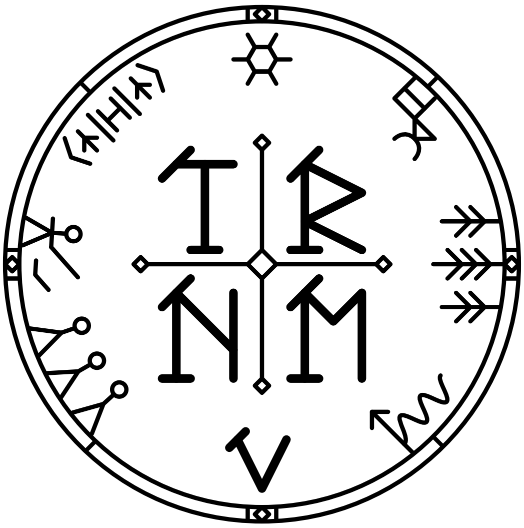
Towards Reality in Nanoscale Materials V

20th — 22nd February 2012
Levi, Lapland, Finland



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Acknowledgement for financial support

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Programme

8:45	intro		
chair	*Rinke*	*Roche*	*Busse*
9:00	Artacho	Busse	Roche
9:40	Bøggild	Lehtinen	Ahlskog
10:00	Sob	Pietrucci	Makarova
10:20	Borlenghi	Booth	Carva
10:40	*coffee*	*coffee*	*coffee*
chair	*Pantelides*	*Perez*	*Artacho*
11:20	Watkins	Liljeroth	Pantelides
12:00	Barth	Ewels	Minato
12:20	Laasonen	Amara	Girard
12:40	Rayson	Kurasch	Uppstu
13:00	*lunch*	*lunch*	*lunch*
chair	*Liljeroth*		*Bøggild*
16:00	Rinke	*posters*	Sinnott
16:40	Susi	16:00 – 18:00	Mittendorfer
17:00	Standop		Perez
17:20	*coffee*		
chair	*Sinnott*		closing
18:00	Chamberlain	*dinner*	
18:20	Björk	18:00 – 21:00	
18:40	Philipp		

Contents

Monday 20/02/2012

8:45	intro
chair	*Rinke*
9:00	Artacho
9:40	Bøggild
10:00	Sob
10:20	Borlenghi
10:40	*coffee*
chair	*Pantelides*
11:20	Watkins
12:00	Barth
12:20	Laasonen
12:40	Rayson
13:00	*lunch*
chair	*Liljeroth*
16:00	Rinke
16:40	Susi
17:00	Standop
17:20	*coffee*
chair	*Sinnott*
18:00	Chamberlain
18:20	Björk
18:40	Philipp

Origin of the 2DEG at oxide interfaces, relation with topology and with redox defects, and possible 1DEG

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When epitaxially depositing a thin film of lanthanum aluminate (LAO) on a strontium titanate (STO) substrate, both band-like insulators, a two-dimensional electron gas (2DEG) emerges at their interface displaying quite interesting and promising properties. The origin of such 2DEG is ascribed to the electrostatic energy build-up in the film due to an effective “chemical" or “compositional" charge at the interface, which destabilises the system towards the appearing of free carriers at the interface screening that charge.

In this talk we will first describe how such chemical charge comes about [1,2], in terms of a discontinuity in the polarisation of both bulk materials. Both STO and LAO are centrosymmetric and thus should be assigned zero effective polarisation, but in fact, while the former has zero polarisation, the latter has half a quantum of polarisation, the two possible distinct values for the formal polarisation of a centrosymmetric material in this context [1,2,3]. The two values correspond to two different values of the Berry phase for polarisation and therefore analogies can be drawn with the topological insulators arising relating to time inversion symmetry.

We will then argue how the electrostatic build-up would promote redox processes on or at the surface of the film [4], which compete with the proposed pure electron transfer (or “electronic reconstruction") as the source of carriers for the 2DEG. Finally, we will propose 1DEG formation possibilities in analogous stepped interfaces [5]. Such ideas will be reviewed and confronted with available experimental results and models based on first-principles calculations.

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On chip synthesis and characterisation of nanostructures in- and outside TEM

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Microfabricated chips with incorporated heater structures allow micro-CVD synthesis of carbon nanotubes and epitaxial silicon nanowires, as well as synthesis insitu TEM. The microheater approach readily gives the experimenter access to high temperatures, fast response times and temperature gradients, which is challenging in any conventional setup. I will overview some of the possibilities that microchip heaters have to offer for studying thermally induced processes such as growth, catalyst roughening and annealing. Resistively heated chips were used to make a linear temperature ramp, which in a single experiment gives a picture of the carbon nanotube growth rate in a continuous range of temperatures. The temperatures were calibrated by micro Raman thermometry and finite element modeling [1]. By using heated single crystalline silicon chips in an environmental TEM, the growth of epitaxial silicon nanowires was tracked in-situ, giving insight in the shape and behavior of the gold catalyst as well as into non-equilibrium effects when hot nanowires form contact to opposing cold silicon walls [2]. Finally, I will point out some of the possibilities for rapid (20 minutes) D.I.Y. fabrication of electron-transparent in-situ TEM heater devices with custom electrode layout by focused ion beam milling of template membrane chips [3], show how this may be used to monitor catalyst surface dynamics directly in TEM, and discuss what else such chips could be used for.

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Ab initio study of mechanical and magnetic properties of Mn-Pt compounds and nanocomposites

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An analysis of mechanical and magnetic properties of Mn–Pt compounds and nanocomposites is provided using DFT calculations. Adding manganese to platinum matrix reduces the bulk modulus and enhances the Young moduli and shear moduli. With increasing Mn content, the theoretical tensile strength is also enhanced and the corresponding maximum deformation is reduced. On the whole, manganese addition makes the Mn–Pt compounds softer, but increases their resistance to shape deformation. Many of these compounds may be considered as natural linear nanocomposites. We studied the magnetic configurations of recently found $MnPt_7$ ordered structure and predict an antiferromagnetic state with spins altering along the [100] direction to be the ground state of this compound. The ferromagnetic state and an alternative antiferromagnetic state with spins altering along the [111] direction have a higher total energy. We further studied Mn–Pt nanocomposites exhibiting the composition of $MnPt_{15}$. The preferential occupation sites of Mn atoms are the corners and centers of the faces of the 2x2x2 supercell. Such a structure with an antiferromagnetic ordering with spins altering along the [100] direction is the ground state of $MnPt_{15}$ nanocomposite. Contrary to $MnPt_7$, the alternative ferromagnetic configurations of different $MnPt_{15}$ nanocomposites exhibit the screening of magnetic moments of Mn atoms by flipping the moments induced on Pt atoms in the opposite direction. This indicates that the Mn spins can be coupled through the Pt atoms similarly as spins of Mn dimers on CuN substrate can be coupled through nitrogen atoms [Phys. Rev. B 83, 014413 (2011)].

This research was supported by the Ministry of Education of the Czech Republic (Project No. COST OC10008), Grant Agency of the Czech Republic (Project No. 202/09/1786), the Grant Agency of the Academy of Sciences of the Czech Republic (Project No. IAA100100920), by the Research Projects AV0Z20410507 and MSM0021622410, and by the Project CEITEC-Central European Institute of Technology (CZ.1.05/1.1.00/02.0068) from the European Regional Development Fund.

Electronic transport and magnetization dynamics in realistic devices: a multiscale approach

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The mutual interaction between spin transport and magnetization dynamics in hybrid nano-devices is at the origin of physical effects, such as Spin Transfer (ST) [1] and Giant Magneto Resistance [2], which act at very different length scales, and depend both on the microscopic characteristics of the material and on the geometry of the device. These effects opened a potential for various applications, such as magnetic memories, reprogrammable logic, and Spin Torque Nano Oscillators (STNO) [3]. The physics of those devices cannot be captured by simple (analytically tractable) models, and numerical simulations that can be easily adapted to different geometries, length scales and materials are of primary importance to describe realistic systems.

We report on a theoretical model, based on Continuous Random Matrix Theory (CRMT) [4] and Non Equilibrium Green Functions [5], that describes on an equal footing transport and magnetic degrees of freedom in realistic devices. The model has been implemented in a simulation code [4,6] that allows one to compute local (spin torque, spin accumulation and spin/charge current) and macroscopic (resistance) transport properties of spin valves. Our approach offers a systematic way to perform multiscale simulations [7] in heterogeneus systems with arbitrary geometry, connected to an arbitrary number of electron reservoirs. Bulk and interface properties of very different materials (magnetic and non-magnetic metals, insulators, semiconductors, superconductors) are properly captured by our model, which can be parametrized using both experimentally accessible parameters and ab initio calculations. As an application of our method, we have coupled CRMT to a micromagnetic simulation code, in order to model a spectroscopic experiment [8], based on a mechanical detection of the ferromagnetic resonance, and performed on a STNO. Our simulations predict correctly the selection rules for spin wave (SW) modes excited by ST, and give a description of the complex dynamics of the magnetization in qualitative agreement with experiments [9]. Our multiscale approach can be coupled to other micromagnetic or spin dynamics codes, and offer a systematic way to compute current driven dynamics in different systems.

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Developing realistic models of interfaces from simulation

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I will describe several recent pieces of work focussing on developing an atomistic-level understanding of a range of interfaces. A variety of computational approaches are used, and connected to state-of-the-art experiments, often using the non-contact atomic force microscope (NC-AFM).

(i) Insulator - molecule - metal. In collaboration with NC-AFM experimental researchers at the University of Hamburg, we unambiguously identified the adsorption configurations of a complex molecule on ionic crystals (NaCl, NiO) and the nature of surface ions [1,2]. These systems can provide a sensitive test system to calibrate the accuracy of computational approaches and also act as a tape measure, providing an accurate measure of tip-sample distance, which is extremely hard to estimate independently.

(ii) Insulator - water. High-resolution imaging and force spectroscopy using AFM in solution opens a wide area of possible applications allowing real-time and real-space imaging of surfaces in solution. To obtain full benefit and provide a significant new analytical ability, it is vital to understand the underlying imaging mechanism(s) that can lead to high (atomic or molecular) resolution. Our simulations of solvated nanoparticles near surfaces show several possible mechanisms that lead to measurable force differences and image contrast over surface sites [3]. We used free-energy perturbation theory to calculate the free energies of nanoparticle-surface interaction. Water-mediated interactions can cause significant force differences above different surface sites, and are in most cases larger, and longer ranged, than the direct vacuum-like interactions.

(iii) Water ice - vacuum. Resolving the atomic structure of the surface of ice particles within clouds, over the temperature range encountered in the atmosphere and relevant to understanding heterogeneous catalysis on ice, remains an experimental challenge. By using first-principles calculations, we show that the surface of crystalline ice exhibits a remarkable variance in vacancy formation energies, akin to an amorphous material. We find vacancy formation energies as low as 0.1-0.2 eV, which leads to a higher than expected vacancy concentration. Because a vacancy's reactivity correlates with its formation energy, ice particles may be more reactive than previously thought. We also show that vacancies significantly reduce the formation energy of neighbouring vacancies, thus facilitating pitting and contributing to pre-melting and quasi-liquid layer formation [4]. These surface properties arise from proton disorder and the relaxation of geometric constraints, which suggests that other frustrated materials may possess unusual surface characteristics.

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Two-dimensional growth of nanoclusters and molecules on Suzuki surfaces

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Patterned surfaces are used for confining the growth of molecules and clusters into nanostructured surface regions, which finds nowadays many applications in nanotechnology. In this contribution it is shown that the nanopatterned surface of Cd doped NaCl crystals [1] (Suzuki surface) can be used to confine the growth of palladium clusters and functionalized brominated pentahelicene molecules [2] into the Suzuki regions of the surface. It is shown that especially the combination of noncontact AFM (nc-AFM) and Kelvin probe force microscopy (KPFM) in ultra-high vacuum (UHV) greatly helps in the characterization of the structure and morphology but also the electrostatics of the considered surfaces [3]. The growth of palladium onto the Suzuki surface results into nanometre sized clusters, which form two-dimensional cluster arrays inside the Suzuki regions. The clusters exhibit a high cluster density, are uniform in size, and due to the specific Suzuki structure the clusters are polarized or charged. Brominated pentahelicene molecules perfectly decorate the Suzuki regions and form two-dimensional islands whereas no molecules can be found inside the pure NaCl regions. The molecules are in a flat configuration, which finds strong support from first principle calculations. Due to the specific adsorption of the molecules, the surface dipole of the Suzuki regions is modified by the molecules. It is shown that changing the functional group of the helicene molecules leads to different adsorption characteristics, self-assembly phenomena and different surface dipoles [4].

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Reaction studies of Al-O clusters in water

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We present several AIMD studies of reactions related on Al-O clusters in water. We have done reaction driven with distance constraint [1,2] and MetaDynamics simulations [3]. Of constraint driven reactions we have studied Cl dissociation from $Al_2O_6H_8Cl_2$ [1] and $Al_2O_8H_{12}$ + AlO_4H_6 association reaction. With MetaDynamics we studied $Al_3O_nH_m$ internal reactions. Also a more general discussion of reaction studies using AIMD is given.

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Towards large-scale accurate Kohn-Sham DFT for the cost of tight-binding

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We present recent, and ongoing, work aimed at highly accurate calculations for large-scale systems. The implementation of the *filtration* method [1,2,3] in the `AIMPRO` Gaussian orbital code is described. Timings and accuracy results are presented for defective semiconducting and metallic systems and a range of quantities, such as formation energies, forces, relaxed structures, vibrational modes and free energies. For example, the time taken to calculate a self-consistent total energy of 1000 silicon atoms (to achieve an average error of less than 10^{-4} angstrom in relaxed structures) is shown to be currently possible in less than 30 minutes on a single 2.8 GHz Intel i7 core.

We finish with a summary of realistic near-term aims, most notably an aim which can be summarised as 'plane-wave accuracy for the cost of a tight-binding calculation'.

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Towards a unified description of ground and excited state properties: RPA *vs GW*

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In the quest for finding an "optimal" electronic structure method, that combines accuracy and tractability with transferability across different chemical environments and dimensionalities (e.g. molecules, wires/tubes, surfaces, solids), the treatment of exchange and correlation in terms of "exact-exchange plus correlation in the random-phase approximation (EX+cRPA)" offers a promising avenue. For quasiparticle spectra as measured by direct and inverse photoemission the GW approach is on the same level of theory as EX+cRPA for the ground state. For molecules and nanosystems the application of GW has steadily gained in popularity and a full assessment of its performance is emerging. In this talk I will extend the assessment of EX+cRPA and GW to small molecules [1] and molecules on surfaces [2,3]. Based on this I will comment on the prospects of these approaches for nanoscience, address current challenges and present avenues for going beyond RPA/GW.

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Core level binding energies of defected and functionalized graphene

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X-ray photoelectron spectroscopy (XPS) is a widely used tool for probing carbon-based nanomaterials. To interpret the binding energies measured by XPS, references to which such energies can be compared is needed. We have employed core-hole calculations utilizing a Delta Kohn-Sham total energy differences method recently implemented [1] in the real-space grid-based projector-augmented wave (GPAW [2]) DFT code to calculate reference core level energies for defected and functionalized graphene.

Our graphene system had a 9x9 unit cell with periodic boundary conditions, treated with 3x3x1 k-points. Using the PBE functional, we calculated C1s and O1s core level energies for simple oxygen and hydrogen functionalities such as the hydroxide, epoxide and carboxylic groups. In addition, we considered the elementary atomic defects [3]: single and double vacancies, and the Stone-Thrower-Wales defect. Finally, modifications of the reactive single vacancy with O and H containing groups were considered. The calculated C1s and formation energies were compared to data in the literature, and Bader analysis [4] employed to elucidate the effect of charge transfer to the observed shifts.

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Spatial Analysis of Ion Beam induced Defects in Graphene

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Defects are expected to play a crucial role when preparing graphene for nanoscaled applications. Only recently the chemically inert graphene layer was found to form chemical bonds to an underlying metal support once vacancies are formed [1]. We employed the impact of noble gas ions on the graphene layer grown on Ir(111) to purposefully create defects. Ions impinging under an angle of 75° with respect to the surface normal are to a large extent able to penetrate the graphene layer and subsequently face scattering with the iridium surface. Depending on the primary energy (1 - 15 keV) and the ion species (He, Ne, Ar, Xe) manifold and complex reflection events take place on both faces between these layers. This leads to the formation of collision trails visible as surface damage in scanning tunneling microscopy. The resulting defect patterns can thus be spatially analysed. Annealing studies of these samples performed in-situ reveal these trails to origin from sputtering of the graphene layer and additional adatom production in the iridium crystal. While the metal surface mainly rebuilds its initial structure, the graphene layer forms rotational domains upon impact annealing. They result from agglomeration of rotated carbon bonds [2]. Besides giving an insight into their thermal stability this enables us to analyse these structures quantitatively and present models for the manifold defect patterns observed.

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Utilizing carbon nanotubes as nanoreactors

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Carbon nanotubes (CNTs) - atomically thin cylinders of sp2 hybridized carbon - have high mechanical and chemical stability and are available in different diameters from sub-nanometre to hundreds of nanometres. Due to the hollow nature of CNTs, it is possible to insert a wide variety of atoms and molecules into the internal cavity resulting in the formation of 1D molecular arrays, some of which do not exist outside of carbon nanotubes and thus can be regarded as products of confinement at the nanoscale.[1] The relative chemical inertness of the concave side of the CNTs makes them ideal candidates for use as both reaction vessels, in which the reactants can be combined, and a 1D template for the controlled formation of products which are unfavoured in the bulk phase.[2] Low-voltage, aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) can be used to visualize these transformations and reactions within the nanotube in real time.[3,4] Encapsulation of the appropriate elemental building blocks, carbon and sulphur, within CNTs results in the formation of sulphur terminated graphene nanoribbons (S-GNRs) in the CNT channel. Such structures represent a new, unexpected hybrid form of carbon, with potentially exciting functional properties.[5] Details of the atomic structure of the novel GNR and the effects of the 1D confinement imposed on the nanoribbon by the CNT have been probed by AC-HRTEM which reveals unusual dynamic behaviour in which the nanoribbon adopts a spiral shape within the CNT. Though the interior surface of carbon nanotubes is known to be chemically inert and typically remains unaffected by reactive species, we have demonstrated that catalytically active atoms of transition metals, when inserted into the internal cavity, can engage the nanotube sidewall in chemical reactions from the inside leading to the formation of nanoprotrusions in the CNT.[6]

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Molecular self-assembly of covalent nanostructures: Unravelingtheir formation mechanisms

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Several experimental studies have illustrated how large macromolecular structures can be formed through molecular self-assembly on surfaces. This success has mainly been obtained via trial and error coupled to insights from organic chemistry, and to date there is little theoretical understanding of how covalent self-assembly proceeds on a submolecular level. We work towards this understanding for two important reaction mechanisms.

A successful approach to generate covalently linked nanostructures through self-assembly is to use molecular building blocks with specific hydrogen atoms replaced by bromine atoms [1]. By splitting-off the bromine atoms one enables the molecules to covalently couple into various structures. In a recent experimental study it was illustrated how graphene nanoribbons (GNRs) self-assemble on the Au(111) surface [2]. In a first step, the debromination strategy is employed to create poly-anthracene from a bianthracene derivative. Secondly, poly-anthracene undergoes a cyclodehydrogenation, resulting in the GNR.

Here we aim to obtain a detailed atomistic view into both of these reaction mechanisms from first principles density functional calculations. In a first part, the mechanism of the debromination will be discussed from a more general viewpoint. The reaction has been studied for bromobenzene on the close-packed (111)-facets of commonly used coinage metals, and we illustrate how the different surfaces catalyzes the reaction.

Secondly, the mechanisms controlling the cyclodehydrogenation of polyanthracene into the GNR on Au(111) will be elucidated. The catalytic role of the Au surface will be discussed by comparing possible reaction pathways. We find that the most favorable transition path is associated with only one barrier, while the other conceivable paths have a second high energetic barrier. Finally, we discuss the cooperative effects involved in the subsequent cyclodehydrogenation, showing how the reaction propagates with a domino-like effect throughout the polyanthracene [3].

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[3] J. Björk, S. Stafström and F. Hanke, J. Am. Chem. Soc. 133 (2011) 14884.

Simulation of defect formation and sputtering of Si(100) surface under low-energy oxygen bombardment using a reactive force field

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The interaction of oxygen atoms with surfaces is of interest for a series of issues and applications. They include the formation of oxides, the interaction of oxygen atoms and ions with surfaces in plasma surface treatments or the bombardment of surfaces with oxygen atoms for sputtering and nano-patterning. For silicon, the formation of the native oxide layer as well as irradiation-induced damage and sputtering has major importance. In previous studies [1-2], results on single impacts of oxygen atoms on amorphous and Si(100) surfaces have been presented. It was shown that the sputtering of Si atoms and clusters largely depends on the damage in the target, i.e. more sputtering and formation of larger Si and SiO clusters was observed for the amorphous target.

In this presentation, we will study the interaction of low-energy oxygen atoms with a silicon surface by Molecular Dynamics (MD) simulations using the reactive force field developed by John Kieffer at the University of Michigan [3-5]. We will show results on continuous 250eV oxygen bombardment of a Si(100) surface and compare them to the aforementioned results. Amorphization, oxide formation and sputter mechanisms are studied with respect to oxygen fluence. Defects are monitored as function of time after a given oxygen impact.

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[2] P. Philipp, T. Wirtz, J. Kieffer, "Sputtering of silicon by low-energy oxygen bombardment studied by MD simulations", submitted to Surf. Interface Anal.
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Tuesday 21/02/2012

chair	*Roche*
9:00	Busse
9:40	Lehtinen
10:00	Pietrucci
10:20	Booth
10:40	*coffee*
chair	*Perez*
11:20	Liljeroth
12:00	Ewels
12:20	Amara
12:40	Kurasch
13:00	*lunch*
16:00	*posters*
18:00	*dinner*
21:00	

Graphene on metal surfaces

C. Busse[1]

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The new material graphene (Noble Prize in Physics 2010) currently receives an enormous attention for its exciting properties [1], caused by its monoatomic thickness and the unique band structure arising from its lattice symmetry.

We study the epitaxial growth of graphene on a metal surface (here: Ir(111)), which leads to graphene of high structural quality which is only weakly bonded to the substrate [1, 2]. Complementing scanning tunneling microscopy (STM), we determined key structural parameters using an x-ray standing wave (XSW) analysis. The results are corroborated by extensive density functional theory (DFT) calculations incorporating non-local interactions [3]. The key finding is that graphene is weakly bound to Ir(111) by global van der Waals forces with an added local covalent-like contribution.

The electronic and geometric properties of graphene can be modified by intercalating alkali metals, rare earths, or oxygen. Important for the subsequent use of epitaxially grown graphene, the intercalation also makes exfoliation of the carbon sheet possible.

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Detailed structure and transformations of grain boundaries in graphene

O. Lehtinen[1], J. Kotakoski[2], S. Kurasch[3], J.C. Meyer[2], V. Skakalova[2],
U. Kaiser[3], A.V. Krasheninnikov[1,4]

[1] *University of Helsinki, Finland*
[2] *University of Vienna, Austria*
[3] *University of Ulm, Germany*
[4] *Aalto University, Finland*

Ideal graphene is formed our of an infinite array of interconnected carbon hexagons. However, large real-life graphene sheets are often not formed of a single crystal domain, but rather consist of multiple differently oriented grains connected by grain boundaries (albeit micromechanically cleaved graphene flakes are monocrystalline). With chemical vapour desposition (CVD) technique, which is perhaps the most promising route to large scale fabrication of graphene, grain boundaries are always present, although recent developments have significantly increased the typical crystal domain sizes.

Several works have been dedicated to the structure of graphene grain boundaries, as they can significantly alter the properties of graphene. However, often the detailed structure of observed grain boundaries in, e.g., high resolution transmission electron microscope (HRTEM) experiments [1] differ significantly from the theoretically proposed optimal boundaries [2].

In this work the gap between the experimental and theoretical observations is bridged by means of multiscale atomistic simulations and HRTEM experiments. A theoretical model is presented, which reproduces charasteristic features observed in real grain boundaries and predicts low energy transformation routes connecting different low-energy boundary configurations.

[1] P. Y. Huang, et al. Nature 469 (2011) 389-392
[2] O. V. Yazyev and S. G. Louie Phys. Rev. B. 81 (2010) 195420

Graph theory meets ab-initio molecular dynamics: atomic structures and transformations at the nanoscale

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[2]*Institute of Theoretical Physics - EPFL Lausanne, Switzerland*

We introduce a set of coordinates which describe the topology of the network of bonds among atoms. These coordinates are obtained from the contact matrix, they are invariant under permutation of identical atoms, and provide a clear signature of the transition between ordered and disordered structures. In combination with first-principles molecular dynamics and metadynamics, the topological coordinates are employed to explore low-energy structures of silicon clusters and organic molecules, demonstrating the possibility of automatically simulating isomerization, association, and decomposition reactions without prior knowledge of the products or mechanisms involved.

Finally we discuss the application of this new approach to the simulation of carbon nanostructures: we obtain transformation pathways for the reconstruction of zig-zag edges of graphene ribbons to 5-7 rings, as well as the folding of graphene into fullerene-like cages. Our results show that it is now feasible the blind exploration of complex structural rearrangements of nanostructures at finite temperature and at density-functional theory level of accuracy.

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Discrete removal of carbon atoms by silver nanoparticles in suspended graphene

T. Booth[1], F. Pizzocchero[1], J. Jinsheck[2], M. Vanin[3], J. B. Wagner[4],
T. W. Hansen[4], R. Dunin-Borkowski[5], P. Boggild[1]

[1]*DTU Department of Micro- and Nanotechnology*
[2]*FEI Eindhoven bb*
[3]*DTU Department of Physics*
[4]*DTU Center for Electron Nanoscopy*
[5]*Ernst Ruska Center fo Electron Microscopy*

In order to realise a number of future applications of graphene, new lithographic technologies capable of patterning graphene down to the few-atom scale are needed. It is critical that these new techniques maintain the desirable proerties of graphene - i.e. high mobility, lack of contamination from resists and applicability to suspended graphene, whilst remaining capable of patterning features down to the few nanometer scale with sub-nanometer edge roughness.

The oxidative channeling behaviour of silver nanoparticles in suspended graphene is a process which can provide these benefits, and in addition produce channels exactly aligned with the <100> (zigzag) direction in monlayer suspended graphene. In-situ TEM provides unparalleled insight into this process [1], and highlights some hitherto unforeseen challenges in the patterning of graphene on the few-atom scale.

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Quantum confined electronic states in atomically well-defined graphene nanostructures

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[2]*Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, University of Utrecht, 3508 TA Utrecht, the Netherlands*

Despite the availability of good quality, large scale graphene layers, the realization of both the room-temperature graphene transistor as well as the more advanced theoretical ideas require well-defined samples, in particular in terms of the graphene edge structure. This level of control is currently not available through conventional lithographic techniques and there is a lack of experimental data on atomically well-defined graphene nanostructures. For example, opening a sufficient gap for room-temperature operation through quantum confinement requires structures in the size range of 10 nm. Furthermore, the electronic structure of graphene nanostructures is sensitive to the structure of the edges (e.g. zig-zag vs. armchair) [1]. There is a possibility of edge reconstructions and attachment of various functional groups, which further complicate the comparison between theory and experiment [2].

We use chemical vapor deposition (CVD) to grow small graphene flakes and on-surface polymerization from molecular precursors to form narrow graphene nanoribbons (GNRs) with well-defined edge structures $[3-6]$. Graphene interacts only weakly with the underlying Ir(111) or Au(111) substrates and retains the electronic structure of isolated graphene. We explore the size-dependent electronic properties of the atomically well-defined graphene nanostructures using low-temperature scanning tunneling microscopy (STM). The CVD growth yields a relatively broad distribution of different GQD sizes and shapes ranging from a couple of nanometers up to ca. 20 nm with a roughly hexagonal shape. All the flakes have edges in the zig-zag direction with a very small roughness (we see steps with a height of a single atomic row at the flake edges). On the contrary, the on-surface polymerization yields very narrow GNRs with arm-chair edge structure. We can readily access individual GQDs and GNRs and measure their atomic structure using STM. The local electronic properties can be probed by scanning tunneling spectroscopy (STS), which shows the presence of quantum confined states with different envelope wavefunction symmetries. We are able to reproduce the experimental results using tight-binding calculations of free-standing GQDs and GNRs with the experimentally determined atomic structure. Our measurements provide the necessary experimental input on the electronic properties of atomically well-defined graphene nanostructures for future electronic devices.

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[3] J. Coraux et al., New J. Phys. 11, (2009) 023006.
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Distorting graphene through mechanics and edge chemistry

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[1]*Institute of Materials, University of Nantes*

Interface formation in three-dimensional crystal lattices involves well characterised processes such as rebonding and rehybridisation, localised strain and dislocation formation. In contrast two dimensional crystal lattices, of which graphene is the archetype, are terminated by lines, and the additional available dimension opens up new topological interfacial possibilities. We show via DFT calculations that graphene sheet edges can adopt a range of topological distortions depending on their nature. Rehybridisation, local bond reordering, chemical functionalisation with bulky, charged, or multi-functional groups can lead to edge buckling to relieve strain [1], folding, rolling [2] and even tube formation [3]. As a result careful chemical control of sheet edge functionalisation allows radical modification of ribbon electronic, mechanical and chemical properties, for example reducing the Young's modulus of thinner ribbons by up to 40

After one-dimensional strain relief at edges we next examine the importance of lattice strain when considering point defect behaviour, and explore the possibilities for formation and glide of dislocation dipoles at vacancy sites [4]. Finally we show how the mechanical constraints of the graphene lattice can lead to new chemistry, taking the example of gas absorption on graphene surfaces [5].

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[5] A. Yaya, C. P. Ewels, I. Suarez-Martinez, Ph. Wagner, S. Lefrant, A. Okotrub, L. Bulusheva, P. R. Briddon, Phys. Rev. B 83 (4), 045411 (2011)

Healing Mechanisms During The Growth of Carbon Nanotubes

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[1]*CINaM, CNRS and Aix-Marseille University, Marseille, France*
[2]*LEM, ONERA-CNRS, Châtillon, France*

Despite considerable progress in synthesis processes, the detailed microscopic mechanisms involved in the growth of carbon nanostructures are still lacking. *In situ* experimental atomic scale investigations are very difficult, whereas computer simulations allow such investigations. Nevertheless, whether the employed method is empirical or semiempirical, all final configurations are plagued by a high concentration of atomic-scale defects. These include, but are not limited to, heptagon-pentagon topological defects, adatoms, and atomic vacancies.

In the present work, we investigate the healing processes of defective carbon nanotubes at atomic scale. We have developed a tight binding (TB) model for nickel and carbon that uses Monte Carlo simulations in the grand canonical ensemble to study the formation of carbon structures (graphene and nanotubes) from a metallic substrate [1, 2]. In particular, we have recently discussed the key role played by metallic atoms in the reconstruction of a defected graphene sheet by annealing defects [3].

We use our TB model to study the evolution at finite temperatures of defected nanotubes. Different lengths and diameters of nanotubes have been investigated at various temperatures ranging from 500 to 3000 K. We have also investigated the role played by the metal catalyst and a vapor of carbon atoms in the healing process. The building up of the tube chirality is analyzed and discussed through electron diffraction patterns. The approach proposed here could help identify individual healing mechanisms during growth that produces perfect tube structures and those favoring a definite chirality [4].

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Graphene: An ideal substrate for TEM imaging and spectroscopy

S. Kurasch[1], P.Y. Huang[2], V. Skakalova[3], A. Srivastava[3], J. Kotakoski[4], A.V. Krasheninnikov[4], R.M. Hovden[2], Q. Mao[2], J.C. Meyer[5], J. Smet[3], D.A. Muller[2], U. Kaiser[1], [1]

[1]*University of Ulm, Germany*
[2]*Cornell University, Ithaca, USA*
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[4]*University of Helsinki, Finland*
[5]*University of Vienna, Austria*

Due to the extremely low thickness, high mechanical stability, low contrast and good electrical and thermal conductivity graphene is an ideal TEM substrate for high resolution studies of deposited crystals or molecules [1,2]. Furthermore it is crystalline and the in-plane lattice spacing is very small. By this the contribution to the HRTEM image is known very well and can presisely be taken into account in the evaluation or be remove by Fourier filtering. This allows to determine the presise atomic configuration of grain boundaries in multiple layers of graphene that are found in CVD grown graphene samples and in high temperature in-situ experiments [3].

Here we demonstrate the strength of this approach for a 2D silica we discovered on graphene: For the first time it is possible to perform structural and spectroscopic (S)TEM studies of glassy materials on an atomic scale. It has been reported previously that crystalline 2D silica forms on Ru (0001) surfaces [4]. Additionally, on graphene we find an amorphous phase as well. The structural images strikingly resemble Zachariasen's cartoons of a 2D continuous random network glass [4].

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[3] B. Westenfelder et al., Nano Lett., 10.1021/nl203224z (2011)
[4] B. Westenfelder, J. C. Meyer, J. Biskupek, S. Kurasch, F. Scholz, C. E. Krill III and U. Kaiser, Nano Letters, 10.1021/nl203224z (2011)
[5] D. Löffler, J. J. Uhlrich, M. Baron, B. Yang, X. Yu, L. Lichtenstein, L. Heinke, C. Büchner, M. Heyde, S. Shaikhutdinov, H.-J. Freund, R. Wodarczyk, M. Sierka and J. Sauer, PRL 105, 146104 (2010)
[6] W. H. Zachariasen, J. Am. Chem. Soc. 54, 3841–3851 (1932)

Wednesday 22/02/2012

chair	*Busse*
9:00	Roche
9:40	Ahlskog
10:00	Makarova
10:20	Carva
10:40	*coffee*
chair	*Artacho*
11:20	Pantelides
12:00	Minato
12:20	Girard
12:40	Uppstu
13:00	*lunch*
chair	*Bøggild*
16:00	Sinnott
16:40	Mittendorfer
17:00	Perez
17:40	closing

Transport Properties in Disordered Graphene : Effects of Atomic Hydrogen and Structural Defects

Stephan Roche [1,2]

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[2] *ICREA, Institució Catalana de Recerca i Estudis Avançats, 08070 Barcelona, Spain*

This talk will focus on the presentation of transport properties in graphene-based-materials, driven by chemical functionalization and structural defects. To circumvent the current hurdles preventing the advent of graphene nanoelectronics, it has become urgent to benefit from engineering complexity at the nanoscale and the unique potential of graphene as a bridging platform between top-down conventional CMOS technologies and (bio)-chemistry self-assembling processes [1].

Here, by using state-of-the-art multiscale simulations (combining first-principles with tight-binding schemes), we present several electronic transport features in complex forms of chemically modified graphene based materials [2, 3]. Past examples include the use of boron or nitrogen-doped to produce graphene-based nanoribbons exhibiting "mobility gaps" of width as large as 1eV, providing an efficient switching behavior principle even in the presence of a vanishing electronic band-gap. The possibility to design a switching effect based on mechanical deformation of graphene nanoribbons. Here, we will explore the effect of atomic hydrogen driving intrinsic magnetic ordering will be presented from a theoretical perspective and in comparison with most recent experiments [3, 4, 5, 6].

It will be shown that the existence of a long range ferromagnetic state in weakly hydrogenated graphene could be related to a highly robust metallic state down to cryogenic temperatures, in contrast to the localization regime obtained in absence of ferromagnetic order. Additionally, the possibility to observe measurable magnetoresistance signals due to magnetism in graphene will be discussed. As a second issue, the presence of structural defects will be shown to yield conventional localization effects.

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Size dependence of electronic transport in multiwalled carbon nanotubes

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In a semiconducting single walled carbon nanotube (SWNT), the electronic conduction can be modulated with a (capacitively) strongly coupled gate electrode. The bandgap Eg, has (in the simple tight-binding theory) the inverse dependence on diameter (D). As graphene does not possess a bandgap, an important direction in current research is to create constricted channels, graphene nanoribbons, where a gap is created via quantum confinement due to the narrow width of the channel. The size of the gap is then roughly in a similar inverse relation with the width of the constriction as in the case of the diameter dependence of semiconducting SWNT's. In SWNT's, however, the diameter range is rather narrow; 1-3 nm.

Reported transport measurements on multiwalled nanotubes (MWNT) have been performed on tubes with diameters of 10 nm or more. In most studies the working assumption has been that the outer layer is solely responsible for the low bias transport properties. In MWNT's with D larger than 10 nm, the semiconducting behavior of the outer wall is smeared out at room temperature. Our group has done pioneering work on the basic transport data of intermediate sized MWNTs ranging in diameter from 2 to almost 20 nm.

We have measured low temperature transport properties of the MWNT's of different diameters. In nearly all samples the gate dependent conductance exhibits a gap whose size increases with decreasing tube diameter and increasing electrode separation. This so called transport gap is attributed, based on the experimental findings, on a combination of localization effects and narrow diameter induced gaps in the electronic band structure.

Our work complements and bridges previous works on both SWNTs and MWNTs. We also find substantial similarities between our results on the size dependence of MWNT's and the comparable current intense research on graphene nanoribbons, whose dimensions are relatively easy to control.

Edge states versus in-plane defects in graphite magnetism

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[2]*Nikolaev Institute of Inorganic Chemistry SBRAS, Russia*
[3]*Ben-Gurion University of the Negev, Israel*

Inclusion compound C2F with the molecules intercalated between layers of graphite fluoride matrix represent a system of loosely bound bilayer graphenes and serve as an excellent model for studying low-dimensional magnetism. We have experimentally studied correlation of the magnetic properties of the samples with the edge structure and the in-plane structure. Fluorination starts from the edges CF termination which causes strong paramagnetism, and the samples obey the Curie-Weiss behaviour. Further fluorination forms CF2 edges which drastically reduce localized spin concentration. At these stages the samples exhibit only low-temperature (< 3K) short-range antiferromagnetic ordering. This is consistent with the predictions that magnetism originates from the localized edge states that give rise to a high density of states at the Fermi level rendering spin-polarization instability. The 1D system is sensitive to thermal disorder destroying the spin arrangement, and magnetism appears only at low T. When fluorine starts to attack the basal plane, it results in strongly coupled localized magnetic moments. The mechanism of fluorination assumes the random attachment of primary fluorine atom to graphite network and further random direction of chain formation. Fluorine fills the basal planes forming both zigzag and armchair chains with the stoichiometry CF-CF-CF-CF alternating with the chains of non-fluorinated C-C-C-C. The areas of formation of C2F structure have limited size and form domains consisting of the C2F bands ordered at different angles. When the formation of chain structures inside the basal planes starts, a kink appears on susceptibility curves at about 150 K. When the wet process is finished, the fluorine atoms continue reorganizing on the basal plane: isolated fluorine atoms diffuse rapidly along a path above C-C bonds till the structure reaches the energetically preferable state. The chains are self-organizing, the metastable lone spins disappear and finally the temperature dependences of magnetic properties does not have anything in common with paramagnetism: susceptibility decays exponentially at low temperatures, which is a characteristic feature of a spin-gap system. Simultaneously a ferrimagnetic contribution to susceptibility is developed due to uncomplete cancellation of magnetic moments; the latter is seen from the M(H) curves. Thus, we observe the formation of bulk magnetic carbon in a self-assembly process. Intrinsic nature of novel carbon magnetism results in its sensitivity to the thermal treatment. Heating up to 400 K destroys antiferromagnetically ordered chains and simultaneously destroys bulk magnetic order. On ageing, room-temperature ferromagnetism spontaneously restores; carbon magnetism is switched ON/OFF. ESR studies and ab initio calculations provide the evidence that magnetic units are the areas of delocalized ?-system between the fluorinated chains.

Defect controlled conductivity of graphene with vacancies and N impurities

K. Carva[1,2], B. Sanyal[2], J. Fransson[2], O. Eriksson[2]

[1] *Charles University in Prague, Czech Republic*
[2] *Uppsala University, Sweden*

The possibility to influence the electronic structure of graphene and hence control its conductivity by adsorption or doping with adatoms is crucial in view of electronics applications. We study electronic structure and transport properties of single and bilayer graphene with vacancy defects, as well as N doped graphene. The theory is based on first principles DFT calculations employing coherent potential approximation (CPA) to describe disorder. We show that increasing the defect concentration increases drastically the conductivity in the limit of zero applied gate voltage [1], by establishing mid-gap states and carriers in originally carrier-free graphene, a fact which is in agreement with recent observations [2]. We calculate the amount of defects needed for a transition from a non-conducting to a conducting regime (i.e. a metal-insulator transition) and establish the threshold of the defect concentration where the increase of impurity scattering dominates over the increase of carrier induced conductivity [1].

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Topics in graphene

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The talk will cover purely theoretical results on doping of graphene by N, oxygen adsorbates, and the formation and healing of self-interstitial complexes; observations using electron-energy-loss spectrum imaging in scanning transmission electron microscopy (STEM), combined with theory, showing that a) a single point defect can act as an atomic antenna in the petaHertz (10^{15} Hz) frequency range, leading to plasmon resonances at the sub-nanometer scale, and b) graphene has highly localized d-states in the conduction bands; and measurements, combined with theory, of electrical transport in multiterminal graphene devices suspended in liquids, showing that non-polar liquids enhance mobility, polar liquids degrade mobility, while all liquids suppress scattering by out-of-plane flexural phonons, which is a dominant scattering mechanism in suspended graphene at room temeperature.

Theory collaborators: Y. S. Puzyrev, J. Lee, L. Tsetseris, B. Wang; microscopy collaborators: W. Zhou, J. C. Idrobo, S. J. Pennycook; graphene device collaborators: A. K. M. Newaz, K. Bolotin. Work supported in part by DTRA, NSF, and by the U.S. Department of Energy, Materials Science and Engineering, Basic Energy Science.

Mechanism of organic chemical reactions on nano-porous gold

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Recently, the catalytic activities of nano-porous (several tens nm) gold for gas phase reactions such as CO or methanol oxidations have been found by several groups [1-3]. The activity of the nano-porous gold is characteristic and is not observed on other catalysts. For example, gold is a chemically stable metal in the bulk form, however, by the formation of nano-porous structure, gold show high catalytic activity for CO or methanol oxidation [1-3]. Although the nano-particle (2-3 nm) of gold also show the catalytic activities, usually supporting materials (metal oxides or carbon materials) which modify the geometric/electronic structure of the gold is necessary to observe the catalytic activity [4-6]. The nano-porous gold show the catalytic activity without supporting materials. Therefore, the elucidation of the reaction mechanism on nano-porous gold catalysts is important to develop new catalysts. We have found that the nano-porous gold show new catalytic activity for organic reactions in liquid phases [7-8]. However, the reaction mechanism is still unclear. To develop new catalysts, we have studied the reaction mechanism of the organic reaction by using surface science techniques (photo-electron spectroscopy and thermal desorption spectroscopy). Based on the observation of surface structure, electronic structure and adsorption structure, we will discuss the mechanism to produce the characteristic reactivity on nano-porous gold.

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Coupling experiments and simulations for the radiation hardening of fiber optics: (I) Experimental results on canonical samples of pure and doped silica

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Silica-based glasses and fibers are considered for use in future facilities associated with very extreme radiative environments like ITER, LMJ, IFMIF, ...For such applications, optical fibers have strong advantages but their integration remains limited by the increase of their linear attenuation observed under irradiation (Radiation-Induced Attenuation). This macroscopic degradation is due to radiation-induced changes at the microscopic level: the generation of point defects in the silica glass of the fiber core and cladding. A predictive model appears necessary to design radiation-hardened fibers and glasses to these challenging environments. The codes necessary for such a prediction are still under development (abstract II by Richard) and need dedicated experimental data allowing the comparison between the simulation results ant the experimental results obtained on comparable samples. We will discuss the approach that we put in place in collaboration between our 4 labs and that is based on the development of specific samples of glasses and fibers (canonical samples), directly comparable to our simulation cells and designed to highlight the impact of one composition or process parameter on the point defects generation. A review of our more recent results based on the spectroscopic analysis (absorption, luminescence, ESR,...) on these canonical samples will be presented.

Electronic transport in graphene-based structures: An effective cross section approach

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We show that transport in low-dimensional carbon structures with finite concentrations of scatterers can be modeled by utilising scaling theory and effective cross sections [1]. Our reults are based on large scale numerical simulations of carbon nanotubes and graphene nanoribbons, using a tight-binding model with parameters obtained from first principles electronic structure calculations. As shown by a comprehensive statistical analysis, the scattering cross sections can be used to estimate the conductance of a quasi-1D system both in the Ohmic and localized regimes. They can be computed with good accuracy from the transmission functions of single defects, greatly reducing the computational cost and paving the way towards using first principles methods to evaluate the conductance of mesoscopic systems, consisting of millions of atoms.

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arXiv:1111.0148v1

Charge Optimized Many-Body (COMB) Potentials for Interfacial Studies

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Graphene has attracted tremendous attention owing to its interesting properties and unique structure. A key intermediate product in the chemical production of graphene is graphene oxide sheets, which are often heavily oxygenated with hydroxyl or epoxide functional groups on the surface and carbonyl or carboxyl groups at the edges. The energetics associated with the interaction of graphene sheets with various levels of oxidation with metal and oxide interfaces is examined in molecular dynamics simulations using charge optimized many-body (COMB) potentials, which enable the investigation of heterogeneous interfacial structures within a single unit cell. The properties of the COMB potentials and their applications to other heterogeneous interfacial systems will also be reviewed.

Graphene on Ni(111): Strong Interaction and Weak Adsorption

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In the recent years, ab-initio modeling has been established as a complementary approach to the experimental nanoscience research. Density functional theory (DFT) based methods usually offer reliable structural models and energetics, and allow to treat systems containing several hundreds of atoms. Yet the accuracy of commonly used semi-local functionals for adsorption studies involving graphene is severely limited, as non-local (van der Waals) contributions are completely neglected. In a recent publication [1], we could demonstrate that the evaluation of the correlation energy in a many-electron approach based on the adiabatic-connection fluctuation-dissipation theorem (ACFDT) in the random phase approximation (RPA) leads to a significant improvement.

In this presentation, I will discuss our recent results [2] for the adsorption of graphene on Ni(111) on the basis of RPA calculations. Although we find a significant hybridization between the graphene π orbitals and Ni d_{z^2} states at an optimized binding distance of 2.17 Å, the adsorption energy is still in the range of a typical physisorption (67 meV per carbon). An important contribution to the energy is related to an decrease in the exchange energy resulting from the adsorption-induced lower symmetry in the graphene layer. The energetics can be well reproduced using the computationally significantly cheaper van der Waals density functional theory (vdW-DF) with an appropriately chosen exchange-correlation functional.

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Probing nanostructures with forces and currents: From atomic-scale contrast on graphene and carbon nanotubes to heterofullerene synthesis with planar aromatic precursors

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In this talk, we focus on the application of Scanning Tunneling (STM) and Frequency-Modulation Atomic Force (AFM) microscopy [1] to carbon nanostructures (graphene, carbon nanotubes and fullerenes). The simple honeycomb structure shared by these materials represents both a perfect testing ground and a fundamental challenge for scanning microscopy imaging. STM can achieve atomic resolution in graphite even in ambient conditions but, after 25 years of research, still there is no consensus whether the maxima in the atomic scale images correspond to atoms or to the hollow sites. To tackle this long-standing problem, we have performed complex first-principles calculations of forces and currents between a tip and carbon nanostructures. Our results explain the rich variety of image patterns observed in both AFM and STM experiments in terms of two factors: (i) the tip-sample distance and (ii) the chemical reactivity of the tip [2]. Based on this work, we have explored the electronic properties of epitaxial graphene on metals, both in the case of the pristine layer and in the presence of carbon vacancies, where the calculations help to correlate the structure of the defect with the experimental STM images [3]. These calculations also shed light on the possible magnetic state associated with these defects, predicted but not experimentally confirmed, in graphite [4].

Finally, we'll discuss the microscopic mechanisms behind the different steps involved in our recent proposal for a controlled synthesis of heterofullerenes based on a surface-catalysed cyclo-dehydrogenation process [5, 6]. With this approach it is possible to transform with an almost 100% efficiency polycyclic aromatic hydrocarbons like C60H30 and C57N3H33, deposited on Pt(111) surfaces, into C60 fullerenes and triazafullerenes C57N3.

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Posters

Ion irradiation induced defects in freestanding graphene: an atomistic simulation study

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We study defect production in graphene using low-energy ion irradiation via atomistic simulations. We show that carbon atoms can be substituted with boron and nitrogen via low energy irradiation with probabilities of 55% for N and 40% for B with the optimum irradiation energy of 50 eV [1]. We have further investigated the effect of pre-existing defects on the irradiation response of graphene, and show that graphene can withstand up to 35% vacancy concentration before subtantial change in its behavior. After this point, the sputtering from graphene increases substantially and leads to breakage of the material.

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A density functional theory study of functionalised silicon surfaces

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Molecular adsorption on silicon surface is studied from first-principles calculations within Density Functional Theory. In particular, we consider the stability of benzene, fluorinated benzene, hexane and thiolated hexane, on [111]- and [100]-silicon slabs and the effect of adsorption on the electronic structure of the slab. Our calculations reveal that fluorinated benzene shows the strongest bonding to the surface whereas thiolated alkanes produce the most significant shift at the edge of the conduction band. A charge analysis at the various sites of slab before and after functionalization allows us to investigate molecular induced charge transfer.

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The role of dispersion forces in the surface stability of oxidised Cu(110)

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There are several methods proposed that can account for or qualitative describe dispersion interactions, with several implementations now available in many density functional theory (DFT) codes. This is largely because it is of current interest, used for studying layered materials, large protein molecules, molecules on surfaces and recently bulk materials. We investigate an additional application for such methods, in surface reconstructions. We performed thermodynamic calculations on several reconstructions of the oxidised Cu(110) surface with different functionals (PBE, PW-91, vdW-DF1 and vdW-DF1) and with the semi-empirical Grimme method (DFT-D2); in addition, in all cases contributions of atomic vibrations to the Gibbs free energy were accounted for. Oxidised Cu(110) has two ground states depending on the pressure oxygen is introduced to the surface, p(2x1) and at higher pressures c(6x2). Our results indicate that without taking into account dispersion forces, the observed p(2x1) appears favourable but reconstructions other than c(6x2) are equally as energetically favourable as the c(6x2) with marginal energy differences. Also taking into account energy due to vibrations had little effect on these results, changing the ordering but not the energy gaps. However, upon accounting for van der Waals (vdW), the c(6x2) reconstruction becomes energetically favourable for the vdW-DF1 and vdW-DF2 functionals and for the DFT-D2 method, with a significantly large energy gap. Thus also demonstrating the importance of describing vdW interactions in a wider scope of materials science.

On heat capacity of superconducting nanoclusters

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The subject of our investigation are ultrasmall Al nanoclusters. Recent experiments have shown that the heat capacity of such systems has a peculiar behavior. Namely there is a peak in the capacity as a function of temperature. This peak is believed to be the sign of superconducting transition, with $T_C\ 200K$. So we had an idea to trace the effects of pairing correlations and shell structure on heat capacity using a simple model with finite particle number. We used the BCS hamiltonian, were the electronic spectrum was represented by two shells but took into account that the particle number was finite. So we obtained qualitative agreement with experiments suggesting the increasing of transition temperature due to increasing of degeneracy of electronic shells and coupling constant. The peak position also appeared to be parity-dependent.

Imaging the carbon K near-edge polarization dependence of a few layer graphene by NEXAFS-TXM

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The near-edge X-ray absorption fine structure technique (NEXAFS) is ideally suited to study graphene-based materials, because the C K-edge is very sensitive to the bonding environment, providing diagnostic information about the structure, defects and doping. Using the NEXAFS method electrons are excited from the initial K-shell state into s* and p* final states, depending on the orientation of the incident photon polarization with respect to the basal plane. The peak positions and lineshapes of the observed NEXAFS resonances represent, to first approximation, a replica of the unoccupied density of states modified by core-hole interactions. Because, in a graphene-based material the C p* exhibits strong linear dichroism, using linearly polarized X-rays, NEXAFS can probe local anisotropy and structural order by varying its relative orientation to a chosen axis of the sample. When combined with microscopy, NEXAFS can be used to study isolated, free-standing, nanostructures.

We use the NEXAFS spectroscopy in a full-field transmission X-ray microscope TXM, to study electronic structure of a few layer graphene. The assignment of the most intense peaks was straightforwardly obtained by comparing the peak positions of the graphite band structure. A pre-peak structure was associated to metal doping due to the presence of metal impurities in the raw material used.

Alternative methods for doping nanocrystals and designing junction offsets

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Low dimensional semiconductor nanostructures have unique properties with no parallel in their bulk counterparts. For this reason, some of the processes long used in the semiconductor industry have to be adapted or reformulated in order to be adopted for the future mass-production of nanostructure-based devices. One example is the doping. In silicon nanocrystals, group-III and group-V elements have higher activation energies and the potential to segregate to the surface where they can lose their dopant character. Using first-principles theoretical calculations, we have investigated possible alternative procedures to change the free carrier concentration or mobility in nanocrystal films, or to tune the electron level offset in silicon nanocrystal hetero-junctions. These include surface doping[1] and coverage with chlorine atoms[2,3]. We explain how the electronic properties of the nanocrystals are changed and how this can be explored for engineering purposes.

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DFT modeling of the interaction of small analyte molecules with a dye/silica receptor center

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The adsorption of small analyte molecules (H2O, NH3, C2H5OH, and (CH3)2CO) and an indicator dye, 9-(diphenylamino)acridine (DPAA), on the surface of amorphous silica particles is studied using electronic structure calculations at the DFT-D level of theory taking into account explicit corrections for van der Waals forces. Cluster models of three different types are used; two of them (Si10O11(OH)18 and Si20O27(OH)29) have been constructed using classical MD methods. The effect of particle size, local environment, and the choice of the exchange-correlation functional and basis set on the adsorption energies is studied, and adsorption energies are extrapolated to nanosized clusters. It is shown that the dye is more strongly bound to amorphous silica particles than the studied analyte molecules and that the energy of DPAA adsorption increases with the particle size, being at least twice as high as the energy of analyte adsorption for nanosized clusters. Electrostatic interactions play an important role in the adsorption of acridine dyes on the surface of silica nanoparticles [1]. We also studied the interaction of analyte molecules in the gas phase with DPAA on dye/silica system. The electronic absorption spectra of the adsorbed dye are calculated within the TDDFT formalism and the effects of dye/analyte interactions are investigated. The spectral line broadening due to molecular vibrations is estimated within the Pekar model. A computationally efficient procedure is proposed for the prediction of changes in the absorption spectra of organic dyes adsorbed on silica upon their interaction with analytes.

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NC-AFM energy dissipation mechanisms

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NC-AFM is an invaluable tool when probing surfaces, providing atomic resolution topography and detailed 3D force maps. As the tip scans the surface, the feedback gain signal associated to the energy dissipated in the oscillation cycles is also recorded, and this often differs from conventional topography images, showing different contrast patterns, periodicity and tip-surface distance dependence. Although many different surfaces have been studied with atomic resolution, a routine interpretation of these measurement has yet to be found, since the atomic processes at the surface responsible for energy dissipation are not well understood and the influence of the tip is not clear. In order to understand better the role of the tip in measured dissipation, we carried out extensive atomistic calculations using a wide variety of different tip materials and structures, and a simple NaCl (100) surface. After studying simple processes with quasi-static calculations [1], testing several tip geometries and materials [2], we are now investigating the atomic-scale dissipative processes using GPU accelerated finite temperature molecular dynamics (MD) simulations, and comparing directly to static force spectroscopy (SFS) and dynamic force spectroscopy (DFS) experiments. Ideal NaCl tips are too stable and do not give dissipation although in presence of defects at the apex, the system shows reversible reconstructions involving the tip and the surface, giving an average dissipation up to 0.02 eV/cycle, smaller than experimentally seen. MgO tips are even more stable but the oxygen's charge at the apex makes the surface unstable leading to formation of atomic chain and, consequently, irreversible surface alteration, which is again in contrast with the experiment, showing no decoration and stable operation. Finally we focused our efforts on simulating the experiment from the very beginning, where an oxidized tip indents the surface adsorbing a NaCl nanocluster at the apex. The average dissipation we calculate with this tip is in a quantitative agreement with DFS data and the distance dependence is also reproduced. We found that dissipation comes from stochastic formation of atomic chains of different lengths.

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Atomic scale dynamics of frictional processes

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Friction has generated a lot of scientific interest in recent years due to its recurrence in almost every aspect of our life. It is one of the most fundamental processes in nature, and remains a key design concept in machines and devices. Friction and wear are the main source of failure in every kind of machinery, macro- and microscopic, as well as biological applications, from prosthetics to drug design/delivery; efforts to reduce and control their effects forms a wide research area. As this field of research has developed alongside modern experimental techniques, it has become evident that friction originates at the nanoscale thus atomic force microscopy became the tool of choice for creating a controllable nanocontact with a surface, where the friction and wear properties and can be studied in detail. Torsional resonance (TR) AFM offers the opportunity to map lateral forces on a sample at extremely high resolution, without damaging the surface as it relies on the same principles of non-contact AFM. The TR frequency shift is related to the lateral force while the excitation signal (or damping) is related to the energy lost to atomic scale frictional processes. While the former is well understood, interpretation of the latter, remains challenging, and an area of intense research, and as yet there are no theoretical or experimental studies of lateral dissipation in TR-AFM. Studying frictional processes at the atomic scale can provide understanding of how materials degrade due to wear, aiding design to improve durability. Our studies focus on NaCl (001) surface, which is an important benchmark system for theoretical models and is easily prepared in the laboratory. Experimental data showed that the vertical interaction with the tip was too weak to give a distinct topography of the surface, whereas lateral interaction, detected via the lateral frequency shift provided surface images with atomic resolution. Although the lateral frequency shift map showed the checkerboard pattern typical of ionic crystals, the damping image looked different. Along a scanline along the atomic rows, the damping signal gives two peaks around one site. In order to understand this, we performed classical molecular dynamics (MD) simulations of the torsional oscillation cycles. We create the model tip via MD, following a procedure similar to the experimental one, and we process it so that vertical dissipative processes are inhibited, as we know from the experiments that no dissipation was detected in the vertical mode. We simulate several cycles, and we repeat the whole calculation placing the tip in several positions on the scanline. Preliminary results show that, while the frequency shift contrast reveals intuitively the surface pattern, the dissipated energy gives a double feature close to one of the two atomic species.

Extreme sensitivity in potential characterization of an insulating step edge

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Understanding potential variations near step edges of surfaces is of cardinal importance to control surface processes such as adsorption, growth, catalysis and friction. Ionic crystal surfaces attract the scientific attention due to their high band gap, and in particular, there is a large interest in studying step edges, for their key role in the adsorption chemistry. In our dynamic force spectroscopy (DFS) experiments, we study the potential variations near a LiF (001) step edge using the flexural and torsional resonance of the cantilever. The flexural oscillation is used to regulate the tip-sample distance, while the torsional one detects the site-dependent interaction. The lateral oscillation is not affected by long range site-independent interactions and thus has a very high sensitivity to the lateral potential gradient. Our measurements show how the vertical interaction is quite weak across the step edge and it does not show a strong dependence on the applied bias voltage. However, the torsional frequency shift, shows a remarkable contrast, and far away from the step, it has a linear dependence on the bias voltage. In order to better understand this effect we performed atomistic calculations with the shell model, using a model LiF (001) surface with a step edge, a planar electrode below the surface and a spherical electrode representing the tip. Because the electrodes in the simulation are applied few atomic layers below the surface, while the real ones have few millimetres of insulating material on top, the effective bias to be used in the atomistic model was evaluated from a finite elements calculation considering the whole cantilever, the macroscopic LiF sample and the grounded vacuum chamber. Such details were found to be quite important since the effective potential calculated in a simpler setup can be 10% larger. After relaxing the surface at different bias voltages and tip positions, we evaluated the gradient of the Coulomb interaction between the resulting surface and a dipole fixed on the tip, and from this, the torsional frequency shift. We found the same linear trend seen in the experiment. The potential change can then be related to the different reconstruction at the step edge, when the ions are more free to move and affect the surface dipole.

Theoretical investigation of the diamond films with implanted oxygen atoms

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The presented work is devoted to the investigation of the diamond films doped by oxygen atoms. Oxygen doping of diamond is interesting both from the theoretical and experimental points of view because diamond despite of different useful properties has the fundamental problem which is prevented to apply in electronics: insulating properties. The doping of diamond by various atoms (e.g. by oxygen) allows to significantly reduce the band gap and transform insulating diamond to semiconducting one with n-type of conductivity. Despite of high perspectives there is only few experimental and theoretical works devoted to the topic of oxygen doping of diamond [1, 2].

The presented work is the result of theoretical and experimental studies. The main goal of our theoretical investigation is the support of experiment where oxygen doped diamond films were manufactured. The main goal of present work is the investigation of dependence of electronic properties of diamond upon the oxygen concentration.

At first step, the dependence of depth lying of implanted oxygen in diamond film depended upon the initial ion energies was established. The good correspondence between experimental and theoretical data was found. At the next step, DFT approach was applied for the analysis of stability of oxygen defects with different charge implanted in different sites of diamond. The investigation of interaction of oxygen with vacancy defects was carried out. Vacancies are a kind of traps, so, oxygen located in an interstitial site could move to the vacancy by directly binding with neighbored to the vacancy carbon atoms. Nudged elastic bend method was applied for the calculation of transition barriers between separate oxygen defects. At the next step the electronic structure of doped diamond was evaluated and compared with available experimental data. Significant contribution of oxygen defects to the band structure was observed. Finally the Raman spectrum of the stablest doped diamond structures was calculated and comparison with experiment was provided.

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From short- to long-range correlations in layered materials

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Exfoliated layered materials commonly exhibit unusual properties in comparison to their bulk counterparts. Apart from a fundamental interest, this attracts an attention also from a practical point of view, having new electronic, optical and other applications in perspective. Reliable theoretical studies of these materials often require more than just the standard density functional theory. Then, such methods as the random-phase approximation and the GW approximation are applied. Recent papers [1,2] show, however, that these two approaches converge slowly with respect to the basis size used in linear-response calculations. We argue that this problem stems from the electron-electron interaction cusp of correlated wavefunctions. Our analysis of the uniform electron gas shows that RPA correlation energies as well as GW quasiparticle energies converge as the negative third power of the cut-off wavevector, and also a further asymptotic expansion is possible. This result is applied for a study of binding in 30 layered solids and the quasiparticle band structure of BN and MoS_2. All obtained exfoliation energies are surprisingly similar and fit into a narrow range around the value of 20 meV/Å^2. The quasiparticle calculations show that the band gaps strongly depend on the width of the vacuum gap between periodic images of single layers, which is another long-range correlation effect along with the van der Waals interaction. Interestingly, the accuracy of these results is strongly influenced by the treatment of the electron-electron interaction in the short range. More generally, if the many-body perturbation theory is applied, the short-range correlation effects have to be taken into account not only for layered materials, but also for all kinds of materials.

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Atomic-scale processes set the critical limit for conventional ion beam thinning of Si lamellae

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The rise of nanoscience has created an ever-increasing need to probe systems on the atomic scale, to which transmission electron microscopy has largely been the answer. Currently, the only method for efficiently thinning an arbitrary bulk sample into a thin lamella in preparation for transmission electron microscopy is using a focused ion beam. However, the conventional method suffers from three harmful effects on the sample which prevent thinning below $\sim$20 nm: warping, shrinking and amorphization. Using atomistic simulations coupled with state-of-the-art experiments to study the thinning of a Si lamella by a focused Ga^+ ion beam, we identify the atomistic processes responsible for the shrinkage of the lamella and explain how they define a fundamental limit for the conventional thinning method. Moreover, we provide insight into why a recently proposed *double-tilt* method is free of the forementioned effects and may thus be applied below the critical limit of the established method.

Structural and electronic properties of GaAs nanotubes.

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It was not long after the discovery of carbon nanotubes that the sythesis of BN nanotubes, which is a III-V compounds, was reported. Novel physical properties re expected in nanotube geometry due to its quasi-1D nature. Therefore, several works [1-3] were devoted to finding nanotubes of common compounds in the semiconducting industry, such as GaN, Si, AlN, AlP, and GaAs. Inspired by these studies, we combine first principles calculations with Tersoff potential based molecular dynamics simulations to predict the structural and electronic properties of single and multi wall Gallium Arsenide nanotubes (GaAs-NTs). Inspired by the geometry of the recently reported GaAs clusters, we choose achiral nanotubes. In GaAs nanotubes, not all atoms are at the same distance from the tube axis, and thus the nanotube surface is corrugated. Therefore, we first determined which element should form the outermost shell in the nanotube surface. We find that As atoms prefer to be the farther from the tube axis, and Ga atoms prefer to be closer to the tube axis. This is due to the charge transfer from Ga to the As atom as it happens also on the GaAs (001) surface. For this reason, even a single wall nanotube could be regarded as dipolar shell. Our calculated bindings energies per formula unit GaAs nanotubes are similar both for armchair and zigzag nanotubes, and they are comparable to that of bulk GaAs. Unless the diameters of the nanotubes are too narrow, the strain due to the bending is eliminated by the corrugated structure of the surface. As to electronic structure of the GaAs nanotubes, we find that all GaAs nanotubes are semiconducting regardless of their chirality. Starting from the atomic structures that we obtained from density functional calculations, we formed multi wall nanotubes, and determined their structural properties in Tersoff potential. We find that strain energies could be modified by formation of multiwall structures.

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Porous Solids Based on Endohedrally Doped CdS Nanoclusters

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Hollow CdS clusters are predicted to trap alkali metals and halogen atoms inside them [1]. Furthermore, the electron affinities (EA) of halogen doped clusters and the potential ionizations (IE) of the alkali doped clusters are calculated to be very similar. This makes them suitable to form cluster-assembled materials, in the same vein as related ZnO, ZnS and MgO porous materials $[2-3]$. With this aim we have focused on the assembling of bare $\mathrm{Cd}_i\mathrm{S}_i$ and endohedral $\mathrm{K@Cd}_i\mathrm{S}_i$-$\mathrm{X@Cd}_i\mathrm{S}_i$ (i=12, 16, X= Cl, Br) clusters in order to obtain new solids with taylored semiconducting and structural properties.

These hollow nanoclusters are built by squares and hexagons, and based on their structures three different orientations have been considered. Namely, edge-to-edge (E-E) square-to-square (S-S) and hexagon-to-hexagon (H-H). These three orientations lead to different zeolite-like nanoporous bulk CdS phases, namely, SOD, LTA and FAU.

Our calculations predict stable solids, with cohesive energies comparable to many soft solids. They exhibit the above mentioned SOD, LTA and FAU zeolite-like structures, with pores of around 0.0, 1.5 and 2 nm respectively. Since endohedral doping decreases the band gaps by 0.5 eV, these solids may be seen as narrow-gap semiconducting materials with potential application in optoelectronics. Moreover, their pore-structure makes them suitable for many other applications such as heterogeneous catalysis, storage, etc.

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Nonlinear behavior of three terminal graphene junctions at room temperature

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Graphene is an attractive material for device applications due to its high carrier mobility in two dimensional charge carrier transport. The transport behavior of three terminal graphene junction has been studied using T-branch shape device. In this study, we present a result of experimental electrical properties of the device at room temperature. We obtained around 10T-branch devices were patterned on exfoliated single layer graphene prepared on a 300-nm-thick silicon dioxide using O2 plasma etching. The width and length of the channel from the left to right is 200 nm and 600 nm, respectively. The center branch is around 100 nm wide and 300 nm long. The metal contact is formed with Ti/Au (5 nm/40 nm) by e-beam evaporation. In the measurement anti-symmetric voltage sources, so-called push-pull configuration (VL=-VR), are applied to the left and right terminals simultaneously and the output voltage is measured at the center branch with various the backgate voltages. The substrate of highly doped silicon is used as a global back gate electrode. All measurements were carried out at room temperature. When the left and right terminals are biased by push-pull manner with a backgate voltage, the output voltage at the center branch is dominantly negative or positive regardless of the sign of input voltage. Moreover, the output voltage becomes almost zero when the backgate voltage reaches the carrier neutrality point as expected. Also, the curvature of rectification becomes stronger when the Fermi level is increased by the backgate voltage. This implies that the curvature of rectification is dependent on the carrier density. Furthermore, the sign of the rectified curve is altered by changing the carrier (hole or electron) type. Positive rectification occurs at electron transport region and negative rectification at the hole transport region.

Molecular Dynamics Simulation of Aluminum Oxidation via Reactive Force Field

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Aluminium-oxide films are actively used in nano-electronic devices due to their high dielectric constant and high barrier for electron tunneling as well as strong resistance to corrosion, significant thermal and mechanical stabilities and good adhesion.

As generally, properties of the system at the nano-scale are sensitive to the geometry, performance of the nano-devices is also strongly affected by the geometry of its components. One manifestation of such correlation is the fact that tunneling current is strongly dependent on the structure of the interface between the metal and the oxide. Therefore, above all, it is important to learn the properties and kinetics of oxide formation. Regardless a large amount of work addressed to this issue, clear picture of the oxide formation is not yet achieved. What is more, most of the works consider only initial stages of oxidation at low coverages.

The goal of the proposed work is to perform atomistic modeling and simulation of tunneling phenomena and barrier structure for metal-oxide interfaces, and to correlate tunneling current properties to the geometry of the barrier. Therefore, the first and the foremost step is to develop detailed understanding of oxide growth. Further, quantitative description of transport relevant barriers can be deduced.

The choice of the inter-atomic potential in the presented problem is crucial. It must be environment-dependent and must be able to describe charge transfer. For our simulations we choose Reactive Force Field (ReaxFF) [1] employed in LAMMPS [2] molecular dynamics code. ReaxFF has been successfully used for aluminum and for Al/Al_2O_3 interface and is claimed to be fully transferable for the description of the oxidation process [3]. Simulated results for the properties and growth kinetics of aluminum oxidation at room temperature will be presented, thereby assessing the applicability of ReaxFF to the current problem.

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Defects in electron irradiated transition metal dichalcogenides

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Transition metal dichalcogenides are a class of layered materials, similar to graphite and BN. Due to recent advances in succesful production of two-dimensional monolayers they have started to attract considerable attention. The prototypical material MoS_2 has been previously used as a dry lubricant, but it also shows promise in applications such as hydrogen production, solar cells, and photocatalysis. In addition, applications in electronics are enabled by the fairly high carrier mobilities. Importantly, as the transition metal chalcogenides comprise of a fairly large set of materials, they offer natural engineering possibilities which are often lacking in other 2D materials. In order to take full advantage of the promise of these materials, a good control over the defect production is required. In particular, defects could be produced intentionally under electron or ion irradiation, whereas unintentional production may be expected during transmission electron microscope (TEM) imaging.

In this work, we investigate the vacancy formation under electron irradiation for a large set of materials. We consider several transition metal species, such as Mo, W, Nb, and Pt, together with S, Se, and Te chalcogenides. We first perform first-principles calculations of vacancy formation energies, which are then complemented with molecular dynamics simulations of the displacement thresholds. In addition, we examine chalcogenide substitution processes within these materials.

Atomic oxygen chemisorption on a zig-zag carbon nanotube

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The interaction of oxygen with carbon nanotubes is of crucial importance for the understanding of their behavior in real environments and also their response to covalent functionalization [1]. However relatively limited attention has been paid to the study of chemisorption of atomic oxygen, especially with theoretical methods (see however [2]).

We present a series of large-scale simulations based on density-functional theory and using different choices for the exchange-correlation functionals aimed at identifying in particular the characteristic configurations of oxygen adsorbates on the side walls of a carbon nanotube as well as the dynamics of desorption and migration processes. In analogy with our previous study of hydrogen chemisorption [3], we shall investigate the variations induced on the electronic and vibrational spectrum of the bare tube. Comparison of our results with recent data from scanning tunneling spectroscopy.

This research was funded in part by Nano-Tera.ch, a program of the Swiss Confederation, evaluated by the SNSF. Part of the computational work was supported by a grant from the Swiss National Supercomputing Centre - CSCS under project ID 245.

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Atomic scale characterization of alumina films grown on the $MgAl_2O_4$ (100) surface

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Metal oxide spinels are an important class of materials in both ceramics technology and materials science. The prototypical ternary metal oxide spinel, magnesium aluminate spinel ($MgAl_2O_4$), is widely used, for instance, as a membrane in solid oxide fuel cells and in heterogeneous catalysis, either as a support for active metal nanoclusters or as a catalyst in its own right. $MgAl_2O_4$ is a ternary metal oxide with the prototypical spinel structure. Its crystal structure defines a larger group of so-called spinel minerals, which adopt the general formula A2+B23+O42-. Recently it was possible in interplay between NC-AFM and surface x-ray diffraction (SXRD) experiment together with density functional theory calculations and NC-AFM simulations to reveal an atomistic model of the (100) surface structure and the prevalent defect types on this metal oxide [1,2]. This was a key step in developing the potential applications of this surface.

In a further step, we used the MgAl2O4 (100) surface as a substrate to grow thin films of aluminium oxide – a particularly common material in studies of catalysis. By combining high- resolution non-contact atomic force microscopy with first principles simulations we demonstrate that this film remains crystalline through several layers of growth. Simulations characterize the structure of the alumina film and its interface, and predict its electronic properties – with particular emphasis on its role as a nanocatalytic substrate.

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Ultrathin diamond nanofilms as possible two-dimensional insulator: electronic and elastic properties

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Hydrogenation of graphene [1] enlarges its potential application in nanoelectronics. Regular adsorption of hydrogen atoms changes graphene electronic structure and opens the band gap depending upon the distance between hydrogen regions. Total hydrogenation of graphene changes the nature of electronic states due to changing of sp^2 hybridization of C-C bonds to sp^3 one and opens the dielectric band gap. Such two-dimensional insulator was called as graphane [2]. Graphane is an offspring of graphene along with graphene nanoribbons and carbon nanotubes. The other type of carbon bonding opens a new way for developing of two-dimensional carbon based materials.

Graphane is only first member in a series of sp3 bonded diamond films with nanometer thickness (or diamanes) consist of a number of adjusted <111> oriented layers which display unique physical properties [3]. The consequent study of graphene, graphane and proposed diamanes can be considered as bottom-up nanotechnological approach opposite to ordinary top-down paradigm. The main goal of this work is the theoretically study of diamane physical properties. We considered diamanes with different thickness; we investigated their stability and compared them with known data for sp3-hybridized hydrocarbon clusters. We studied the elastic properties of the structures and obtained phonon dispersion (as well as Raman spectra), wave velocities and elastic constants of the films. We calculated phase diagram depended upon the diamond film thickness and discussed possible ways of synthesis of the considered structures and their application in nanoelectronics and nanooptics.

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Transport properties of graphene-based branched nanoribbons. Theoretical study

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Today scientific hot topic is graphene [1]. Graphene have attracted considerable attension as a main candidate material for future nanoscale electronics. But because of unique electronic properties graphene application in nanoelectronis becomes difficult because of a lack of band gap in the electronic structure. Therefore it seems that more usefull to use graphene nanoribbons as possible semiconducting devices in nanotechnologies because it displays such large band gap due to quantum confienment effect. In recent report different types of graphene nanoribbons in particular Y-junctions were considered. The I-V characteristics of current objects were studied All investigations in recent work were making with density function theory (DFT-GGA implemented in TranSiesta package [2]). The transmission spectrum of such systems were obtained. As a result, it was found that the transmission spectrum has a similar behavior as the spectrum of Y-junctions carbon nanotubes [3].

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Optical properties of thermocromic VO_2 nanoparticles

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Thermochromic VO_2 undergoes metal-insulator transition at temperatures relatively near room temperature. The transition affects its optical properties especially at the near-infrared (NIR) wavelengths. Consequently, thin films of VO_2 have been proposed for energy-saving applications such as window coatings. At high temperatures, metal VO_2 has high reflectivity of NIR light which is absorbed or transmitted at low temperatures. However, if used as nanoparticles instead of thin films, the optical properties of the high-temperature metal VO_2 are significantly different.[1] Metal nanoparticles show strong surface plasmon resonance absorption which for VO_2 is at NIR wavelengths changing the high reflectivity of NIR light in thin films to absorption in nanoparticles.

We have studied the optical spectrum of VO_2 nanoparticles using two different methods suitable for the calculation of optical properties of nanoparticles embedded in a dielectric coating layer. Effective medium theory (EMT), in this case in the form of Maxwell Garnett theory, can describe the absorption properties of nanoparticles but does not consider scattering of light. It can be taken into account by using the four-flux method with scattering and absorption efficiencies calculated with the Mie theory. The results from the two methods agree well at both low and high temperatures for small VO_2 nanoparticles where the scattering contribution to the spectrum is small.

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Imaging and energy dissipation mechanisms on metallic and insulating surfaces studied with AFM in pendulum geometry

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Mechanism of the energy dissipation and accompanied friction in the nanoscale is a widely studied field. For a surfaces in contact the dissipation is dominated by the Van der Waals (VdW) and short range (SR) forces. Surfaces seperated by a finite distance, larger than the decay length of short range forces, dissipate energy via (VdW) and electronic interaction. To investigate the electronic contribution to the non-contact energy dissipation [1], we successfully utilize an Atomic Force Microscope (AFM) in the pendulum geometry [2].

In pendulum geometry the Cantilever is oscillating perpendicular to the sample surface. This opens the possibility to use ultra sensitive cantilever with spring constants of mN/m with a force sensitivity of $10\mathrm{aN}/\sqrt{\mathrm{Hz}}$. For surface characterisation of mixed materials its useful to image the surface topography first. Calculations show that in pendulum geometry the contrast mechanism is influenced by two types of forces - the axial force and the lateral force gradient. This is confirmed experimentally. To study the electronic contribution in detail, it is necessary to compensate the electrostatic force present due to contact potential difference between the cantilever tip and the sample surface. We used frequency modulated - Kelvin Probe Force Microscopy (fm-KPFM) to compensate the contact potential.

We can distinguish between metallic and insulating surfaces an determine the electronic contribution to the energy dissipation. This effect is enhanced, if we gently functionalize the probe, by covering the tip apex with an insulator or metal.

The measurements are performed on Cu(100) substrate with $0.6ML$ coverage of NaCl. All experiments are done under UHV and cryogenic conditions (77K).

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Lattice parameter local determination for trigonal crystal systems using several coplanar X-ray reflections

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The method for determining the local lattice parameters using quasi-multiple X-ray diffraction (which was proposed and used only for crystals of the cubic system [1]) has been expanded to measure the local crystal lattice parameters for the trigonal, hexagonal, and tetragonal systems [2]. Local variations in the lattice parameters in the trigonal lanthanum-gallium tantalite (La3Ga5.5Ta0.5O14) crystals have been investigated. Reflections necessary for implementing the quasi-multiple X-ray diffraction scheme are found for these crystals.

The pairs of reflections that were found were used to complete quasi-multiple X-ray diffraction schemes on a laboratory X-ray source and determine the variation in the lattice parameter a along the surface of these crystals. The relative measurement error was 4×10^{-6} at a spatial resolution of 140 m.

The results of determination of the linear coefficient of thermal expansion of the crystal LGT were obtained. Measurement of the relative variation of the lattice parameter a at different temperatures and linear approximation of these results gave the value of the coefficient of thermal 11 expansion equals to 4,6 - 10^{-6} (K^{-1}).The accuracy of the method and the parameters determining this characteristic were analyzed based on the results. The locality of the method and the limits of the spatial resolution of an X-ray diffraction measurement of lattice parameters are estimated.

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Atomic defects on titanium dioxide surface
-Electronic structure and manipulation-

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Titanium dioxide (TiO2) has many important applications in chemistry and physics. The chemical and physical properties of TiO2 are strongly affected by atomic defects like hydrogen atoms (H), oxygen vacancies and Ti interstitials [1-4]. The control of atomic defects on the TiO2 surface is important for creating new properties. Previously, it was found that by applying a bias voltage from a scanning tunneling microscope (STM) tip, individual H can be desorbed from the TiO2 surface [1-4]. This gives ideal control of an atomic defect. However, the reaction mechanism is not well understood. In this work, we have studied the H desorption mechanism on the TiO2 surface by measuring how the reaction yield. By applying a voltage pulse (positive sample bias) to the H from an STM tip, desorption of an individual H is observed. The reaction yield for injected electrons showed two threshold voltages for H desorption in the positive sample voltage range. With decreasing tip-sample distance, these threshold voltages shifted towards a lower energy region. In contrast, H desorption was not observed in the negative sample voltage range. From density functional theory and by probing isotope effects on the reaction yields, the shift of the spectrum was explained by changes of the barrier width of the potential curve for H desorption induced by the electronic field between tip and sample.

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d^0 ferromagnetic interface between non-magnetic perovskites

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d^0 magnetism results from spin-polarized p orbitals, whereas conventional magnetic materials have partially filled d or f states. Magnetic effects in hole-doped oxides are a common experimental observation, and holes in oxygen p orbitals have been widely predicted to result in magnetic moments [1]. In perovskite oxides, oxygen p bands are narrow and have a high density of states just below the band gap. Also, oxygen p electrons have a strong exchange coupling. Hence, Stoner's criterion for itinerant ferromagnetism is fulfilled, if the hole density is high enough [2].

Obtaining such high hole densities, moving the Fermi level to the oxygen p band, is easily done by so-called *intrinsic* doping, by a charge-imbalanced interface between two d^0 perovskites. In our model $KTaO_3/SrTiO_3$ interface, SrO and TiO_2 layers are nominally neutral, but $(KO)^-$ and $(TaO_2)^+$ layers have preferred ionic charges. To retain charge neutrality and compensate for interface dipole, 0.5 holes per p type interface unit cell are localized in the interface region. The n type interface, on the other hand, introduces 0.5 electrons per unit cell above the band gap, on the Ti d orbitals. Usually, a 2D electron gas is formed at a charge-imbalanced perovskite interface [3].

We have performed LSDA, LSDA+U and GGA+U calculations of p and n type $KTaO_3/SrTiO_3$ interfaces. The hole on oxygen $2p$ orbitals is partially magnetized. Very small values of on-site Hubbard interaction U on oxygen p orbitals stabilize complete spin-polarization and half-metallic, ferromagnetic holes. For the n type interface, on the other hand, the electrons on Ti d orbitals do not magnetize completely, and doped electrons can have a variety of competing magnetic states [4]. The density of states at the top of the O p band is higher than at the bottom of the Ti d band, making p type interfaces between d^0 perovskites candidate materials for combining ferromagnetism and ferroelectricity.

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Ehrenfest molecular dynamics within the projector augmented-wave method: an ab initio insight on electronic stopping in nanostructures

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Modeling nonadiabatic processes, such as ion-atom collisions and electron transfer in molecular and biological systems, represents major computational challenges because multiple potential energy surfaces (PES) are involved in the dynamics. Consequently, traditional ab initio molecular dynamics (AIMD) methods, founded on the assumption that the electronic subsystem is in its ground state, cannot be used. Ehrenfest molecular dynamics (Ehrenfest MD) within time-dependent density functional theory (TDDFT) offers a computationally affordable approach to simulating nonadiabatic processes by coupling the quantum equations of motion for electrons with classical equations of motion for nuclei via an average potential surface.

In ion bombardment of materials, the projectile loses kinetic energy while traversing the target due to two different processes. In nuclear stopping, the energy loss is due to the collisions with the nuclei in the target, whereas in electronic stopping, the projectile loses energy due to the interaction with the electrons of the target material. Ab initio modeling of electronic stopping is difficult because of the nonadiabatic nature of the process.

We have implemented [1] Ehrenfest MD within the projector augmented wave (PAW) method. The electronic structure program used for the implementation is GPAW [2, 3], which uses real space grids and finite differences. First, we present and discuss the Ehrenfest TD Kohn-Sham equations within the PAW method and their implementation in GPAW. Second, we demonstrate the applicability of our method by studying electronic stopping in graphene and boron nitride. We find that our PAW-based Ehrenfest MD results agree well with experiments as long as the effect of core electron excitations is small.

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Interfacial characteristics of in situ CVD-seeded ALD oxide layers on graphene

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As pristine graphene does not possess dangling bonds atomic layer deposition (ALD) generally should be preceded with surface funcionalization to initiate uniform growth. Currently, metal oxide seed layers for ALD have been deposited by physical vapour deposition with success by others [1]. In addition, the oxidation of a thin aluminum layer on graphene has also been demonstrated[2]. Other methods exist such as functionalization using nitrogen dioxide (NO2) and trimethylaluminum (Al[CH3]3) or using parlyene have been demonstrated [3,4].

In the present work, interfacial characteristics of graphene and ALD oxides of Al2O3 and TiO2 films, which are preceded with in situ chemical vapour deposition CVD-seeding, are examined.

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Direct density functional theory simulation of single sequential transmission electron microscope images

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High resolution transmission electron microscopy now enables the study of materials on the few atom level in real-time. We describe here our recent efforts to model using density functional theory single sequential exposures of suspended graphene obtained in the high brightness gun equipped, chromatically and Cs corrected PICO transmission electron microscope based at the Ernst Ruska Center, Jülich.

Single frames obtained in recent experiments show unprecedented levels of detail, enabling a one-to-one mapping between DFT models and experimental results. The rate of knock on damage and motion of adatoms can be inferred on a frame-by-frames basis, allowing more information to be extracted about nanoscale systems than ever before.

Coupling experiments and simulations for the radiation hardening of fiber optics: (II) Ab initio characterization of electronic and optical properties of defects in amorphous silica

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The changes of the transmitted signal in optical fibers occurring under irradiation depend on the point defects generated at atomic scale in the amorphous silica core of the fiber and of their optical properties. The goal of this study is to characterize using ab initio the electronic and optical properties of some of these defects, in order to help the design of specific fibers dedicated for use in the future radiative environments. The first step of our study was to generate an amorphous silica cell. This 108 atoms amorphous silica cell is then used in the framework of the the Density Functional Theory (DFT) with the Local Density Approximation (LDA) to obtain defect configurations (in particular oxygen vacancies and oxygen interstitials) in pure and doped silica. Starting from these configurations, we applied the GW approximation to obtain a right value of the band gap and to evaluate the effects of point defects, dopants and impurities on the electronic properties of silica. Finally, the optical properties (particularly the absorption spectra) of pure and doped silica are given including excitonic effects with resolution of the Bethe-Salpeter equation (BSE). The results obtained and the theoretical spectra obtained will be discussed and compared to the results coming from the literature and from our experiments (abstract I by Girard).

Magnetic resonance properties of $Sc_3C_2@C_{80}$ in finite temperatures

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Nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) are modes of spectroscopy applied to chemical species with zero, one or more unpaired electrons. They allow, e.g., the determination of molecular structures by exciting nuclear (NMR) or electron (EPR) spins of a sample by using an external magnetic field and studying the electromagnetic response of interactions caused by the perturbation.

Endohedral fullerenes are hollow carbon structures enclosing atoms or small clusters. These nanomaterials have become a subject of great interest because of their properties and potential applications, e.g., in medicine [1] and technology [2]. In the present work, the magnetic resonance parameters of $Sc_3C_2@C_{80}$ are studied computationally, continuing earlier research by S. Taubert et al. [3] by extending the study to finite temperature effects. Quantum chemical calculations and molecular dynamics simulations at various temperatures are used to obtain time-averaged properties comparable to real-life experimental results [4, 5, 6].

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Time-dependent DFT approach for the dielectric response of nanoscale systems

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Spectroscopic methods can probe the electronic structure and excitations of condensed matter systems. Non-resonant inelastic x-ray scattering (NRIXS) provides the dynamic structure factor (analogous to the electron energy loss function) that closely relates to the macroscopic dielectric function of the studied material, and is applicable in an exceptionally wide energy range: vibrational, valence and core electron excitations of various materials can be studied with this technique. Due to the rapid development of the experimental techniques, there is an increasing need for reliable computational methods that can simulate the scattering event. This work reviews our recent developments for calculating the NRIXS energy loss spectrum using time-dependent density functional theory (TDDFT).[1,2] We describe the theory behind our scheme and demonstrate the applicability for various molecular systems. We discuss the information that can be obtained from the momentum transfer dependent NRIXS spectrum, and give an overview for future developments.

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Resonant scattering in graphene: adsorbate fingerprints from ab initio calculations

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Experimental evidence indicates that the presence of resonant impurities, such as vacancies and adsorbates, is a key factor in explaining the conductance of intrinsic graphene samples [1]. Understanding of resonant scattering is also important if graphene is to be functionalized: a transport gap can be created by adsorbates while Klein tunneling makes electrostatic gating ineffective.

We have recently shown that by using a scaling approach for randomly distributed defects reliable estimates for transmission properties can be calculated based on even single defect calculations [2]. This is done by defining a scattering cross-section, a quantity that only depends on energy and defect type. Estimates of transmission and all the related transport properties, such as localization lengths and mean free paths, can then be calculated for a macroscopic system with an arbitrary defect density.

We now extend our analysis to the case of adsorbates on graphene by studying the experimentally important epoxide and hydroxyl groups. We calculate the transmission using a first-principles density functional theory nonequilibrium Green's function method [3, 4] and use the scattering cross section approach to generalize into larger and more experimentally relevant systems.

We show that a qualitative understanding of resonant scattering can be gained even from a single bulk graphene calculation, which thus provides an useful transmission "fingerprint" for each adsorbate. For graphene nanoribbons on the other hand the scattering cross section needs to be calculated from an ensemble containing all the relevant adsorption sites across the whole ribbon. The transmission in ribbons is also strongly affected by the van Hove singularities at band edges making the scattering cross section specific to a particular ribbon width.

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Nanoscale friction of ice

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The freezing of water and melting of ice are among the most dramatic examples of phase transitions is nature. Everyday experience suggests why ice surface should be slippery: water spilled on a kitchen floor or rainwater on asphalt creates some kinds of hazards for walkers. Presumably, the liquid makes the surface slippery because liquids are mobile. Since the ice crystal structure demonstrates lower friction coefficient than other solids, asking why ice is slippery is thus roughly equivalent to asking how a liquid or liquid-like layer can appear on the ice surface. Significant efforts have been made to understand the properties of this liquid layer, particularly its thickness and atomic structure. However, very little work has been done to study the friction or slipperiness at the atomic scale. This contrasts strongly with the development of the field of atomic friction in general (AFM). In this work we use atomistic simulations to understand the atomic processes involved dominating friction in ice. As a first test of our simulation tools, we study regelation in bulk ice around a nanowire using Molecular Dynamics. In particular, we show that the symmetry and continuity of the transition from a stationary to a moving system due to increased driving force changes if a hydrophilic wire is replaced by a hydrophobic one. We then investigate the frictional contact between a model polymer and an ice surface, and study how the predicted forces depend on tempereture and sliding velocity. Particular emphasis is placed on understanding the formation of the liquid layer at the surface of ice and its role in the observed properties of the interface.

Interplay of geometric and electronic structure in metalloid gallium clusters

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Over the last two decades, the so-called “renaissance of main group chemistry” has led to significant advances in the synthesis, isolation and characterization of metalloid gallium clusters. What distinguishes these from other metalloid species (e.g. ligand-protected gold, silver, palladium, etc.) is their structural diversity, with the existence of four different Ga_{22} frameworks being a particularly striking example. To gain more insight into this polymorphism, we carried out electronic structure calculations using density functional theory. Our calculations verify that two of the ligand-protected Ga_{22} isomers can to some degree be viewed as super-atom complexes - their respective metalloid cores are more or less close-packed, roughly spherical, and exhibit a well-defined electronic shell structure with a completely filled outer-most shell. The other two frameworks contain a slightly distorted icosahedral Ga_{12} core without a central atom - an unusual arrangement for metals - and the underlying electronic structure is more complex. This talk will serve as a summary of our calculations and illustrate the interplay of geometric and electronic structure in metalloid gallium clusters.

Local tunneling spectroscopy of the Hydrogen-induced impurity state in quasi-freestanding graphene

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Graphene has a unique electronic structure, which is expected to exhibit a linear dispersion near the Fermi edge. Usually this peculiar feature is difficult to observe due to proximity effect from the substrate. However, the fabrication of quasi-freestanding graphene on specific multi-layer metal surfaces has recently been demonstrated [1].

Manipulation of such graphene through selective insertion of impurities may allow to tune the electronic structure and thus to open up new routes towards graphene based device functionalities. Hydrogenation leads to a reversible gap opening at the Fermi edge. Also a dispersionless, hydrogen-induced state appears in the center of this gap [2]. The precise adsorption nature of this kind of functionalization is unclear up to the present.

Here we use scanning tunneling microscopy and spectroscopy (STM/STS) to study graphene samples with an outstanding cleanness obtained by in-situ preparation under UHV conditions. The surfaces are investigated by STM and atomically resolved images of the pristine graphene as well as the hydrogen adsorbate sites were achieved. STS measurements reveal an enhanced DOS near the Fermi edge after hydrogenation, consistent with theoretical predictions and ARPES experiments [3].

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Corrugation-enhanced graphene reactivity boosting the graphene/SiC(0001) interface stability

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Epitaxial graphenes can be grown on SiC by thermal decomposition, offering a convenient template for future carbon-based electronic devices [1]. On the Si-face, a thin carbon interface layer, usually called "buffer layer", forms between the SiC surface and the epitaxial graphene, partially decoupling electronically the latter from the substrate. This interface structure is commonly understood as a coincidence lattice between a $6\sqrt{3}\times6\sqrt{3}R30^\circ$ SiC(0001) surface reconstruction and a 13×13 graphene layer, with part of the buffer C atoms covalently bonded to the underlying surface Si atoms [2]. Using large-scale density functional theory (DFT) simulations, we have recently addressed the energetic stability of the buffer layer, poorly explored by theory so-far, showing that a model interface with the experimentally observed $6\sqrt{3}\times6\sqrt{3}R30^\circ$ periodicity is indeed stable [3]. However, the mechanism which drives the energetics has not been clarified until now: the fact that the $6\sqrt{3}\times6\sqrt{3}R30^\circ$ SiC and the 13×13 unstrained graphene lattices are perfectly commensurate does not provide alone an explanation [3, 4]. In this work, we perform DFT structural optimizations for a set of model graphene/SiC(0001) interface structures with low graphene strains [4] and we show that the energetic stability is closely related to the degree of local corrugation of the graphene (at the *atomic scale*) superimposed on the long-range Moiré rippling. We find that the most stable interfaces generally present larger deformation energies of the buffer layer due to the corrugation. This can be explained by the increased reactivity of the C atoms undergoing a partial sp_2 to sp_3 rehybridization (pyramidalization) associated with the atomic-scale buckling in the graphene. Those buffer C atoms which participate in the formation of covalent bonds with the surface Si atoms are found to have, on average, a considerably larger degree of pyramidalization than the others. Moreover, this component of Si-bonded C atoms is more reactive (i.e., has larger pyramidalization angles) in the more stable interfaces, thus explaining their higher binding energies. Finally, we find a strong dependence of the interfacial binding energies on the rotation angle between SiC and graphene favoring those interface structures with angles close to 30°, which is also the experimentally observed relative rotation for graphene on SiC(0001).

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New Method for Measuring Rocking Curves in X- Ray Diffractometry for time resolving observation of the crystal defects by Ultrasonic Modulation of the Lattice Parameter

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A new method for measuring angular distribution of X-ray beam diffraction intensity (method for measuring X-Ray rocking curves) is represented. Intensity distribution analysis in this method is conducted by ultrasonic modulation of a lattice parameter of X-ray acoustic crystal, used as an analyzer. The distinctive feature of this method is the possibility to lead precise time-resolved measurements of X-ray rocking curves without using sophisticated goniometry system.

Special elements of the X-ray acoustooptics - X-ray acoustic resonators, consisting of a piezoelectric crystal (quartz) and X-ray optical crystal (silicone) was developed to implement the method. Piezoelectric crystal was used to create a standing acoustic wave and control effectively a tension-compression deformation in the X-ray optical crystal [1]. Developed X-ray optical scheme and optical elements allow us to create uniform (within X-ray beam footprint) time-variable deformation of crystal lattice [2] and use these X-ray acoustic resonators as analyzers of scattered X-rays beam.

Rocking curves, measured by proposed X-ray acoustic method by shape and halfwidth agrees well to curves measured according to traditional way - by rotating a crystal. Experimental results of method approbation - examples of rocking curves of (440) reflection silicon crystal and (220) paratellurite crystals measured on laboratory diffractometer using X-ray acoustic method will be presented.

The angular and time resolution of the method is determined by speed of detecting apparatus (the minimum possible changing of phase and minimal width of stroboscopic window or number of channels of the multichannel scaler) and depends on parameters such as ultrasound frequency and amplitude of ultrasonic oscillation. Experimentally achieved resolution of the method is 0.1 arcsec. Accuracy can be increased by no less than an order by using an ultra-fast multichannel scaler. Developed method and experimental schemes are totally applicable for synchrotron radiation conditions.

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Molecular dynamics simulations of initial stages of growth of nitrogen-doped carbon nanotubes

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Although growing carbon nanotubes on catalytic metal nanoparticles is today a routine task, the reaction mechanisms involved remain elusive. Recently, efforts have been made to synthesize nitrogen-doped carbon nanotube in a controlled manner, since every nitrogen atom affects the properties of the doped nanotube [1, 2]. Therefore, the mechanisms of nitrogen and carbon diffusion and reactivity on catalyst nanoparticles deserves to be explored.

We have investigated the diffusion and clustering of carbon and nitrogen on the surface of the Fe_{55} nanoparticle by means of molecular dynamics simulations at the density-functional tight-binding (DFTB) level. The transport and clustering of carbon and nitrogen atoms on the catalytic nanoparticles are the first steps towards the nanotube formation and growth. Different degrees of carbon coverage on the Fe_{55} nanoparticle surface are considered. Short molecular dynamics simulations on nitrogen-doped carbon nanotube segments on a catalytic iron nanoparticle are also presented.

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Modelling of radiation damage recovery in concentrated Fe-Cr alloys: a multi-scale modelling approach

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High-Cr ferritic/martensitic steels (containing 7-14Currently, an essential emphasis is made on the development of numerical models to describe accumulation and annealing of radiation damage in Fe-Cr alloys depending on Cr content so as to optimize composition of the high-Cr steels. The mean field theory is the only approach currently available to study the accumulation of damage over substantial period of time (i.e. dose) at the relevant space scale. Development, parameterization and validation of the mean field theory model for the concentrated Fe-Cr alloys is the subject of the present work. Here, we apply a combination of simulation tools such as Density Functional Theory (DFT), molecular dynamics (MD), atomistic kinetic Monte Carlo (AKMC) and mean field theory (MFT) to model recovery in electron-irradiated concentrated Fe-Cr alloys and provide comparison with experimental resistivity recovery studies. MD simulations were used to generate the primary damage state due to electron bombardment to be used in AKMC. The latter method was used to model short term annealing i.e. correlated and close-pair recombination processes. An applied AKMC techniques was parameterized using Artificial Neural Network (ANN) method, trained with a set of DFT-fitted interatomic potentials. Firstly, the migration energy of diffusing point defects (i.e. vacancies or self-interstitials) is calculated using the nudged elastic band method, as a function of the local atomic environment (i.e. solutes and other point defects), which become variables describing the migrating defect's neighbourhood in the ANN regression. The defect distribution after short term annealing obtained from AKMC was then passed to MFT model, where the mobility of point defects (depending on Cr content) was parameterized with the same AKMC tool. The stability and mobility of clusters of point defects was obtained by means of MD and partially fitted to achieve agreement with experiment. The above constructed setup was used to simulate defect recovery up to stage III (vacancy migration) in electron-irradiated Fe-5Cr, Fe-10Cr and Fe-15Cr alloys during isochronal annealing.

Nanomanipulation of Graphene using E-beam and Block Copolymers

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Since the discovery of graphene, the possibilities for manipulating the properties have been intensively studied. Generation of a customised electron bandgap in combination with a high carrier mobility is an key issue for electronic applications. There are numerous possibilities for opening a bandgap, and a pathway studied recently is that of dense periodic lattices, either antidot lattices (periodic holes) [1], [2], [3], [4] or chemical functionalisation [5]. While conventional top-down approaches are inadequate in terms of reaching the dimensions predicted to result in bandgaps of a useful size [1], self-assembled structures such as block copolymers (BCP) and hydrogen superstructures can be used to deliver the ultra-high density of structures needed, with the periodicities down to 5 nm.

In the present work, several options for tuning the properties of graphene through lithographic modulation are studied; either by partially suspending graphene on nanoporous surfaces or structuring graphene as has already been demonstrated experimentally [3], [4]. These are compared to graphene structured with conventional lithography teqniques. Apart from the direct influence of the periodic, alternating contact with polymer/substrate and air for partially suspended graphene, which may itself open a bandgap, it has been predicted that graphene may conform mechanically to a nanostructured surface, which should contribute to the electronic bandgap as well. The properties of nanomanipulated graphene will be investigated in a controlled environment and in ambient conditions.

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NMR parameter of chemically modified graphanes

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Two dimensional carbon layer, graphene has reached high interest among many fields. It serves many interesting physical phenomena due to the unique electron structure [1]. Graphene's chemically modified counterparts, hydrogenated (graphane), and fluorinated graphene (F-graphene), are also under active study in material science [2].

In this work NMR parameters are calculated with density functional level (DFT) for graphane and F-graphene. Calculations are implemented using two different kinds of basis set paradigm; i) periodic plane wave based and ii) cluster method based with Gaussian type basis set. In latter case, the method of completeness-optimized (co) basis set is used [3]. The utilization of co enables to generate basis set close to the basis set limit for desired molecular properties.

Graphene's NMR parameters were first ever predicted some years ago [4]. This work offers not only predictions of NMR parameters of graphane and F-graphane for use of experimentalists, but also comparison of two different kinds of computational methods with interesting way.

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Hybrid-Functional Study of Band-Structures of GaAs$_{1-x}$N$_x$ and GaSb$_{1-x}$N$_x$ Alloys

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Conduction band-structures of III-V nitrides can be strongly modified by replacing the V component by just a small fraction of nitrogen. That is why dilute III-V nitrides have attained considerable attention during the past two decades in research. Opposite to the expectations arising from large nitride band gaps, the band gaps in dilute nitride alloys decrease with increasing nitrogen concentration. Archetypal examples are the GaAs$_{1-x}$N$_x$ alloys that show band gap reduction with the increasing nitrogen concentration. The effect of nitrogen is even more dramatic in GaSb$_{1-x}$N$_x$ alloys with the maximum electronegativity difference between two group-V species.

In this work we consider GaAs$_{1-x}$N$_x$ and GaSb$_{1-x}$N$_x$ alloys. Density functional theory calculations made to this day to model these materials have been performed within the local or semilocal approximation for the electron exchange and correlation. The drawback of these methods is a substantial underestimation of energy band gaps. In contrast, in the present work, we make use of the hybrid functionals in which part of the semilocal exchange-correlation functional is substituted by the Hartree-Fock exchange[1] . Hybrid functionals give band gaps near to the experimental ones and makes it possible to study band structures of GaSb$_{1-x}$N$_x$ alloys *ab initio* without any parameter fitting.

In this work we found that nitrogen affects both GaAs and GaSb in a similar way, by creating well-localized states above the band gap, related to the bonding of nitrogen to the surrounding Ga atoms. According to our calculations in the case of a single nitrogen atom in the supercell, the tail in DOS due to the nitrogen induced states hybridize with bulk conduction band states and extends towards the band gap by the same amount in both materials. This is due to similar Ga-N bonds. The tails enter into the bulk band gap regions causing the observed band gap reductions. The reason for the observed stronger band gap reduction in GaSb$_{1-x}$N$_x$ than in GaAs$_{1-x}$N$_x$ was found to be the positions of bulk band edges relative to the Ga-N bond energy, i.e. the position of the nitrogen induced states. Our findings do not support the common suggestion that the greater electronegativity mismatch between N and Sb compared to that between N and Ga should explain the stronger band gap reduction in GaSb$_{1-x}$N$_x$ than in GaAs$_{1-x}$N$_x$.

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The effect of non-magnetic impurities on magnetic and cohesive properties of grain boundaries in nickel

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The macroscopic mechanical behaviour of polycrystalline metallic materials is largely determined by cohesion of the grain boundaries (GB) which is strongly affected by segregated impurities. Here we present an ab initio study of segregation of 12 non-magnetic sp-impurities (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) at $\Sigma5(210)$ GB and (210) free surface (FS) in fcc ferromagnetic nickel and analyze their effect on structure, magnetic and mechanical properties. We determine the preferred segregation sites of the impurity atoms at the $\Sigma5(210)$ GB, their segregation enthalpies and strengthening/embrittling energies with their decomposition into the chemical and mechanical components. We find interstitially segregated Si as a GB cohesion enhancer, substitutionally segregated Al and interstitially segregated P with none or minimum strengthening effect and interstitially segregated S, Ge, As, Se and substitutionally segregated Ga, In, Sn, Sb and Te as GB embrittlers in nickel. Interstitial impurities modify the magnetic moments at the GB and in its immediate neighbourhood stronger than substitutional ones. Whereas there is a slight enhancement of magnetization at the clean GB and FS with respect to bulk nickel (3-7 % and 24 %, respectively), most of the above impurities nearly kill or substantially reduce the magnetic moments at the FS and, when segregating interstitially at the GB (i.e. Si, P, S, Ge, As, and Se), they produce magnetically dead layers at the boundary, which are caused by a strong hybridization of sp-states of the impurities with the d-states of nickel and a redistribution of electron states in both majority and minority bands.

This research was supported by the Grant Agency of the Czech Republic (Projects No. 202/09/1786 and 106/09/H035), the Grant Agency of the Academy of Sciences of the Czech Republic (Project No. IAA100100920), by the Research Projects AV0Z20410507 and MSM0021622410 and by the Project CEITEC-Central European Institute of Technology (CZ.1.05/1.1.00/02.0068) from the European Regional Development Fund.

Influence of boron doping on the defect-induced magnetism of oxygen-eroded graphite

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Magnetic properties of pure carbon materials or carbon materials, doped with elements of the first rows of the periodic table such as B or N, have been in focus during the last decade, yet, the true nature of magnetism of carbon remains unclear. Pristine graphite is diamagnetic. Structural disorder, topological defects or absorbed guest atoms are believed to change the localized electronic states of carbon materials and trigger anomalous behavior in magnetic field. Magnetic ordering has been observed in irradiated graphite [1-2], as well as nanoporous carbon structures [3]. At the same time, very large amount of defects is predicted to destroy magnetism [4]. Surface oxidation route turns bulk graphite into a foamy-like highly-defective graphitic structure. Boron is well-known as a catalyst of graphite-oxidation reaction. On the other hand, it acts as a dopant for carbon system and can change the relative occupancy of pi-bands. The theoretical studies conducted in [5] predict a significant influence of relative concentration of boron atoms vs vacancies on defect-induced magnetism in graphene. We present a comparative experimental study of structural and magnetic properties of nanoporous oxygen-eroded graphite with varying boron content. DC magnetic measurements were performed at a Quantum Design SQUID magnetometer (MPMS-XL-1) on microcrystalline powder samples. The impurity analysis performed with HR-ICP-MS proved that magnetism of the samples does not correlate with content of magnetic impurities.

We have found that introduction of boron affects the magnetic behaviour of nanoporous carbon in a complex way, changing both paramagnetic and diamagnetic contributions. Small concentrations of dopant enhance magnetic response from the system, while higher concentrations suppress magnetism.

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First-principles investigation of the martensitic transformation in Co-doped Ni_2MnGa shape memory alloys.

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The ferromagnetic Ni_2MnGa alloy has attracted a lot of interest because it exhibits interesting magneto-mechanical effects such as magnetic field-induced martensite (MIM) and magnetic field-induced reorientation of martensite (MIR) [1]. These effects are the consequence of coupling between the magnetic microstructure and twin microstructure of the alloy and high mobility of twin boundaries. The MIM and MIR occur near or below martensitic transformation temperature, which is about 200 K for stoichiometric Ni_2MnGa. Controlling the martensitic transformation temperature is important task for the practical exploitation of the MIM and MIR. The transformation temperature can be adjusted by doping by an additional element such as Fe, Co or Cu [2].

The purpose of the present contribution is to describe the influence of Co-doping on the martensitic transformation using the first-principle calculation techniques. The exact muffin-tin orbitals (EMTO) method [3] in combination with coherent potential approximation (CPA) [4] was found to describe accurately the total energy of a system with chemical and magnetic disorder. The exchange correlation term is described within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [5]. The EMTO basis sets include s, p and d components.

In this work, we compute the structural parameters, total energy and magnetic moments of non-modulated structures as a function of tetragonal ratio c/a. We have found the ground state of tetragonal phase for $c/a = 1.33$. The metastable state corresponds to the cubic $L2_1$ structure ($c/a = 1$). Because the previous theoretical work shows that Co has a strong tendency to occupy the Ni-sublattice [6], the effect of Co-doping is also included in the present work. The calculations shows, that c/a ratio of equilibrium state can be reduced by Co-doping. Also the structural energy difference between cubic and tetragonal phase decreases with increasing content of Co.

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Index