

Studying the properties of materials with numerical simulations



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Exciting new materials can now be grown or synthesized with very good atomic and chemical structures. Some of these materials do not even exist naturally and can only be obtained in research laboratories, by clever manipulation of matter at the nanometre scale. These materials possess unexpected physical properties. They are currently the object of fundamental investigations with the aim of understanding the origin of their interesting behaviour. These materials can be used for technological applications in various fields like bio-nanotechnologies, microelectronics, magnetic memories and structural materials.

Supercomputer

Numerical simulations must be used to understand the microscopic origin of the physical properties of these materials and to interpret results of experimental studies on these systems. These simulations are complicated because we usually need to describe the behaviour of a huge number of electrons and nuclei interacting together. The mathematical equations describing the physical properties of these materials can only be solved with a supercomputer like the one provided by CALMIP (Calculations in Midi-Pyrénées). The researchers of the main laboratories in Toulouse studying the physical properties of materials (at CEMES¹, CIRIMAT², LAAS³, and laboratories belonging to the IRSAMC⁴ institute) routinely use this kind of computer.

Each year, these laboratories apply for calculating time on the CALMIP computer and about 30 research project proposals are submitted each year. In 2011, CALMIP allocated 5 000 000 hours to these labs for calculating the physical properties of materials. This represents 22% of the total available computer time. The codes that calculate the physical properties of materials are well suited to massively parallel architectures and run on Hyperion, the most recent supercomputer at CALMIP.

1 Centre d'élaboration des matériaux et d'études structurales/ Center for Material Elaboration & Structural Studies

2 Centre Inter-universitaire de Recherche Ingénierie Matériaux/Interuniversity Research and Engineering Centre on Materials
3 Laboratoire d'analyse et d'architecture des systèmes/ Laboratory for Analysis and Architecture of Systems
4 Institut de Recherche sur les Systèmes Atomiques et Moléculaires Complexes/ Research Institute on Complex Atomic and Molecular Systems
LPCNO: Laboratoire de Physique et Chimie des Nano-objet/Laboratory of Physics and Chemistry of Nano-objects
LPT: Laboratoire de Physique théorique/Laboratory of Theoretical Physics

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CALMIP and the Hyperion supercomputer:

Thanks to the active support of UPS, and in collaboration with the PRES University of Toulouse, CALMIP is able to provide a high-performance calculation platform to the local scientific community. Hyperion (2912 cores, 33 Teraflops) was acquired in 2009 thanks to CPER funding. This computer is hosted and managed by the DTSI staff (head office for information technologies and systems) of UPS. Interaction between researchers and the CALMIP technical staff allows to optimize the return time of each calculation. For instance, the time needed to calculate the electronic structure near structural defects in a magnetite crystal has been shortened from 5h45min to 17 min.

We can also mention the case of calculations to study an Fe nanocube: the use of 256 processors means that one calculation loop can be performed in just 30 seconds (this is important since convergence requires thousands of loops). The active collaboration between CALMIP technical staff and new users with little experience in numerical calculations and computing allows to parallelize the codes that they have developed. This has been the case for a code written for studying the electromagnetic properties of nano-objects using more than 200 Go of shared memory. To carry on meeting such needs and further increasing computer capability, CALMIP will acquire several hundreds of processors and several TeraOctets of shared memory in 2012, in the framework of the EQUIP@MESO (EQUIPEX) project.

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>>> Self-organization of atoms induced by a standing acoustic wave (a molecular dynamics simulation). Because of the standing acoustic wave, atoms diffusing on the substrate tend to localise preferentially in the vicinity of the anti-nodes (N. Combe, CEMES).



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Simulations at the atomic scale in metallurgy

Certain mechanisms are difficult to test experimentally in metallurgy. The subject has greatly benefited from numerical simulations over the last 20 years, and the research performed at CIRIMAT is emblematic of recent progress in this domain.

Calculations and phase diagram predictions

Scientists are now able to describe the phase diagrams of various complex systems such as those containing just one atomic species as multi-phase systems (like ternaries). These ab initio simulations, based on quantum mechanics principles, provide data that can then be entered into thermodynamic equilibrium equations. Researchers can thus optimize many stable and meta-stable structures existing at equilibrium between phases.

The energies obtained are subsequently used at the same time as experimental data to optimize thermodynamic data bases destined for phase diagram simulations. These data bases can then be combined with diffusion coefficient data bases (such as those implemented in the DICTRA software, for example) in phase transformation calculations.

Defect migration

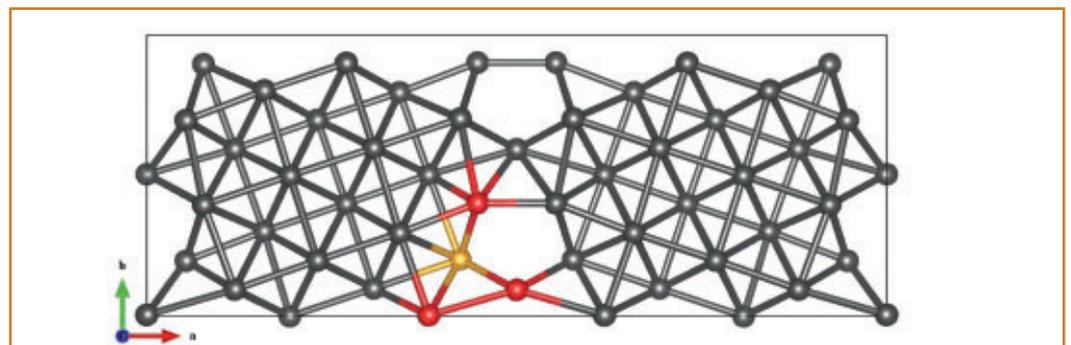
Another major worry for metallurgists is understanding the process of defect migration. Defect include vacancies, species in solution and extended defects. This information is very important for understanding how materials and structures age and is linked to experimental studies on degradation

mechanisms or premature ageing (for example, by corrosion or hydrogen embrittlement). Nickel - a metal routinely studied by our group - is widely used in the aerospace and nuclear industries. Network vacancies in the metal are important for a number of mechanisms, such as corrosion, diffusion and cavity formation. At CIRIMAT, for example, researchers have calculated how such vacancies form and migrate. They have also observed that the energy of formation of 1.41 eV, and migration energy of 1.05 eV are in very good agreement with experimental data (1.46 to 1.72 eV and 0.97 to 1.04 eV, respectively).

Diffusion

CIRIMAT is also interested in interfaces, and in particular grain boundaries - where segregation, cracking and fast diffusion can occur. These systems are studied for just these reasons. For example, our simulations of niobium segregation in nickel grain boundaries suggest that it can easily concentrate at this interface. These results indicate that Nb atoms may change the mobility of the grain boundaries in the alloy and then influence its mechanical properties.

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>>> Nickel Σ 5-(012) symmetric grain boundary. In red and yellow, we underline the configurations used to study niobium segregation.



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Numerical simulations for understanding the behaviour of electrons in materials for spintronics

Spintronics has given rise to several industrial applications. However, the conception of new spintronic devices and an understanding of the fundamental physical principles that govern their behaviour requires high quality numerical simulations.

Spintronics is a relatively new research field in physics. The most important spintronic devices, namely spin valves and magnetic tunnel junctions, are made with thin magnetic metallic layers (the magnetic electrodes) separated by a thin non-magnetic spacer that has a thickness of a few nanometres. The electrical resistance of these multilayers depends on their magnetic configuration: it is smaller when the two electrodes have parallel rather than antiparallel directions.

Albert Fert and Peter Grunberg received the Nobel prize for physics in 2007 for discovering this magnetoresistance effect, which can be used to write and read a magnetic bit of information. This initial discovery has been followed by much fundamental and applied research based on the utilization of spin-polarized electric currents. The magnetoresistive properties of spin valves and magnetic tunnel junctions are used in the fields of magnetic memories and media - hard disk drive read heads or MRAM (Magnetic Random Access Memories) in computers use this effect.

Fundamental research

The physical phenomena that govern the electronic and magnetic properties of materials for spintronic applications are the subject of many fundamental studies. To understand the behaviour of electrons in these multilayers, we must use a quantum description of matter and numerical simulations must be performed in this framework. In general, these simulations use density functional theory (DFT), which allows to calculate the ground state density and energy of magnetic crystals. The basic equations that must be solved in this theory were proposed by Peter Hohenberg, Walter Kohn et Lu Sham in the 1960s. These are the basic equations of the codes used to calculate the electronic structure of crystalline materials. Solving these equations gives access to the total energy of the magnetic crystal, the density of states and the magnetic moment of the different atoms.

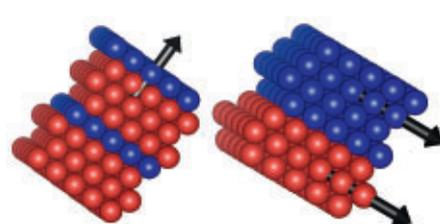
Tunnel current

Materials for spintronics have been studied for many years at CEMES by the Nanomaterials team. The numerical calculations and simulations performed allow for a better understanding of which electron states contribute to the tunnel current in magnetic tunnel junctions with Fe-based alloy magnetic electrodes (the physical properties depend on the electrode alloy composition for $Fe_{1-x}Co_x$ or $Fe_{1-x}V_x$ electrodes), or with magnetite (Fe_3O_4) electrodes. Important magnetoresistive effects should be measured with magnetite electrodes, this material being half-metallic - that is, with metallic behaviour for spin-up electrons and with insulating behaviour for spin-down electrons.

Magnetic nanostructures

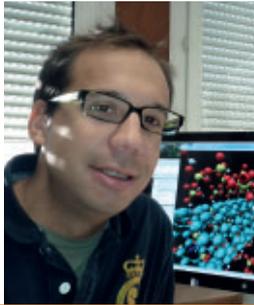
Recent research has also focused on tuning the magnetic anisotropy of multilayers with the aim of obtaining nanostructures with a magnetic anisotropy perpendicular to the thin magnetic layers. The systems with this magnetic configuration are very interesting: they can be used to record magnetic information with a very high density, and their magnetization can be switched using spin-polarized electric current with a relatively small intensity. The perpendicular anisotropy is actually due to the presence of interfaces between magnetic layers. In Ni/Co superlattices, the magnetization direction depends on the thickness of the successive Co and Ni layers (see figure). Another hot topic concerns the modification of the magnetic moments of metallic atoms near the interfaces of magnetic oxides.

Our numerical simulations are performed on the Hyperion supercomputer (CALMIP/UPS).



>>> Magnetic configuration of Co/Ni(111)
superlattices: the magnetic anisotropy is
perpendicular to interfaces when all the cobalt
layers contain a single cobalt atom, and parallel
to the interfaces when they contain four cobalt
atomic layers.

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Theoretical study of the physical and chemical properties of carbon-based nanostructures

Thanks to their huge potential in terms of applications, graphene and carbon nanotubes are among the most exciting of nanomaterials.

Although the unique properties of graphene were theoretically predicted 60 years ago, the material (which is a single sheet of carbon atoms organized in a honeycomb lattice) was only isolated in experiments for the first time in 2004. This real breakthrough was acknowledged by the Nobel prize in Physics in 2010.

Graphene could be an ideal candidate for next-generation nanoelectronic devices, thanks to its amazing electron transport properties. Indeed electrons can whiz through the material at extremely high speeds.

Numerical simulations

Nanotubes, discovered at the beginning of the 1990s, are also emblematic systems in nanoscience. They can be thought of as rolled-up graphene sheets. Numerous fruitful experimental and theoretical studies, dealing with the chemical, mechanical, thermal and electronic properties of these materials have been performed over the last 20 years, with the development of sophisticated numerical simulations, and more particularly first-principles methods.

In this context, electronic-structure calculations, based on density functional theory, can be of great value. Thanks to the 1D or 2D character of these nanomaterials, calculations concerning just a few hundreds of atoms can be routinely performed now.

Electronic structure

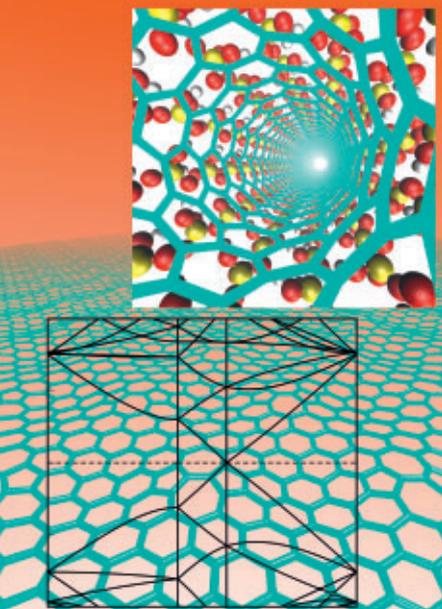
A deeper understanding of the surface chemistry of such systems is one of the main objectives of the Physical and Chemical Modelling team at LPCNO, in conjunction

with theoretical investigations of these electronic structures. In collaboration with experimentalists - led by Prof. Serp (LCC-ENSIACET), B. Lassigne (LPCNO) and P. Puech (CEMES), we are currently studying defect formation and stability, functionalization of sidewalls and metal-nanocarbon structure interactions. Indeed this interaction governs the behaviour of the growth of nanocatalysts based on metallic (Ru/Pt) atoms, the anchorage mode of a single magnetic nanoparticle on a carbon nanotube nanoresonator or even the catalytic activity of subnanometric clusters.

Superacids such as sulphuric acid are well known to be reversible p-dopants for nanotubes. Recent calculations have helped to interpret Raman spectroscopy results that suggest that the origin of the doping process is a non-covalent functionalization that induces a charge transfer between the tube and the acid.

Nitric Acid

Recently a combined experimental/theoretical study has led us to propose a reaction path, thanks to defect reactivity, that describes a fundamental step in the process of nanotube functionalization, that is, after the nitric acid treatment. Experimentally, this step is used to remove amorphous carbon, to oxidise the surface and yield carboxylic groups before complete destruction of the tubes.



>>> Top: The centre of a nanotube interacting with a nematic phase of sulphuric acid. Bottom: Band structure of pristine graphene.

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Uncovering the mystery of high-temperature superconductivity

Why do some materials superconduct when cooled down to “only” -150°C , rather than to temperatures near absolute zero (-273°C)? Research carried out at the Theoretical Physics Lab in Toulouse shows that these materials may host novel quantum states of matter.



>>> Left to right, researchers at the Theoretical Physics Laboratory (LPT, UPS/CNRS): Fabien ALET, Revaz RAMAZASHVILI, Matthieu MAMBRINI, CNRS scientists; Sylvain CAPPONI, professor at UPS; Nicolas LAFLORENCIE, CNRS scientist; Didier POILBLANC, senior CNRS researcher and Pierre PUJOL, professor at UPS.

In 1900, the work of Paul Drude allowed to describe the phenomenon of electric current in a common metal such as aluminum by considering the motion of each electron independently and classically. However, soon after, the 1911 experiments by Kammerlingh Onnes in Leiden - and then the theory developed by Bardeen, Cooper and Schrieffer in 1957 - ushered in a revolution concerning the physics of metals. The latter theory explained how cooling a metal down to a temperature near absolute zero (-273°C) turns “normal” electric conductivity into “super”-conductivity. By contrast with the former, where the electrons scatter off the crystal lattice of the conductor and thus heat it up, the latter implies perfect conduction without any resistance to electric current, and thus no heating whatsoever! This seemingly magic effect can only be explained by quantum mechanics; in particular, the electrons tend to form pairs, which turns out to be key in the phenomenon of superconductivity. This effect begins at sufficiently low temperatures (-272°C for aluminum), ordering the electrons into a collective state that allows them to move through a metal without experiencing any resistance.

The mystery deepens

A major surprise came in 1986, when Karl Müller and Johannes Bednorz discovered superconductivity in a new family of materials, based on copper and oxygen: the cuprates. These ceramics turn superconducting at the relatively “high” temperatures of about -150°C , where electron pairing is not expected at all! This is even more startling, given that at room temperature the cuprates conduct rather poorly.

What happens to these materials upon cooling? What mechanism pairs up the electrons and makes them superconduct? These questions, raised 25 years ago by materials now commonly called “strongly correlated”,

still await an answer. Here, “strongly correlated” implies that charge carriers in these materials cannot be regarded as independent: it is the collective behaviour due to strong interparticle interactions, that gives rise to novel physics. Along with experiments carried out in laboratories across the world (such as the High Magnetic Field National Laboratory of Toulouse) understanding the physics at work in these “unconventional” superconductors represents a major challenge to theorists.

Novel quantum states

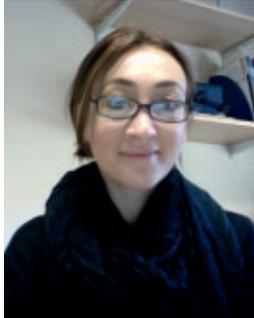
To solve these mysteries, the Strongly Correlated Fermion research team at the Theoretical Physics Laboratory (LPT) of the Institute for the Studies of Complex Atomic and Molecular Systems (IRSAMC) uses powerful analytic and numerical methods. Understanding and describing the collective behaviour of interacting quantum systems requires enormous computational power. With the help of supercomputers at LPT and at the computational meso-centre CALMIP, the researchers in our team use various cutting-edge methods. These involve the Lanczos algorithm that allows us to diagonalise giant matrices of many billion numbers, as well as the Quantum Monte Carlo method, whereby supercomputers simulate the dynamics of very large ensembles of interacting particles. The problem of strong correlations gives rise to a variety of new concepts from novel quantum states of matter to frustrated quantum magnetism and quantum entanglement. It is through pursuing these new ideas that novel theoretical methods develop, allowing us to step beyond established concepts. This year, we celebrate the centennial of the discovery of superconductivity, but the great adventure has only just begun!



>>> The LPT calculation cluster.

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Atomic-scale modelling for biohybrid molecules



>>> Marie BRUT,
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(CNRS lab associated to UPS).

Nanobiotechnology exploits biological and biohybrid molecules as structural materials and integrates them into nanodevices. The objective is to modify and control these complex systems provided by nature and couple them with technologically traditional materials (such as semiconductors, metals and oxides). These new developments should lead to a wide range of applications, notably in the fields of health and the environment.

Proteins can be considered as real molecular machines, with specific, sophisticated and adjustable functions. Nucleic acids also have unique self-assembly and hybridization properties that offer endless possibilities for nanopatterning, for instance. Although the idea of adapting these molecular objects to create new biohybrid devices has been considered for years, we are still far from using these structures in real-world applications. To be able to ensure the design and manufacture of DNA-based devices, it is crucial to understand molecular mechanisms at the atomic scale. This level of comprehension requires sophisticated numerical simulations. Today, modelling these biomolecules and integrating them into non-biological environments is our greatest challenge.

Multiscale simulation

At the LAAS-CNRS, in the nanoengineering team, we are developing models to predict both the structure and activity of biological and biohybrid molecules. We are especially interested in the way they may be affected by different modifications and a non-biological environment, as they are at the core of a nanodevice. To this end, we are developing innovative and dedicated tools, with the aim of integrating the materials into the larger context of multiscale simulations. To this end, we first designed the "Static Mode" method that allows us to compute the deformation of macromolecules induced by external excitations. The idea is to use this method directly to explore the intrinsic properties of biomolecules, but also to adapt it in a "docking" procedure - that is, to predict interactions with a view to assessing the impact of intermolecular interactions on partner structures and activity.

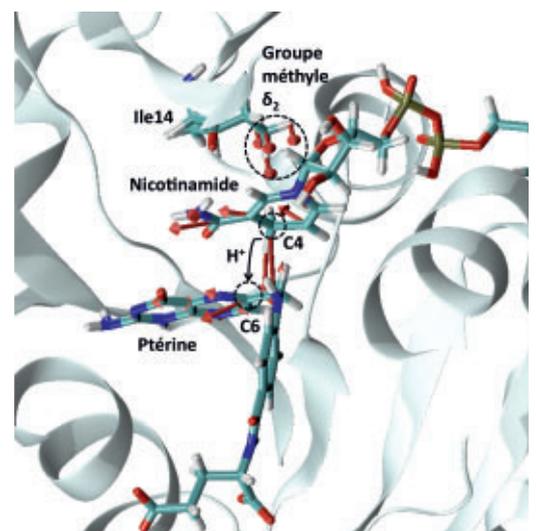
Bioinspired technologies

This approach can be used on "traditional" biological samples (particularly enzymes for pharmaceutical and medical applications: HIV protease, and DHFR). Pioneering work has also been performed in the field of bioinspired technologies in various fields of activity that include molecular motors (Ca^{2+} ATPase, myosin

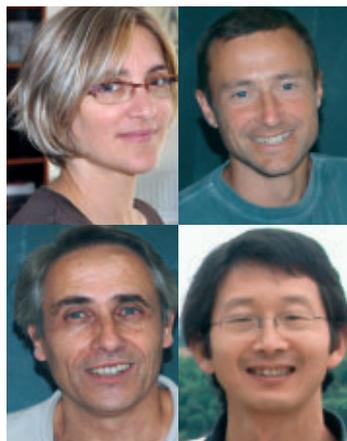
and chaperonin) and modified/functionalized DNA. These calculations accompany the LAAS experimental developments in DNA-based technologies, notably directed towards the development of aptamer sensors for medical diagnostics (cancer, for example) and the environment/health fields (water pollution).

The design of these devices raises many questions, such as how the environment influences aptamer folding, the choice of the detection device and its effect on the aptamer, the aptamer/target interaction mechanism, or the specificity of the sensor, to name but a few. To date, these issues are fundamental and generally applicable to all processes of bio/non-bio functional coupling.

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>>> Structure of the dihydrofolate reductase (DHFR) catalytic site. Nicotinamide and pterin rings are shown, as well as the C4 and C6 atoms involved in hydrid transfer. We have shown that the δ_2 methyl group allows to adjust the C4-C6 distance in a preferred direction and thus play a crucial role in catalysis.



Atomic scale modelling: defects and self-organization in materials

Simulations at the atomic scale are crucial for the development of nanotechnologies and the elaboration of new materials. Three typical examples of such simulations, from the “matériaux cristallins sous contrainte” group at CEMES are presented herein.

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Joseph MORILLO, professor at UPS,
Hao TANG, CNRS scientist, at the Centre
d'élaboration des matériaux et d'études
structurales (CEMES, CNRS laboratory
associated to UPS).

While glass is fragile (it breaks), metals are easily deformed under an applied external stress. This ductility, the ability to be deformed without breaking, comes thanks to the presence, inside the material, of particular kinds of defects known as dislocations. Under an applied stress, the density of dislocations increases and they move, allowing the material to plastically deform. The study of dislocations and how they move is therefore crucial to understanding the plasticity of materials.

Among the different kinds of dislocations that exist, screw dislocations are particularly important in some metals like titanium, an important metal for the aeronautics industry. Their atomic structure cannot be determined experimentally and atomistic simulations are therefore used to study these structures using a quantum mechanics approach. Evidence for numerous metastable structures have been found and the results could explain how dislocations move in titanium and thus the plastic deformation behaviour in this metal.

They self-assemble...

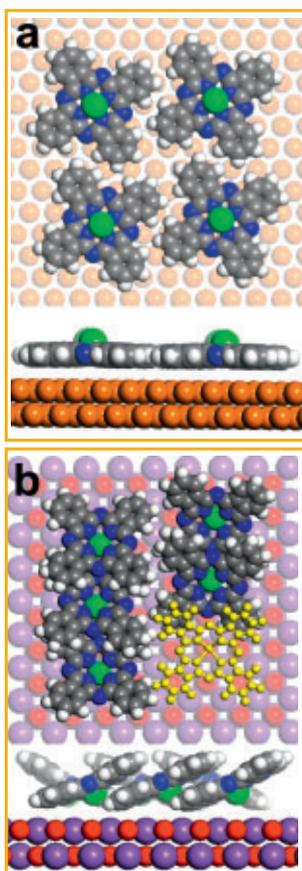
Many other physicochemical phenomena have also been understood using atomistic modelling. Another example studied by the CEMES scientists is the self-assembly of some molecules when they are deposited on a substrate. Many applications are expected from the growth of organic molecules on crystalline substrates: elaboration of Organic Light Emitting Diodes (which would be very cheap to produce compared to existing technologies) or Organic Field Effect Transistors.

Due to their weak interactions, these molecules can self-assemble on a substrate. A precise knowledge of the molecule-molecule and molecule-substrate interactions is required to fully understand these self-assembling architectures, as well as their electronic and optical properties. For instance, phthalocyanines (Pc), a very well-known family of molecules used as dyes for solar energy conversion or for rewritable optical discs, can self-assemble in different ways. On a gold surface, they self-assemble parallel to the surface plane in a bidimensional lattice, whereas on the surface of salt (NaCl), they come together in a tridimensional structure. Using atomistic simulations (molecular mechanics), we have shown that the interaction Pc-gold is stronger than the interaction Pc-Pc, whereas it is the opposite in the case of the NaCl surface. This difference can explain the origin of the diverse self-assembling properties.

Acoustic waves

Similarly to the self-assembly of molecules, the self-organization of semiconductors and metallic nanostructures on a substrate surface is a promising approach for the electronics and optoelectronics industries. Indeed, such an approach would avoid the expensive and delicate process of lithography. The scientists in the group have also recently proposed a new elaboration technique that would potentially allow better control of self-organization at the nanoscale.

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>>> GROWTH MODEL OF SN-PC (SN-PHTHALOCYANINE) MOLECULES. MOLECULAR MECHANIC SIMULATIONS.
(A) ON A GOLD (111) SUBSTRATE : THE GROWTH MODE IS BI-DIMENSIONAL.
(B) ON A ULTRATHIN LAYER OF NaCl (001)/Au(111) THE GROWTH MODE IS 3D. (J. AM. CHEM. SOC., 132, 12547, 2010).