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Editorial

This present issue is strongly focused on novel physical and chemical properties of carbon materials and their interaction with nanostructures. IPCMS is one of the most active European laboratories on such materials, taking advantage from a large variety of available experimental techniques such as scanning tunneling microscopy, atomic-force microscopy, micro magneto-Raman spectroscopy, electron tomography and spatially resolved electron energy loss spectroscopy. In the examples shown hereafter, carbon can take the form of multi-layer and monolayer graphene, graphite and nanotubes and act as a support or as a system bearing intrinsic properties still not fully exploited. In the contribution by Frederiksen et al. (Nature Comm. 5:6359, (2014)) a new insight is provided on the electronic transport between a C60 molecule and single metallic atoms. The study by Melinte et al. (Nature Comm. 5:4109, (2014)) addresses the morphology of iron-based nanoparticles in contact with a few-layer graphene system. This turns out to be strongly dependent on the topology of the underlying carbon substrate. The results by Berciaud et al. (Nano Letters 14, 4548 (2014)) demonstrate the variety of the electronic excitation spectra in N-layer graphene, fostering the understanding of many-body effects on the magneto-optical conductivity. As a last highlight on carbon materials properties, the sliding properties of a nanostructure on graphite are addressed by M.V. Rastei et al. (Phys. Rev. B 90, 041409(R) (2014)).

To what extent spin transport properties across the prototypical MgO system are affected by the presence of defects sites? This issue is addressed by describing thermally activated defect-assisted magneto-transport via solid-state tunneling spectroscopy (Nature Comm. 5:4547, (2014)). Another stimulating highlight in material science is provided by the paper of Lenertz et al. (J. Phys. Chem. C 118, 13981 (2014)) investigating by powder neutron diffraction measurements the antiferromagnetic, ferrimagnetic, and ferromagnetic configurations of the magnetic moments in γ-CoV₂O₆.

The present issue ends with two interdisciplinary contributions in which concepts of photonics and biophysics (the first) as well as physics and soft matter (the second), are intimately related. J Léonard et al. (Lab. Chip 14, 4338 (2014)) present a new method of high-throughput (bio-)molecular screening by time-correlated single photon counting of the fluorescence from microfluidic droplets. The contribution by A. Debacker et al. (Phys. Rev. Lett. 113, 028301 (2014)) establishes the atomic-scale foundations of a very common and widespread phenomenon, the dispersion of a powder in a liquid.

Stefan Haacke, Director
The electronic properties of bilayer graphene drastically differ from those of monolayer graphene. These two (quasi) bidimensional systems are the building blocks necessary to describe the electronic properties of the family of stacks of N-layer graphene, up to the limit of the bulk material, graphite. A detailed study of the members of this family of electronic systems could reveal new quantum transport regimes, potentially useful for future applications. A team of physicists from IPCMS and Grenoble’s High Magnetic Field Laboratory (LNCMI) has measured for the first time the evolution of the electronic band structure of stacks of N-layer graphene, from the mono- to the pentalayer, using Raman scattering spectroscopy with an applied transverse magnetic field. These studies have recently been published in Nano Letters (cf. reference below).

In our experiments, we have deposited high crystalline quality graphene flakes onto a substrate, pre-patterned with micrometer scale holes. In such conditions, it is possible to find graphene flakes suspended over holes, hence, non-affected by the substrate and from which the intrinsic properties can be probed. When a magnetic field is applied, electronic states of N-layer graphene specimens transform into discrete and highly degenerated Landau levels, with an evolution as a function of the magnetic field which directly reflects the number of graphene layers. The Raman scattering response of N-layer graphene has been measured at low temperature and with an applied magnetic field up to 29 T. In addition to the well-known vibrational Raman peaks, new features showing pronounced dispersions with the magnetic field appear. The latter are attributed to an electronic Raman scattering process, involving electronic transitions between Landau levels. Tracing the evolution of such excitations as a function of the magnetic field allows imaging the characteristic Landau level structure of a N-layer graphene specimen, to finally deduce the electronic band structure at zero magnetic field and, in particular, the Fermi velocity. Because of dielectric screening, the Fermi velocity is found to decrease when increasing the number of graphene layers to reach the value measured in bulk graphite. The electronic Raman scattering process observed for the first time in suspended graphene, opens new avenues in the research on graphene and on 2D semiconductors, in particular in the search for effects of many body interactions in the optical response of graphene. Magneto-Raman spectroscopy appears as a well-adapted, contactless technique to probe electronic excitations at the micrometer scale. This approach could be applied to the study of other bidimensional crystals such as silicene, phosphorene and the large family of transition metal dichalcogenides.

S. Berciaud, M. Potemski, & C. Faugeras, Nano Letters, 2014, 14, 4548

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Structural defects and spin-polarized transport: a 10+ year-old enigma solved

The magnetic tunnel junction (MTJ), which consists in two ferromagnetic electrodes separated by a tunnel barrier, is an essential brick for spin electronics, a strategic research field toward information science and technology. In quantum mechanics, electron transport through solid-state tunneling (SST) across an ultrathin dielectric layer conserves the properties of this electron, including its spin and symmetry. The conservation of these electronic parameters can thus be studied using MTJs. Our understanding of SST has been considerably strengthened over 10 years ago thanks to the convergence between theory and experiment on crystalline junctions with Fe electrodes and a MgO barrier. However, the energetic height of the barrier as measured experimentally has always been lower than expected, or even in complete contradiction with theory. After two years of research, scientists from the Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS) have, in collaboration with the Institut Jean Lamour, solved this enigma.

Within the scope of ANR project SpinMarvel (2009-2013), these scientists revealed the impact of structural defects present within the MgO tunnel barrier on spin- and symmetry-polarized transport. They characterized the temperature dependence of photoluminescence spectra acquired on this MgO, and in the process revealed the presence of oxygen vacancies at a concentration reaching the percent (which is huge!). They then confirmed that the electronic occupation of these vacancies evolves, with increasing temperature, from the ground to the excited state of a given vacancy type. This alters the barrier height perceived by tunneling charge carriers. These vacancies, according to their structure, can in turn asymmetrically mix the symmetry-polarized transport channels. This yields different barrier heights in each channel. By combining these elements, one can explain how the spintronic performance of these junctions is in agreement with theory if it takes into account the impact on magnetotransport of the structural and electronic nature of these vacancies.

In publishing this work in August 2014 in Nature Communications, and to affirm this new scientific perspective, these scientists propose to their colleagues that the presence of defects within the MgO of their MTJs, and its impact on spintronics, be better documented. In addition, this work constitutes a manifesto for the numerous scientific communities working on advanced dielectrics (eg. strongly correlated oxides): one must take defects into account when assessing that dielectric’s intrinsic functionality (eg ferroelectricity, multiferroicity), especially at the nanoscale.

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IPCMS meets NIMS

At the end of January 2015, five IPCMS researchers have attended a joint meeting with the NIMS institute for Material Science (Tsukuba, Japan) having a twofold purpose: setting the scene for the establishment of scientific exchanges and allow the formal signature of a bilateral exchange convention between the University of Strasbourg (represented by the IPCMS) and the NIMS. The IPCMS researchers attending this event were Stefan Haacke, Carlo Massobrio, Hicham Majad, Stéphane Bellemin-Laponnaz et Guillaume Rogez. The picture refers to the convention signature featuring the director of IPCMS, Stefan Haacke and the director of NIMS, Sukekatsu Ushioda.
Low-dimensional magnetic oxides built up of one-dimensional magnetic chains show generally unusual properties such as a stepped magnetization reversal, a particularly strong anisotropy, or interesting magnetodielectric coupling. Many of these properties result from geometrical frustrations, structural modulations or mixed valence magnetic ions.

CoV₂O₆ is such a one-dimensional magnetic oxide that exhibits an antiferromagnetic (AF) ground state, a strong anisotropy and a magnetization plateau at one-third of the saturation magnetization (MS). It presents two polymorphs: one monoclinic called α-CoV₂O₆ and one triclinic called γ-CoV₂O₆. Both phases are constituted of magnetic chains of CO₆ octahedra, separated by nonmagnetic VO₄/₆ units (fig. a). While all Co atoms are equivalent in the α phase (Co-Co-Co angles of 180°), in the γ phase they occupy two different atomic positions (Co-Co-Co angles of 170° or 180°). For this reason the magnetic structure of the γ phase has never been described correctly. In our work, the structural and magnetic properties of γ-CoV₂O₆ have been investigated with an emphasis on its magnetic structure.

Powder neutron diffraction measurements were carried out under magnetic fields of 0, 0.52, and 1 T, corresponding to the antiferromagnetic (AF), ferrimagnetic (Fi), and ferromagnetic (F) configurations of the magnetic moments (fig. b). The magnetic moments are not collinear, but lie mostly along the b direction (i.e., inside structural edge-sharing CoO₆ chains), which corresponds to the experimental easy magnetization axis (fig. c). In the ground state, the moments are ferromagnetically ordered along the b and c directions, and AF ordered along a axis. The ground state magnetic structure can be described in a (4a, 2b, c) supercell using two AF propagation vectors k₁ₐF = (1/2, 0, 0) and k₂ₐF = (1/4, 1/2, 0). The second propagation vector modulates the first one, tuning the orientation of the spin in a 8-fold unit cell (fig. c). The ferri- and ferromagnetic structures are characterized by k₁ₕ = (1/3, 0, −1/3) and k = (0, 0, 0) propagation vectors, respectively (fig. d and e). The existence of a vector modulation along the b axis agrees with the difficulty to reach the full magnetic saturation and could explain the slope of the magnetization curve above 1 T.


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Structuring few-layer graphene sheets

To develop electronic devices based on the use of carbon nanotubes (CNTs) with the desired chirality or structured catalytic graphene layers one must envisage tailoring processes like cutting for example. Researchers from the IPCMS and ICPEES Institutes in Strasbourg have joined their efforts to acquire deep understanding of the catalytic cutting of few-layer graphene sheets, by using advanced electron microscopy.

Iron oxide nanoparticles are first deposited onto a graphene sheet of a few layers, which was prepared through mechanical exfoliation of massive graphite. As a result of the exfoliation process the surface of the sheets is randomly decorated with steps and the overall thickness is an integer number of graphene layers. The samples are submitted to a reducing flow of hydrogen before their study by means of 3D electron tomography. During the hydrogen treatment, the particles situated at the step foots start to move along the high sym-
Neutron diffraction: a powerful tool for the resolution of complex magnetic structures. 3D analysis of the catalytic cutting of graphene by Fe-based nanoparticles as explored by electron tomography. Different trajectories are drawn by the catalytic particles on graphene by following well defined crystallographic directions shown schematically (upper side). 2D TEM micrographs and 3D volume sections identify two different cutting nanoparticles and the corresponding trench (down left side) and tunnel (down right side).

The friction between two bodies in relative motion is of paramount importance in a large variety of applications. This includes nanodevices which directly rely on friction forces at atomic and nanometer scale. In this context, lamellar materials such as graphite, graphene or MoS$_2$ are considered key materials for reducing friction, yet very little is known on the exact physical processes at work at the same scale.

After having shown that the sliding of a nanostructure on graphite occurs through a puckering friction mechanism, we recently report in a PRB Rapid Communication that the surface of graphite exhibits a surprising nanoscale frictional mosaicity due to the same puckering effect. Using an Atomic Force Microscope operating in vacuum we found that sliding along a stiff crystallographic axis promotes a low friction. Depending on sliding speed and angle between the pulling direction and the local stiff crystal axis, friction can vary by more than one order of magnitude. The results are significant as graphite surface was thought to be one of the most homogeneous in terms of friction. Our findings are also useful to understand how single nanoparticles and molecules can be manipulated on these lamellar surfaces.

M.V. Rastei, P. Guzman, and J.L. Gallani, Phys. Rev. B 2014, 90, 041409(R)

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Nanoscale Friction: The Secret to Sparing Energy

The friction between two bodies in relative motion is of paramount importance in a large variety of applications. This includes nanodevices which directly rely on friction forces at atomic and nanometer scale. In this context, lamellar materials such as graphite, graphene or MoS$_2$ are considered key materials for reducing friction, yet very little is known on the exact physical processes at work at the same scale.

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M.V. Rastei, P. Guzman, and J.L. Gallani, Phys. Rev. B 2014, 90, 041409(R)

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How fast does a curd swell?

How fast does your morning chocolate powder disperse in milk? Could you be lazy enough to wait for the dispersion of flour in the crêpe pastry? How to avoid unpleasant curds when pills are dispersed in water? These everyday situations involve the dispersion of a powder in a liquid. Powder dispersion plays a role in many industrial processes in the building activity or in the food and pharmaceutical industries. It is of the utmost importance in the tyre process, where the quality of powder dispersion directly controls the mechanical properties of the final product.

In its dry state, and because attractive surface forces, powder consists in small agglomerated particles. During the dispersion, the aggregates must be disrupted. This can be done through the aid of mechanical forces (by mixing the powder with the solvent) or induced by the wetting of the particles by the solvent, leading to the imbibition of aggregates. When this happens, capillary forces pull the solvent inside the pores of the aggregates. The imbibition is governed by the difference of pressure between the inner part of the aggregates and the outside pressure: on one hand, capillary pressure drives the infiltration, on the other hand, charge loss slows down the flow. Such a very simple description of the capillary rise inside a pore has been known for almost a century and can be used to describe the imbibition of a porous medium whose one side remains in contact with the atmosphere. Nevertheless, despite attempts to use it to describe the imbibition of powders, much complex kinetics, in which the rate of imbibition slows down and rapidly accelerates after a waiting time, are observed and are yet to be understood. We have observed that this complex kinetics is due to the trapping of air inside the aggregates, that is compressed by the advancing front. A state where the pressure of trapped air is equal to the capillary pressure is reached. The imbibition then stops, but the system is in a metastable state: any increase of the pressure inside the aggregate leads to drainage of air out of the aggregate. This is responsible for the front instability, finally leading to the complete imbibition of the aggregate.


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![Image of the aggregate during the imbibition (a) and (b) and after complete imbibition (c). The dry core appears black due to refraction at the air/particles interface whereas the imbibed shell is more transparent.](image)

![Evolution of the square of the non-infiltrated core radius as a function of time for aggregates of radius 1 mm (black squares), 1.5 mm (dark grey squares), 2 mm (medium grey squares) and 2.5 mm (light grey squares). Insert: Same data represented in a log-log scale. The first imbibition kinetics (corresponding to the trapping of air) is clearly defined.](chart)
Fluorescence detection is a very sensitive technique for biosensing and in particular biomolecular interactions assaying (DNA-protein, protein-drug, etc...). In that case, biomolecules are fluorescently-labeled with molecular probes. Upon light excitation, the latter undergoes an excited-state reaction (e.g. energy transfer or "FRET", charge transfer, etc...) which is strongly influenced by the interaction with its near environment, hence by changes in biomolecular structures or interactions. Most commonly a change in fluorescence intensity is detected as a diagnosis for the interactions of interest. However, fluorescence intensity may also be affected by other, non-relevant parameters, such as inhomogeneity or fluctuations in excitation light or in fluorophore concentration. Instead fluorescence lifetime (FL) detection is an intrinsic measure of the excited-state lifetime of the chromophore, hence of biomolecular interactions. This is for instance the reason why FL imaging microscopy (FLIM) has been largely developed to monitor biomolecular interactions in cellulo and distinguish regions of the cell where a biomolecule interacts (change in FL), from regions where it is simply less concentrated (change in fluorescence intensity but not in lifetime).

We propose to develop the use of FL detection for high-throughput (HT) biomolecular interaction assays. As a platform for HT sample manipulation we use droplet microfluidics, which is very promising for biotechnologies because it allows accurate and rapid manipulation of very small samples (picoL or less). The most sensitive technique for FL detection is certainly time-correlated single photon counting (TCSPC), in which single photon detection events are dated (correlated in time) with respect to the preceding laser excitation pulse. After accumulating a large number of single detection events, the histogram of the fluorescence detection times yields the fluorescence decay kinetics (and FL) of the chromophore. The technique has long been well established and is very accurate. However counting photons one by one is reputed to be relatively slow and therefore not suited for HT fluorescence assays.

In a proof-of-principle experiment, we demonstrated that TCSPC can be implemented with a cheap, low-power, picosecond laser diode to detect "on-the-fly" the passage and FL of water-in-oil droplets of diameter 50 µm, containing as little as a few 100 nM fluorescein, and circulating at a rate as high as 1000 droplets/sec in a microfluidic channel. We explored the experimental and fundamental limitations (single photon detection statistics) to demonstrate that i) several $10^3$ photons per droplet can be detected in that regime, and ii) the corresponding accuracy of the FL determination enables reliable HT screening assays based on FL detection by TCSPC. The technology was patented and further microelectronics developments are presently carried out (collaboration with Prof. W. Uhring, ICube) towards concrete applications.


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Thanks to their unique mechanical and electronic properties, carbon-based materials such as nanotubes, graphene sheets, and nanoribbons are intensively scrutinized and promising applications ranging from energy storage to nano-electronic devices are envisioned. A close attention is paid to the electrical connections of these graphitic structures to external metallic leads where the injection and the collection of electric charges occur. Indeed, bad interfaces might ruin the desired properties of such carbon-based devices. In this respect, the chemical nature of the contacting leads is of major importance; it affects the electronic properties and the geometry of the contact. The impact of these two aspects on the transport properties are entangled, and for large structures it is challenging to address them separately.

An important step has been surmounted to solve this issue by researchers from the CNRS in Strasbourg, France, and from the Donostia International Physics Center in San Sebastian, Spain, who explored the evolution of these parameters for contacts shrunk to the limit of individual atoms. To this end the researchers studied a prototype carbon-based molecule made of 60 carbon atoms arranged in a sphere that can be viewed as a graphene sheet rolled into a tiny ball. The experimental team in Strasbourg led by G. Schull, attached this molecule to the apex of an extremely tiny metal needle of a scanning tunnelling microscope. The molecule-terminated needle was then cautiously approached to individual metallic atoms of different chemical nature up to the formation of a robust connection. By simultaneously measuring the electrical current passing through these connections, they could deduce which of the individual metallic atom is injecting charges to the carbon-made molecule with the greatest efficiency.

The theoretical team in San Sebastian led by T. Frederiksen, performed large-scale computer simulations that revealed a fascinating and unexpected aspect of these extremely small connections: their electric and mechanical properties are in fact representative for much larger carbon-based materials. In other words, this study of single-atom connections turned out to be a basic model to explore and intuit the general properties of electrical contacts between metals and structures made of carbon atoms, whatever their dimension, size, or shape. These results, published in Nature Communications, suggest that in a near future a great number of different metallic species (as well as small alloys made of two or three different metallic atoms) will be probed, allowing for a systematic classification of their abilities to inject electrons into carbon-based electronic devices.


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A special award

During the first edition of the conference « Instrumenter et Innover en Chimie Physique pour Préparer l’Avenir » that did take place January 22nd and 23rd 2015 in Paris, Christian Mény and Pierre Panissod received the 2014 prize for instrumental developments of the Division of Chemistry and Physics of the French Society of Physics. The prize has been awarded for the development of a broadband spectrometer for Nuclear Magnetic Resonance in ferromagnets and for the recent methodological developments that have been performed in order to study assemblies of nano-objects. The 2014 prize is shared with Alexandra Sereda of the Institut d’Optique in Palaiseau.