from micro-CT images and transforming it onto finite elements by means of SCAN/IP and SCAN/FE software. The material models used in the FEM computations are the three conservation equations with a linear elastic constitutive equation for the ceramic and an elasto-plastic constitutive equation for the metal phase. Numerical calculations of thermal residual stresses and the resulting material damage were done using FEAP and Abaqus programmes.



Processing-induced microcracking in metal-ceramic composites due to mismatch of thermal properties of the constituent materials was calculated by micromechanical models with configurational forces considered to be the driving forces of macroscopic cracks and defects. The parameters of the macroscopic constitutive equations were either obtained by measurements or by micromechanical modelling. The micromechanical models were solved on a grid of voxels representing either the metal or the ceramics phase of the composite with the microstructural data coming from micro-CT scans or from a randomly generated microstructure. A voxel based generation of three dimensional FE models based on Mishnaevsky (2007) numerical procedures was used in the computations.

A phenomenological model of contact wear has been formulated which provides a constitutive equation relating the local wear rate (wear volume per unit area and per unit time) to contact variables (contact pressure, sliding velocity, etc.) and material properties (e.g. hardness, composition of an FGM layer, etc.). The model is a generalization of the classical Archard wear model. The wear model is a part of the contact and wear problem in which the equilibrium equations (balance of linear momentum) are solved on a varying domain, and the evolution of the domain is determined by the wear model. Thus two problems are solved simultaneously: the deformation (contact) problem and the shape evolution problem. The main focus of the work is on development of a solution strategy based on an unconditionally stable implicit time integration scheme and on development implementation of efficient computational algorithms suitable for this class of problems. The finite element implementation and the computations are performed using the AceGen/AceFEM system. Efficient computational algorithms have been developed which are not part of the existing commercial FEM codes.

A phenomenological model of oxidation coupled with wear was proposed for the aluminacopper FGM developed for the brake disk application. The model gives the oxide mass evolution (the wear and oxide change rates) as function of temperature, contact stress and time. The model is based on experimental observations from Thermo-Gravimetric Analysis (TGA) at a given temperature, tribological wear test (ball on disk) and real surface topography measurement. The wear-oxidation process was solved using a two scale approach. The first scale is the macroscopic level, corresponding e.g. to the ball on disc test of a braking system, the second scale is the asperity microscale level. On the microscale Finite Element Analysis with thermo-mechanical coupling was used for the calculation of averaged wear-oxidation parameters. Finally, on the macroscale the evolution of shape, stress and temperature (affected by the wear-oxidation processes) was calculated using FEM (Abaqus).

Models of mechanical and thermal fatigue of the copper-alumina FGM intended for the thruster application were developed using micromechanical and continuum mechanics approaches. The low-cycle fatigue behaviour of composite is treated as a localized damage development phenomenon activated by applied cyclic loading. The modelling is based in part on the analytical analysis on the microscale of the representative cell, formed by a composite element of a specified size and particle volume ratio. The energy equations are formulated to describe the energy balance with account for the stress transfer between the brittle-particles and ductile-matrix with different possible scenarios of damage localisation. On the macroscale the numerical analysis by the FEM (Abaqus) is used in which the representative damage parameter is introduced affecting the stiffness moduli of the macro element. The predictive result of these models is a relationship between the number of loading cycles (fatigue life) and the critical stress/accumulated equivalent plastic strain sustained by the material.

A series of fully coupled linear thermoelastic models of brake disk demonstrator solved with FE techniques were developed and tested. The focus was on the optimal design of the brake disk and on simulation of mechanical strength. The effective material properties were used as input in phenomenological model.

A new constitutive model defining the relationship between tensile strength of functionally graded materials (FGMs) and volume fraction of ceramic phase has been developed to simplify complicated mechanical behaviour of FGMs.

In oxidation modelling a new constitutive relation has been proposed between the oxide growth rate and the surface temperature. Since the calculated macro temperatures are too low to allow for the oxidation, only closer look at surface asperities can provide the mathematical model for the experimentally observed oxidation phenomena. A user-defined FORTRAN code for the developed constitutive relation has been added to a commercial FE software.

matrans.kmm-vin.eu

Project Acronym and Number: MATRANS 228869 Project Title: Micro and Nanocrystalline Functionally Graded Materials for Transport Applications Start and End Dates: 01/02/2010 till 31/01/2013 EC Contribution: 3.600.000 € Coordinator: Michal Basista, KMM-VIN AISBL, <u>Michal.Basista@kmm-vin.eu</u>


in METACHEM 228762

Subject of the modelling

Characterisation of electro-magnetic properties of thin-film metamaterials with well-defined boundaries

Extraction of optical constants from measured optical data (variable angle spectroscopic ellipsometry, transmission, reflection, phase.)

Models used

Continuum: electromagnetism models:

Maxwell equations with boundary conditions and different types of sources (plane wave; wave port; Gaussian beam; point dipole, etc)

Models developed for extraction of bulk properties of the materials (mainly real and imaginary parts of permittivity)

Generalized Mie Model (GMM) of scattering by clusters of simple and core-shell spheres

Simulation software and type of numerics used

Ansoft HFSS

CST Studio Suite

Original analytical method of dynamic homogenization for so-called Bloch lattices Original analytical method of dynamic homogenization for so-called metasurfaces Fresnel modelling using commercial WVASE software, a corrected Sivukhin-Debye model Integral equation approach and discretization of the surfaces with the help of GMSH, Accelerations:

- Exponentially converging (and tabulated) periodic Green's functions.

- Compression of matrix of system of equations using the incomplete-QR approach

- Matrix reduction using multiple-scattering Macro Basis Functions

Achievements of the model beyond experiments

The model predicts whether the metamaterial can be described within effective media theory. The model extracts parameters not directly measurable.

The model can determine individual polarizabilities of a complex scatterer (electric and magnetic), surface susceptibilities of metasurfaces (electric, magnetic and magnetoelectric), refractive index of the wave in a lattice and wave impedance of the wave in a lattice.

Application

Optical devices Characterization of metamaterials

Relevant review articles

http://ec.europa.eu/research/industrial_technologies/pdf/metamaterials-brochure_en.pdf

The objective of the METACHEM collaborative project is to use the extreme versatility of nanochemistry and the physical-chemistry routes of self-assembly to design and manufacture bulk meta-materials exhibiting non-conventional electromagnetic properties in the range of visible light.

Summary of the modelling

<u>ElectroMagnetism theory</u> and numerical simulations provide guidance for designs by calculating which materials, shape of particles and range of sizes can provide new metamaterial properties. The aim is also to understand the consequences of disorder (in size and position). The models will give the effective optical parameters of the metamaterial (refractive indices, thickness, bi-anisotropy, etc.).

Plane wave models are used for the extraction of bulk properties of the materials (mainly real and imaginary parts of permittivity).

The generalized Mie Model (GMM) is used to study scattering by clusters of simple and core-shell spheres and also for the study of gain media, in combination with appropriate periodic Green's functions.

Ansoft HFSS and CST Studio Suite are used for infinite-array simulations of periodic metavolumes and meta-surfaces in combination with plane-wave models (see above) for the extraction of material parameters.

Integral-equation approaches are used for the accelerated analysis of large finite structures and structures made of complex inclusions (systematic reduction of complexity with "macro basis functions"). It easily allows for the computation of "point spread functions" (response of a metamaterial to a nearby localized source). This approach is used for fast infinite-array response of magnetic nano-particles, point-spread function of arrays of nanorods, and study of disorder in large finite arrays.

The transmission, reflection and ellipsometry spectra measured at different angles of incidence (ellipsometric data) are used to extract values of optical constants of metamaterial. The spectroscopic data will be also analyzed with the help of the Sivukhin-Debye approach, which has a much better accuracy than effective medium theories in case of small film thickness.

https://www.metachem-fp7.eu/

Project Acronym and Number: METACHEM 228762 Project Title: Nanochemistry and self-assembly routes to metamaterials for visible light Start and End Dates: 15/09/2009 till 15/09/2013 EU Contribution: 3.499.820 € Coordinator: Philippe Barois, CNRS-Bordeaux, FR, <u>barois@crpp-bordeaux.cnrs.fr</u>



in MINOTOR 228424

Subject of the modelling

Electronic phenomena at interfaces in organic-based electronic devices

Models used

Electronic: <u>Hartree-Fock methods</u>, <u>DFT methods</u> Atomistic: <u>Molecular Dynamics</u> (MD), <u>QM/MM</u>, <u>Monte Carlo</u> algorithms, Continuum: <u>Classical electromagnetism</u> (microelectrostatic models)

Software code and type of numerics used

Gaussian, Ampac, Fireball, VASP, SIESTA, Gromacs, Materials Studio, Tinker, NAMD

Achievements of the model beyond experiments

Modelling allows material design of multilayer devices with optimized proprieties as follows:

- The model has predicted the contributions to the discontinuity between the electronic structure at the interface and the bulk material
- The model explained the origin of the electronic level alignments at organic/organic interfaces as measured in short-circuit current and the open circuit voltage of solar cell devices, two key quantities that directly dictate the efficiency of those cells.
- The model has shown that modifying the surface of electrodes, can tune the charge or spin injection barriers in devices such as OLEDs.
- The model predicted the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties.

Application

OLEDs, transistors, sensors and storage devices, solar cells

Relevant review articles

"Electronic structure and geminate pair energetics at organic - organic interfaces: the case of pentacene/ C60 heterojunctions". S.Verlaak, D.Beljonne, D.Cheyns, C.Rolin, M.Linares, F.Castet, J.Cornil and P.Heremans. Advanced Functional Materials 2009, 19, 3809-3814 "Electronic Processes at Organic-Organic Interfaces: Insight from Modeling and Implications for Opto-Electronic Devices". D.Beljonne, J.Cornil, L.Muccioli, C.Zannoni, J.L.Brédas and F.Castet. Chemistry of materials 2011, 23, 591-609

"Barrier Height formation for the PTCDA/Au (111) interface" J.I.Martinez, E.Abad, F.Flores, J.Ortega, G.Brocks Chemical Physics, 2011, 390, 14-19.

The main goal of MINOTOR is to develop a multiscale theoretical approach to model the interfaces in organic-based electronic devices and the electronic phenomena taking place at these interfaces in order to optimize the device efficiency. Organic electronics and spin-based electronics use organic conjugated molecules and polymers in multi-layer devices. Many key electronic processes (such as charge injection from metallic electrodes, charge recombination into light or light conversion into charges, spin injection) occur at interfaces and predictive models need to be developed to reproduce and fine tune new materials characteristics.

Summary of the modeling

The project applied modelling approaches to investigate electronic and structural properties at organic-organic, organic-metal, and organic-inorganic interfaces, in close conjunction with corresponding experimental measurements.

MINOTOR aimed at a multi-scale modelling approach ranging from the atomistic to the mesoscopic scale. In particular, the modelling could predict and explain:

- Changes in the work function of metal electrodes upon deposition of self-assembled monolayers or organic semiconductors using <u>DFT</u> calculations with Periodic Boundary Conditions (as implemented in VASP, SIESTA, FIREBALL)

- The nature of interface dipoles formed at organic/organic interfaces by modelling the morphology at the atomistic level with <u>Molecular Dynamics</u> simulations and by computing the electronic properties of model systems or aggregates extracted from the MD snapshots using semi-empirical <u>Hartree-Fock techniques</u> or DFT calculations validated against <u>highly correlated CASSCF and MP2</u> approaches.

- The nature of the dipoles at interfaces between organic semiconductors and oxide layers (ZnO, TiO2) and the resulting shift in the workfunction of the oxide layer at the DFT and tight-binding DFT levels; realistic morphologies have also been generated at the MD level.

- The mechanism of free charge carrier generation in organic solar cells by computing the energetic profile of the charge carriers around the interface with a classical <u>microelectrostatic model</u> with all relevant parameters provided by quantum-chemical calculations.

- The mechanism of chemical doping of organic layers to yield enhanced conductivities by determining the energy landscape of the charge carriers with a classical microelectrostatic model. The goal of the calculations is to find the energy of a positive charge or negative charge localized on each individual molecule of a large cluster. To do so, classical electrostatic laws were used to estimate the dominant interactions (charge-induced dipole and charge

permanent quadrupole moment) with all relevant molecular parameters (polarizability tensor, molecular charge distribution, and quadrupole moment tensor) provided by quantum-chemical calculations In a next step, the charge carriers are propagated in the doped layer by means of Monte-Carlo simulations relying on hopping transfer rates (with all molecular ingredients provided by quantum-chemical calculations and the energetic disorder by the microelectrostatic model) in order to evaluate the density of free carriers.

http://www.materianova.be/minotor

Project Acronym and Number: MINOTOR 228424 Project Title: Modelling of electronic processes at interfaces in organic-based electronic devices Start and End Dates: 01/06/2009 till 31/5/2012 EU Contribution: 3.080.098 € Coordinator: Jerome Cornil, MONS University, Belgium, Jerome.Cornil@umons.ac.be



in MINTWELD 229108

Subject of the modelling

Welding processes of metal alloys

Models used

 Atomistic: <u>Ab-initio molecular dynamics</u> (MD) with plane wave pseudo potential <u>Born-Oppenheimer molecular dynamics</u> (BOMD), <u>classical MD simulations</u>, by using the abinitio fitted EAM potentials, Molecular dynamics simulation of solid-liquid interfaces with newly developed force fields.
 Mesoscopic: <u>Phase fields model</u> Continuum: <u>Thermodynamic modelling</u>

computational fluid dynamics modelling

Simulation software and type of numerics used

Quantum-Espresso software Potfit force-matching code to fit a new EAM potential to ab-initio forces Finite Element Analysis Front-Tracking method Adaptive interpolation scheme that is suitable for phase field simulations of relevant systems

Achievements of the model beyond experiments

The software predicted the failure of components under in-service loading conditions. By doing so, it accelerated the development of new welding fillers and processes and it thus reduced costs.

Application

Manufacturing industry, metal alloys, welding, EAM (electric active materials) modeling

The ability to weld a metal to itself (similar welding) and to other materials (dissimilar welding) strongly depends on the chemical segregation and morphology of the advancing solidification interfaces, in particular at grain boundaries where individual crystals meet near the weld centre. The advancing solidification interfaces and the resulting grain boundaries have critical nano- and sub-micron scale features. These boundaries have different alloy concentrations due to chemical segregation during solidification, and are the regions where failure most probably occurs by cracking during solidification of the weld pool (hot cracking) or by cracking in service (cold cracking), an example is hydrogen embrittlement. Cracking is the most common failure mode in welds, and many expensive failures have occurred in welded components. This project aims at producing an integrated suite of modelling software, with special emphasis on the solid-liquid interface evolution in industrially relevant systems, such as steel/steel and steel/nickel-based alloys.

Summary of the modelling

The computational aspects of this project aim at incorporating the realistic effects of alloy chemistry and process parameters in modelling the interface evolution during welding and the in-service failure of weld components. Multi-scale approaches which link atomistic ab-initio and Molecular Dynamic models (interface properties and issues of chemistry in the crack) with micro/nanoscale Phase-Field Models (grain boundary and interface chemistry and structure), and continuum Computational Fluid Dynamics models (heat and mass flow) are required to go beyond the current single scale model. The current challenge facing modelling of weld hot cracking is the use of existing models to describe the formation of the weld pool, the advance of the solidification interface, element segregation at the grain boundary and the influence of the welding process parameters and mechanical constraints that arise from the geometry of the work-piece. The project will use models for fluid flow, solidification, phase field and front tracking to provide thermodynamic, kinetic and element segregation information relevant to the solidification interface evolution and resulting grain boundaries. Ab-initio and molecular dynamics studies will provide surface and interface energies and develop new interatomic potentials of selected EAM. For the representation of the sample mesoscope Front-Tracking calculations (crystal growth, grain size distribution) are used.

This information will be combined within the framework of the variational principle to predict component life time.

Validation of the predictions will be ensured by novel experiments at each scale, including realtime synchrotron imaging to observe morphological evolution of the welding fronts, electron probe micro-analysis and atom probe to characterise alloy chemistry near grain boundaries. Strategies for intelligent design of new weld materials with improved properties of the nanoorganized interfaces and grain boundaries will be developed and passed on to the welding industry.

Multi-scale structure integrity analysis is taking advantage of the continuum CFD, mesoscope grain structure modelling, micro-scale phase field modelling and atomistic modelling to provide thermodynamic, kinetic and element segregation information relevant to the properties and failures in welded components. It is hoped that this new approach can provide us a better understanding of physical process during welding and the welded components in use.

http://www2.le.ac.uk/projects/mintweld

Project Acronym and Number: MintWeld 229108 Project Title: Modelling of Interface Evolution in Advanced Welding Start and End Dates: 01/09/2009 till 31/08/2013 EU Contribution: 3.550.000 € Coordinator: Prof. Hongbiao Dong, UNIVERSITY OF LEICESTER, UK, <u>hd38@le.ac.uk</u>



in MODIFY 228320

Subject of the modelling

Stress-induced deformation of pressure sensitive adhesive materials (PSAs) consisting of complex formulations of acrylic polymers

Models used

Atomistic: All-atom <u>molecular dynamic</u> models using <u>force-fields</u> from quantum-mechanics calculations and parameterization on the basis of experimental data. Mesoscopic: <u>Statistical Mechanics rheology model</u> (in-house)

Continuum: Closed-form differential constitutive equation for the <u>rheology</u> of highly elastic polymer-based materials.

Non-equilibrium thermodynamics model for interfacial phenomena.

Simulation software and type of numerics used

LAMMPS software for MD

Molecular Dynamics structural code using the NPxxPyyPzzT statistical ensemble, where N denotes the number of interacting atomistic units in the system, Pii the normal pressure in the i-direction, and T the temperature

Mesoscopic (network) geometry representation based on particle-to-particle transient forces and chain-to-chain entanglements

In-house Statistical Mechanics mesoscopic rheology model

CFD rheology: In-house finite element code to solve the set of partial differential equations describing transport phenomena during the stretching deformation of acrylic adhesives at macro-scale accommodating several boundary conditions (slip, no-slip, generalized slip, etc).

The deformation equations were solved using (a) the mixed Galerkin/finite element method for the velocities, pressure and location of mesh nodes, and (b) the DEVSS-G with streamline upwinding method for the stress components.

Phase field formulations (in-house thermodynamics codes)

Achievements of the model beyond experiments

Modelling has explained the interplay between the chemical composition of the synthesized PSA samples and the degree, strength and life-time of the specific hydrogen forces developing in the polymer, which in turn governs the unique cohesive properties and strong elasticity of these materials. Models also explained the big role played by particle-to-particle transient forces on the elasticity-to-viscosity ratio which seems to be at the heart of the design task for new adhesives. Modelling explained the connection between bulk rheological properties in extension and shear and the debonding mechanisms during stretching of PSAs.

Application

Pressure sensitive adhesive materials for cosmetics, food, paints, and coatings

MODIFY has developed a hierarchical modelling framework for soft nanostructured adhesives based on acrylic polymers. These codes address a multitude of phenomena governing the performance of PSAs in real applications: cavitation, diffuse particle-particle interfaces that can transfer stress, adhesion on hard substrates and slip at high levels of stretching, elasticity-versus-viscosity, density of hydrogen bonds versus density of chain entanglements, and degree of chain cross-linking.

Summary of the modelling

The modelling framework of the MODIFY project consists of the following components:

a) The GENERIC framework of non-equilibrium thermodynamics (<u>phase fields</u>) was first utilized and extended to handle mixed systems consisting of bulk regions and interfaces based on a specific treatment of interfacial fields built on the concept of gauge invariance to atomistic displacements of the interface. The outcome of this effort has been a new type of boundary condition for elastic polymers strongly adhered on hard substrates.

b) For the solution of equations of motion at the atomistic level in the presence of a flow field, a generalized non-equilibrium <u>molecular dynamics</u> (NEMD) algorithm was developed, capable of predicting nano-scale structural changes both in the bulk of an acrylic PSA and at the interface with a substrate. The LAMMPS software was equipped with potential energy functions of relevance to the chemistry of the PSA materials.

c) Information from the atomistic simulations was used to parameterize a continuum model describing the bulk <u>rheology</u> of the PSA systems specifically synthesized in the course of the MODIFY project using the Pom-Pom tube constitutive equation, and a mesoscopic <u>statistical mechanics</u> <u>transport</u> model based on a particle-based coarse-grained picture of the latex particles. The tube-based model enabled accurate empirical fits both of the linear and of the non-linear extensional rheology of the synthesized adhesives. The particle-based coarse-grained model enabled semi-quantitative predictions of their linear and non-linear rheology, using input parameters which were estimated from experiment, statistical reasoning, or more detailed (atomistic) simulations.

Constitutive equations

A macroscopic <u>constitutive model</u> was developed capable of describing quite reliably the deformation equations (e.g., the shear and elongational behaviour) of the synthesized PSA materials. The new equation utilizes generalized expressions for the strain energy density as a function of the three invariants of the conformation or deformation gradient tensor. In limiting cases, it reduces to known laws widely used to describe hyper-elastic materials, such as the Rivlin-Saunders and Hart-Smith theories.

Representation of the sample

An advanced geometrical code was developed to monitor moleculare structural changes upon stretching at the atomistic level; this code can compute the entanglement network, and provide information to higher-level models for the response of polymer acrylics to elongational deformation fields.

Numerics

A powerful finite-element code was developed for the full three-dimensional (3-d) simulation of the deformation of acrylic adhesives. It is based on a consistent coupling of an elliptic-mesh generation methodology with domain decomposition and local mesh refinement around deforming and moving interfaces. The transport code can follow the large adhesive and bubble deformations inside the material (which lead to fibrillation); it can also trace the elastic boundary layers that form at the moving interfaces. It can therefore reliably simulate the force-deformation history of the material under industrially relevant conditions. This is one of the biggest achievements of the MODIFY project.

http://modify.chemeng.upatras.gr/

Project Acronym and Number: MODIFY 228320 Project Title: Multi-scale modelling of interfacial phenomena in acrylic adhesives undergoing deformation Start and End Dates: 01/6/2009 till 31/05/2012 EC Contribution: 2.863.126 € Coordinator: Prof Vlasis Mavrantzas, University of Patras, GR, <u>vlasis@chemeng.upatras.gr</u>



in MONAMI 233513

Subject of the modelling

Molecular- and nano-magnetism, spintronics and magnonics Quantum transport through materials at nano-scale Magnetism

Models used

Electronic: <u>Density Functional Theory</u> and <u>quantum chemistry models</u> with exchange-correlation (XC) energy density functional for excited states and time-dependent phenomena <u>Dynamical Mean Field theory</u> to study material dependent properties of strongly correlated systems like high temperature superconductors <u>Tight-binding model</u>

Atomistic: simulation of physical properties of nanostructured materials, using <u>coarse-grained</u> <u>models</u> with effective soft potentials: stochastic terms for essential motions and large-scale structures

Simulation software and type of numerics used

RSPt: Matrix diagonalization and invertion, quantum Monte Carlo simulations NMTO Wannier-like functions for bonding in intermetallic systems VASP plane wave pseudopotential treatment, Fourier analysis DALTON quantum chemical first principle theory

UppAS: Stochastic differential equation, Fokker-Plank equation

Achievements of the model beyond experiments

Modelling of materials properties allows the search for new materials or to make accurate interpretations of observed materials phenomena. An example can be found for magnetic materials where two properties are most important from an application point of view, namely the size of the magnetic saturation moment at room temperature and a large magnetic hardness (or synonymously, a large magnetic anisotropy energy – MAE). These two properties can be predicted for any material, with an accuracy that is needed to make the search for novel permanent magnetic materials much more efficient. The MONAMI project has also led to a soft-ware which enables simulations of magnetization dynamics, where the dynamical movement can be followed for each atom in the simulation, an ability which goes way beyond experimental possibilities.

Application

Electronic and spintronic devices, sensors Nuclear Magnetic Response probes of electrons in nanoscale system

Relevant review articles

Review of Modern Physics, 82, 1633 (2010); Nature Commun. 105, 1109 (2010); Analen der Physik 523, (2011); Phys. Rev. Lett. 93 27203 (2004) and Phys. Rev. Lett. 96 037205 (2006) Computational Materials Science 55, 295 (2012)

The project develops novel techniques and paradigms concerning theoretical modelling of nano-scale advanced materials. An important aspect here is the ability to carry out this development all the way from idea and concept to working computer softwares. The project has made contributions to the application of a quantum mechanics - molecular dynamics response approach and made applications for calculations of large solvated systems (including more than 10,000 atoms) on their magnetic properties, EPR, NMR parameters, solvatochromism, and non-linear optical properties, like hyperpolarizability and two-photon absorption. In this methodology, the full quantum mechanical interactions are accounted for in the evaluation of a given property. Underlying structures and trajectories are obtained by molecular dynamics or Car-Parrinello methods. Results on protein environments have been obtained and a new technique for parameterization of the electrostatic and polarization interactions in such environments has been developed.

Summary of the modelling

The project did a study of V2O3 to validate a <u>DFT</u> model that was developed within MONAMI, and is a theoretical technique for calculating the effect of electron-electron correlations. The developed models are an elaboration of existing models to make the theory general to treat complex crystal structures like that of V2O3. To be specific, testing of models have been executed to see which one describes the measurements best: a so called N-th order Muffin-Tin Orbital (NMTO) software, with features like massive down folding, generation of Wannier combined, and <u>dynamical mean field theory</u> (DMFT) for the study of strongly correlated system, has been used to investigate the electronic structure of V2O3. Also, the development of a full-potential software with incorporation of DMFT has been completed. These theoretical analysis methods are geared towards calculations of spectral properties, which are important when analysing and interpreting the data now emerging from synchrotron radiation facilities and x-ray free electron lasers.

The development of an overlapping muffin-tin approximation (OMTA) transport code has involved replacing the condition of "tail cancellation" of muffin-tin orbitals (MTOs) with "kink cancellation" in an existing <u>tight-binding MTO (TB-MTO) model</u> so as to make maximum use of all of numerical features such as the extensive use of sparse matrix algorithms. The tail cancellation of orbitals goes long back to a paper by O.K.Andersen, in the 70'ies. It provided new physical insight in how electrons move around in solids, and how to best describe their quantum mechanical equation of motion. In the model developed in MONAMI, several conceptual steps and mathematical derivations have been made to come to a set of equations which enable a numerical implementation. The model now allows accurate and fast calculations of ground state properties of solids.

Non-newtonian dynamics was discovered to be necessary for nano-sized magnetic systems of particular symmetries. This was a discovery and/or a numerical result of a simulation tool which was developed under MONAMI, i.e. the UppASD stochastical simulation package for <u>spin-dynamics</u>. Simulations of nano-magnetism and the dynamical response of small magnetic clusters have been completed and revealed several unexpected phenomena.

http://www.iacs.res.in/monami/Home.html

Project Acronym and Number: MONAMI 233513 Project Title: Modeling of Nano-Scaled Advanced Materials Intelligently Start and End Dates: 01/07/2009 till 30/06/2012 EU Contribution: 930.000 € Coordinator: Olle Eriksson, Uppsala University, <u>olle.eriksson@physics.uu.se</u>



in MORDRED 261868

Subject of the modelling

Nanoelectronic devices, oxide interfaces

Models used

Electronic: <u>Density functional theory (DFT)</u>, electronic <u>drift diffusion (DD)</u> and non-equilibrium Green's function (NEGF) for electron transport Atomistic: <u>MD</u> using <u>force fields</u> for dynamic charge transfer, Mesoscopic: <u>Statistical models</u>: Monte Carlo (MC) Continuum: compact <u>models for electrical circuit</u> behaviour

Simulation software and type of numerics used

VASP (DFT), CP2k (DFT) GARAND (DD, NEGF, MC) Pysic (Molecular Dynamics) Mystic and RandomSPICE (for compact modeling) Numerics: genetic algorithms, Bayesian statistics

Achievements of the model beyond experiments

Predict defect character and density that causes device breakdown in realistic environments and over realistic performance times. Characterize this for a variety of new, industrially untested materials. Suggest routes for device design that should eliminate or reduce reliability problems

Application

Nanoelectronic devices, transistor and memory design, semiconductors.

Relevant review articles

Nature Insight: Silicon electronics and beyond, Nature 479, 309 (2011).

Building upon fundamental analysis of the structure and electronic properties of relevant materials and interfaces at the quantum mechanical level, we will construct mesoscopic models to account for defect generation and impact on Complimentary-Metal-Oxide-Semiconductor (CMOS) transistor and circuit performance and yield. The models will provide detailed understanding of the common reliability issues and degradation routes of next generation devices. Results will be supported by comprehensive experimental characterization techniques.

Summary of the modelling

The project is performing calculations and characterisation of oxide/semiconductor interfaces in stacks and films.

First principles (e.g. <u>DFT</u>) calculations are used for calculation of interface electronic structure and the impact of defects.

Semi-empirical <u>(classical) MD</u> codes are used for e.g. dynamic charge transfer atomistic simulations, for calculations of the structure of large models of the oxide interface. <u>Statistical charge transport models</u> are used to calculate statistical variability of electrical impact of defects and their behaviour as a function of applied bias and time. These are supported by NEGF and drift diffusion simulations directly modelling current within interfaces. The NEGF formalism provides a powerful conceptual and computational framework for treating quantum transport in nanodevices. It goes beyond the Landauer approach for ballistic, non-interacting electronics to include inelastic scattering and strong correlation effects at an atomistic level. <u>Electrical circuit compact models</u> are semi-physical/phenomenological models of an active circuit component designed to perform high level circuit simulation. There are several variations of the models generally with over 100 Parameters, often tied to a specific simulation methodology.

This results in a realistic description of interfaces in gate stacks, based on combinations of high-k oxides with III-V (GaAs, InGaAs, InP) and IV semiconductors (Si, SiGe, Ge, graphene) and gate metals (TiN, TaN, Ru).

Schottky barrier performance and defects in new gate stack materials are calculated with these models with the goal of improving the reliability of CMOS devices. The thermal stability of defects in different charge states, gap states, optical, electron spin resonance and vibrational properties are calculated. The empirical defect potentials have been optimised using the output of DFT calculations (energy levels, adiabatic potentials, metastable states, vibrational properties). The main defects are associated with oxygen deficiency, interdiffusion of cations, hydrogen and dopants.

The calculated properties of grain boundaries in polycrystalline films, which serve as sinks for vacancies and impurities are used to calculate stress-induced leakage current breakdown mechanisms. Also the dynamic behaviour of the defects and impurities creation and annealing has been studied, in particular the most common defects as oxygen vacancies in their various charge states, dangling bonds at the interface, hydrogen bridges, K centres, etc.

Models and corresponding drift diffusion (DD), monte carlo (MC) and non-equilibrium Green's function (NEGF) simulation tools have been developed that can describe the statistical impact of bias temperature instabilities and hot carriers on the electrical characteristics of CMOS transistors. The simulations are 'frozen' in time. At a particular stage of the degradation process the areal density of defect states and trapped charges is transformed in random defect states and trapped charge distribution that will be introduced in DD, MC and NEGF simulation tools in addition to the initial variability sources. Methods to capture the impact of local defect generation in the gate dielectric on the statistical variation of the gate leakage current have also been developed.

https://webhotel2.tut.fi/fys/mordred

Project Acronym and Number: MORDRED 261868 Project Title: Modelling of the reliability and degradation of next generation nanoelectronic devices Start and End Dates: 01/04/2011 till 31/03/2015 EU Contribution: 3.624.853 € Coordinator: Adam S. Foster, Tampere University of Technology, <u>adam.foster@tut.fi</u>



in MULTIHY 263335

Subject of the modelling

Microstructure and mechanical properties of materials under the effect of hydrogen embrittlement

Models used

Electronic: First-principles <u>DFT</u> calculations for calculations of the energetics of hydrogen in bulk phases and around point defects

<u>Semi empirical Tight Binding (TB)</u> and <u>Bond Order Potential (BOP)</u> models for hydrogen interactions with extended defects

Mesoscopic: kinetic Monte Carlo simulations for hydrogen diffusion as function of defect distribution finite element models of hydrogen diffusion at the continuum, specimen and component levels

Continuum: Fluid Dynamics models of hydrogen diffusion at the continuum

Simulation software and type of numerics used

DFT (self-developed codes employing mixed-basis pseudopotential approach, VASP) TB and BOP codes (self-developed), ElectricActiveMaterials-Potentials (LAMMPS) Kinetic Monte Carlo (self-developed codes) for diffusion Continuum mechanics (Abaqus, Comsol, Marc, self-developed codes) finite element for diffusion

Achievements of the model beyond experiments

Optimisation of the pulse-plating process used in the fabrication of the combustion chamber of the Ariane satellite delivery vehicle in a fast and efficient way.

Mechanistic understanding of the susceptibility of advanced high strength steels to HE by absorbed H that could not be provided by experiments alone.

Prediction of the influence of H on the fatigue lifetime of wind turbine bearings enabling the choice of materials.

Application

Materials for manufacturing, wind turbine, automobile industry, plates for rocket combustion chambers

Relevant review articles

S.M. Myers, M.I. Baskes, H.K. Birnbaum, J.W. Corbett, G.G. DeLeo, S.K. Estreicher, E.E. Haller, P. Jena, N.M. Johnson, R. Kirchheim, S.J. Pearton, M.J. Stavola, *Rev. Mod. Phys.*, 64 (1992) pp559-617

A. Pundt, R. Kirchheim, Annu. Rev. Mater. Res., 36 (2006) pp555-608

I.M. Robertson, H.K. Birnbaum, P. Sofronis, in *Dislocation in Solids*, J.P. Hirth, L. Kubin (Eds.), Vol. 15 (2009) ch91

Summary of project

The aim of the project is to develop a modelling framework to predict the susceptibility of materials and components to hydrogen embrittlement (HE) under conditions representative of those actually occurring in the aerospace, automobile and wind energy industries. To achieve this, the description of H transport in modern advanced materials with complex microstructures is created, through a multiscale modelling framework.

Summary of the modelling

The key aspect of this project is the incorporation of atomistically-derived diffusion barriers for critical H trapping sites into continuum and component level models, and their application to real industrial problems involving HE.

The project is applying density functional theory (DFT) to the evaluation of energy barriers and binding energies of H in normal interstitial sites and around point defects, based on quantum-mechanical effects. <u>Semi-empirical tight-binding models</u> and classical potentials for the evaluation of H trapping at extended crystal defects such as grain boundaries and dislocations are employed.

The results will be used in mesoscopic kinetic Monte Carlo (KMC) simulations to evaluate the effective H diffusivities under different strain conditions and trap densities. The ultimate aim of the atomistic-KMC calculations is to develop a database of H diffusivities as a function of defect distribution, stress/strain and temperature. This database would serve as the input for continuum diffusion equation (solved by FE) of H diffusion that could be applied to full components. The models will be applied at the continuum, specimen and component scales using boundary conditions furnished by data collected in-service and from experimental measurements.

The continuum models will be based on novel set of constitutive equations for H diffusion capable of exploiting the information being derived from the atomistic calculations. The equations are more generalised than those commonly used in the literature, enabling the description of hydrogen diffusion under a broader range of conditions (e.g. temperature variations, trap occupancies) as before. The equations are being implemented on a number of platforms, including as bespoke codes and as subroutines in commercial fluid dynamics packages, e.g. ABAQUS. Possibilities for the licensing or commercialisation of these codes will be evaluated during the course of the project.

The modelling will be validated at all levels using advanced experimental techniques (in situ hydrogen permeation tests, thermal desorption spectroscopy, fractography).

The effectiveness of the proposed simulation framework will be demonstrated by investigating the role of microstructure in three contrasting industrial problems, which have been specified by companies involved in the development and application of advanced materials.

www.multihy.eu

Project Acronym and Number: MULTIHY 263335 Project Title: Multiscale Modelling of Hydrogen Embrittlement Start and End Dates: 01/05/2011 till 30/04/2015 EU Contribution: 3.390.722 € Coordinator: Nicholas Winzer, FhG, DE; <u>nicholas.winzer@iwm.fraunhofer.de</u>



in MUST 214261

Subject of the modelling

Inhibitor release, self-healing mechanisms and nanocontainers, formation of containers with membrane emulsification, multifunctional coatings

Models used

Atomistic: <u>QM/MM</u>

Mesoscopic: <u>Dissipative Particle Dynamics (DPD)</u> lattice gas model of the inhibitor/healing agent

release under mechanical impact.

Continuum: Multi-phase <u>diffusion equations</u> for water, ions, corrosion products and inhibitor particles in a multilayer anticorrosive film

Simulation software and type of numerics used

Software for MD calculations, force field Amber 99 – Hyperchem v.8.0, Crystal Maker Gaussian 03 for QM/MM Monte Carlo simulations – lattice gas algorithm for statistical mechanics Finite Elements and Finite Differences simulation of diffusion Mathcad 14.0

Achievements of the model beyond experiments

The model can be used do give recommendation concerning optimal composition and structure of the coating to delay corrosion of metallic and polymeric substrates and structures, thus reducing development costs.

The model predicts service-life time via the probability of the scratch healing or inhibition based on the physico-chemical properties of the materials and realistic scratch geometries and thus enables an optimal material choice without having to do extensive service-life tests.

Application

Coating and surface treatment of metallic and polymeric substrates and structures

Relevant review articles

Z. Tabor, et.al. .Water Diffusion In Polymer Coatings Containing Water-Trapping Particles,
Part 1. Finite Difference - Based Simulations, Progress in Organic Coatings. 75 (2012) 200– 206.
Małgorzata Krzak et. al. . Water diffusion in the polymer coatings containing water-trapping particles, Part 2. Experimental verification of the mathematical model, Progress in Organic Coatings, 75 (2012) 207–214.

N. Filipovic A. Jovanovic et. al. . Modelling of self-healing materials using discrete and continuum methods, Surface Coatings Int., 95 2012 74-79.

The project MUST developed new active multi-level protective self-healing coatings and adhesives for future vehicle materials that improve the long-term performance of metallic and polymeric substrates and structures. These materials are based on "smart" release nanocontainers incorporated into the polymer matrix of current commercial products.

A nanocontainer (or nanoreservoir) is a nanosized volume filled with an active substance confined in a porous core and/or a shell which prevents direct contact of the active agent with the adjacent environment. The purpose of nanocontainers is to release the inhibitor before corrosion has happened (e.g. in case of presence of aggressive environment) or just after the corrosion has started. The role of traps is to delay corrosion agents reaching the protected surface.

Summary of the modelling

Two basic mechanisms of corrosion have been modelled. First, the diffusion of corrosive species (e.g. water, chloride ions) through the intact coatings containing traps and inhibitor nanoreservoirs has been modelled atcontinuum level by <u>diffusion equations</u>. Second, the release of inhibitor/healing agent from the microcontainers and its propagation upon the mechanical impact during formation of mechanical defects is modelled at mesoscopic with the analytical geometry representation and the <u>DPD lattice gas model</u>.

Constitutive equations for the active feedback and self-healing processes have been based on the experimental results obtained on nanoreservoirs and the nanocontainer-containing coatings providing the conditions of effective self-healing (self-healing rate higher than corrosion rate). This has been used to develop new nanocontainers. The constitutive equations can be used to determine the probability of successful healing, i.e. for evaluation of technical risks of application of multilevel protective coating.

Numerical approach for simulation of the layer-by-layer encapsulation process has been developed using combination of QM and MD calculations (<u>QM/MM</u>). Surfactants and polyelectrolytes in solution, their interactions, adsorption at interface and formation of the polyelectrolyte membrane has been simulated according to the following steps:

- Quantum molecular computations for single surfactant molecules and polyelectrolyte monomers for determination of partial atomic charges and electric dipoles.

Molecular dynamics simulations of polyelectrolyte chains to determine their average conformations, chain stiffness and degree of counterion condensation using AMBER99 force field with corrected van Waals interaction parameters for polyelectrolites in the aqueous medium.
Molecular dynamics simulation of formation of surfactant-polyelectrolyte complexes and adsorption of single polyelectrolyte chains.

- Molecular dynamics simulation of formation of polyelectrolyte multilayer.

The mean porosity of the polyelectrolyte multilayer membrane was determined taking into account the sum of the solvent accessible volumes of polyelectrolyte chains.

A phenomenological constitutive equation of formation of liquid emulsion cores by membrane emulsification has been developed. It is based on the balance of hydrodynamic, capillary and buoyancy forces, taking into account the hydrodynamic instability at the formation of droplet at the mouth of the membrane pore. Key parameters for the constitutive equation have been identified, estimated and verified by measuring the interfacial tension in the system pertinent for emulsification.

Modelling of the release of corrosion inhibitor based on the solution of the multiphase diffusion equation (in spherical geometry) was developed and applied to the release of 2-mercaptobenzothiazole from the emulsion based nanocapsules.

www.must-eu.com

Project Acronym and Number: MUST 214261 Project Title: Multi-level protection of materials for vehicles by "smart" nanocontainers Start and End Dates: 01/06/2008 till 31/05/2012 EU Contribution: 7.143.481 € Coordinator: Theo Hack EADS DEUTSCHLAND GMBH <u>theo.hack@eads.net</u>



in NAMASTE 214499

Subject of the modelling

Magnetic and magnetotransport properties of magnetic materials (diluted magnetic semiconductors and transition metal ferromagnets) manipulated by electric fields and strain.

Models used

Electronic: Ab-initio <u>density functional theory</u> band structure calculations, damping based on the band structures from the <u>ab-initio</u>, tight-binding, and <u>k•p kinetic-exchange effective</u> <u>Hamiltonian models</u> for Band structure calculations in ferromagnetic metal nanostructures Atomistic: Statistical mechanics model for <u>magneto-transport</u> in nano-devices Mesoscopic: <u>Micromagnetic Landau-Lifshitz models</u> for magnetisation and magneto-crystalline anisotropies

Continuum: micromechanics elastic theory

Simulation software and type of numerics used

Revised k-space integration schemes

Landauer-Buttiker approach for the strongly SO-coupled transition metal systems and for the diluted magnetic semiconductors.

Prague Library of codes suitable for solving these numerical problems

Achievements of the model beyond experiments

Reproduction of the valence band nature of Fermi level states the archetypical ferromagnetic semiconductor (Ga,Mn)As.

Prediction and explanation of the observed magnetic and magneto-transport properties in ferromagnetic semiconductors

Understanding of the observed spin-torque effects which lead to the discovery of new ferromagnetic resonance (FMR) effects.

Based on the developed capabilities to model spin-orbit in metals, it was shown that appropriate antiferromagnetic materials could be employed as active layers in spintronic devices (GMR, etc), thus opening up the possibility of the new field of antiferromagnetic spintronics.

Application

Spintronic and magneto-electronic devices using control and manipulation of the nanoscale magnetic properties through the application of local strain or electric fields. Antiferromagnetic materials for spintronics

Single ElectronTransistors and Fast Precessional Switching Devices

Relevant review articles

"Spin-orbit coupling induced anisotropy effects in bimetallic antiferromagnets: A route towards antiferromagnetic spintronics", Shick A. B et al., PhysRevB. 81 212409 (2010) "Magnetocrystalline anisotropies in (Ga,Mn)As: Systematic theoretical study and comparison with

experiment", Phys Rev. B 80, 155203 (2009) "Semiclassical framework for the calculation of transport anisotropies", K. Výborný et al, Phys. Rev. B, 79, 045427 (2009)

The NAMASTE project aimed to control and manipulate the nanoscale properties of magnetic materials which have strong spin-orbit coupling by local strain and electric fields. This should make possible new types of magneto-electronic and spintronic devices. The project explored two parallel complementary strands based on ferromagnetic semiconductors and ferromagnetic metal materials.

Summary of the modelling

The project made detailed microscopic theoretical descriptions of the interrelated structural, magnetic, and electrical properties and their dependencies on a large number of degrees of freedom ranging from the choice of semiconductor host and doping densities to the geometry and arrangement of the nanostructures and spintronic nanodevices.

The spin-orbit band structure was calculated by electronic models

- a) <u>ab-initio density functional theory</u>
- b) <u>multi-orbital tight-binding theory</u>
- c) <u>k•p kinetic-exchange effective Hamiltonian models</u>

Spin-orbit (SO) interaction is at the heart of the materials physics involved and the majority of physical quantities relevant to the experimental work can be derived directly from the SO-coupled band structure of the considered systems. The relevant microscopic micromagnetic parameters include the magnetisation, relativistic magneto-crystalline anisotropy constants, Gilbert damping coefficient, and extraordinary MR coefficients. These have been calculated for metals (ferromagnetic and antiferromagnetic metal alloys), diluted magnetic semiconductors and metal/semiconductor hybrid structures.

Magneto-crystalline anisotropies, e.g., reflect the dependence of the system total energy on magnetization orientation and are sensitive to changes in electron concentration (charge accumulation/depletion in conventional field effect transistor structures) or lattice strains (electrical voltage on piezoelectric transducers). Magneto-crystalline anisotropy then represents the key microscopic input parameter for the micromagnetic Landau-Lifshitz simulations to be employed to describe the magnetization dynamics experiments explored within the project.

Another quantity that can be directly derived from the SO-coupled band structure is the dependence of the position of the chemical potential, at a fixed electron density, on the orientation of the magnetization. The chemical potential anisotropy influences the magnetization reorientation induced Coulomb blockade oscillations, a property exploited in a ferromagnetic Single Electron Transistor and modelled with micromagnetism.

Statistical mechanics based atomistic transport anisotropies in tunnelling or ohmic regime employed the Boltzmann or Kubo <u>transport theories</u> for uniform systems, whereas Landauer-Buttiker and Green's function formalisms were employed for spatially non-uniform nanogeometries and non-equilibrium conditions.

Finally, the magnetic and magneto-transport properties of ferromagnetic semiconductors nanostructures were successfully modelled by combining continuum<u>micromechanics elastic</u> theory and the microscopic relativistic band structure modelling.

http://namaste-project.net/

Project Acronym and Number: NAMASTE 214499 Project Title: Nanostructured Magnetic Materials for nano-spintronics Start and End Dates: 1/9/2008 till 31/8/2011 EU Contribution: 2.299.963 € Coordinator: Bryan Gallagher, University of Nottingham, UK, <u>bryan.gallagher@nottingham.ac.uk</u>



in NANOINTERFACE 214371

Subject of the modelling

Metal-oxide-polymer adhesion and interface fracture

Models used

Electronic: <u>many-body models for (band) structure</u> based on <u>interatomic potentials</u> Atomistic: <u>classical molecular dynamics</u> Mesoscopic simulations; statistical mechanics particle-based models (<u>coarse-grained molecular</u> <u>dynamics</u> and <u>DPD</u>) for cross-linked epoxy structure Continuum: <u>mechanical models</u> to describe delamination behaviour

Simulation software and type of numerics used

Electronic models for (band) structure /interatomic potentials: Forcite (universal and COMPASS forcefields) and Gulp (EAM) modules within Materials Studio (Accelrys), as well as LAMMPS (open source code)

Cross-linking algorithms for epoxy moulding

Materials Studio incorporating Mesocite and COMPASS & EAM for atomistic modelling Implicit finite local arc-length methodes element for delamination

Achievements of the model beyond experiments

A set of design and reliability guidelines for microelectronic packages with respect to delamination risk has been elaborated, which can only be generated in a systematic way by accurate models.

A better, quantitative understanding of adhesion mechanisms at the very small to macroscopic scale and of the effect of surface roughening on adhesion properties has been provided. This was only possible via mesoscope semi-analytical and numerical fracture mechanics models.

Application

Prevention of delamination phenomena in microelectronic packages

Relevant review articles

Chen J, Bull SJ (2011) Approaches to investigate delamination and interfacial toughness in coated systems: an overview. J.Phys.D: Appl. Phys. 44: 034001.

DeVries KL, Adams DO (2002) Mechanical testing of adhesive joints. In D.A. Dillard, A.V. Pocius (Eds.) The Mechanics of Adhesion, Elsevier.

Hutchinson J, Suo Z (1992) Mixed mode cracking in layered materials. Advances in Applied Mechanics 29: 63–191.

Litteken CS, Dauskardt RH (2003) Adhesion of polymer thin-films and patterned lines. International Journal of Fracture 119/120: 475-485

In the NanoInterface project a multi-scale modeling approach (electronic, atomic, mesoscopic, continuum scale) has been applied to describe the failure behaviour of metal-oxide-polymer materials systems. In addition, micro- and nano-scale characterization techniques have been developed and applied. The project focused on the simple and complex carrier systems, defined and processed by industrial partners.

Summary of the modelling

Large scale molecular statics and dynamics simulations were conducted on Cu-Cu tilt grain boundary interface, results of which are used as input to develop interfacial constitutive laws at larger scale. We have used <u>Coarse</u> <u>Graining Molecular Dynamics</u> (CGMD) and <u>Discrete Particle Dynamics</u> (DPD). The interaction parameters are here obtained from molecular simulations. Both of the methods have been used in the project to generate a cross-linked epoxy structure. Such models are paramount in developing predictive capabilities related to reliability and failure of microelectronic components. Molecular simulations were conducted on two Cu-Cu tilt grain boundary structures using ElectricActiveMaterial potential and open source LAMMPS MD simulation code. After obtaining relaxed equilibrium structure (using the coincident-site lattice theory to get the GB interface and conjugate gradient algorithm for energy minimization), it is subjected to Nose-Hoover NPT <u>molecular dynamics</u> with modified Hoover equation of motion under constant strain rate loading. An intergranular crack is introduced and local traction and crack opening displacement data is extracted from the simulation results. To bridge length scales between atomistics and continuum, the data obtained from MD simulations is re-casted within the framework of continuum cohesive zone model (CZM) to quantify the cohesive zone law. Atomistic simulations on the epoxy resin were conducted to compute its material properties, and interfacial interaction energy on its interfaces with copper and cuprous oxide.

To take into account the influence of roughness on adhesion properties, semi-analytical <u>micromechanics</u> <u>models</u> solved by FE at the micro-scale on Cu/Polymer interface are also developed to establish cohesive/adhesive interfacial delamination criteria under external loading.

A crosslinking procedure consisting of cyclic molecular dynamics simulation/energy minimization and covalent bond creation between reactive sites based on close contact calculation is developed to simulate polymer network formation of the epoxy resin. The cross-linked structure was then fully relaxed to achieve geometry optimization and equilibrated to get rid of artifacts introduced during crosslinking simulation. Subsequent molecular dynamics/molecular statics simulation predicts well material properties, including densities, glass transition temperature, volumetric coefficient of thermal expansion and isotropic mechanical properties, indicating the validity of the adopted polymer network formation methodology. Using the same crosslinking approach, <u>constitutive equations</u> for interfaces between a 2D polymer network and copper as well as cuprous oxide were constructed and subjected to energy minimization. Using energy minimization calculations based on force fields, the interfacial interaction energy for both systems was extracted by the energy difference between the total energy of the entire interface system and the sum of energies of individual components. The system was also subjected to external tensile loading and results related to the interfacial debonding strength are also reported. Interfacial excess energy computation methodology and results for Cu-Cu and Cu-Cu2O interfaces are also presented. Appropriate interatomic potential (IP) formalism is very important to conduct any molecular simulations, as it should be able to capture the correct physics at those loading and environmental conditions. The project also details the IP development framework and results for copper oxide system which is of paramount importance in addressing the failure behavior of the copper/polymer interface which encompasses a thin layer of copper oxide (both, CuO and Cu2O) and invariably influences its failure characteristics. The micromechanical delamination model at macroscopic level used to predict delamination in a microelectronic device is called the cohesive zone model. This is a model that describes the degradation process between 'crack surfaces' from initially closed to entirely open (i.e., a true crack). The input is interface strength and interface toughness (collected in a so-called traction-separation law, the constitutive equation for this model). The output is a transient crack path.

www.nanointerface.eu

Project Acronym and Number: NanoInterface 214371 Project Title: Knowledge-based multi-scale modelling of metal-oxide-polymer interface behaviour for microand nano electronics Start and End Dates: 01/09/2009 till 31/08/2011 EU Contribution : 3.300.000 € Coordinator: Dr. Olaf van der Sluis, Philips Applied Technologies, <u>olaf.van.der.sluis@philips.com</u>



in NANOMAGMA 214107

Subject of the modelling

Magneto-plasmonic nanostructures

Models used

Continuum: <u>Maxwell equations</u> in dipole approximation (coupled)

Simulation software and type of numerics used

Generalized Scattering Matrix Methods to solve Maxwell's equations in presence of magnetooptical effects. In various situations it involves a nonlinear eigenvalue problem that, in this case, has been solved by a linearization procedure. The linearization involves an increase in the dimension of the problem. A direct solution would be convenient.

Finite Difference Time Domain solvers, it would be desirable to extend this technology to cope with non-diagonal dielectric tensors for dispersive materials.

Achievements of the model beyond experiments

The model predicted that the optical and magneto-optical response of complex structures where metals and magneto-optical materials are simultaneously present is proportional to the electromagnetic field in the magnetic material. This guided the design and now the whole structure is grown to try to maximize the field in that material.

Application

Non reciprocal devices (Information Technologies devices), Magneto-optical Surface Plasmon Resonance Sensors.

The goal of this project was the study development and application of a novel concept of nanostructured materials formed by the combination of components with plasmonic and magneto-optic (MO) activity, in order to produce "magneto-plasmonic" nanomaterials tailored on the nanoscale. Both bottom-up and top-down approaches were applied to obtain the desired magneto-plasmonic materials. The goal was to develop films, nanoparticles and coreshell structures. Also proof of concept for applications based on magneto-plasmonic activity is provided including identification of applications for microelectronics and information technology. Testing for specific applications in the field of chemical sensors and biosensors has taken place.

Summary of the modelling

The project modelled the optical response of MO-plasmonic nanostructures using two different approaches: analytical modelling (including the use of approximate methods) and quantitative numerical simulation. Both approaches are complementary and necessary in order to reach the main objectives.

Using the procedure described above the project explored the mechanisms that would allow: i) Investigate the correlation between the optical, magnetic, magneto-optical and magnetoplasmonic properties.

- ii) Controlling the plasmon (either surface or localized) using an external magnetic field.
- iii) Analyzing the interplay between plasmon excitation and MO response.
- iv) Amplifying the MO response from local field enhancements

The project performed <u>electromagnetic</u> studies:

• Numerical calculation of the MO response of continuous trilayered structures solving the Maxwell equations using transfer and scattering matrix techniques (layer thickness optimization for maximum sensor signal in Au/Fe/Au structures).

• Analysis of magneto-plasmonic periodic arrays of small particles coupled to a multilayer structure described by the Maxwell equations in the dipole approximation.

• Analysis of the MO properties of a random dispersion of magnetic nanoparticles (using the coupled dipole method).

• Comparison between SNOM measurements and calculations of near-field signals on magnetoplasmonic structures.

• Numerical study of field enhancements on magneto-plasmonic structures for molecular sensing.

• Quantitative study of single-molecule fluorescence control by magneto-plasmonic structured substrates or nanoparticles.

http://www.phantomsnet.net/Nanomagma/indexMagma.php?project=5&f=1

Project Acronym and Number: NANOMAGMA 214107 Project Title: NANOstructured active MAGneto-plasmonic MAterials Start and End Dates: 01/11/2008 till 31/10/2011 EU Contribution: 2.963.156 € Coordinator: Antonio Garcia-Martin, Instituto de Microelectronica de Madrid, Consejo Superior de Investigaciones Cientificas, Madrid, ES, e-mail: <u>a.garcia.martin@csic.es</u>



in NANOMODEL 211778

Subject of the modelling

Mechanical, thermochemical and viscous flow behaviour of nano-filled polymeric materials

Models used

Atomistic: <u>Coarse grained MD</u> (CG-MD) for nanostructure and nanomechanics Mesoscopic: <u>statistical mechanics Monte Carlo</u> model (Fti-MC) for nanostructures <u>Dissipative Particle Dynamics</u> (DPD) for nanostructures

Continuum: <u>Micromechanics model</u> and <u>viscous flow models</u> for behaviour of nano-filled polymeric materials

Simulation software and type of numerics used

FEM for micromechanics Coupling schemes between Molecular Dynamics and Continuum Mechanics, based on modified Arlequin algorithm Integrated software product Culgi to model and visualize nanocomposites

Achievements of the model beyond experiments

The role of the interphase (structure and dynamics) is difficult to investigate experimentally. Only modelling can give access to the very structure of matrix, nanoparticles and their interphases. Modelling revealed details how the interface is influenced by the chemistry. In particular, the glass transition temperature (Tg) was reported in the literature to depend strongly on the nature of the fillers. This effect was not found (experimentally) in our systems where Tg was not much affected (within the error bars). The reason for this could be rationalized computing the structure and dynamics of the grafted silica particles by means of MD (atomistic, CG, DPD) which showed there is now pronounced interface, at least not an overlap of the interfacial area. From the modelling it was argued that in order to incease Tg (or lower Tg), the mobility of polymer units has to be modifed. We saw this is the case close (very close!) to the surface of the NP, but this effect was not long range. However, with only 1-2 wt% NP in the polymer, there is no macroscopic effect,

Application

Reinforcement of polymeric material Surface modifiers ensuring stable particle dispersion under melt mixing conditions

Relevant review articles

Attinger, S., Koumoutsakos, P. (Eds.), Multiscale Modelling and Simulation, Lecture Notes in Computational Science and Engineering Vol. 39 (Springer, Heidelberg, 2004)

The project targets the reinforcement of polymers via the decrease of viscosity through a mixture of nanoparticles. The project has studied the detailed structure of matrix, nanoparticles and interface region. By detailed comparisons of computed structures and experimental ones, new composites were explored.

Summary of the modelling

The project used coupled <u>continuum fluid</u> and <u>micro-mechanics</u> (CM) models and particle based Molecular Dynamics (MD) methods.

The CM and MD part have been adapted as follows: in the MD part, the necessary number of degrees of freedom has been reduced by <u>coarse graining</u>, i.e. groups of atoms are considered as single super atoms. Furthermore, the periodic boundary conditions (PBC), which avoid surface effects in the MD simulation box, have been replaced by stochastic boundary conditions (SBC), combined with a DPD thermostat. Using a certain probability function in the boundary domain, a part of the super atoms in that region is tethered via a harmonic interaction potential to so-called anchor points. These additional artificial particles transfer information (forces and positions) from the MD region to the FE domain and vice versa. The main advantage of this approach is the spatial fixing of the anchor points during the MD run, thus there is no dynamic coupling to FE required. The rigid frame of anchor points enclosing the MD domain is coupled to the FE domain by using the Arlequin method which is based on an energy blending of the different domains.

A coupling algorithm between MD (Molecular Dynamics) and CM allows for the computation of forces externally exerted on a nanocomposite. The multiscale approach to study the structure and dynamics of e.g. silica-polystyrene nanocomposite systems consisted of four levels of description: an atomistic one, several coarse grained ones where each "superatom" or bead represents e.g. a monomeric unit or a meso or racemo diad of styrene monomers, parametrized using Iterative Boltzmann Inversion (Coarse Grained Monte Carlo (CG-MC)), or DPD, and a third one describing the system at a length scale comparable to that of the Kuhn length, by exploiting the polymer mean field approximation (Field Theory - inspired Monte Carlo, FT-i MC), and a micromechanical approach based on mesoscale morphologies. The first two levels of modelling are closely connected, via forward and reverse mapping schemes. Initial configurations have been subjected to CG-MC simulations, where polymeric chains were e.g. treated as chains of diads and nanoparticles as solid spherical Hamaker interaction sites. Based on atomistic molecular dynamics trajectories of the equilibrated structures, local packing and dynamics were addressed by calculating pair distribution functions, bond orientational autocorrelation functions and H-NMR spectra. The third level of modeling at mesoscale (FT-i MC) has enabled simulations of micrometer-sized domains of the nanocomposite system, wherein the nanofillers are represented as solid spheres (interacting via Hamaker integrated potentials) and the polymer chains as freely jointed sequences of Kuhn segments.

The protocols developed for the model Polystyrene systems were applied to other systems identified by the consortium as interesting for applications, such as PMMA, Nylon 66, and PBT SiO2 based nanocomposites. A pseudo core-shell model to account for interface phenomena in the multiscale procedure was developed and tested on unmodified spherical and cylindrical nanoparticles based nanocomposites.

https://nanomodel.eu/

Project Acronym and Number: NANOMODEL 211778 Project Title: Multi-Scale Modeling of Nano-Structured Polymeric Materials: From Chemistry to Materials Performance Start and End Dates: 01/11/2008 till 30/11/ 2011 EU Contribution: 3.481.149 € Coordinator: Horst Weiss, BASF SE, <u>Horst.weiss@basf.com</u>



in NANOPIGMY 280393

Subject of the modelling

Adsorption behavior of different molecules in porous solid multifunctional ceramic pigments

Models used

Atomistic: Monte Carlo simulations for molecular adsorption

Simulation software and type of numerics used

Materials Studio 5.0 (molecular modeling software form Accelrys): Sorption module (specific to study adsorption of molecules in solids through Monte Carlo Methods)

Achievements of the model beyond experiments

The use of Monte Carlo simulations can help to select the more suitable conditions for adsorption (pressure and temperature) and to perform successful experiments at the laboratory. It is also helpful to select the kind of molecules that can be adsorbed (type of functional groups and sizes of the molecules) and preferred adsorption sites.

Application

Pigment applications in automotive and construction

Relevant review articles

EJ Maginn et al. J. Phys. Chem., 99 (7), pp 2057–2079 (1995)
J. Phys. Chem , 100, 17573-17581 (1996)
H-J Son et al. Chinese Journal of Chemical Engineering, 16(1) 108–111 (2008)
I Daems et al, J. Phys. Chem. C, 111, 2191-2197 (2007)

NANOPIGMY project seeks to produce cost-efficient multi-functional ceramic pigments to give to the automobile and construction materials (plastic, paint and concrete) additional functionalities apart from colour (such as antibacterial, anti-corrosion, self-cleaning, selfhealing, energy efficiency). The aim is to avoid changes in manufacturing processes.

Summary of the modelling

In order to help in the design and development of the multi-functional pigments, computer modeling tools are used. Adsorption sites of Phase Change Materials (PCMs) molecules inside the pigment will be analysed using <u>Monte Carlo molecular simulations</u> of molecular adsorption at different pressures and temperatures. The interactions between nanoparticles/pigment surfaces will be analysed by studying the interaction energies between inorganic coatings and Phase Change Materials (PCMs) as well as pigment PCMs interaction energies.

http://www.nanopigmy.eu/

Project Acronym and Number: NANOPIGMY 280393 Project Title: More than color: Applying nanotechnologies for the multifunctional ceramic pigments development Start and End Dates: 01/03/2012 till 01/03/2015 EU Contribution: 3,299,596 € Coordinator: Pedro Villasante, Nubiola, Spain, <u>p.villasante@nubiola.com</u>



in NANOPYME 310516

Subject of the modelling

Magnetic properties of thin polycrystalline magnetic films Magnetic properties of bulk nanocomposite materials consisting of several magnetic phases Characteristics of permanent magnets made of magnetic nanocomposites

Models used

Electronic model: <u>DFT</u> calculations for thin film systems (single layers and bilayers) Mesoscopic: <u>micromagnetic</u> models applied to thin films and nanocomposite magnets Continuum: <u>modelling of magnetic performance of macroscopic magnetic components</u>

Simulation software and type of numerics used

Electronic: SIESTA and Quantum ESPRESSO fro DFT calculations Mesoscopic: OOMMF and MicroMagus Continuum: Infolytica

Achievements of the model beyond experiments

Electronic properties (critical temperatures and magnetic anisotropy) calculated by DFT will allow exploration of the influence of the electronic correlations at the interface in hybrid metal/oxide-based magnetic bilayers in a nanocomposite system. The model will allowa systematic investigation on the exchange coupling phenomena between metal and oxidebased magnetic phases based on large scale density functional theory calculations and provide information that experiments can not give.

Application

permanent magnets which do not contain rare-earth elements.

Relevant review articles

D. Goll, Micromagnetism-Microstructure Relations and the Hysteresis Loop.

Summary of project

The NANOPYME project addresses the design and development of permanent magnets without rare-earths but instead with hybrid nanostructures of metals and metal ferrite oxides. The metallic nanostructures offer high magnetization values while the ferrite oxide ones provide high anisotropy. NANOPYME intends to design and process novel permanent magnets based on traditional hard ferrites and additional new magnetic phases combined with a soft magnetic phase to achieve high magnetic performance through effective exchange-coupling of both magnetic phases

Summary of the modelling

In the NANOPYME project, numerical simulations performed on the electronic scale (density functional theory (<u>DFT</u>)), on the mesocale (<u>micromagnetic simulations</u>) and on the macroscale (<u>modeling of magnetic performance for magnetic components</u>) will be carried out.

Input to the DFT calculations will be the experimental crystal structure coordinates, while the output will be the electronic properties: critical temperatures (Curie temperature for magnetic systems and Verwey temperature for Co-ferrites systems) and magnetic anisotropy. In order to understand the coupling phenomena between different magnetic phases at their interface, DFT calculations will be done to gain a fundamental insight into these phenomena at the atomistic level.

Next, micromagnetic modeling of thin films, bilayers and two-phase nanocomposites (composed by magnetically soft/hard grains coupled through the grain boundaries) will allow to evaluate which magnetisation processes take place in these systems and which structural and magnetic parameters (characteristics) determine the hysteretic behaviour of such materials. In addition, we shall study how the exchange coupling through the interphase boundary affects magnetisation processes. This information is expected to be crucial for optimizing the preparation of two-phase nanocomposite magnets.

At the final stage, <u>device models</u> solved by finite element techniques for e.g. electric motors will allow us to predict magnetic performance of NANOPYME magnets in operation conditions. Particularly important will be predicting any possible performance decay of these magnetic components due to temperature and demagnetisation effects under operation conditions.

www.nanopyme-project.eu

Project Acronym and Number: NANOPYME 310516 Project Title: Nanocrystalline Permanent Magnets Based on Hybrid Metal-Ferrites Start and End Dates: 01/12/2012 till 30/11/2015 EU Contribution: 3.479.493 € Coordinator: Dr. Alberto Bollero, IMDEA Nanociencia, <u>alberto.bollero@imdea.org</u>



in NEXT-GEN-CAT 280890

Subject of the modelling

Catalysts consisting of transition element metal nano-particles without Platinum Group Metals (PGM)

Models used

Electronic modelling: <u>ab initio quantum mechanical model</u> and <u>DFT</u> for surface energies and activation energies of the catalytic nanoparticles Continuum modelling: models for the species concentration in the gas and <u>the kinetics of the reactions</u> and a <u>process model</u>

Simulation software and type of numerics used

Home made codes (on Matlab etc) and a process simulator like ASPEN and CFD simulator will be used. Additionally commercial/open source codes include Cantera, CHEMKIN, DETCHEM, Comsol

Commercial and/or academic programs Gaussian 03/ Vasp/ Quantum Expresso/ ADF

Achievements of the model beyond experiments

Improved understanding of catalytic reactivity on non-PGM catalysts

Application

Nanoparticles of transition elements based catalysts for automotive sector

Relevant review articles

L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, A critical evaluation of Navier– Stokes, boundary-layer, and plug-flow models of the flow and chemistry in a catalytic-combustion monolith, Catalysis Today 59 (2000) 47-60.

Paolo Giannozzi, et al. "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials" J. Phys. Cond.

Matter, 21 (2009) 395502.

H. Santos and M. Costa "Modelling transport phenomena and chemical reactions in automotive three-way catalytic converters" Chemical Engineering Journal 148 (2009) 173–183.

The main objective of NEXTGENCAT proposal is the development of novel eco-friendly nanostructured automotive catalysts utilizing transition metal nano-particles (Cu, Ni, Co Zn, Fe etc) that can partially or completely replace the PGMs.

Summary of the modelling

The project addressed physicochemical phenomena concerning nanostructured catalysts. The project will apply existing models and the aim of the modelling activities within the NEXT-GEN-CAT is to check initially the validity of the current available models and /or to adjust their parameters in order to comply with the experimental data obtained either by the literature or by experiments performed by the consortium. After the validation of the models certain runs will be performed in order to predict the behaviour of a catalytic system without the need to perform the experiments. Therefore, only selected catalyst will be evaluated using real feed conditions. The results of the nano-scale modelling will be used later for the process engineering and the optimization of the catalytic performance.

Materials at nanoscale

The surface of the catalysts will be calculated at the atomic level in order to understand the interaction between the gas phase molecule and the catalyst. The stability of all exposed surfaces will be computed from <u>first principles calculations</u>. It will be possible to modify the composition of the surface to determine the most promising catalysts. These studies will the focus on the active phase composed of catalysts. The computed surface energies will be used to build the most probable shape of the nanoparticles. The chemical properties of the surfaces will be computed using the <u>quantum formalism</u> (Schrödinger Equation). Due to the size of the system model, <u>DFT approach</u> (Kohn- Sham equation) will also be applied.

In a second step, the <u>reaction mechanism</u> will be calculated as well as the activation energies that can be used latter in kinetic models for the process simulation of the catalysis.

The equilibrium shape of crystals can be predicted from the Wulff construction, which in turn is obtained from the surface energies of the most stable surfaces of the material.

Process Simulation

The models to be applied will simulate the performance of the catalytic converters and predict the concentration distribution of the chemical species in the gas and the temperature profile inside the converter as well as the velocity profile. More specific the models will enable the:

- simulation of the species concentration in the gas (near and far from the catalytic surface, along the flow direction), on the surface, and the corresponding temperature, pressure and velocity variation along the converter.

- tuning of a kinetic submodel, including detailed surface chemistry and possibly gas-phase reactions, able to make simulation consistent with experimental data. Initial kinetic parameter will hopefully be provided within the project dedicated to more fundamental approaches (nanoscale modelling).

The equations governing the simulation are the kinetic equations, and the equations produced from the mass balances of the chemical species, the heat balance and the momentum balance, will be applied. Furthermore, material, energy and momentum balances, in differential form and at any direction where gradients are expected (along and across the flow) will be considered using ordinary differential equations (ODEs) or partial differential equations (PDEs)

www.nextgencat.eu

Project Acronym and Number: Next-Gen-Cat 280890 Project Title: Development of NEXT GENeration cost efficient automotive CATalysts behaviour for microand nano electronics Start and End Dates: 01/02/2012 till 31/01/2016 EU Contribution: 3.940.000 € Coordinator: Fotis Katsaros, Demokritos, EL, <u>fkats@chem.demokritos.gr</u>



in NIM_NIL 228637

Subject of the modelling

Characterisation of electromagnetic metamaterials

Models

Application

<u>Electromagnetic wave theory</u> for characterisation, Maxwell's equations coupled to <u>constitutive</u> <u>equations</u> for material response; constitutive equations are dispersive models (Drude, Drude-Lorentz) or experimentally obtained material constants; Rigorous Coupled Wave Analysis (RCWA) method is used to calculate transmission and reflection and field distributions inside the metamaterial structures.

Development Models for losses

Simulation software and type of numerics used

Commercial software, DiffractMOD (RSoft inc.), Reticolo and RCWA solver Self-written Mathematica and Matlab codes for implementation of Berreman formalism for oblique incidence retrieval and visualization purposes

Finite-difference time-domain method, finite-elements method (COMSOL), finite integration technique (CST Microwave Studio), retrieval procedure based on scattering parameters. RCWA method solving Maxwell's equations for stratified structures like gratings and metamaterials

Simulated structures are assumed periodic in lateral dimension and the accuracy can arbitrarily be increased by taking a higher number of Fourier harmonics and better discretization

Achievements of the modelling beyond experiments

Negative refractive indices cannot be measured directly but need to be carefully derived from measurements.

Determination that silver is the best conducting material for use in optical metamaterials Design and optimization of 3D metamaterial structures

Unambiguous demonstration of negative refraction with wedge configuration for designed negative index metamaterial in the visible regime

Application

Optical devices for communications and imaging

Relevant review articles

http://ec.europa.eu/research/industrial_technologies/pdf/metamaterials-brochure_en.pdf C. M. Soukoulis and M. Wegener, "Past achievements and future challenges in the development of three-dimensional photonic metamaterials," Nature Photon. **5**, 523-530 (2011).

G. W. Hanson, J. Appl. Phys. 103, 064302 (2008).J.W. Weber et al., Applied Physics Letters 99, 061909 (2011)Oates et al., Optics Express 20(10) 11166 (2012)

Summary of project

The aim of NIM_NIL is the development of a production process for 3D negative refractive index materials in the visible regime combining UV-based nanoimprint lithography (UV-NIL) on wafer scale using the new material graphene and innovative geometrical designs.

A micro-optical prism will be fabricated to directly verify and demonstrate the negative refractive index.

Summary of the modelling

<u>Electromagnetic characterisation tools</u> are used to interpret the measured reflection and transmission by spectroscopic ellipsometry to determine the region of negative refractive index and its dispersion as a function of wavelength. Dependence on the wave vector is also investigated. During the characterization stage ellipsometry and normal incidence responses of the models were compared with post fabrication measurements to calculate effective parameters of the product. Then necessary feedback was given to the fabrication team for further optimizations.

The optical properties of graphene are not completely characterized experimentally, especially in the infrared and Terahertz frequency regions. Relations between the density of free carriers and the frequency dependent conductivity as a function of the temperature and the Fermi level (which may be influenced by external bias) are established. The relation is based on the Drude model using the Kubo formula. We used these formulas as input to the dielectric functions to fit our infrared ellipsometry measurements. We used the Airy-Fresnel formulas to create a layer model of the substrate and graphene layer, and fit the optical conductivity (dielectric functions) in the range from 600-4000 cm-1. In this way we could estimate the Fermi level shift due to chemical doping from atmospheric exposure.

We also characterized the plasmonic modes of silver fishnet metamaterials fabricated using nanoimprint lithography. Coupling of obliquely incident radiation to surface plasmon polaritons (SPPs) at a metal-dielectric interface is affected when the incident wave vector matches an SPP wave vector. We used the SPP formulas coupled to the grating formulas to show the angular dependence of the SPP modes in spectroscopic ellipsometry data.

Full-wave simulations are used for the calculation of scattering parameters of metamaterial structures. The scattering parameters can subsequently be used to determine the effective material constants of the metamaterials. The models were used for the design of the metamaterial samples. Full-wave simulations were performed for metamaterial wedges. This effort used our existing numerical simulation capabilities, but it was scaled up to accommodate the large computational problem involved. Wedges contain many circuits and require resolving the electromagnetic on both the microscopic and macroscopic scales. Possible candidates for optical metamaterials with negative index of refraction were identified. The improved wedge configuration shows unambiguous phenomenon of negative refraction with designed optical metamaterials. Single and multiple functional layer Fishnet metamaterial in IR and visible regions were designed and simulated using ab-initio Maxwell solver (RCWA).

A EM model was developed to describe the dissipative loss in resonant electromagnetic metamaterials. The model takes into account the radiation damping of the resonant currents, which is necessary to model metamaterials made from low-loss conducting materials. This model led to an identification of which conducting materials are useful for metamaterials. Silver was found to be the best conducting material at optical wavelength. Graphene was ruled out.

www.nimnil.org

Project Acronym and Number: NIM_NIL 228637 Project Title: Large Area Fabrication of 3D Negative Index Metamaterials by Nanoimprint Lithography Start and End Dates: 01/09/2009 till 31/08/2012 EU Contribution: 3.373.100 € Coordinator: Iris Bergmair, Profactor, DE, <u>iris.bergmair@profactor.at</u>



in NPMIMETIC 246351

Subject of the modelling

biomaterials, biomimetic nano-polymer gel, synthetic scaffolds

Models used

Continuum: Model for <u>hyperviscoelastic behavior</u> in biomaterials <u>Multibody system dynamics model</u> (MBS) for intervertebral disc loading conditions incorporating local (biomaterial) physics

Simulation software and type of numerics used

Partial differential equations for finite element methods (model for hyper viscoelastic materials) and multibody system dynamics

Algorithms for image analysis (denoising, segmentation, smoothing, sampling and visualisation)

Achievements of the model beyond experiments

The study of the intervertebral disc (IVD) mechanical behaviour presents a high level of difficulty, due to intrinsic uncertainty on the quantification of real working loads (coupling compression forces, flections and torsion moments). Post-mortem analysis doesn't allow a full understanding of these phenomena, mainly due to the highly hydrated nature and the fact that the osmotic role of nucleus function is not achieved in those conditions. Modelling can overcome these restrictions and predict two fundamental situations:

i)degenerated IVD – stress/strain conditions due to nucleus degeneration (geometry, stress conditions, prediction of overstretched annulus' fibres)

ii) restored IVD – prediction of restoration conditions, annulus rupture state and/or failure risks on the nucleus 'refilling' process, influence of nucleus prosthetic materials characteristics on overall mechanical stability

Application

Biomedical implants for intervertebral discs

Relevant review articles

Cavalcanti, C; Alves, JL, Mechanical behaviour and constitutive modelling of the annulus fibrosus: a literature review, ESB-2012, 18th Congr. European Society of Biomechanics, Lisbon, Portugal, Jul. 2012

Araújo, A; Peixinho, N; Marques Pinho, AC, Stress characterization of intervertebral disc on radial direction: an experimental approach, ESB-2012, 18th Congr. European Society of Biomechanics, Lisbon, Portugal, Jul. 2012

The NPmimetic project will develop a biomimetic nano-polymer based gel for minimally invasive disc regeneration treatment: Electro-spinning technology will be exploited to design and develop a nano-fiber based, biocompatible, biodegradable, synthetic scaffold that will mimic the mechanical properties of the native nucleus pulposus (NP) for immediate and short term treatment. Anti-inflammatory drugs will be carried by the biodegradable nano-fibers to be gradually released in situ for healing and preventing inflammation.

Summary of the modelling

The continuum <u>mechanical models</u> applied are focused on

1. prediction of the mechanical behaviour of an undamaged intervertebral discs, and possible geometrical/mechanical effects of a NP pathology

2. the behaviour of bio-mimetic gels withstanding loads and behaviour characteristics under working conditions.

<u>A hyper-viscoelastic mechanical model</u> for bulk material, with an almost-incompressibility assumption was used in a non-linear finite elements model (FEM) approach to mimic Nucleus pulposus (NP) behaviour within the intervertebral discs.

Intervertebral disc loading conditions were simulated with a multibody system <u>mechanical model</u>. This can, with a much lighter computational effort than FEM, simulate the dynamic behaviour of the mechanical phenomena inside the intervertebral discs, either under endogenous or exogenous actuations, and a detailed analyse of the localized deformation on intervertebral disc's soft tissues can be achieved.

Combining all these aspects, a hybrid model can be developed, using the multi body system tool to predict the motion of the segment and the FEM tool to detail the localized deformation on IVD's soft tissues. The kinematics, stress distribution and its effects can be analysed simultaneously, allowing a more precise definition of the loading state of the different parts in different situations, as well as the prediction of the overall behaviour of the set under 'real' use.

Image –processing: Intervertebral disc geometry definition involved the development of an automated image-based procedure, capable of making an identification of soft tissues and substrate bone (i.e., capable of distinguishing between muscle and ligaments, tendons and bones, cortical and trabecular bone, fibrous and pulpous regions, etc.), extracted from 2D high resolution MRI or other available technique images. A subroutine was created to build up geometrically consistent boundaries/regions, through analysis, parameterization and high-degree regression of 2D topographic curves, in order to produce suitable 3D meshed 'solid' entities.

With these models assistance in the evaluation of eventual different proposals for the therapeutic modalities and/or techniques of regeneration can be given.

www.npmimetic.com

Project Acronym and Number: MODIFY 228320 Project Title: Biomimetic nano-fiber-based nucleus pulposus regeneration for the treatment of degenerative disc disease Start and End Dates: 01/02/2011 till 31/01/2015 EC Contribution: 3.985.587 € Coordinator: Marco N Helder, Vrije Universiteit medical center, Amsterdam, NL <u>m.helder@vumc.nl</u>



in ONE-P 212311

Subject of the modelling

Electronic processes occurring in organic-based devices (charge transport, light conversion into current, charge injection) and their dependence on system morphology.

Models used

Electronic: Ab initio or semi-empirical <u>Hartree-Fock methods</u>, <u>DFT methods</u> Atomistics: <u>Molecular Dynamics</u>, <u>Molecular Mechanics</u>

Simulation software and type of numerics used

Gaussian, Ampac, ADF, SIESTA for DFT Gromacs, Materials Studio, Tinker, NAMD for MD with the numerical Kinetic Monte Carlo procedure

Achievements of the model beyond experiments

Material design targeted to the optimization of physical properties and to yield devices with enhanced efficiencies. Modelling allowed the fast screening of candidate molecules for electron transport in devices, IR emitters and lasing applications. It predicted organic semiconductor crystal structures and explained the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties; and predicted its implications for charge separation in organic solar cells.

Application

OLEDs, field-effect transistors, sensors and storage devices, solar cells

Relevant review articles

"An Atomistic Description of Polymer Dielectrics/Pentacene Interfaces: Influence of Electrostatic Interactions on Charge Mobility Values". N.G. Martinelli, M. Savini, L. Muccioli, Y. Olivier, F. Castet, C. Zannoni, D. Beljonne, and J. Cornil. Advanced Functional Materials 19 (2009) 3254-3261.

"Control of the Mutual Disposition of Cyclometalated Ligands in Cationic Ir(III) Complexes: Synthesis, Spectroscopy, and Device Efficiency of the Different Isomers". J.M. Fernandez-Hernandez, C.H. Yang, J. Beltran, V. Lemaur, F. Polo, R. Frölich, J. Cornil, and L. De Cola. Journal of the American Chemical Society 133 (2011) 10543-10558.

Photoinduced Work Function Changes by Isomerization of a Densely Packed Azobenzene-Based SAM on Au: A Joint Experimental and Theoretical Study". N. Crivillers, A. Liscio, F. Di Stasio, C. Van Dyck, S. Osella, D. Cornil, S. Mian, G.M. Lazzerini, O. Fenwick, E. Orgiu, F. Reinders, S. Braun, M. Fahlman, M. Mayor, J. Cornil, V. Palermo, F. Cacialli, and P. Samori. Physical Chemistry Chemical Physics 13 (2011) 14302-14310.

ONE-P developed new functional organic materials for organic electronics and photonics and some applications such as organic light-emitting diodes, photovoltaics and active matrices. These materials provided enhanced properties in electron transport, conversion of photons into electrons and/or conversion of electrons into photons and can be printed in a continuous process.

Summary of the modelling

ONE-P applied electronic and atomistic modelling approaches in order to investigate electronic and structural properties of the next generation of organic conjugated compounds for applications in organic electronics. The project combined <u>quantum-chemical models</u> (a.o. by means of Non-Equilibrium Green's Function <u>DFT</u> calculations) for the evaluation of the molecular parameters defining the rate of charge transfer between molecules and <u>Kinetic Monte Carlo numerical algorithms</u> for the propagation of the charge and the evaluation of the charge carrier mobility and <u>Molecular Dynamics</u> simulations for the prediction of the bulk organization,

The project developed a methodology to model the triplet energy transfer at the molecular scale from quantum-chemical calculations to end up with exciton diffusion length using Kinetic Monte Carlo.

Results: with these models the project could

- model realistic donor-acceptor interfaces (such as polymer-fullerene) using Molecular Dynamics simulations and then extract by means of quantum-chemical calculations the dipole at the interface between organic layers.

- design functional molecules for SAMs for application in molecular electronics

predict the changes in the work function of metal electrodes upon deposition of self-assembled monolayers or organic semiconductors using DFT calculations with Periodic Boundary Conditions (as implemented in SIESTA) to tune the charge or spin injection barriers.
find a relationship was found between the structural organization of polymer chains (modelled by Molecular Dynamics) and the solid-state optical properties (described by

phenomenological models).

- elaborate a design rules for improving the charge transport properties of n-type as well as ambipolar organic semiconductors.

-study the impact of the nature of the insulating layer in field-effect transistors on the electrostatic disorder at the interface between the dielectric layer and the organic semiconducting layer. We have used here a combination of <u>Molecular Dynamics</u> simulations to generate realistic interfaces between the insulating layer and the organic semiconductor at the nanometre scale, <u>quantum-chemistry</u> and <u>Kinetic Monte Carlo</u> approaches to quantify the impact of different dielectrics on the charge carrier mobility.

http://www.one-p.eu/public/

Project: 212311 ONE-P Title: Organic Nanomaterials for Organics and Electronics Start and End Dates: 01/01/09/2009 till 31/12/2012 EC Contribution: 17.989.000€ Coordinator: Prof. Yves Geerts, ULB, BE, <u>ygeerts@ulb.ac.be</u>


in ORAMA 246334

Subject of the modelling

Multifunctional oxides (Active Semiconductor Oxides (ASO)) Passive n-type amorphous Transparent Conducting Oxides (a-TCOs) and p-n type junctions thereof

Models

Electronic: First principle modelling (<u>DFT</u>) of oxide materials for the electronic structure of oxides Atomistic: <u>Generalized Boltzmann Transport Equations models</u> for plasma and thin film growth Continuum: <u>Computational fluid dynamics</u> for droplet formation

Simulation software and type of numerics used

Own codes: BEM for electric field computation by Poisson's equation PICMC Parallel Particle-in-Cell Monte-Carlo code including routines for particle motion (DSMC) BEM for electric field computation by Poisson's equation RIG-VM for computation of magnetic fields using the Boundary Element Method CFX Ansys (CFD) Commercial software: Advanced, Essential Macleod, Code and OptiLayer Scripting language used for scheduling of parallel simulation tasks, for specialized post-processing and for optimization issues. Direct Simulation Monte-Carlo (DSMC) techniques. Optical analysis codes

Achievements of the modelling beyond experiments

Using modelling, we understood the relevance of the grain boundaries for shallow acceptor levels which are the prerequisite for p-doping in ZnO films with substantial resource savings compared with an experimental approach. Similar savings are achieved for the layout of deposition chambers and coating processes. Our modelling allows for an in depth understanding of the plasma parameters and growth conditions particular in PVD processes. The modeling of particle fluxes and energies allows for substantial time savings and deeper understanding compared to experiments.

Application

Electronic devices (automotive), thin film photovoltaics, Displays, LED and OLED technology

Relevant review articles

B. Szyszka et al., Development of new transparent conductors and device applications utilizing a multidisciplinary approach, Thin Solid Films 518 (2010) 3109

B. Szyszka et al., Recent developments in the field of transparent conductive oxide films for spectral selective coatings, electronics and photovoltaics, Current Applied Physics 2012, in press, doi: 10.1016/j.cap.2012.07.022

W. Körner et al., First-principles density functional study of dopant elements at grain boundaries in ZnO, Phys. Rev. B 81 (2010) 085324

M.Putti, et al., "New Fe-based superconductors: properties relevant for applications" Supercond. Sci. Technol. **23** (2010) 034003

K. Tanabe and H. Hosono "Frontiers of Research on Iron-Based Superconductors toward Their Application" Japanese Journal of Applied Physics **51** (2012) 010005

G. R. Stewart "Superconductivity in iron compounds" Reviews of Modern Physics, 83 (2011) 1589

Summary of project

Orama deals with the development of multifunctional oxide based electronic materials, processable at low temperatures, including flexible substrates. Orama will address the potential of oxides as electronic materials in the automotive industry. It will achieve this by addressing the four key elements being essential for building up the new era of oxide based electronic industry: 1st principle material modelling, synthesis of new materials, development of low temperature and damage free deposition and patterning techniques and novel characterization methods.

Summary of the modelling

The materials modeling in Orama aims at understanding of semiconductor properties for realistic life materials including doping and defect related phenomena. An important issue is the understanding of p-conductivity in doped ZnO films and novel p- and n-type oxide materials. Another important issue is the suppression of plasma damage due to high energetic species impinging on the substrate.

A multiscale model for coating processes is used. To achieve this, we use different approaches to model electronic structure, plasma process and thin film growth phenomena and for continuum modelling of ink-jet processes.

First principle modeling of the electronic structure of oxides

Own code developments or source codes available for academic purposes were utilised to solve the Kohn-Sham equations of <u>density functional theory</u> for the first principle modelling of the electronic structure including defect effects, such as doping and grain boundary related issues. <u>Plasma and thin film growth related phenomena</u>

For these areas, codes developed earlier were used. Monte-Carlo techniques Direct Simulation Monte-Carlo (DSMC) were used to solve the <u>statistical mechanics (Boltzmann) transport equation</u> for the description of gas flow phenomena. With self-consistent electric field computation that approach is extended to Particle-in-Cell Monte-Carlo Techniques (PIC-MC) for plasma phenomena. The simulation environment is entitled "picmc". RIG-VM is used for scheduling and parameterization of the parallel computing jobs. Further, it can be used for specialized postprocessing and optimization issues. Besides PIC-MC simulation, RIG-VM comprises a module for optical simulation of multilayer stacks.

<u>Computational fluid dynamics</u> (CFD) modelling is used for various tasks in the optimization of Ink-Jet and Sol-Gel processes. Here, we use commercial software, from suppliers such as CFX / Ansys. <u>Optical analysis</u>

Here, we use also the RIG-VM code to analyse optical spectra and X-ray reflectometry data besides several commercial products in this field (such as Advanced Fit by Sentech, Essential Macleod, Code or OptiLayer.An important application is the analysis code of RF-superimposed DC-sputtering of TCOs serving as front contact for thin films LEDs where intense bombardment reveals plasma damage (due to release of N from the GaN substrates) which increases the operation voltage of the device.

www.orama-fp7.eu

Project Acronym and Number: ORAMA 246334 Project Title: Oxide Materials Towards a Matured Post-silicon Electronics Era Start and End Dates: 01/10/2010 till 30/09/2014 EU Contribution: 9.742.506 € Coordinator: Bernd Szyszka FhG, DE, <u>coordination@orama-fp7.eu</u>



in OXIDES 228989

Subject of the modelling

Oxide interfaces and nanostructures (structural, electronic and functional properties)

Models used

Electronic models:

First-principles description within the <u>Density Functional Theory</u> formalism Second-principles modeling: <u>Tight-binding Hamiltonians</u> for electrons, <u>Effective Hamiltonians</u> for the lattice-related properties at finite temperatures <u>Bloch-Boltzmann theory</u> for transport and thermoelectric properties

Simulation software and type of numerics used

Standard packages for first-principle simulations (SIESTA, ABINIT, CRYSTAL, VASP) and homemade/open-source codes (BoltzTraP) for second-principles simulations. Iterative resolution using either a variational formulation and a minimization method or a diagonalization procedure. In house arallelised code

Achievements of modelling beyond experiments

Theoretical predictions to be further validated experimentally:

The unexpected possibility to induce multiferroism in epitaxially strained CaMnO₃

The unexpected possibility to achieve exploitable Tunnel Electro-Resistance (TER) in symmetric Ferroelectric Tunnel Junction (FTJ); for memory applications

The prediction of the unexpected appearance of a half-metallic ferromagnetic highly-confined 2-dimensional electron gas (2DEG) in SrTiO₃/SrRuO₃ superlattices

The unexpected role of oxygen rotation in shifting by 300 K the ferroelectric phase transition of PbTiO₃;

Joined theoretical-experimental breakthroughs

Improper ferroelectricity in oxide superlattices in which modelling identified a new microscopic mechanism (the so-called trilinear coupling of structural instabilites) as observed in parallel experimentally

Exchange bias in LaNiO₃/LaMnO₃ superlattices; modelling allowed the proper understanding of the unusual spin order giving rise to the experimental results

Compelling evidence of the intrinsic nature of the 2DEG at polar oxide interfaces; modelling of ideal interfaces was required to unambiguously distinguish between intrinsic and extrinsic effects

Confinement properties of the 2DEG at the LaAlO₃/SrTiO₃ interface; modelling provides key information on the electronic band structure, mandatory to interprete measured properties

Application

Nanostructures for electronic and spintronic applications, ferroelectric and multiferroic memories, thermoelectric devices for energy conversion and energy harvesting

Relevant review articles

ABINIT: first-principles approach to material and nanosystem properties X. Gonze et al.Computer Physics Communications 180, 2582 (2009)

The OxIDes project develops advanced techniques for the atomic scale modelling of the most relevant types of oxide interfaces and uses these tools to design a new generation of layered materials with unique experimentally-confirmed properties.

Summary of the modelling

OxIDes addresses the physics of three types of interfaces: (i) insulating interfaces between insulating oxides, where coupling between lattice modes can lead to unusual phenomena; (ii) conducting interfaces between insulating oxides, where an interfacial 2-dimensional electron gas (2DEG) might exhibit large thermoelectric power; and (iii) interfaces between metallic and insulating oxides, for a deeper understanding of screening.

OxIDes relies at a first level on advanced electronic modelling based on first-principles Density Functional Theory (DFT) techniques where the study of highly-correlated electron sytems and/or specific interfaces (like metal/insulator interfaces) requires going beyond the usual approximations. Significant methodological advances concern the use of pseudo self-interaction correction local density functional method pSIC and B1-WC hybrid functional techniques for these interfaces. The pSIC method removes in complex systems the spurious self-interaction repulsion present in local or semilocal density functionals (LDA, GGA). The B1-WC functional was introduced only recently and implemented in CRYSTAL code during the project. Hybrid functionals are well known but this is a new functional that was adjusted to properly describe at the same time the lattice dynamics and electronic properties of functional ferroelectric and related perovskites. Previous hybrid functionals were not satisfactory for those systems.

A variational pSIC extension was developed within Oxides allowing atomic relaxation at the pSIC level. In the VPSIC approach, the atomic forces formulation follows from the usual Hellmann-Feynmann procedure. It is obtained as the LSDA expression augmented by a further additive contribution due to the atomic-site dependence of the SI projectors.

The first-principles techniques have been used to study single- and poly-domain structures of ferroelectric capacitors and various ABO₃/A'BO₃ superlattices, the origin and confinement of the 2DEG at the LaAlO₃/SrTiO₃ interface or in SrRuO₃/SrTiO₃ superlattices, the magnetic properties of nickelates, etc.

The second-principle modelling includes a <u>tight-binding</u> Hamiltonian for electrons to determine the equilibrium distribution of the conduction charge in 2DEG, extended effective Hamiltonians for finite-temperature simulations of ferroelectric-related properties, an approach based on <u>Bloch-Boltzmann theory</u> for the prediction of thermoelectric properties and the Brinkman-Dynes-Rowel relation for the determination of electronic transport properties (The voltage dependent tunneling conductance has been calculated using two extreme models of the WKB approximation)

OxIDes developed a totally new effective Hamiltonian approach, that properly includes all ionic degrees of freedom, for the study of structural phase transitions with temperature, implemented a method including a temperature-dependent relaxation time for the description of the transport properties within the Bloch-Boltzmann approach, proposed a simple electrostatic model properly including incomplete screening for the description of ferroelectric capacitors in zero and finite bias and also realized the first ever ab initio simulation of a realistic ferroelectric tunnel junction under finite bias, combining DFT and non-equilibrium Green's function formalism.

http://www.oxides.ulg.ac.be/

Project Acronym and Number: OXIDES 228989 Project Title: Engineering exotic phenomena at oxide interfaces Start and End Dates: 01/09/2009 till 31/08/2012 EU Contribution: 2.150.000 € Coordinator: Philippe Ghosez, University of Liège, B, <u>Philippe.Ghosez@ulg.ac.be</u>



Modelling in PMJOIN 309993

Subject of the modelling

Polymer-metal laser joining

Models used

Continuum: heatflow and thermodynamical models ; electromagnetic models

Simulation software and type of numerics used

Simulation software: Comsol Multiphysics / Matlab/ABAQUS Type of numerics: Analytical / Finite Elements/Monte Carlo

Achievements of the model beyond experiments

Thermal modelling of joining of parts will help to determine the viable parameter space and provide thermal cycles at all points of the part. Structuring modeling will assist to numerically evaluate the generation and the effect of different patterns on the joint. Finally mechanical modelling will clarify the constitutive behaviour and the nature of breaking of the joint interface.

All these models save precious resources and provide in-depth understanding of the underlying physical processes, as opposed to a purely experimental approach.

Application

Polymer-metal joined structures for automotive industry

Relevant review articles

Farazila,Y.; Miyashita, Y.; Hua, Wang; et al, YAG Laser Spot Welding of PET and Metallic Materials,

Journal of Laser Micro Nanoengineering, Volume 6, Issue 1, Pages: 69-74

- A.P. Mackwood, R.C. Crafer, Thermal modelling of laser welding and related processes: a literature review, Optics & Laser Technology, Volume 37, Issue 2, March 2005, Pages 99-115, ISSN 0030-3992, 10.1016/j.optlastec.2004.02.017.
- Giuseppe Casalino, Elhem Ghorbel, Numerical model of CO2 laser welding of thermoplastic polymers, Journal of Materials Processing Technology, Volume 207, Issues 1–3, 16 October 2008, Pages 63-71, ISSN 0924-0136, 10.1016/j.jmatprotec.2007.12.092.
- Bappa Acherjee, Arunanshu S. Kuar, Souren Mitra, Dipten Misra, Effect of carbon black on temperature field and weld profile during laser transmission welding of polymers: A FEM study, Optics & Laser Technology, Volume 44, Issue 3, April 2012, Pages 514-521, ISSN 0030-3992, 10.1016/j.optlastec.2011.08.008.
- M. Ilie, E. Cicala, D. Grevey, S. Mattei, V. Stoica, Diode laser welding of ABS: Experiments and process modeling, Optics & Laser Technology, Volume 41, Issue 5, July 2009, Pages 608-614, ISSN 0030-3992, 10.1016/j.optlastec.2008.10.005.
- Experimental and Numerical Investigation of Laser Welding of long Fiber Thermoplastic Composites, M. Oumarou, J. Renard, D. Jeulin, W. Knapp, S. Clément, ICALEO 2011, Orlando, Florida, USA, 2011.

Summary of project

The projects targets lightweight structures for the automotive industry to replace metal parts and to achieve reduced energy consumption. As metals cannot fully be replaced by plastics in many applications, many products are made of multi-components consisting of several types of materials. The present project aims to develop a new innovative joining concept for Plastic and Metal materials using a direct non-contact laser joining process without extra filler, adhesive bonds or mechanical union.

Summary of the modeling

<u>Thermal modeling</u> will provide thermal gradients, weld seam geometry and thermal distortions, as a function of laser parameters, material properties and clamping conditions. A finite elements model (FEM) commercial <u>thermodynamics package</u>, COMSOL Multiphysics, will be used for fast heating and joining while ZEMAX will be the tool to model the <u>scattering behaviour</u> of the laser beam through the polymer, via ray tracing and Monte-Carlo methods. With this, the laser input parameters will be predicted that yield the required polymer melting temperature independently of the required joining configuration (through the polymer or the metal). Possible joint distortions (generated during the cooling of both materials) will be also determined.

<u>Structuring modelling</u> of the micro-structured pattern geometry in the metallic part will identify the most appropriate structure facilitating anchorage of the melted polymer during the joining operation. The code COMSOL is used. This modeling does not describe the physical phenomena in laser ablation but it links the laser processing parameters for the structuring to the resulting structures and the subsequent joining process. It will be a MIMO (Multiple Input/Multiple Output) matrix relation definition in order to obtain a starting point in a process development and to better understand the complete process chain. In terms of the structuring model the approaches from the laser material interaction model known from laser drilling applications will be adapted to the structuring process.

Process descriptions for manufacturing technologies in terms of correlating manufacturing parameters e.g. laser power, feed rate with the joining results e.g. tensile strength. These relations follows the approach of RSM (Response Surface Model) which is utilized in DOE (Design of Experiments) methods to link process results to input parameter using Statpoint Statgraphics Centurion.

<u>Mechanical modeling</u> with ABAQUS will clarifying the behaviour and the nature of breaking of the joint interface and how to obtain the best rigidity and weld seam strength. Generally, the joint interface has a complex behaviour and depends on the loading condition and rate. The variables (internal variable) written at meso or macro scales for structural calculation, are directly linked to the physical mechanisms occurring in the material at microscopic scale. We obtain the constitutive law of the welded zone thanks to our testing system, which is able to test the assembly in 3D. By this way we get the real behavior of the in situ seam. Concerning the link with the physical mechanisms, we are able to perform tensile and shear tests through a scanning microscope and then to observe the microstructure. By this way we don't get a mechanical characterization because the tested volume is too small to be representative, but we can understand the evolution of the microstructure. That means that we identify the domain of elasticity and then damage, the type of damage and its evolution till breaking of the join.

Project Acronym and Number: PMJOIN 309993 Project Title: Development of a Direct Laser Joining of hybrid Plastic-Metal components for industrial applications Start and End Dates: 1/2/2012 till 31/1/2015 EU Contribution: 2.670.335 € Coordinator: Carmen Sanz, Fundación Tekniker, ES <u>csanz@tekniker.es</u>



in POCO 213939

Subject of the modelling

Interactions of functionalised carbon nanotubes with polymer matrices and influence of processing parameters on different properties of the nanocomposites

Models used

Atomistic: <u>Molecular Dynamics</u> for interfacial interactions between CNTs and polymeric matrices.

Continuum: <u>Solid mechanics</u> to describe the elastic behaviour of the nanofilled composites as whole i.e matrix+CNTs.

Simulation software and type of numerics used

Materials Studio (Molecular Dynamics)

ANSYS Finite Elements method (FEM) for continuum mechanics

Minimization algorithms (Steepest descents, Conjugate gradient, Newton) Ewald summation method, Finite Differences method (Verlet integrator) with Andersen numerical thermostat and barostat to simulate the NVT and NPT statistical ensembles

Achievements of the model beyond experiments

Molecular models of functionalized CNTs and polymer matrices could predict the influence of the functional groups on the mechanical properties of the CNT and the interfacial shear strength (IFSS) of the nanocomposites. The influence of the functionalization of CNTs on the IFSS of the nanocomposite was demonstrated, something that would otherwise have cost many experiments.

The pull-out of CNTs from molecular matrices is difficult to analyze by experimental methods due to the scales involved. In this case, the process modelling of the pull-out was necessary to analyze the interfacial shear strength of the nanocomposites.

Application

Polymer composites filled with CNT for automotive, aeronautics, building, aerospace, wind power generation (blades), ship building and biomedicine applications

Relevant review articles

Molecular dynamics modelling for the analysis and prediction of miscibility in polylactide/polyvinilphenol blends; de Arenaza, et al Polymer 2010 51-19 pp4431-4438 Molecular dynamics study of the influence of functionalization on the elastic properties of single and multiwall carbon nanotubes. Coto, B.et al. Comp Mat Science 2011 50-12 pp. Poly(ethylene oxide)-b-poly(L-lactide) Diblock Copolymer/Carbon Nanotube-Based Nanocomposites: LiCl as Supramolecular Structure-Directing Agent. Meyer et al Biomacromolecules 2011 12-11 pp4086-4094

POCO develops innovative polymer composites filled with CNT, a nanostructured material with tailor made and superior properties. This involves development of CNT confinement strategies.

Summary of the modelling

CNTs/Polymer matrices were modelled with the following approaches for the different properties:

The influence of the functionalisation on the mechanical properties of the CNTs was analysed using a <u>Molecular Dynamics</u> approach and by calculating the stress-strain slopes with <u>mechanics models</u>.

The interfacial interactions between CNTs and polymer matrices were analysed using <u>Molecular</u> <u>Dynamics</u> pull-out simulations, where the interaction energy between the CNT and the polymer matrices is monitored while the CNT is being pulled-out from the matrix. This energy can be related to the interfacial shear strength. Analytical relations were developed from the analysis of the curing of the thermosetting polymers (kinetic, chemo-rheology) and used Ozawa's and Avrami's models to study the crystallization of thermoplastics semi-crystalline matrices both pure and with CNTs. For the alignment of CNTs in viscous media under electric fields, POCO developed an electro-dynamics <u>constitutive equation</u> relating the polarisability of the CNTs, the electric field applied and the viscosity of the polymer with the torque.

The mechanical properties such as Young's modulus, shear modulus and Poisson's ratio of nanofilled systems have been obtained by a <u>macromechanical model</u> using stress-strain <u>constitutive equations</u>, which was solved with a finite element approach implemented in a dedicated simulation code called ANSYS.

The project has proven that a moderate degree of chemical functionalization of the CNTs can increase the interfacial shear strength up to a 300% (depending on the functional groups used) when compared to pristine CNTs.

The influence of functional groups on the properties of the CNTs has been proven to be detrimental for the mechanical properties of the SWCNTs. This detrimental effect is less critical in the case of MWCNT.

http://www.poco-project.org/home.asp

Project Acronym and Number: POCO 213939 Project Title: Carbon nanotube confinement strategies to develop novel polymer matrix composites Start and End Dates: 01/11/2008 till 31/10/2012 EU Contribution: 5.520.000 € Coordinator: Borja Coto, Fundacion Tekniker, ES, <u>bcoto@tekniker.es</u>



in RADINTERFACES 263273

Subject of the modelling

Damage mechanisms and effects on mechanical properties for novel crystalline materials with large interfacial areas

Models used

Electronic: <u>DFT</u> and <u>fitted many body potentials</u> for calculation of diffusion barrier Atomistic: <u>Molecular Dynamics (MD)</u> <u>Hybrid kinetic Monte Carlo-Molecular Dynamics</u> Continuum: <u>Mechanical modeling</u> for interface defect and dislocation mechanics

Simulation software and type of numerics used

LAMMPS Molecular Dynamics Simulator for fast and precise modelling of multilayer systems and nanostructured systems

Micromechanics model: Dislocation Dynamics Simulator solved by FE methods for interface motion and damage

Achievements of the model beyond experiments

The modelling is going to guide the appropriate tuning of interfaces within multi-laminate composite materials to obtain defect absorption materials with a self-healing mechanism.

Application

Nuclear reactors, radiation damage

Radiation damage is known to lead to materials failure and thus is of critical importance to lifetime of and safety within nuclear reactors. The purpose of the project is to create self-healing materials using nanoscience in the design and control of nanostructures and complex defect structures. The materials should self-heal radiation-induced defects and avoid impurities that can yield radiation impervious (inpenetrable) materials.

Summary of the modelling

This project aims at developing general modelling tools to predict the effect of interface composition (monophase, heterophase) and structure (geometry, roughness) on its propensity to resist radiation damage (both via defect localization and creep) using a multiscale multiphysics approach. Model validation will arise through direct comparison with materials testing for a wide array of materials systems (metal/metal, metal/oxide, oxide/oxide).

First using DFT and <u>fitted many body potentials</u> the project will quantify the energies required to activate diffusion (diffusion barriers). For the sake of simplicity, diffusion of vacancies will be studied first. The simulations will be conducted on bilayer interfaces for the Cu/Nb system in the Kurdjimov Sachs orientation, for the Zr/Nb system in all three Burgers, Potter and Pistch Schraeder orientations such as to extract their excess energy and structure. Comparison with experimentally observations will serve as a validation. Based on experimental observation and ab initio simulations of the different interface structures -such as those in the Zr/Nb system, inter-atomic potentials will be developed and improved.

Atomistic models of interfaces representing bi-material interfaces (e.g. metal/metal, oxide/oxide, metal/oxide) and substrate/layer interfaces will be developed based on <u>molecular dynamics (MD)</u>. The code will be based on LAMMPS. A <u>hybrid kinetic Monte Carlo-Molecular Dynamics</u> (Object Oriented kinetic Monte Carlo) model will be developed aiming at studying the irreversible processes taking place in the irradiation conditions at the atomic scale and in cascade events. This is done by listing all possible reactions and paths that a given defect could follow and by then choosing the most probable one based on Monte Carlo statistical method. All possible events are quantified by migration energies, formation energies (leading to binding energies). These energies are quantified with the numerical Nudged Elastic Band method in MD. It will be based on a newly developed synchronous parallel kinetic Monte Carlo algorithm capable of reaching longer times in larger systems and will allow following the evolution of individual defects (i.e. vacancies, interstitials, He and their clusters).

At the continuum scale, a damage accumulation <u>constitutive equation</u> for macromechanical modelling will be developed based on a micromechanical model (differential equations) to describe the thermodynamical and kinetic response of the synthesized materials to microstructural features. This <u>micromechanical model</u> is 3-D cluster dynamics model -where transport and reactions in the form of absorption and emission of defects are taken into account in constitutive equations. Here rather than following individual defects within the nanolayered system, defect quantities are followed as densities. This leads to a great decrease in the amount of information (i.e. defects) to be followed which then allows to simulate the evolution of defect for long time scales.

Discrete dislocation dynamics simulations (micromechanics), accounting for the symmetry of the crystals considered, will be performed to predict the mechanical response of layered systems and to extract latent hardening parameters. To describe phenomena in the interface regions a constitutive equation based on point defect and dislocation mechanics concepts capable of accounting for interface morphology, diffusive processes, radiation-induced hardening, and the effect of dislocation/vacancy interactions will be developed. For example, the effect of defect penetration on the presence of disconnections (i.e. interfacial defect with both dislocation and step characters) will be considered.

A continuum <u>mechanics model</u> incorporating the above constitutive models will be implemented capable of accounting for coupled diffusion-mechanical bulk and interfacial phenomena. Numerically this is going to be implemented with the Finite Element method. The code will be based on a two level approach in order to account for the coupling between interfacial motion and defect diffusion, and at each finite element time step, driving forces for interfacial motion will be calculated.

http://www.radinterfaces.eu/

Project Acronym and Number: RADINTERFACES 263273 Project Title: Multiscale Modelling and Materials by Design of interface-controlled Radiation Damage in Crystalline Materials Start and End Dates: 01/09/2011 till 31/08/2014 EU Contribution: 3.223.002 € Coordinator: Mohammed Cherkaoui, CNRS, France mcherkaoui@me.gatech.edu



in REFREEPERMAG 280670

Subject of the modelling

Magneto-crystalline and shape anisotropy in RE-free magnets

Models used

Electronic: <u>Density functional theory (DFT)</u> for crystalline anisotropy Mesocale: <u>Micromagnetics dynamics</u> for shape anisotropy

Simulation software and type of numerics used

WIEN2k, Elk, muffin-tin orbitals (EMTO) pseudopotential approaches with plane waves (VASP) or numerical local orbitals (SIESTA, OpenMX) for DFT calculations

Most of these codes provide MPI-parallel versions suitable for large-scale computations. MAGPAR, FEMME will be used for micromagnetics together with finite element discretisation codes (GID, Salome)

Achievements of the model beyond experiments

The theory can pre-identify interesting materials prior to the actual synthesis and experiments and thus save time and resources.

Application

Magnets

Relevant review articles

Gillelen and Dronskowski • Vol. 31, No. 3 • Journal of Computational Chemistry, 2011 J. Buschbeck, et al, PRL 103, 216101 (2009)

The project REFREEPERMAG aims at developing new permanent magnets (PM) with high energy product without use of rare-earths or platinum. High-aspect-ratio nano-structured materials with large magnetic moments will be studied theoretically and synthetized in environment-friendly ways.

Summary of the modelling

Two different kinds of magnetic anisotropies, namely the magneto-crystalline anisotropy and shape anisotropy are investigated. Due to their inherently different nature, they will also be studied with two different approaches. The magneto-crystalline anisotropy will be studied by first-principles electronic structure calculations with <u>DFT</u> using both full-potential and <u>pseudopotentials</u> methods. The project will use various <u>basis sets</u>, e.g., augmented plane waves with local orbitals. High-throughput algorithms will be employed to search the parameter-space of ternary compounds. An additional alloying element will be added to these selected systems to obtain additional degrees of freedom and the modeling will determine whether this improves the system. For alloys, some of the DFT codes implement the coherent potential approximation, which was shown to be the best single-site approximation for alloys.

The shape-anisotropy will be studied with a <u>micromagnetics code</u> solved with a finite element discretization approach in order to study the influence of realistic microstructures on the magnetic switching behaviour of nano and mesoscopic structures in order to predict optimised structures and packing densities for a nanocomposite PM. In every iteration step the contribution of the Zeman field, the anisotropy field, and the stray field components of the particles/grains are calculated by the hybrid finite element method with boundary element method. Energy barriers for thermal switching are calculated by the implemented nudged elastic band method, which calculates the minimum energy path, i. e. the saddle point between two local energy minima of the system. Starting from an initial guess a highly probable path is found moving the points along the path according to an algorithm which resembles tensioning an elastic band across maximum energy range. Micromagnetics can predict the hysteresis properties of mesoscopic magnetic structures including the coercive field and switching times and their thermal stability depending on the geometry and the size of the magnetic volumes.

The ultimate aim is to compact powders of magnetic nanostructures with intrinsic large coercivities.

http://refreepermag-fp7.eu/project/what-is-refreepermag/

Project Acronym and Number: REFREEPERMAG 280670 Project Title: Rare earth free permanent magnets Start and End Dates: 01/05/2012 till 30/04/2015 EU Contribution: 3.850.000 € Coordinator: Dr. D. Niarchos, NCSR Demokritos, Athens, Greece <u>dniarchos@ims.demokritos.gr</u>



in ROLICER 263476

Subject of the modelling

Damage and degradation of ceramics (silicon nitride, mechanical and thermal loading)

Models used

Electronic: <u>DFT</u> and Mixed-Basis<u>PseudoPotential</u> (MBPP) Atmoistic: <u>Molecular Dynamics</u> (MD: based on inter-atomic empirical potentials) Continuum:<u>micromechanical models</u> for thermoelasticity, plasticity, sliding interaction, cohesive interfaces and dynamic analysis) and an elastohydrodynamic lubrication (EHL) model (Reynolds equation)

Simulation software and type of numerics used

Quantum Espresso for ab initio QM DFT LAMMPS for MD EHL (Fourier analysis) ABAQUS, ANSYS (FEM) and numerical methods of homogenization for continuum mechanics SIMPLEWARE for 3D microstructure generation

Achievements of the model beyond experiments

The ab initio models provide reliable properties of the bulk material and solid-solid interfaces as criteria for crack initiation, which are very difficult to obtain by experiments. Molecular dynamics models are used in modelling hybrid steel-ceramic contact to study the interaction between additives in lubricants and bearing surfaces. Experiments that provide such information are not possible.

The micromechanical and macroscopic models calculate stress distributions in undamaged and damaged regions of components, which cannot be obtained experimentally. The fracture models describe crack nucleation based on traction-separation laws which provide a phenomenological lifetime prediction tool without the need for extensive experiments. The microscale models results are homogenised to arrive at thermoelastic properties and thermomechanical homogenisation of strengthening effects in ceramics. Such simulations provide information that cannot be obtained experimentally.

Application

Metalforming tools; hybrid bearings

Relevant review articles

J. Wippler, T. Böhlke, Structure and fracture property relation for silicon nitride on the microscale, Computational Materials Science, DOI 10.1016/j.commatsci.2012.02.042

Wippler, J., Fünfschilling, S., Fritzen, F., Böhlke, T., Hoffmann, M.J.: Homogenization of the thermoelastic properties of silicon nitride. Acta Materialia 59, 6029-6038 (2011) DOI:10.1016/j.actamat.2011.06.011

I. Khader, A. Hashibon, J.-M. Albina, A. Kailer, Wear and corrosion of silicon nitride rolling tools in copper rolling, Wear 271 (2011) 2531-2541.

A. Hashibon, C. Elsässer, Approaches to atomistic triple-line properties from first-principles, Scripta Materialia 62 (2010) 939-944

J.H Beynon, Finite-element modelling of thermomechanical processing, Phil. Trans. R. Soc. Lond. A, 357 (1999) 1573-158.

J.H Beynon, Tribology of hot metal forming, Tribology International 31 (1998) Pages 73-77

Summary of project

RoliCer relies on multiscale predictive models to assess damage and simulate degradation mechanisms in engineering ceramics under realistic working conditions. This will include tribology, damage analysis and lifetime predictions. The project aims at a systematic tailoring of ceramic materials for new applications, where modelling is supported by measuring techniques. The project concentrates on silicon nitride ceramics which are wear corrosion and contact fatigue resistant materials and potential materials for high temperature metal-forming tools and rolling elements for bearings

Summary of the modelling

RoliCer develops multiscale simulations based on continuum <u>mechanics</u> (finite-element FE numerics and numerical homogenization) and elastohydrodynamic lubrication (EHL) to predict time-dependent mechanical, tribological and thermal material stresses arising in contact. The micromechanical models use coupled thermal-mechanical analysis techniques to obtain material stresses as a function of material properties and realistic working conditions. Within the homogenization schemes, efficient numerical estimates of the failure probabilities depending on microstructural parameters are obtained. The modeling focuses a reliable failure prediction also for non-proportional and cyclic loading. The EHL simulations provide information on the lubrication film thickness, local stress, pressure distribution, temperature and deformation and factors affecting the breakdown of the lubrication films on real rough surfaces in mechanical contacts; the applied methodology is based on Fourier analysis of the harmonic components of the surface microgeometry to predict stresses and the induced lubricant film.

Continuum models depend on the availability of material parameters suitable for describing the behaviour of the bulk material, and in RoliCer they are partially provided through electronic and atomistic simulations. These include the elastic constants, physical and mechanical properties of the materials involved.

First, an electronic model based on <u>density functional theory (DFT)</u> calculations will be conducted to investigate the adhesion of relevant metal-ceramic interfaces, and internal grain boundaries. The adhesion energy will provide direct information on the tribological aspects which relate to the degradation mechanisms. Additionally, the influence of the environment on the degradation mechanisms will be investigated. This will be achieved by considering the effects of impurities and point defects on the bonding and structure of both metal-ceramic interfaces and grain boundaries. The main assumption here is that impurities are correlated with the environment, such as (i) temperature, which enhances the diffusion and leads, for example, to higher concentration of point defects; (ii) foreign impurities originating from the metal or lubricant. As a result, the role of DFT calculations will be twofold: to investigate the correlation between the interface structure, point defects and adhesion and to provide input to the microscale simulations through constitutive equations, hence enabling the simulation of realistic working conditions.

The second atomistic method describes the interactions between atoms with semi-empirical potentials, which allow performing large-scale <u>molecular dynamics</u> and static relaxation. Such methods can be used to study large scale defect structures in the ceramics, such as dislocations and general incoherent grain boundary models. The effect of temperature, or thermal stresses will be studied large-scale molecular dynamics and static relaxation; two distinct approaches will be tackled, by inducing large thermal gradients, or via coupling to statistical physics (fluctuation-dissipation theorem) where one can estimate via statistical mechanics the rate of <u>thermal transport</u>, and its effect on the degradation of the materials, for example, through the interaction of dislocations and phonons (which are the means by which the thermal energy is transported in the system). The initiation and propagation of cracks will be investigated efficiently using molecular dynamics and static (relaxation of atomic positions at absolute zero temperature) simulation techniques. Such simulations require reliable interatomic potentials. <u>Constitutive equations</u> will also be derived from the results of the interatomic potentials, which would have the advantage of dealing with incoherent interface models, and take temperature effects into account as well.

http://www.rolicer.eu

Project Acronym and Number: ROLICER 263476 Project Title: Enhanced reliability and lifetime of ceramic components through multiscale modelling of degradation and damage Start and End Dates: 01/12/2011 till 30/11/2014 EU Contribution: 2.600.000 € Coordinator: Andreas Kailer, Fraunhofer Institute for Mechanics of Materials IWM, Germany andreas.kailer@iwm.fraunhofer.de



in ROMEO 309729

Subject of the modelling

Magnetic material with reduced content of critical raw materials

Models used

Electronic: <u>spin-polarized</u> <u>density</u> <u>functional</u> <u>theory</u> to predict new phases that exhibit ferromagnetism and to compute the magneto-crystalline anisotropy as function lattice constant in permanent magnetic materials

Mesoscopic: <u>micromagnetics dynamic models</u> based on Landau-Lifshitz-Gilbert equation to calculate magnetization reversal in permanent magnets as function of microstructure and intrinsic magnetic properties

Simulation software and type of numerics used

Ab-intio packages VASP and WIEN2K for spin-polarized density functional calculations Micromagnetic software FEMME for the calculation of magnetization reversal Hybrid boundary element / finite element method for micromagnetic simulations

Achievements of the model beyond experiments

Fast database screening combined with spin-polarized density functional theory can be used to find candidate materials for new permanent magnets and this saves a huge amount of time.

Application

Permanent magnetic stuctures for energy automotive and wind power applications

Relevant review articles covering the topic (not necessarily their own):

Schrefl, Thomas, Gino Hrkac, Simon Bance, Dieter Suess, Otmar Ertl, and Josef Fidler. 2007. "Numerical Methods in Micromagnetics (Finite Element Method)." In *Handbook of Magnetism and Advanced Magnetic Materials*. Helmut Kronmüller, Stuart Parkin (eds) John Wiley & Sons, Ltd.

Summary of project

Currently, magnets are based on the rare earth elements neodymium and dysprosium, which are predominantly mined in China (>95%). ROMEO targets to remove, or greatly reduce, the need for heavy rare earths in permanent magnets, by developing several novel microstructural-engineering strategies that will dramatically improve the properties of magnets based purely on light rare earths elements, especially the coercivity, which will enable them to be used for applications above 100°C. ROMEO's second goal is to develop a totally rare-earth-free magnet.

Summary of the modelling

Inter-granular phases of sintered RareEarth-TransitionMetal-Boron magnets create a lattice distortion in the hard magnetic grains. The role of the specific structural distortion near grain boundaries on the magneto-crystalline anisotropy and magnetization will be determined by means of first principles <u>DFT</u> calculations using the WIEN2K package. The project will perform ab-initio calculations of the magnetic properties of Pr2Fe14B, Nd2Fe14B and tetragonally-distorted tetragonally distorted FeCo-compounds. The computed intrinsic magnetic properties (magnetization and anisotropy) serve as input for mesoscopic simulations.

Using non-zero temperature <u>micromagnetics</u> based on the elastic band method. The project computes the influence of the local change of intrinsic magnetic properties near grain-boundaries in grain-boundary engineered magnets. The minimum required thickness of the layer that contains heavy-rare-earths will be computed. Magnetic properties will be computed as a function of grain size. Magnets containing a grain boundary phase that is anti-ferromagnetically coupled to the main phase may lead to high coercive field at the expense of remanent magnetization. The optimal structure (grain size versus boundary phase thickness) with respect to specific requirements of key applications (EV, HEV, wind power) will be searched for using numerical optimisation techniques combined with micromagnetic simulations The results will be compared with temperature dependent measurements of the coercive field..

Analytical expressions will be sought for the relations between parameters and results. Micromagnetic and global relations between the coercive field and the activation volume will be compared to find analytical relations expressing the role of various structural and physical parameters. The relation expressing the coercive field for different superferrimagnetic structures (for example Nd₂Fe₁₄B in a GdFe₂ matrix) and nanostructures will be used to find an optimum solution. The relations will be compared with experimental data.

First a database will be created of electronic structures of 50,000 existing and new Heuslers by performing spin-polarized DFT calculations for prototype compositions. This will be used in a search for materials exhibiting specific intrinsic properties such as magnetization and anisotropy with a ground-state crystal structure which is uni-axially distorted (tetragonal). The experimental data will be used to develop the database and to improve the predictive power.

http://www.romeo-fp7.eu/

Project Acronym and Number: ROMEO 309729 Project Title: Replacement and Original Magnet Engineering Options Start and End Dates: 01/12/2012 – 30/11/2015 EU Contribution: 3.977.500 € Coordinator: Prof. Dr. Spomenka Kobe, Jožef Stefan Institute, Slovenia <u>spomenka.kobe@ijs.si</u>



in SIMBA 229034

Subject of the modelling

Synthesis of silicon nanopowders in Inductively Coupled Plasma (ICP) systems

Models used

Atomistic: <u>statistical mechanics transport model</u> (kinetic gas equation) for plasma thermodynamic and transport properties

Continuum: <u>Computational Fluid-Dynamics</u> (CFD) for plasma physics, precursor evaporation and nanopowder transport and growth

Simulation software and type of numerics used

Commercial CFD code ANSYS FLUENT extended to take into account plasma physics, precursor evaporation and nanopowder synthesis.

Numerical routines written in C for the Chapman-Enskog method to solve the Boltzmann kinetic gas equation

Achievements of the model beyond experiments

The modelling of the plasma flow dynamics and particle trajectories permitted to define the process at different scales and to predict the influences of the main process parameters (e.g. effects on nanopowder production yield when changing the reactor geometry and operating conditions).

The model enabled the design of an optimum reactor chamber with increased flow of particles for collection thus avoiding an expensive try-and-fail approach, and saving time and effort in optimising the lab scale process and in transferring main results to an industrial ICP installation.

Application

Production of anode material (nano-silicon based) for Li-Ion battery and photovoltaic applications

Relevant review articles

Colombo V et alii, Journal of Physics D: Applied Physics 42 (5), 2009

Colombo V et alii, Plasma Sources Sci. Technol. 19 (2010) 065024

Colombo V et alii, J. Phys. D: Appl. Phys. 43, 105202 - 105214 (2010).

Colombo V et alii, IEEE Trans. Plasma Sci, 6th Triennial Special Issue on Images in Plasma Science, 2011.

Colombo V et alii, Plasma Sources Sci. Technol. 21, 025001 (2012)

The project SIMBA addresses the upscaling of synthesis of metallic nanoparticles with the Inductively Coupled Plasma (ICP) technique. This project developed an industrial production line including on-line monitoring systems for silicon and silicon-based alloyed nanoparticles, which can be applied as anode material in battery applications. It included an on-line functionalisation technique and an industrial powder injection system to ensure a continuous production.

Summary of the modelling

An advanced <u>CFD</u> model FLUENT (including electromagnetics, non-LongTermEvolution effects, chemical non equilibrium, turbulence models, discrete-phase model with plasma-particle interaction, plasma thermodynamic and transport properties) was used in SIMBA. This code uses parallel computing, and is capable of capturing the fine geometric details. The existing model can predict temperature and flow fields of different plasma mixtures of a variety of gases together with injected particle temperature and trajectory prediction. This model for plasma fluid-dynamics has been extended to simulate non-equilibrium plasma (low pressure operating conditions and the strong temperature gradients due to the quenching system) and for the nanopowder nucleation out of the gas phase (aerosol model to track the particle size-distribution and particle population in the reactor region and to calculate process yield). This model for the precursor particle thermal history and trajectory prediction is using a Lagrangian approach for continuum <u>CFD</u> methods. The first order perturbation solution of the **Boltzmann kinetic equation**, i.e. the Chapman Enskog method, has been used for the calculation of the transport properties of SIMBA gas mixtures. The model is applied to the actual lab-scale Empa reactor (plasma torch and reaction chamber) and has been proven to calculate temperature, velocity, viscosity profiles of plasma flow in the whole system. The model has been validated through comparison with enthalpy probe measurements of temperature under different operating conditions and calorimetric measurements for energy balance of the plasma system. The computational effort of this calculations is reduced by a) limiting the computational domain to the most important regions of the reaction chamber (e.g.: the quenching zone); b) decoupling the plasma torch with the reaction chamber domain, using the calculated plasma torch outflow fields (temperature, velocity, concentration, ...) as boundary condition for the reaction chamber.

The model has allowed a design-oriented modelling approach to optimize the lab scale process and then to transfer main results to an industrial ICP installation.

www.simba-project.eu

Project Acronym and Number: SIMBA 229034 Project Title: Scaling-up of Inductively Coupled Plasma technology for continuous production of Metallic nanopowders for Battery Applications Start and End Dates: 01/9/2009 till 01/08/2012 EU Contribution: 2.869.275 € Coordinator: Stijn Put, Umicore, BE, stijn.put@umicore.com



in SIMUGLASS 233524

Subject of the modelling

Precision glass moulding

Models used

Continuum: <u>CFD</u> for Laminar flow of ideal gas (protection gas): Navier–Stokes equations (continuum equation, momentum equation and thermal equation), for conduction, convection, radiation <u>Mechanics model</u>s: Elastic model (for mould) and visco-elastic models (for glass) Thermo-rheologically model for viscoelastic material based on Kelvin equation, Burgers equation, Newton's fluid, WLF shift function, Narayanaswamy equation

Simulation software and type of numerics used

ABAQUS, ANSYS (Finite Element codes) Transient solving, implicit method

Achievements of the model beyond experiments

Shape of moulds can be now predicted with the help of modelling of the glass shrinkages, which had to be done previously by expensive try-out experiments.

Index drop inside glass lens can be now predicted with the help of modelling of the structure relaxation behaviour of glass material, which was unknown only by pure experiments. Material flow and temperature during forming process can be predicted, which can not be observed and measured in the real moulding process.

Application

Optics for lighting and photovoltaic Optics for imaging Optics for laser apparatus

Relevant review articles

O. Dambon, F. Wang, Y. Chen, A. Y. Yi, F. Klocke, G. Pongs, "Efficient Mould Manufacturing for Precision Glass Moulding," J. Vac. Sci Technol. B, 27 (3), 1445-1449 (2009). A. Jain, A. Y. Yi, X. Xie, R. Sooryakumar, "Finite Element Modeling of Stress Relaxation in Glass Lens Moulding Using Measured, Temperature-Dependent Elastic Modulus and Viscosity Data of Glass," Model Simul Mater SC, 14 (3), 465-477, Mar (2006).

This project has developed a FEM-tool for material modelling, process simulation and optimization of optical glass moulding. The relevant thermal, mechanical, rheological and optical glass material properties and their dependence on the moulding parameters (forming velocity, temperature, force, etc.) were investigated.

Summary of the modelling

The simulation of hot glass deformation is a complex thermo-mechanical problem comprising interactions between radiative/conductive thermal transport phenomena, incompressible, viscous fluid dynamics of softened glass and the large strain/large displacement visco-elastic/visco-plastic deformation of glass due to pressing in the mould. Some of the important issues to be addressed by modelling are (a) large free surface deformations (b) complex contact phenomenon (c) high deformation rate (d) time and temperature dependent boundary conditions and (e) high degree of material non-linearity

The project has developed a generalized simulation tool covering the whole cycle of glass moulding for the whole relevant temperature range incl. newly developed glass material models.

The <u>micromechanics</u> code is based on the commercial packages MARC, DEFORM 3D, FIDAP, POLYFLOW, SYSTUS, ANSYS, ABAQUS, and LS-DYNA. The project developed a <u>CFD model</u> for the behaviour of the laminar flow of the protection gas, which is usually nitrogen gas. Such protection gas is used only not to prevent the heated glass material from being oxidised, but also to help the heat flow convect more efficiently inside the machine chamber. This is used to determine the thermal boundary conditions for the FEM model of the glass forming process. New glass material model for the thermo-rheologically viscoelastic material behaviour, which occurs in the moulding process, is developed based on existing models like Hooks, Maxwell, Kelvin, Burgers fluid, Newton's viscosity materials model, in which the strain rate and time dependency is considered.

The result is a complete process simulation including structural and thermal analysis, which covers all the important procedures during the moulding process: heating, soaking, moulding, holding and cooling.

www.simuglass.com

Project Acronym and Number: SIMUGLASS 233524 Project Title: Development of a Synergistic Computational Tool for Material Modeling, Process Simulation and Optimization of Optical Glass Moulding Start and End Dates: 01/01/2010 till 31/12/2013 EU Contribution: 899.994 € Coordinator: Dr. Olaf Dambon, Fraunhofer Institute for Production Technology IPT, olaf.dambon@ipt.fraunhofer.de



in SMASH 228999

Subject of the modelling

GaN nanocolumn LEDs

Models used

Electronic:

Quantum mechanical models for eigenstates of confined particles in nanostructures in continuous medium (EFA k·p) and empirical tight-binding level Statistical mechanics based electron and hole transport models Continuum: EM models for optical properties

Simulation software and type of numerics used

TiberCAD for strain/electronic modeling QUATRA/CELS for luminescence modelling OptiWave for electromagnetic properties Numerical libraries, such as portable extensible toolkit for scientific computation and scalable library for eigenvalue problem computations (PETSc, SLEPc)

Achievements of the model beyond experiments

The modelling and simulation of GaN-based LEDs is able to guide the device design, by optimizing strain, polarization and quantum effects in order to improve the performance of the devices. Atomistic simulations can shed light on the effect of clustering in the alloy active regions.

Application

LEDs

Relevant review articles

Auf der Mau, M et al; IEEE TRANSACTIONS ON ELECTRON DEVICES, Vol. 58, No. 5, May2011, overview on the multi-scale approach is given, and on what is essential to simulate the growth and the electro-optic properties of nanowires.

The project SMASH has developed LEDs of high efficiency and low cost. An epitaxial growth technique based on nano-rod coalescence on ultra-low defect density templates has been realised. Also growth of directly emitting Gallium Nitride based nano-rod structures has been developed. High efficiency devices covering the entire visible spectrum and phosphor-free white LEDs have been manufactured.

Summary of the modelling

The multiscale simulation tool TiberCAD includes all the relevant physical models, at electronic, atomistic and continuous level, for the investigation of strain, transport and optoelectronic properties of GaN nanocolumn structures.

The calculation of strain in lattice mismatched heterostructures is based on <u>linear elasticity theory of solids</u>, assuming pseudomorphic interfaces between different materials.

Transport of electrons and holes is treated in a semi-classical picture based on the <u>drift-diffusion model</u>. The particle fluxes are written in terms of the electrochemical potentials. The carrier statistics are given by Boltzmann or Fermi-Dirac statistics, assuming as usual local equilibrium. The conduction and valence band edges and effective masses are obtained from bulk <u>k.p calculations</u>, which include the local corrections due to strain. Quantum mechanical models used for the calculation of eigenstates of confined particles in nanostructures, are based on the <u>envelope function approximation</u> (EFA) and on <u>the empirical tight binding</u> (<u>ETB</u>) model. In the first case, the Hamiltonian of the system is constructed in the framework of single-band and multiband k.p theory. The ETB method is an atomistic approach where electron and hole states of the QD states are written as a linear combination of atomic orbitals (LCAO). Self consistent band profiles have been calculated by concurrently solving the Poisson/drift-diffusion and the quantum mechanical models. Carrier capture and escape in and out of the well is described with a combination of a drift-diffusion model in the contact region and more sophisticated quantum description in the region close to the quantum well is used. The atomistic structure, which is needed for ETB calculations, is generated internally in TiberCAD according to the macroscopic device description and crystallographic orientation.

Strain maps and the effects of strain, piezo and spontaneous polarizations, as well as surface states, on band profiles have been studied in GaN nanocolumn p-i-n diode structures with different active regions, such as Quantum Disk (QD) and Core Shell.

Electroluminescence spectra are obtained with a custom developed quantum kinetic model (CELS/QUATRA). Optical properties of nanorods, in particular the extraction efficiency, emission directionality and polarization, are calculated with the <u>electromagnetic</u> simulation tool OptiWave. Optical emission spectra and the dependence of transition energies on geometrical and material parameters have been found. The microscopic complex refractive index is taken as input, as well as the different absorption by metals and semiconductors. The wave guiding properties of a single nanorod, as well as the electromagnetic coupling of the rod arrays forming a collective photonic crystal emitter or bottom distributed reflector are investigated, and an optimum design is developed.

Coupled electro-optical properties in a LED device are studied by applying a combination of the described above. Exciton and carrier distributions, polarization states of emitted photons, radiation characteristics are calculated also by finite element tools FDmax and CELS/QUATRA. Finally, key device specifications such as the internal and external efficiency of nanorods in LED geometries are simulated and structure parameters for an optimized LED performance are determined. In particular, the design for phosphor-free white light emitting devices is optimized, which is crucial to meet specific colour coordinates. The model results have been used as input to adjust epitaxial growth conditions and stamp design.

www.smash-fp7.eu

Project Acronym and Number: SMASH 228999 Project Title: Smart Nanostructured Semiconductors for Energy-Saving Light Solutions Start and End Dates: 01/09/2009 till 31/8/2012 EC Contribution: 8.299.360 € Coordinator: Martin Strassburg, OSRAM Opto Semiconductors GmbH, DE, <u>martin.strassburg@osram-os.com</u>



in SOLARDESIGN 310220

Subject of the modelling

Solar cells (flexible thin film $Cu(In,Ga)(S,Se)_2$)

Models used

Electronic: <u>quantum mechanics</u>, <u>electronic transport</u> Atomistic: <u>Monte Carlo simulation</u> Continuum: <u>electrical</u>, <u>thermal</u> and <u>mechanical modelling</u> of the device Continuum: <u>fabrication process modelling</u>

Simulation software and type of numerics used

Electronic and atomistic: TCAD for charge generation and transport Modelling of manufacturing processes and computing mechanical stress with TCAD SENTAURUS PROCESS

Electrical, thermal and optical modelling with TCAD SENTAURUS DEVICE for the device behavior Different optical solvers will be used to handle light propagation and absorption (e.g. transfer matrix method, ray tracing, beam propagation method, but also solution of the Maxwell's wave equation using with the Finite-Difference Time-Domain method (FDTD).

Achievements of the model beyond experiments

The methodological toolbox provides design rules for the best $Cu(In,Ga)(S,Se)_2$ solar cell superstructure and module design layout for a given application reducing significantly the number of experimental trials and reducing costs. Models are used to correlate the impact of process variation to parametric yield, thereby lowering production costs, as well as the geometrical design of the solar module in order to meet the custom product requirements.

Application

Custom designed thin film Cu(In,Ga)(S,Se)₂ solar cells for energy harvesting in buildings, products and textiles.

Relevant review articles

- U. Malm, M. Edoff, 2D device modelling and finite element simulations for thin-film solar cells, Solar Energy Materials & Solar Cells 93 (2009) 1066–1069
 Joar Johansson, Modelling and Optimization of CIGS Solar Cell Modules, Master's Thesis, Lunds
- universitet, 2008 - M. Lee, D. Pramanik, H. Liang, E. Korczynski, J. van Duren, Optimization of Graded CIGS Solar Cells Using TCAD Simulations, MRS Proceedings, Volume 1447 / 2012,

DOI: http://dx.doi.org/10.1557/opl.2012.1167

- J.Malmström, On Generation and Recombination in Cu(In, Ga)Se2 Thin-Film SolarCells, PhD Thesis, ppsalaUniversity,2005

URL: http:// www.diva-portal.org/diva/getDocument?urn_nbn_se_uu_diva-5721-1__fulltext. pdf

 J. Lähnemann, Spectrally Resolved Current Losses in Cu(In,Ga)Se2 Thin-film Solar Cells, Diploma Thesis at the Freie Universit at Berlin carried out at the Institut des Materiaux Jean Rouxel /Universit e de Nantes, France, 2008

Summary of project

SolarDesign has the goal to deliver innovative and cost-effective custom designed solar cell prototypes suitable for the integration into building skins, roof tiles or electric devices. The aim is to obtain new custom designed systems for decentralized solar power generation ranging from low- to high power applications.

For these applications the solar cells need to be flexible and obey certain electrical constraints. This project is developing interconnection of thin- film solar cells created with a simplified production process of thin-film modules that allows adjustment the specifications of a PV module "on-the-fly" without excessive set-up times.

Summary of the modelling

Simulations will provide a detailed physical description of the new solar cells operation, allowing researchers, designers and architects to explore new cell/module concepts and meet specific requirements as well as to optimize current fabrication technologies.

SolarDesign will use an advanced multiscale device (TCAD) simulator capable of simulating electrical, thermal, and optical characteristics of CIGS solar cells/modules, for development and optimization of their performance.

TCAD 1D <u>QM electronic simulations</u> for small geometries in SolarDesign will provide insights into the physical mechanisms affecting charge transport within the solar cell such as optical generation, surface and bulk recombination processes, grain boundary effects, contact design, and interconnect losses, texturing. These quantum effects will be included in continuum models.

<u>Process simulation</u> TCAD SENTAURUS PROCESS will deal with modelling (2D- or 3D-) of the fabrication steps of solar cells/modules, like e.g. different types of depositions, etching, oxidation, diffusion, and implementation of models for custom solar cell processes. The <u>mechanical models</u> (particularly doping and material growth) are either based on basic diffusion equations or an analytic Gaussian solution is assumed. Process conditions like the ambient chemical composition, pressure, temperature etc. during individual fabrication steps can be implemented in the model. The simulation tool will allow the researcher to select parameters to be investigated and visualize the influence of each parameter, as well as to compute the influence of mechanical stresses in PV cells.

The <u>continuum electrical models</u> are based on Poisson and continuity equation together with the material relations and a carrier transport model (either electronic <u>drift-diffusion</u>, atomistic <u>Monte</u> <u>Carlo</u> or continuum <u>hydrodynamics</u>). The material properties are given by the carrier mobilities, the susceptibility and eventually the band structure from the electronic modeling. The project will explore solar cell/module design alternatives in order to meet the performance goals. The model will simulate dark and light I-V curves, internal and external quantum efficiency, fill factor and other key cell performance attributes using monochromatic, and standard solar spectra (e.g. AM1.5g) as well as other illumination spectra (indoor applications).

The project will use the electrical <u>device design</u> code TCAD SENTAURUS DEVICE in a customized approach. The simulation tool will support mixed-mode simulations, combining numerical simulations and lumped circuit elements to analyze, for example, resistive losses in the metallisation and will allow exploring different device designs.

http://www.solar-design.eu/

Project Acronym and Number: SolarDesign, 310220 Project Title: On-the-fly alterable thin-film solar modules for design driven applications Start and End Dates: 01/01/2013 till 31/12/2015 EU Contribution: 2.716.423 € Coordinator: Dr. Nadja Adamovic, Vienna University of Technology, Austria, <u>nadja.adamovic@tuwien.ac.at</u>



in SSEEC 214864

Subject of the modelling

Magnetic materials, micromagnetism, magnetic cooling engines

Models used

Electronic: Ab initio <u>DFT</u> models of non-collinear magnetic material groundstates (electronic quantum mechanical models using 10s of atoms)

Mesoscopic: <u>Micromagnetic</u> (mesocale) models, including exchange-coupled nanocomposites (1-10 nm)

Continuum: modelling of materials including conductive and convective <u>heat flow equations</u>, <u>Maxwell equations</u> and <u>fluid dynamics equations</u> and <u>magnetic cooling engine modelling</u>

Simulation software and type of numerics used

Ab initio DFT models: OpenMX (http://www.openmx-square.org/) and VASP (http://www.vasp.at/). Site-based magnetic moments were calculated using the Voskown analysis within the general gradient approximation scheme.

Preisach model of hysteresis: original C++ code written and solved in-house.

Micromagnetics: Free energy of a magnetic solid, solved using in-house C++ code.

Magnetic cooling engine prototypes: COMSOL Multiphysics, Matlab, Mathematica. Finite element and analytical treatments were used. The entropy generation method was developed for efficiency analysis.

Achievements of the model beyond experiments

The materials modelling gave us invaluable feedback on experimental development, reducing the time that would otherwise be required to make multiple measurements or a full phase space of physical samples.

Regarding the cooling engines, the 2D model of an active magnetic regenerator (AMR) enabled accurate optimisation of geometry (packing density, absolute length scales), system operating parameters (frequency, flow rate) and identification of optimal (or ideal) refrigerant material properties (magnetocaloric effect and heat capacity) against overall efficiency and power requirements.

Application

Magnetic materials, manufacturing industry, magnetic cooling engines

Relevant review articles

The papers containing the DFT work are: Barcza, Gercsi, Knight and Sandeman, Phys. Rev. Lett. **104** 247202 (2010) Gercsi and Sandeman, Phys. Rev. B. **81**, 224426 (2010) Gercsi, Hono and Sandeman, Phys. Rev. B. **83**, 174403 (2011) Micromagnetics: Basso, J. Phys. Condens. Matt. **23** 226004 (2011). Reviews: "Gas-free refrigeration" K.G. Sandeman, Magnetics Technology International, **1** 30 (2011); "Magnetocaloric materials: the search for new systems" K.G. Sandeman, Scripta Materalia **67** 566-571 (2012)

The ultimate goal of this project was to lower the economic barrier to entry of magnetic cooling as a high efficiency cooling technology free from greenhouse gas refrigerants. SSEEC's efforts in this direction centred around the development of a low power heat pump based on a highly efficient magnetic refrigeration cycle. The device features a magnetic refrigerant that is magnetised and demagnetised by movement relative to a permanent magnet. The core materials research concerned the identification, synthesis, modelling and production of low cost, environmentally friendly magnetic refrigerant materials based on new (nano)-architectures.

Summary of the modelling

SSEEC aimed to develop an integrated approach to magnetic cooling for an end-user application. This entailed characterisation of materials, integration of those into prototype cooling engines, and integration of those engines into an end-user (heat pump) system. The modelling work examined magnetic refrigerants (novel physical mechanisms of magnetic cooling) and magnetic cooling engines (an integrated view of the impact of design on cost and performance).

Magnetic refrigerants: <u>DFT</u> models were used to calculate site-based magnetic moments using the Voskown analysis within the general gradient approximation scheme. Giant magneto-elastic coupling in CoMnSi (a metamagnetic refrigerant material) and thereby the dependence of magnetism on Mn-Mn interatomic distance in Mn-based materials of the same structure (*Pnma* space group) was modelled as it can be used to understand and control magnetic phase transitions. This modelling led to predictive synthesis of new metamagnets. The exchange coupling between the phases in the composite material was calculated (note this is at nano-scale).

The phenomelogical Preisach model of hysteresis (irreversibility) was applied for phase transformations at the mesoscale. It was found that the entropic, or cooling effect of a nano-scale spin reorientation-based refrigerant is diluted by any amount of second, exchange-coupled phase, and that, for the oxide systems synthesised, retention of a single phase is more desirable. However, for other systems a second phase could be of use in broadening the temperature range of use of a candidate refrigerant.

<u>Micromagnetics models</u> used exchange couplings, dependent on composite geometry, as an input. First the effect of mixing a spin reorientation material with a ferromagnet in a nano-composite in which the constituent phases were exchange coupled was modelled. It was demonstrated that the total entropy change of the composite was reduced, but spread over a wider temperature range. Secondly a nano-scale magnetic heterostructure comprised of two different hard magnetic materials with orthogonal axes of unaxial anisotropy was designed and proved to function as a theoretical anisotropy switch, the optimal dimensions of which were determined by the composition of each layer.

<u>Magnetic cooling engines</u>: different cooling cycles were modelled using "real" magnetic materials that have magnetic phase transitions (required for magnetic cooling) which exhibit magnetic hysteresis (a source of loss). Experimental data were used to generate a detailed picture of the magnetic cooling effect of La-Fe-Si when deployed in a relevant, "regenerative" cooling cycle. Cooling engine modelling underpinned a comprehensive design approach for the development of magnetic cooling engine prototypes as well as optimising the design of individual components. The model couples the different aspects at work within a magnetic cooling engine: <u>heat transfer</u>, <u>fluid flow</u>, <u>magnetic fields and loss processes</u>, and uses the material properties calculated with DFT as input. Over 100 magnet designs were examined and tuned, valves were optimised for flow, pressure drops and flow rates, and magnetic forces inside the cooling engine (both regenerators and magnetic valves) were optimised. Accurate optimisation of an overall system design that can meet the power, weight, span, volume and cost targets needed for a commercial system was achieved.

http://www.sseec.eu

Project Acronym and Number: SSEEC 214864 Project Title: Solid State Energy Efficient Cooling Start and End Dates: 1/12/2008 till 31/11/2011 EC Contribution: 1.885.534 € Coordinator: Karl G. Sandeman Imperial College London UK <u>k.sandeman@imperial.ac.uk</u>



in SUPER-IRON 283204

Subject of the modelling

Physical properties of iron-pnictides superconductors (spin susceptibility and effective electronelectron interaction) in superlattices, thin-films, interfaces, grain or twin boundaries

Models

Electronic: Various <u>Density Functional</u> implementation and <u>effective tight binding model</u> Bogoliubov-de Gennes model for the superconducting and magnetic phases

Simulation software and type of numerics used

All-electron codes (Fleur, Elk and FLAPW)
Plane-waves implementations (VASP, Quantum-Espresso)
Local basis, linear scaling DFT codes (Siesta, OpenMX)
The DFT implementations are all stable, optimized, parallelized and highly maintained codes. They are mainly based on complex matrix manipulations and Fast Fourier Transform operations.
Specific developed software will be based on iterative matrix diagonalization and many-body multiband Hamiltonian solution.

Achievements of the modelling beyond experiments

Prediction of high-pressure phase transitions in $Ba(Ca)Fe_2As_2$ and of non-hydrostatic effect, confirmed by high-pressure XRD measurements

Prediction of the peculiar structural and electronic modification upon doping with rare-earth metals in $CaFe_2As_2$

Understanding of disorder, surface and interface effects

Model calculations, joined with DFT calculations, were able to predict a tri-critical point in the phase diagram of iron-pnictides, now a hot subject for experimental confirmation

Application

Non-conventional iron-based superconductors systems

Relevant review articles

M.Putti, et al., "New Fe-based superconductors: properties relevant for applications" Supercond. Sci. Technol. **23** (2010) 034003

K. Tanabe and H. Hosono "Frontiers of Research on Iron-Based Superconductors toward Their Application" Japanese Journal of Applied Physics **51** (2012) 010005

G. R. Stewart "Superconductivity in iron compounds" Reviews of Modern Physics, 83 (2011) 1589

Summary of project

The topic is to investigate Fe-based superconductors characterized by FeAs (or FeSe) planes separated by different layers. Among these compounds there are the so called 1111 phase (represented by the LaFeAsO), the 122 (BaFe₂As₂), the 111 (LiFeAs) and the 11 (FeSe) phases as well as the new pnictide oxide superconductors intercalated by oxides blocking layers. Superconducting properties will be investigated also under high magnetic field and/or pressure and visualization of local electric field and current will be carried out with a number of techniques. SUPERIRON will then depict the roadmap for exploring and exploiting the potentialities of Fe-based superconductors (FeSC).

Summary of the modelling

SUPER-IRON will use models to predict structural, electronic and superconducting properties of interfaces in FeSCs. In particular, they will study: single crystal properties (superlattices), the interface between two layers of the same material but with differently oriented crystalline axes and properties of interfaces between two different materials (blocking layers, superconductor/metal interface).

Bulk samples of single crystals will be simulated with parameter free first-principles simulations (<u>Density Functional Theory, DFT</u>). The effect of substitutions, various kinds of defects and applied pressure on the structural, electronic, magnetic and superconducting properties of FeAs superconductors will be investigated. This will provide input parameters for multiband analyses of superconducting and normal state properties.

Interface properties will be simulated by first-principles structural models. The study will address layers with misoriented crystalline axes, the stability and energetics of thin film geometry and superlattices formed by different layers of various FeAs superconductors. Lattice mismatch, uni-axial pressure effects, interface and surface states will be investigated.

Also the possibility of incorporating perovskite and metal blocking layers intercalated with FeAs planes will be studied. The structural stability of the terminations, defect formations and their effect on the electronic, magnetic and superconducting properties will be predicted.

The interplay of temperature and pressure, structural and magnetic transition will be studied by Landau theory developed from <u>ab-initio calculations</u> fully taking into account the effect of the crystalline structure.

<u>Effective tight-binding Hamiltonians</u> will be constructed starting from first-principles to describe the electronic properties of defects, superlattices and grain boundaries and simulate the superconducting properties (Jc, Hc, Tc) by means of Bogoliubov-De Gennes equations. This will give information on the superconducting properties: order parameters in real space across the boundary, superconducting current flow at the boundary and critical currents (Jc^o and how the superconducting properties of FeSCs are affected by the mis-orientation angle will be predicted. First-principles models of effective interactions between electrons, including spin fluctuations, will be elaborated to provide fundamental information on the superconducting properties will be done extending the ab-initio SuperConducting Density Functional Theory with electronic pairing interactions.

A different crystallographic orientation of the grains and different properties of the grain boundaries result in a strongly inhomogeneous current flow. A model, based on an approach for percolation in MgB₂, will be developed, which predicts loss-free macroscopic currents.

http://www.super-iron.eu/

Project Acronym and Number: SUPER-IRON 283204 Project Title: Exploring the potential of iron-based superconductors Start and End Dates: 01/10/2011 till 30/09/2014 EU Contribution: 1.725.659 € Coordinator: Marina Putti, CNR-SPIN, <u>putti@fisica.unige.it</u>



in SUPERLION 214832

Subject of the modelling

Nano-architectured battery materials and 3D microbattery components

Models used

Atomistic: <u>Molecular Dynamics (MD)</u> for electrochemical phenomena for material/battery/production process optimisation Mesoscopic: <u>Lattice Gas Model</u> for charge and mass transport Continuum: <u>Fluid dynamics</u> and <u>electrochemical modelling</u>

Simulation software and type of numerics used

COMSOL multiphysics for the flow and electrochemical phenomena DL_POLY for MD MCGEN for nanoscale battery architecture

Achievements of the model beyond experiments

The model allowed shortened and better-informed selection of the most efficient cell architectures and geometries, and the optimal cell materials. Modelling can avoid excessive and often futile efforts to create more impressive micro-architectured electrodes, since these will often not result in improved battery performance.

Application

On board microbatteries for electronic and medical devices

Relevant review articles

Kasemägi et al., Solid State Ionics, 168 (2004) 249 Brandell et al., J. Mater. Chem., 15 (2005) 4338 Thomas et al., ECS Meeting Abstracts, Los Angeles, Oct. 2005 Thomas et al., Modelling studies of 3D-Microbatteries, IMLB-13, Biarritz, May 2006 Liivat et al., Polymer, doi: 10.1016/j.polymer.2007.08.05 Liivat et al., J. Mater. Chem., doi:10.1039/b706938c

The project SUPERLION has contributed to improved materials synthesis, and the design and fabrication of novel 3D nano-architectured microbattery components.

Summary of the modelling

<u>Molecular Dynamics (MD)</u> modelling of branched PE/PEO as a host matrix for Li-ion battery electrolytes, and electrochemical and transport modelling with Finite Element (FE) modelling is made of the individual materials considered for relevant battery architectures and geometries.

<u>Electrochemical system modelling</u> (with the code Comsol) has provided new and invaluable insights into the optimal device configurations, given the technological and materials limitations. A first approach exploiting <u>Newmann theory</u> has simulated the porous electrodes in prospective micro-scale Li-ion batteries and has given current-voltage relationships for the complete 3D-MB device. This work has provided valuable input for material/battery/production process optimisation.

This approach has been accompanied by simulation of charge and mass transfer in the 3D-MB structures. The description of equilibrium potential of the electrode material has been based on <u>the Lattice Gas Model</u> with COMSOL. Diffusion of Li ions inside the electrode material is simulated by numerically solving the relevant diffusion equations for appropriate geometries. Simulation of electrolyte phenomena has been made by applying the Nernst-Planck approximation.

Simulations of complete 3D-MB geometries are done at both an atomic- and continuum-level to better understand the underlying reasons for critical current distributions within micro-/nanomicro-battery systems. Work at both levels is needed in understanding the basic functionality/design relationships in 3D micro- and nanoscale battery architectures. DL_POLY is the software codes used for atomic-scale polymer Molecular Dynamics and MCGEN and COMSOL are used for FEA modelling of 3D-microbattery architectures.

SUPERLION investigated a link between MD and a continuum mechanical model but the statistics in the MD did not contain enough ion jumps to be able to extract meaningful classical ion diffusion constants (D). The runs were exceptionally long - up to 6 months (shared time) on a "supercomputer" and the models contained up to 50 000 atoms - but nevertheless "MD boxsizes" and run-times were still too small/short to accumulate enough "ion-jump events".

www.superlion.eu

Project Acronym and Number: SUPERLION 214832 Project Title: Superior Energy and Power Density Li-Ion Microbatteries Start and End Dates: 01/9/2008 till 31/08/2011 EU Contribution: 2.800.000 € Coordinator: Josh Thomas, Dept. of Chemistry, Uppsala University, Sweden, <u>Josh.Thomas@kemi.uu.se</u>



in SURFUNCELL 214653

Subject of the modelling

Adsorption phenomena at the interface of cellulose surfaces

Models used

Electronic: <u>DFT</u> for hydrogen bonding and dispersion interaction between cellobiose and glucose

Coupled-Cluster electronic calculations

Atomistic: Molecular Mechanics for cellulose/water interface with molecular mechanics using the GLYCAM06 <u>force field</u>

Mesoscopic: <u>Coarse grained grid-based model</u> of the interaction of nanoparticles among each other and with cellulose substrate

Simulation software and type of numerics used

Molecular mechanics (MM) using the GLYCAM06 force field(supercell approach with periodic boundary condition). Programs: ChemShell, DL_POLY DFT and DFT-D functionals used: BP86, B3LYP, M06 TURBOMOLE, TERACHEM In-house code for CGMD

Achievements of the model beyond experiments

Modeling reproduced and predicted the strength and structured buildup of hydrogen bonds of water to the cellulose surface and inside the water layer as a function of the water layer thickness. This led to suggestions for the design of the surface structure and charge distribution at cellulose surfaces.

Application

Interfacial chemistry

The aim of the project is the creation of functional surface modifications using polysaccharides and nano-particles leading to four different demonstrators in the fields of pulp and paper, cellulosic yarns, cellulose films and filter membranes.

Summary of the modelling

Adsorption of water or small or large carbohydrates on cellulose surfaces is frequently attributed to the formation of highly stable hydrogen bonds. Adsorption phenomena at the interface of cellulose surfaces require modeling of a system that is composed of two subsystems: the cellulose bulk and the adsorbate. The modelling of the interaction between cellulose and water using <u>force fields</u> is very delicate: water-water interaction in bulk water can be described with water models, which are not part of the force fields used for cellulose. Therefore the modelling of the interaction at the interface has to be considered as crucial and this can only be done by comparing results at different level of theory ((electronic) <u>quantum mechanical</u> and (atomistic) <u>molecular mechanics</u> model).

Within the Surfuncell project, a study was started with <u>classical molecular dynamics</u> using CHEMSHELL and DL-POLY on the strength of different H-bonds in cellulose, separating the intrinsic H-bond dissociation energy (H-bond strength) from the atom-pair van der Waals interactions. The interaction of cellulose surface of different morphologies and any kind of adsorbates as a function of the water layer thickness using molecular dynamics simulations was also studied to get a feeling for the number of water molecules that are necessary for the adsorption of solvated molecules at the cellulose surface.

<u>Coarse grained modelling</u> with in-house codes was used to simulate the formation of layers of nanoparticles on cellulose surfaces. For this purpose, a grid-based, discrete model operating at the scale of the nanoparticles has been developed. The model assumes a simplified geometry of the particles, a limited discrete set of particle locations and orientations and a simplified, short ranged interaction between particles and the surface. In return, this coarse-grained approach allows the simulation of layer formation involving millions of particles and a subsequent analysis of the layers' statistical properties.

www.surfuncell.eu

Project Acronym and Number: SURFUNCELL 214653 Project Title: Surface functionalisation of cellulose matrices using coatings of functionalized polysaccharides with embedded nano-particles Start and End Dates: 01/12/2008 until 30/11/2012 EU Contribution: 7.916.259 € Coordinator: Prof Volker Ribitsch Uni Graz, AT <u>volker.ribitsch@uni-graz.at</u>



in SYNAPSE 310339

Subject of the modelling

Electro-thermal behavior of chalcogenide nanowires (NWs) in simple structures, including coreshell

Models used

Electronic: DFT

Atomistic: <u>classical molecular dynamics</u> (MD) simulations, based on an interatomic potential generated by means of a neural network (NN) scheme.

Continuum: coupled models for <u>electrical</u> and <u>thermal behavior</u> based on Poisson's equation for electrical conductivity and the Fourier's heat law

Simulation software and type of numerics used

CP2k open source code for ab-initio molecular dynamics simulations based on Density Functional Theory and a Car-Parrinello-like scheme

Proprietary RuNNer code for molecular dynamics simulations with the NN interatomic potentials (several thousand atoms and several tens of ns)

The electrical and thermal models will be solved numerically by employing both MATLAB and COMSOL software suites

Achievements of the model beyond experiments

DFT simulations allowed uncovering the atomistic structure of the amorphous phase of several phase change compounds, the microscopic origin of the resistivity and optical contrast between the crystalline and amorphous phases and the vibrational signature of different local atomic configurations in the amorphous network.

Large scale molecular dynamics simulations based on the NN potential have provided insights on the origin of thermal conductivity in the bulk and on the origin of the fast phase change. Thermo-electrical models have helped to understand, or predict, several effects occurring in nanoscaled devices and they thus provide crucial insight for the actual implementation of memory devices.

Application

multi-level phase change memory devices.

Relevant review articles

S. Caravati, M. Bernasconi, T.D. Kuehne, M. Krack, and M. Parrinello, Appl. Phys. Lett., 91 (2007) 171906; S. Caravati, et al., J. Phys. Cond. Matt. 21 (2010) 255501; ibidem 22 (2010) 315801; B. Huang and J. Robertson, Phys. Rev. B 81 (2010) 081204; Mazzarello et al., Phys. Rev. Lett., 104 (2010) 085503

T. D. Kuehne, M. Krack, F. R. Mohamed, and M. Parrinello, Phys. Rev. Lett. 98 (2007) 66401 G.C. Sosso, et al., Phys. Rev. B, 85 (2012) 174103; G.C. Sosso et al, Phys. Stat. Solidi, 249 (2012) 1880; J. Behler and M. Parrinello, Phys. Rev. Lett. 98 (2007) 146401

D. Yu, S. Brittman, J. S. Lee, A. L. Falk, H. Park, Nano Lett., 8 (2008) 3429

J. P. Reifenberg, D. L. Kencke, K. E. Goodson, IEEE Electron Device Lett.

J. Liu, B. Yu, M. P. Anantram, IEEE Electron Device Letters, 32, 1340

F. Leonard, Applied Physics Letters 98 (2011) 103101

Summary of project

The SYNAPSE project will study metal-organic chemical vapor phase deposition (MOCVD) and study chalcogenide single material (core) and double material (core-shell) nanowires (NWs), to be used for multi-level phase change memories (PCM).

The project aims to downscale PCM cells by employing chalcogenide Ge-based and In-based NWs, deposited by MOCVD on different substrates and using bottom-up approaches like the vapor-liquid-solid deposition technology(VLS) and selective area growth technique (SAG). Different material combinations (Ge-Sb-Te/In-Sb-Te/In-GeTe) will be explored to expand the memory level operational features of PCM devices. The NW synthesis will be supported by the development and test of precursors for MOCVD. A detailed study of the NW phase switching behaviour (reversible amorphous-crystalline transitions) will be carried out with special attention to electrical and thermal properties of the NWs, their phase formation/crystallization dynamics, size-dependent effects and structural/chemical composition.

Summary of the modelling

SYNAPSE will do theoretical modelling and simulation of both crystallisation dynamics and electro-thermal behavior. <u>Car-Parrinello-like molecular dynamics</u> simulations based on <u>density</u> <u>functional theory</u> will be performed to uncover the atomistic structure of the amorphous and crystalline phases of the involved chalcogenide alloys. A comparison between theory and the experimental data will be used to aid the interpretation of the experiments. Secondly, large scale classical molecular dynamics simulations will be carried out to study the crystallization dynamics and thermal properties of the amorphous phase in the bulk and in NWs, by using suitably devised interatomic potentials. An interatomic potential (with accuracy close to that resulting from a full DFT calculation) has been already generated for bulk GeTe by fitting a huge DFT database by means of Neural Network (NN) techniques. The NN potential was able to successfully reproduce structural, dynamical and thermo-dynamical properties (including melting and crystallization) of liquid, crystalline and amorphous GeTe. We aim at extending the NN potential to GeTe NWs and to other phase change materials.

Existing <u>electro-thermal</u> models based on Poisson's equation for electrical conductivity and Fourier's heat law, can be tailored to fit different materials (In-Sb/In-Te, In-Sb-Te) and architectures (confined cell PCM, free-standing NWs, confined NWs) will be considered and solved with COMSOL and MATLAB. The model takes into account the thermal boundary resistance and the crystallization rate of the phase-change materials. At the same time, inhouse custom models will be possibly developed, if needed to cope with novel phenomena (such as scaling, core-shell interaction, etc...). Material properties, source terms and boundary conditions of known materials will be used, or extracted from experimental data available in literature, if needed. Moreover, all boundary conditions (electrical and thermal) will be set so as to match those of the actual device. The modeling will be performed both at steady-state conditions and in transient.

Project Acronym and Number: SYNAPSE 310339 Project Title: Synthesis and functionality of chalcogenide nanostructures for phase change memories Start and End Dates: 1/12/2012 till 30/11/2015 EU Contribution: € 2,206.640 Coordinator: Massimo Longo, Consiglio Nazionale delle Ricerche (CNR-IMM, Unit of Agrate Brianza – Italy), massimo.longo@mdm.imm.cnr.it



in ULTRAMAGNETRON 214469

Subject of the modelling

Optical control of nanomagnets (rare earth transition metals, diluted magnetic semiconductors) including reversal and (thermal) relaxation

Models used

Electronic: <u>ab-initio QM</u> for ultrafast laser-induced magnetization reversal based on the use of the Heisenberg formalism for the exchange interaction between atomic spins Atomistic: <u>Atomistic spin model</u> of a ferrimagnetic material with magnetic compensation points Landau-Lifshitz-Bloch (LLB) equation

Simulation software and type of numerics used

Parallel version of the codes

Achievements of the model beyond experiments

Materials with a compensation point are shown to be very promising media for magnetic recording.

The magnetization reversal by a single circularly polarized laser pulse has been successfully simulated.

A phase diagram for opto-magnetic reversal was obtained, demonstrating a window of peak electron temperature and effective magnetic field pulse duration for opto-magnetic switching A new mechanism of linear magnetization reversal was discovered

Experimentally the two sublattices of a ferrimagnetic alloy (GdFeCo) were found to demagnetise at different rates which was then confirmed by the model

The model predicted that the ferrimagnet transitioned into a transient ferromagnetic phase stable for only around 300femtoseconds which was found experimentally (Nature 2011) The theoretical model predicted that the magnetisation of the ferrimagnet reversed spontaneously on application of a heat pulse, which was then experimentally verified (Nature Comm.2012)

Application

THz magnetic recording and information processing devices (opto-magnetic read-head and the required picosecond laser and write heads)

Relevant review articles

Nature, <u>472</u>, 205 (2011); Nature Communications 3, #666 (2012)

The objective of the EU-India project was to develop "opto-nano-magnetism" that is, the manipulation of the magnetic properties of nanomagnetic materials with light using (magneto-) optical effects, as a novel approach for future magnetic recording and information processing technology. This topic is situated at the junction of coherent nonlinear optics, nanophotonics and magnetism. In particular, we investigated the effects of light on magnetic order at the nanoscale, optimized materials and conditions for highly efficient and ultrafast (10-12 seconds and faster) optical control of nanomagnets and in this way tried to initiate a development of novel technology for unprecedented fast (THz) magnetic recording and information processing.

Summary of the modelling

Models have been developed for the physical understanding of the opto-magnetic process. The models have given an understanding of the thermal processes involved in the opto-magnetic reversal process. The electronic ab-initio QM model is based on the use of the Heisenberg formalism for the exchange interaction between atomic spins. It is demonstrated that ultrafast reversal can occur on heating close to the Curie temperature in the presence of a large applied field

After establishing the basic physics of the reversal detailed calculations were carried out using an <u>atomistic spin model</u> based on the Landau-Lifshitz-Bloch (LLB) equation. The LLB equation has the property that the magnetisation is not conserved which means that it can be used in calculations at elevated temperatures up to and even beyond the Curie temperature. In a single spin approximation, the LLB equation is computationally efficient and the influence of a magnetic field on the recovery phase following a rapid heat-pulse was investigated. This field originates in the laser-pulse due to the inverse Faraday effect.

The micromagnetic modelling is applied to ferrimagnetic material such as GdFeCo. Ferrimagnets have a magnetic compensation point which may contribute to the ultrafast reversal. It is important to study the dynamics of ferrimagnetic materials in order to understand their ultrafast dynamic magnetisation properties. For the modelling of laserinduced magnetization reversal at the nano level opto-magnetic switching processes of a single macro-spin in the framework of the Landau-Lifshitz-Bloch (LLB) equation recently derived by D. Garanin [Phys. Rev. B 55, 3050 (1997)] was investigated. It was found that the maximal electron temperature, as well as the field pulse duration, influences the reversal of the magnetic system. These findings coincide with observations found experimentally. Furthermore, it has been shown numerically as well as experimentally that the occurring reversal is not precessional in nature, but has instead a linear character, proceeding via a strongly-nonequilibrium state. The so-called linear reversal mode previously investigated analytically for a single LLB macro-spin leads to reversal processes on an ultra-short time scale. The next step went beyond this single-macro spin approach and extended the approach to a LLB based multi-macro spin simulation. The exchange coupling as well as the dipolar interaction is taken into account. Here, the long-range dipole-dipole interaction is calculated with the aid of the well-established fast-Fourier transformation (FFT). Furthermore, the code was paralellised in order to simulate extended systems of realistic size up to 107 macro-spins on our computer cluster at Konstanz.

With these new programs, systems were simulated with up to 4*106 macro-spins. A Gaussian electron temperature profile was assumed in order to model a realistic laser spot as used in the experiments. The magnetization evolution corresponds to those found in the experiment.

http://www.ultramagnetron.org

Project Acronym and Number: ULTRAMAGNETRON 214469 Project Title: Ultrafast all optical magnetization reversal for magnetic recording and laser controlled spintronics Start and End Dates: 01/12/2008 till 31/11/2011 EU Contribution: 3.147.150 € Coordinator: Theo Rasing Radboud University NL <u>th.rasing@science.ru.nl</u>


Modelling

in YBRIDIO 309560

Subject of the modeling

The induction heating of composite laminates and metal composite hybrids via electromagnetic induction and laser radiation to facilitate the joining of two dissimilar materials

Models used

Continuum:

<u>macro mechanics</u> of materials and <u>heat transfer in solids</u> <u>electromagnetism modeling</u> (Maxwell equations in the eddy current (induction-diffusion) approximation)

Simulation software and type of numerics used

Finite Element Analysis (FEA) codes COMSOL AB's COMSOL Multiphysics and LSTC's LS-DYNA 980 solver for electromagnetism, solid mechanics and heat transfer. Boundary element (BEM) and finite element (FEM) methods

Achievements of the model beyond experiments

Models help understand the effects of the many processing parameters and gives information of material (e.g. temperature and pressure at the bond line or at the connection interface of the two parts being joined) which is extremely difficult to measure to the necessary level.

Application

Automotive, aerospace industry, consumer goods, electronics

Relevant review articles

- P. L'Eplattenier, G. Cook, C. Ashcraft, M. Burger, A. Shapiro, G. Daehn, M. Seith, "Introduction of an Electromagnetism Module in LS-DYNA for Coupled Mechanical-Thermal-Electromagnetic Simulations", 9th International LS-DYNA Users conference", Dearborn, Michigan, June 2005.
 Duhovic M, Moser L, Mitschang P, Maier M, Caldichoury I, L'Eplattenier P: Simulating the Joining of
- Duhovic M, Moser L, Mitschang P, Maier M, Caldichoury I, L'Eplattenier P: Simulating the Joining of Composite Materials by Electromagnetic Induction. In Proceedings of the 12th International LS-DYNA® Users Conference, Detroit, 2012, Electromagnetic (2)
- L. Huiping, Z. Guoqun, N. Shating and H. Chuanzhen, "FEM simulation of quenching process and experimental verification of simulation results", in Materials Science and Engineering A, April 2007, pp. 705-714
- Martínez, S., Ukar, E., Lamikiz, A., Liébana, F. "Laser hardening prediction tool based on a solid state transformation numerical model". Proceedings of AMPT 2010 ISBN: 978-0-7354-0871-5 Advances in materials and processing, 2010. Paris.

Summary of project

Within the YBRIDIO project the necessary know-how and equipment will be created to join thermoplastics and thermoplastic based composites with dissimilar materials, especially metals. The goal is to replace common methods (adhesive bonding, mechanical joining, ultrasonic welding, injection moulding, etc.) by a more efficient process. As a consequence, productivity can be increased while energy and raw material consumption are decreased. In addition, new knowledge-based materials, such as enhanced composites and metals with improved surfaces, will be created. Moreover new process control systems for laser and induction joining will be developed.

Summary of the modelling

Computational models are used to simulate the joining process.

The simulation of material processing using electromagnetic induction is a multiphysics problem involving the theories of <u>electromagnetism</u> and <u>heat transfer</u>. If the thermal and <u>mechanical stresses</u> are also to be taken into account then a three-way Electro-Thermal-Mechanical (ETM) simulation coupling is required. Joule heating of composite laminates via electromagnetic induction will be modeled using general multiphysics Finite Element Analysis (FEA) codes which use a "continuum modelling approach" of the mechanics of materials in particular applying the physics of electromagnetism, solid mechanics and heat transfer using either a finite element or boundary element formulation.

Two Finite Element Analysis (FEA) software codes capable of such simulations are COMSOL AB's COMSOL Multiphysics and LSTC's LS-DYNA 980 solver. The electromagnetic behaviour is calculated by solving Maxwell's equations in the eddy current (induction-diffusion) approximation using boundary elements (rather than FE) coupled to the outer surfaces of the parts meshed using solid 3D finite elements which take care of the model's thermal and mechanical behaviour. There are advantages and disadvantages with both methods. The former, for example, provides a more efficient formulation for large (component scale) static induction heating simulations while the latter is more suited for smaller dynamic simulations where a moving coil or workpiece is required.

Given a 2D or 3D geometry, mechanical properties of the composite laminate, its thermal conductivity, specific heat capacity, thermal expansion, electrical conductivity, induction skin effect depth, heat transfer conductance, heat convection coefficient and properties of the tooling and induction equipment (mechanical properties and thermal conductivity, applied pressure, induction frequency, current amplitude, electrical conductivity, heat convection coefficient), the outputs available from the modelling are an optimized induction coil and flux concentrator, shape design, velocity, distance from work piece; induction generator: voltage, current, power; material: temperature and pressure at the bond line (or connection interface of the two parts being joined). The modelling will predict also the Joule heating temperatures, cooling behaviour, pressure requirements for consolidation, magnetic fields, electric fields, Lorentz forces, thermal expansion/deflection.

All physics equations are solved in a coupled model within each completely independent FEA code. There is no need for data transfer between the two codes. The characterization experiments necessary for gathering the verification data for such simulations is captured for both the heating and cooling cycles and is then used to verify simulation models of the same experiment before more complex joining scenarios through simulation are considered.

Project Acronym and Number: YBRIDIO 309560 Project Title: Novel technologies for dissimilar materials joining Start and End Dates: 01/03/2013 till 29/02/2016 EU Contribution: 2.196.827 € Coordinator: Fernando Liébana, Fundación Tecnalia Research & Innovation, ES, <u>fernando.liebana@tecnalia.com</u>



Annex II List of software codes used in NMP projects

SOFTWARE	where they are used by the NMP projects	website
ABAQUS	Continuum solid mechanics (micro and macro); fluid dynamics; process	www.3ds.com/fr/products/simulia/por tfolio/abaqus/overview
ABINIT	Electronic: quantum mechanical	www.abinit.org
ACEFEM	Continuum solid mechanics (micro and macro)	www.wolfram.com/products/applicati ons/acefem
ADF	Electronic: quantum mechanical and and many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.scm.com/Products/ADF
AMBER	Atomistic: ab-initio molecular dynamics and Quantum Mechanics/Molecular Dynamics	www.ambermd.org
AMPAC	Electronic: quantum mechanical and many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.semichem.com
ANSYS (FLUENT)	Continuum solid mechanics (micro and macro); fluid dynamics	www.ansys.com
ANSYS HFSS	Continuum: Electomagnetism	www.ansys.com
BOLTZTRAP	Electronic: many-body and semi-empirical or parametrised electronic models	www.icams.de/content/departments/ ams/madsen/boltztrap
CANTERA		code.google.com/p/cantera
CASTEP	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics and Quantum Mechanics/Molecular Dynamics	www.castep.org
CHEMKIN	Continuum: chemistry	www.reactiondesign.com/products/op en/chemkin
CHEMSHELL	Continuum: chemistry	chemcell.sandia.gov
CFX ANSYS	Continuum: fluid mechanics	www.ansys.com/Products/Simulation+ Technology//ANSYS+CFX
CODICE_DEG	Continuum: solid mechanics (micro)	www.codice-project.eu/codes and demos
CODICE_MEC	Continuum: solid mechanics (micro)	www.codice-project.eu/codes and demos
COMSOL	Mesoscopic: statistical methods, Continuum solid mechanics (micro) ; continuum thermodynamics; electrochemistry; continuum EM	www.comsol.com

СР2К	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics and Quantum Mechanics/Molecular Mechanics	www.cp2k.org
CRYSTAL MAKER	Electronic: quantum mechanical	www.crystalmaker.com
СТQMC	Electronic: many-body and semi-empirical or parametrised electronic models	inhouse (<u>GOFAST</u>)
CTS studio suite	continuum EM	www.cst.com/2010
DALTON	Electronic: quantum mechanical	www.dirac.chem.sdu.dk/daltonprogram .org/
DEFORM3D	Continuum mechanics (macro)	www.deform.com/products/deform- 3d/
DEMON2K	Electronic: quantum mechanical	www.demon-software.com
DESSIS	Device modelling	www.iue.tuwien.ac.at/phd/klima/node8
DETCHEM	Continuum: Chemistry	www.detchem.com
DIFFRACMOD	Continuum EM	www.foservice.com/SOFTWARE/diffrac tmod
DGCA	Mesoscopic: micromagnetics, file compression	inhouse (<u>DYNAMAG</u>)
DL_POLY	Electronic: quantum mechanical and device level	http://www.stfc.ac.uk/cse/25526.aspx
DMM	Mesoscopic: micromagnetics This is a frequency domain technique rather a simulation code	In-house [DYNAMAG and MAGNONICS]
ELK	Electronic: quantum mechanical	www.elk.sourceforge.net
Elmer	Continuum: flow	http://www.csc.fi/english/pages/elmer) http://www.simpartix.com/
FDMAX	Continuum: Electomagnetics	
FEAP	Continuum solid mechanics (micro) and process	www.ce.berkeley.edu/feap
FEMAP	Commercial continuum solid: pre-processor	www.plm.automation.siemens.com
FEMME	Mesoscopic: micromagnetics	www.suessco.com/simulations/solution s/femme-software
FIREBALL	Electronic: quantum mechanical	http://onlinelibrary.wiley.com/doi/10.1 002/pssb.201147259/abstract;jsessioni d=7E7A482F6EFD483AEB9979289EDEE 0EE.d03t04)
FLAPW-FLEUR	Electronic: quantum mechanical, DFT	www.flapw.de
GARAND	Atomistic: statistical methods; drift diffusion	www.goldstandardsimulations.com/ser vices/service-simulations/statistical- variability/atomistic-simulator
GAUSSIAN	Electronic: quantum mechanical and many-body and semi-empirical or parametrised electronic models and Atomistci Quantum Mechanics/Molecular Dynamics and Atomistic: statistical methods	www.gaussian.com
GPAW	Electronic: quantum mechanical	www.csc.fi/english/research/software/

GROMACS	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods, molecular dynamics	www.gromacs.org/About_Gromacs
GROMOS	Mesoscopic: molecular dynamics	www.gromos.net
HYPERCHEM	Electronic: semi-empirical and ab-initio molecular orbital methods, as well as density functional theory Atomistic: molecular mechanics, molecular dynamics	www.hyper.com
INFOLYTICA	Continuum: behaviour of magnets	www.infolytica.com/en/products/magn et
KMC-MD	Atomistic: statistical methods (Molecular Dynamics - kinetic Monte Carlo)	www.kintechlab.com/products/md-kmc
LAMMPS	Atomistic: statistical methods (molecular dynamics)	www.lammps.sandia.gov
LLG	Mesoscopic: Micromagnetics	http://llgmicro.home.mindspring.com
Madrid/Konstanz code	Mesoscopic: micromagnetics	Inhouse (<u>FEMTOSPIN</u>)
MAGPAR	Mesoscopic: micromagnetics	www.magpar.net
MARC	Continuum mechancis (macro)	www.mscsoftware.com/Products/CAE- Tools/Marc.aspx
MATERIALS STUDIO	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods and Mesoscopic: statistical methods	www.accelrys.com/products/materials- studio
MCGEN	Macro-scale: device modelling	Inhouse (<u>SUPERLION</u>)
MicroMagus	Mesoscopic: micromagnetics	http://www.micromagus.de/
MSC.MARC/MENTAT	Macro-scale: Continuum solid mechanics (micro and macro); fluid dynamics; process	www.mscsoftware.com
MSINDO	Electronic: many-body and semi-empirical or parametrised electronic models	www.thch.uni-bonn.de
MUMAX	Mesoscope: micromagnetics	code.google.com/p/mumax
NAMD	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.ks.uiuc.edu/Research/namd
NMAG	Mesoscopic: micromagnetics	www.nmag.soton.ac.uk
NMTO	Electronic: many-body and semi-empirical or parametrised electronic models	www2.fkf.mpg.de/andersen
NXNastran	Continuum solid mechanics	http://www.plm.automation.siemens.c om
OCTOPUS	Electronic: quantum mechanical in response of time dependent fields	www.tddft.org
OOMMF	Mesoscopic: micromagnetics	www.ngs.ac.uk/use/applications/engin eering/oommf

OpenKIM	Atomistic: interatomic potentials and simulations	www.openkim.org
OPENMX	Electronic: quantum mechanical	www.openmx-square.org
OPTILAYER	Continuum: EM	www.optilayer.com
OPTIWAVE	Continuum: EM	www.optiwave.com
PICMC (DSMC)	Atomistic: statistical methods	Inhouse (<u>ORAMA</u>)
POM-POM TUBE	Macro-scale: fluid dynamics: polymer melt rheology This is a constitutive equation not a simulation package!	Inhouse (<u>MODIFY</u>)
PWM	Mesoscopic: micromagnetics	inhouse (<u>DYNAMAG</u>)
PWSIC	Electronic: quantum mechanical	Inhouse (<u>ATHENA</u>)
QUATRA/CELS	Atomistic: semi-classical drift-diffusion method and quantum kinetic model	inhouse (<u>SMASH</u>)
QLDFT	Electronic: quantum mechanical	physics.joacobs.university.de/theine/re search/qldft/
QUANTUM ESPRESSO	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics	www.quantum-espresso.org
QUIP	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics and Quantum Mechanics/Molecular Mechanics	www.libatoms.org
RANDOMSPICE	Device modelling: statistical circuit simulator	www.goldstandardsimulations.com/pro ducts/randomspice
RETICOLO	Continuum: Electromagnetism	Inhouse (<u>NIM-NIL</u>)
RIG-VM	Boltzmann transport equation solver, Direct Simulation Monte-Carlo and Particle in Cell plasma modelling for coating processes, optical modelling	http://www.ist.fraunhofer.de/en/servic es/simulation.html
RSPt	Electronic: many-body and semi-empirical or parametrised electronic models	www.fplmto-rspt.org
SE-MARGL	Mesoscopic: micromagnetics This software for post-processing the data from micromagnetic simulations	www.magnonics.org/semargl/
SIESTA	Electronic: quantum mechanical and and many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.nanotec.es/products/siesta.php
SIMPARTIX	Continuum: flow	www.simpartix.com
SPINPM	Mesoscopic: micromagnetics	www.apl.aip.org/resource/1/applab/v9 6/i2/p022504_s1?view=refs
TIBERCAD	Electronic: many-body and semi-empirical or parametrised electronic models, Atomistic: continuum mechanics (micro)	www.tibercad.org/
TINKER	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.dasher.wustl.edu/ffe/
TURBOMOLE	Electronic: quantum mechanical and quantum mechanical in response of time dependent fields	www.turbomole.com/
UppASD	Atomistic: statistical methods and Mesoscopic: micromagnetics	Inhouse (<u>MONAMI</u>)

Uppsala code	Electronic: quantum mechanical in response of time dependent fields	Inhouse (<u>FEMTOSPIN</u>)
VASP	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics and Quantum Mechanics/Molecular Mechanics	www.vasp.at
WANT	Electronic: quantum mechanical	Inhouse (<u>ATHENA</u>)
WIEN2K	Electronic: quantum mechanical	www.wien2k.at
WISETEX	Continuum: solid and fluid mechanics	www.mtm.kuleuven.be/Onderzoek/Co mposites/software/wisetex
YORK code	Atomistic: statistical methods	Inhouse (<u>FEMTOSPIN</u>)

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The future of the European industry is associated with a strong modelling capacity. An efficient modelling approach is needed to shorten the development process of materials-enabled products.

This brochure describes modelling of materials, their properties and use in industrial applications illustrated by FP7 Industrial Technologies NMP Materials projects. It does not require prior knowledge of the subject. It is written for anybody interested. It contains no equations. The brochure is to provide insight into the work of the modellers and help the reader to see the models as more than mere "black boxes".

This brochure shows that industry is a very active player both in modelling for production and in modelling research areas. Industry identifies the specifications for material properties and the modelling then finds which material composition can meet the specs and how production can be done. This Materials by Design approach has been supported during the last decade in the EU Framework Programmes.

Application areas of modelling span all industrial sectors. The bulk of the projects are applying existing models to new materials, which shows that the current state of the art of modelling can be characterised as "mature".

