Atomic structure of nanosystems from first-principles simulations and microscopy experiments

Physics Boat 2015

9th – 11th June 2015
Helsinki, Finland – Stockholm, Sweden

Organizers

Prof. Adam Foster
Department of Applied Physics, Aalto University

Dr. Teemu Hynninen
Department of Physics and Astronomy, University of Turku

Dr. Arkady Krasheninnikov
Department of Applied Physics, Aalto University

Dr. Peter Spijker
Department of Applied Physics, Aalto University

Acknowledgements for financial support

Aalto University

Programme

Tuesday

10:40	*Registration*
11:10	*Opening*
	chair: Voitchovsky
11:20	**Onishi**
12:00	**Grutter**
12:40	Stocker
13:00	*Lunch*
	chair: Kühnle
14:00	**Voitchovsky**
14:40	**Fukuma**
15:20	Federici Canova
15:40	Loukonen
16:00	Komsa
16:20	*Departure/coffee*
	chair: Kantorovich
18:00	**Hornekaer**
18:40	**Yazyev**
20:00	*Dinner*

Wednesday

13:40	*Coffee*
	chair: Grutter
14:00	**Kühnle**
14:40	**Kantorovich**
15:20	**Kawai**
16:00	Coffee at posters
	chair: Hornkaer
17:40	**Gröning**
18:20	Kimouche
18:40	Åhlgren
19:00	Hummel
20:00	*Dinner*

Thursday

	chair: Groening
9:00	**Sloan**
9:40	**Arenal**
10:20	Booth
10:40	Dienel
11:00	*Coffee*
	chair: Arenal
11:40	**Ramasse**
12:20	Temirov
12:40	Schulz
13:00	*Lunch*
	chair: Komsa
14:00	**Ternes**
14:40	Hlawacek
15:00	*Closing*

Contents

Tuesday 09.06.2015

10:40	–	11:10	*Registration*
11:10	–	11:20	*Opening*
			chair: Voitchovsky
11:20	–	12:00	**Onishi**
			Interfacial liquids, Most soft materials probed by AFM
12:00	–	12:40	**Grutter**
			Atomic Force Microscopy combined with Field Ion Microscopy: structure-function determination for nanoelectronics
12:40	–	13:00	Stocker
			The hydrogen molecule in a vice
13:00	–	14:00	*Lunch*
			chair: Kuehnle
14:00	–	14:40	**Voitchovsky**
			Amplitude-modulation atomic force microscopy at the solid/liquid interface: imaging water, ions and liquid self-assembly
14:40	–	15:20	**Fukuma**
			Visualizing atomic-scale calcite dissolution processes by high-speed frequency modulation atomic force microscopy
15:20	–	15:40	Federici Canova
			Structure and shear dynamics of nano confined ionic liquids
15:40	–	16:00	Loukonen
			Entropy drives the self-assembly of water on calcite?
16:00	–	16:20	Komsa
			Observation and stability of one-dimensional ionic BN and CsI chains in electron microscope
16:20	–	18:00	*Departure/coffee*
			chair: Kantorovich
18:00	–	18:40	**Hornekaer**
			The interaction of atoms and molecules with graphene on metal substrates
18:40	–	19:20	**Yazyev**
			Predicting and observing topological defects in 2D materials
20:00	–	22:00	*Dinner*

Interfacial liquids, Most soft materials probed by AFM

H. Onishi[1]

[1]Kobe University, Japan

In the present talk, our recent effort in visualizing interfacial liquids by frequency-modulation atomic force microscopy (FM-AFM) is reviewed. We have examined structured liquids at a number of interfacial liquids over TiO2 [1], Al2O3 [2], hydrophilic [3] and hydrophobic [4] self-assembled monolayers, p-nitroaniline [5, 6], CaCO3 [7], and graphite [8]. The observed force curves were sensitive to the composition of the solid and liquid, while insensitive to tips of different apex radii [9]. This suggests that the observed force distribution was not much affected by the presence of the AFM tip. On the basis of these results, we now propose that heteroepitaxial relationship functions at liquid-solid interfaces. This proposal is open to discussion on the boat.

[1] T. Hiasa et al., *Jpn. J. Appl. Phys.* **48**, 08JB19 (2009).
[2] T. Hiasa et al., *J. Phys. Chem. C* **114**, 21423 (2010).
[3] T. Hiasa et al., *Phys. Chem. Chem. Phys.* **14**, 8419 (2012).
[4] T. Hiasa et al., *Coll. Surf. A* **396**, 203 (2012).
[5] R. Nishioka et al., *J. Phys. Chem. C* **117**, 2939 (2013).
[6] P. Spijker et al., *J. Phys. Chem. C* **118**, 2058 (2014).
[7] H. Imada, *Langmuir* **29**, 10744 (2013).
[8] T. Hiasa et al., *J. Phys. Chem. C* **116**, 26475 (2012).
[9] T. Hiasa et al., *Jpn. J. Appl. Phys.* **51**, 025073 (2012).

Atomic Force Microscopy combined with Field Ion Microscopy: structure-function determination for nanoelectronics

P. Grutter[1]

[1]Department of Physics, McGill University, Montreal (Canada) grutter@physics.mcgill.ca

It is experimentally well established that AFM can image the structure of surfaces with very high spatial resolution. Determination of structural information from this data needs theoretical modeling to compare to experimentally observed contrast. This is challenging, in particular if other properties such as electrical conductivity should be determined simultaneously, thus enabling powerful, quantitative structure-function relationships to be extracted from AFM experiments. On a fundamental level the major reason why this is challenging is because theoretical models need to make assumptions and experiments typically don't know enough atomic scale details of the AFM tip, leaving substantial room for approximations. I will discuss our experimental work using a combined STM/AFM-field ion microscopy (FIM) UHV system that allows the creation and investigation of atomically defined electrical and mechanical contacts [1]. Both contact electrodes can be characterized on an atomic scale, which in combination with state-of-the art transport and MD theory allows deep insights into the conductance of nanoscale metallic contacts. Based on detailed, atomic scale experimental characterization of the clean W tip – Au(111) sample system immediately before contact we demonstrate that the observed electronic transport has conductance values factors below that expected from simple ballistic transport models [2]. Furthermore, these experiments allow detailed insights into the energetics of mechanical contact formation and the initiation of plastic deformation [3]. Finally, I will discuss some of the experimental limitations in addition to the theoretical challenges.

[1] W. Paul, P. Grutter, *Phys. Chem. Chem. Phys.* **16**, 8201 (2014).
[2] D. J. Oliver, J. Maassen, M. El Ouali, W. Paul, T. Hagedorn, Y. Miyahara, Y. Qi, H. Guo, and P. Grutter, *Proc. Natl. Acad. Sci. USA* **109**, 19097 (2012).
[3] D. Oliver, W. Paul, M. El Ouali, T. Hagedorn, Y. Miyahara, Y. Qi, and P. Grutter, *Nanotechnology* **25**, 025701 (2014).

The hydrogen molecule in a vice

M. Stocker[1] S. Röger[1] B. Koslowski[1]
[1]Universität Ulm, Institute of Solid States

Molecular Hydrogen physisorbed on metal surfaces leads to strong characteristic features in scanning tunneling spectroscopy [1][2]. At low bias not only a strong inelastic signature occurs but also a huge change of the elastic channel is observed. We show that the molecular vibration opens an inelastic channel as expected but stalls concurrently the entire elastic channel due to the forces exerted on the electrodes by the vibrating molecule. The required compliance of the stylus is surprisingly large but is possible in the wide spectrum of experimental conditions. Additionally, the inelastic channel experiences a saturation from which the lifetime of the molecular vibration can be deduced to be approximately 1 ns. This experiment allows resolving the forces corresponding to specific vibrational states of a single molecule.[3]

[1] F. Natterer, F. Patthey, H. Brune, *PRL* **111**, 175303 (2013).
[2] S. Li, A. Yu, F. Toledo, Z. Han, H. Wang, H.Y. He,R. Wu, W. Ho, *PRL* **111**, 146102 (2013).
[3] M. Stocker, S. Röger, B. Koslowski, *arXiv* **1503**, 07702 (2015).

Amplitude-modulation atomic force microscopy at the solid/liquid interface: imaging water, ions and liquid self-assembly

K. Voitchovsky[1] M. Ricci[2] P. Spijker[3] W. Trewby[1]

[1]Durham University, UK
[2]EPFL, Switzerland
[3]Aalto University, Finland

Recent development in the field of atomic force microscopy have made it possible to routinely achieve atomic- or molecular-level images of solid/liquid interfaces and quantify the behaviour of solvation structures locally. Typical measurements are based on the frequency- or amplitude-modulation of a cantilever vibrating with sub-nanometre amplitude. Here I present high-resolution amplitude-modulation measurements over two different types of interfaces. The first type involves solids in contact with aqueous solutions containing ions. Such interfaces are of fundamental importance in biology and in electrochemical processes. The results, complemented by MD simulations, show that interfacial water can induce correlations between single metal ions at various soft and hard interfaces, create ordered ionic structures, and dramatically slow down the dynamics of adsorbed ions. The second system is composed of soluble liquid mixtures that tend to demix at the interface, creating dynamical self-assembled structures that can rapidly heal when damaged. Aside from its enormous potential in technology, this type of interfaces offer unique insights into the poorly understood transition between bulk and surface thermodynamics. In both cases, I discuss the impact of the measurement process on the results and on the resolution achieved.

Visualizing atomic-scale calcite dissolution processes by high-speed frequency modulation atomic force microscopy

T. Fukuma[1] K. Miyata[1]

[1]Division of Electrical Engineering and Computer Science, Kanazawa University, Kakuma-machi, 920-1192 Kanazawa, Japan

Recent advancement of frequency modulation atomic force microscopy (FM-AFM) has enabled true atomic-resolution imaging even in liquid environments. In addition, combined with three-dimensional (3D) imaging techniques, it has also enabled to visualize 3D hydration structures and flexible surface structures. These previous works highlighted excellent spatial resolution of liquid-environment FM-AFM. However, imaging speed of the present FM-AFM is typically 1 min/frame, which is often insufficient to visualize dynamic atomic-scale processes at a solid-liquid interface. Examples include crystal growth and dissolution, catalytic reactions and metal corrosion processes. To overcome this limitation, we have recently developed a high-speed FM-AFM that allows true atomic-resolution imaging at 1 sec/frame in liquid. In this talk, I would like to present direct FM-AFM imaging of calcite dissolution processes. To date, the calcite growth and dissolution processes have been extensively studied by AFM. There previous works clarified dynamic behavior of single atomic steps. However, the actual atomic-scale dissolution processes take place at the vicinity of a step edges. Due to the insufficient resolution or imaging speed of the conventional AFM, atomistic details at the step edges have remained unknown. In this study, we succeeded in visualizing atomic-scale processes near the step edges. In addition, the obtained FM-AFM images revealed the existence of a transition region along step edges. The region appears to be a layer having a width of a few nanometers and a height of 0.1-0.2 nm. This height is much lower than the single atomic step height of a cleaved calcite surface (0.31 nm). Detailed analysis of a large number of FM-AFM images obtained at this interface suggests that the transition region corresponds to a layer of adsorbed hydrated ions. Based on this finding, here we make a major improvement in the atomic-scale model of crystal dissolution processes.

Structure and shear dynamics of nano confined ionic liquids

F. Federici Canova[1,2] A. L. Shluger[3]
[1]Advanced institute for materials research, Tohoku University, Japan
[2]Aalto Science Institute, Aalto School of Science, Finland
[3]University College London, United Kingdom

Ionic liquids (ILs) are molten salts usually composed of organic molecules, typically in liquid state at room temperature. Initially quite popular solvents for synthesis and catalysis [1], recent studies showed how IL lubricants reduce friction between sliding surfaces [2]. Moreover, thanks to their ionic nature, they can form stable, charged layers on surfaces, providing remarkable wear protection [3]. Another interesting feature is the endless variety of ILs that can be obtained from anion and cation combinations. Each pair has different properties, and this in principle allows the design of lubricants with optimal properties for a particular application. Unfortunately it is still not possible to do so, because the relationship between molecular shape/size and viscous properties, and the effect of confinement, are not well known at the atomic scale. Such detailed information is not always accessible in experiments, and theoretical models become necessary. Following our previous investigation of [BMIM][BF4] and [BMIM][NTF2] between crystalline silica [4], we extended the study to amorphous surfaces. Using classical models, we performed molecular dynamics (MD) simulations of the equilibrium structure of the two ILs on glass, and their nano-confined shear dynamics. We found that the main structural properties of the solid-liquid interface seen on the crystal surface, are still present on amorphous ones. However, the atomic scale roughness and the irregular distribution of hydroxyl groups, weaken the liquid order. Under nano-confinement, the layered structure of [BMIM][BF4] does not show a strong dependence on the detailed structure of the amorphous surface, as the small anions adapt to the topography. However, the surface disorder is amplified by the larger anions of [BMIM][NTF2], and even the number of layers appear to change between different amorphous surfaces. Higher friction is seen in [BMIM][NTF2], compared to [BMIM][BF4], as seen with crystal surfaces, but the difference appears more remarked. Contrary to expectations, higher lateral forces are observed when shearing the less ordered liquids, between amorphous surfaces. This suggests that the layered structures of ILs are stiff, despite their corrugation, and molecular collisions are triggered more often, resulting in higher friction.

[1] J. S. Wilkes, P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis* –, Wiley (2008).
[2] M. Placio and B. Bhushan, *Tribology Letters* **40**, 247 (2010).
[3] M. Placio and B. Bhushan, *Advanced Materials* **20**, 1194 (2008).
[4] F. Federici Canova, et al., *Phys. Chem. Chem. Phys.* **16**, 8247 (2014).

Entropy drives the self-assembly of water on calcite?

V. Loukonen[1] F. Kling[2] R. Bechstein[2] P. Spijker[1] A. Kühnle[2] A. S. Foster[1]

[1]Department of Applied Physics, COMP Centre of Excellence, Aalto University, P.O. Box 11100, 00076 Aalto, Espoo, Finland
[2]Institut für Physikalische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

The phenomenon of self-assembly — the emergence of order out of disorder — encompasses the physical world on several scales [1]. In aspirations towards manufacturing nanoscale structures and devices, molecular self-assembly on surfaces has aroused plenty of attention [2]. Simplifying, molecular self-assembly on surfaces is governed by the competition between the molecule-molecule and the molecule-surface interactions. These interactions are always present whenever molecules meet surfaces — however, only seldom do they lead into self-assembly. Consequently, much of the research concentrates in finding/designing specialised molecules to self-assemble on targeted surfaces. Recently, however, we observed interesting molecular self-assembly of water on calcium carbonate surface — both of the species are fairly common in nature.

According to non-contact atomic force microscope measurements on calcite (10.4) surface (the natural cleavage plane of the most stable crystal structure of calcium carbonate $CaCO_3$ [3]), in a perfect water monolayer coverage, each Ca^{2+} ion accommodates one water molecule. This is intuitively easy to understand: the Ca^{2+} ions attract water oxygen and the water hydrogen atoms try to form hydrogen bonds with the carbonate group (CO_3^{2-}) oxygens. However, with a sub-monolayer concentration of water something unexpected happens: water fills the surface with regular zigzag lines with an equal spacing. The bonding patterns are likely still the same, but now every second Ca^{2+} row is skipped. Thus, water spontaneously self-assembles into a sparse but regular packing on the surface.

We present a first-principles investigation aiming at explaining this curious observation. Dispersion-corrected density functional theory calculations and simulations are used. Preliminary computations show that both at zero and non-zero temperatures, the perfect monolayer packing is energetically slightly more favourable than the observed sparse packing. However, this energy barrier can be overcome if the change in entropy is large enough between the dense and sparse packing. If the free energy change ΔF(from dense to sparse) $=$ $\Delta E - T\Delta S < 0$, eventually the sparse packing should occur spontaneously; in other words this should happen if $\Delta S > \Delta E/T$, where E is the internal energy of the system and T is the temperature. Here, we evaluate the entropy change

ΔS from first-principles molecular dynamics simulations and try to answer this pressing question.

Besides illuminating the particular case studied here, on a more general level the results give new insight on the behaviour of confined water and on the fundamental mechanisms of self-assembly.

[1] Whitesides, G. M., and Grzybowski, *Science* **295**, 2418–2421 (2002).
[2] Barth, J. V., Costantini, G., and Kern, K., *Nature* **437**, 671–679 (2005).
[3] Rahe, P., Kuhn, S., and Kühnle, A., *JUnQ* **3**, 21–25 (2013).

Observation and stability of one-dimensional ionic BN and CsI chains in electron microscope

H. Komsa[1] A. V. Krasheninnikov[2]

[1]COMP, Department of Applied Physics, Aalto University, Finland
[2]Department of Applied Physics, Aalto University, Finland

Single atom thick one-dimensional chains have been previously observed when consisting of a single element such as carbon or gold. Chains consisting of two or more different atoms, and in particular chains of ionic character, have not been previously reported. The first scanning tunneling electron microscope observation of two such chains, consisting of BN and CsI ions, were recently reported [1,2].

Boron nitride chains were constructed via electron beam etching from two-dimensional (few layer) h-BN sheets. The chains were found to behave rather similarly to the carbon chains created from graphene, and thus completes the analogy between various boron nitride and carbon polymorphs. In the case of CsI chains, the chains were stabilized through encapsulation inside carbon nanotubes. In order to find out if such sensitive structures can remain stable in the conditions prevailing inside the electron microscope, we performed density functional theory (DFT) calculations to study the equilibrium energetics of the chains and DFT molecular dynamics calculations to study their thermal stability and ability to withstand knock-on events.

In both cases, dynamical effects were found to complicate characterization and identification of the observed features. Suspended BN chains were found to break easily, while BN chains supported on a BN sheet were rather stable, but were also found to vibrate strongly. In the case of CsI, I ions are located at the center of the tube, whereas Cs atoms are attracted to nanotube wall and undergo rapid circular motion along the wall. Finally, the electronic properties of the chains were found to retain the insulating properties of their bulk counterparts.

[1] R. Senga, H.-P. Komsa, Z. Liu, K. Hirose-Takai, A. V. Krasheninnikov, and K. Suenaga, *Nature Materials* **13**, 1050 (2014).

[2] O. Cretu, H.-P. Komsa, O. Lehtinen, G. Algara-Siller, U. Kaiser, K. Suenaga, and A. V. Krasheninnikov, *ACS Nano* **8**, 11950 (2014).

The interaction of atoms and molecules with graphene on metal substrates

L. Hornekaer[1]

[1]Dept. Physics and Astronomy and Interdisciplinary Nanoscience Center (iNANO), Aarhus University

Two approaches to control graphene electronic properties and graphene-substrate interactions are chemical functionalization of graphene and intercalation at the graphene-metal interface. Both of these processes are highly dependent on the graphene-metal substrate interaction, edge effects and defects in the system, as well as the registry between the graphene and the metal lattices. In some cases Moire patterns lead to preferential intercalation and functionalization in some areas, leading to ordered nano-patterning, while in other cases disordered functionalization structures and uniform intercalation are observed.

In my talk I will present combined, scanning tunnelling microscopy, thermal desorption spectroscopy, angle resolved photoemission spectroscopy and density functional theory calculations on intercalation and functionalization of graphene on Ir(111)[1-4] and Pt(100) [5-8] substrates and discuss the mechanisms governing hydrogen functionalization of, as well as intercalation of gaseous species under graphene on transition metal substrates.

[1] S. Ulstrup, M. Andersen, M. Bianchi, L. Barreto, B. Hammer, L. Hornekær and P. Hofmann, *2D Materials* **1**, 025002 (2014).

[2] R. Balog, M. Andersen, B. Jørgensen, Z. Sljivancanin, B. Hammer, A. Baraldi, R. Larciprete, P. Hofmann, L. Hornekær, and S. Lizzit, *ACS Nano* **7**, 3823 (2013).

[3] R. Larciprete, S. Ulstrup, P. Lacovig, M. Dalmiglio, M. Bianchi, F. Mazzola, L. Hornekaer, F. Orlando, A. Baraldi, P. Hofmann, and S. Lizzit, *ACS Nano* **6**, 9551 (2012).

[4] R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann and L. Hornekær, *Nature Materials* **9**, 315 (2010).

[5] L. Nilsson, M. Andersen, B. Hammer, I. Stensgaard, and L. Hornekær, *J. Phys. Chem. Lett.* **4**, 3770 (2013).

[6] S. Ulstrup, L. Nilsson, J. A. Miwa, R. Balog, M. Bianchi, L. Hornekær and P. Hofmann, *Phys. Rev. B* **88**, 125425 (2013).

[7] L. Nilsson, M. Andersen, R. Balog, E. Lægsgaard, P. Hofmann, F. Besenbacher, B. Hammer, I. Stensgaard, L. Hornekær, *ACS Nano* **6**, 10258 (2012).

[8] . Kyhl, S. F. Nielsen, A. G. Cabo, A. Cassidy, J. A. Miwa and L. Hornekær, *Faraday Discussions* 10.1039/c4fd00259h (2015).

Predicting and observing topological defects in 2D materials

O. V. Yazyev[1]

[1] Institute of Theoretical Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Grain boundaries and dislocations are intrinsic topological defects of polycrystalline materials that inevitably affect their physical properties. In my talk, I will first discuss the structure of topological defects in two-dimensional (2D) materials such as graphene and monolayer transition metal dichalcogenides [1,2] as well as their electronic transport properties predicted by theory [3,4]. Our most recent efforts involved joint experiment-theory studies of well-ordered topological defects in graphene. In particular, a line defect with valley-filtering properties has been produced in a controlled way at the transmission electron microscopy (TEM) conditions [5]. Periodic grain boundary defects have been investigated in polycrystalline samples of epitaxial graphene grown on SiC substrates using scanning tunneling microscopy (STM) [6]. The latter study allowed observing the buckling transition of grain boundaries predicted to occur in 2D polycrystals. Unlike graphen e, monolayer transition metal dichalcogenides (MoS_2 and alike) combine a two-valley electronic band structure with strong spin-orbit effects. The latter can be employed for creating spin-polarized currents and adds yet another conservation law of the electronic transport across regular defects [7], such as the inversion domain boundaries frequently observed in dichalcogenide materials [8].

[1] O. V. Yazyev, Y. P. Chen, *Nature Nanotechnol.* **9**, 755 (2014).
[2] O. V. Yazyev, S. G. Louie, *Phys. Rev. B* **81**, 195420 (2010).
[3] O. V. Yazyev, S. G. Louie, *Nature Mater.* **9**, 806 (2010).
[4] F. Gargiulo, O. V. Yazyev, *Nano Lett.* **14**, 250 (2014).
[5] J. H. Chen et al. , *Phys. Rev. B* **89**, 121407(R) (2014).
[6] Y. Tison et al., *Nano Lett.* **14**, 6382 (2014).
[7] A. Pulkin, O. V. Yazyev, *submitted* (2015).
[8] O. Lehtinen et al., *ACS Nano* **9**, 3274 (2015).

Wednesday 10.06.2015

13:40	-	14:00	*Coffee*
			chair: Grutter
14:00	-	14:40	**Kühnle** Molecular self-assembly on an insulating surface: Long-range order induced by an intrinsic repulsion mechanism
14:40	-	15:20	**Kantorovich** Dynamics at nano-scale: Modeling AFM manipulation and kinetics of self-assembly
15:20	-	16:00	**Kawai** Chemical structures and mechanical properties of molecules studied by high-resolution force microscopy
16:00	-	17:40	Coffee at posters
			chair: Hornkaer
17:40	-	18:20	**Gröning** Trapping, reacting and switching molecules on metal supported h-BN monolayer
18:20	-	18:40	Kimouche Electronic states in ultra-narrow metallic armchair graphene nanoribbons
18:40	-	19:00	Åhlgren Creating nanoporous graphene with swift heavy ions
19:00	-	19:20	Hummel Amorphization of Graphene at the micrometer-scale by electron irradiation
20:00	-	22:00	*Dinner*

Molecular self-assembly on an insulating surface: Long-range order induced by an intrinsic repulsion mechanism

J. L. Neff[1] H. Söngen[1] R. Bechstein[1] A. Kühnle[1]
[1]University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

The success of future molecular electronics will critically rely on our capability to fine-tune the structure of functional molecules on surfaces. Adjusting the subtle balance between intermolecular and molecule-surface interactions is known to provide a versatile strategy for tailoring the on-surface structure formation. A very promising, yet rarely explored approach is using long-range interactions for creating well-controlled molecular arrangements on the surface of interest. In this talk, we present a generic mechanism for the formation of an ordered array of molecular stripes on an insulating surface based on long-range repulsive interactions. Upon adsorption of 3-hydroxybenzoic acid (HBA) onto calcite(10.4) held at room temperature, molecular stripes are formed. A detailed analysis of the stripe-to-stripe distances obtained from non-contact atomic force microscopy (NC-AFM) reveals an equidistant appearance with a periodicity that can be tuned by the molecular coverage.

Dynamics at nano-scale: Modeling AFM manipulation and kinetics of self-assembly

L. N. Kantorovich[1]

[1]Physics, King's College London, London, WC2R 2LS, U.K.

In this talk I will present several joint theory-experiment projects in which dynamic simulations were pivotal for understanding experimental findings.

In the first project [1] done in collaboration with Y. Sugawara (Osaka, Japan) and I. Stich (Bratislava, Slovakia) groups, we studied vertical manipulations of ”super”-Cu atoms on the p(2x1) Cu(110):O surface observed in low-temperature non-contact AFM (NC-AFM) experiments. Both extractions to and depositions from the tip were frequently observed. In all cases the imaging contrast remained the same. These results are rationalized employing a novel and completely general method that combines density functional theory (DFT) calculations for obtaining energy barriers as a function of the tip height and stochastic simulations for studying the tip dynamics that allow extracting manipulation statistics. The latter method is reminiscent of a well-known Kinetic Monte Carlo (KMC) method, however, it is applicable even when transition rates change dramatically with time during the experiment, as is the case of NC-AFM. The model reveals a novel multi-step manipulation mechanism com bining activated jumps of ”super”-Cu atoms to/from the tip with their drag by and diffusion on the tip.

In the second project [2] (in collaboration with J. Recio, Oviedo, Spain) we modeled self-assembly of p-Terphenyl-m-Dicarbonitrile molecules on the Ag(111) surface at room temperature. It was claimed [3] that upon self-assembly in which molecules form intercepting filaments and ring structures-vertices trans isomers prevail upon cis ones. By studying in detail with DFT molecular diffusion and isomerization mechanisms and then performing the appropriate KMC modeling, we found the underlying mechanisms of self-assembly of the observed structures, but found alleged abundance of trans upon cis unfounded.

In the third project [4] done in collaboration with the group of R. Raval (Liverpool, U.K.), we considered a bimolecular system comprising a simple divalent molecule that is shown to "walk" at room temperature along a specific pathway terminated at each end by oligomeric "fences" constructed on the Cu(110) surface by porphyrin molecules. STM experiments demonstrated high mobility and directional selectivity of the diffusion of the walker molecule preferably along Cu rows. DFT calculations show that the walker moves by attaching and detaching the nitrogen atoms in its imidazolyl ”legs” (stepping with one leg at a time) either in an inchworm fashion or by pivoting, depending on how it is adsorbed on Cu rows.

[1] J. Bamidele et al. , *Nature Comm.* **5**, 4476 (2014).
[2] D. Abbasi-Perez et al., *PCCP [published online]* **XX**, XX (2015).
[3] M. Marschall et al., *ChemPhysChem* **11**, 1446 (2010).
[4] Sam Haq, et al. , *Angewante Chemie Int. Ed. [accepted]* **XX**, XX (2015).

Chemical structures and mechanical properties of molecules studied by high-resolution force microscopy

S. Kawai[1,2]
[1]Department of Physics, University of Basel
[2]PRESTO, Japan Science and Tehcnology Agency

Since the first direct observation of the chemical structure of pentacene, atomic force microscopy (AFM) became a powerful tool for surface chemistry.[1] The low reactivity and the tilting effect of a carbon monoxide tip, prepared at low temperature, allow us to image inner structures of molecules. Such direct observation is quite beneficial to identify the conformation of molecules on the surface, such as position, bend, tilt, and rotation. We studied supramolecular structures formed with partially fluoro-substituted phenyleneethynylene.[2] The molecules are aligned alternatively. The assembly is established by a weak C-F$\cdots$C-H hydrogen bonding but the adoption on the corrugated substrate of Au(110)-1$\times$2 induces the bending of molecule and consequently the length and angle of the hydrogen bond vary. Further, the different extents of the π-electron induces the different diameters of non- and fluoro-substituted benzene rings (smaller: fluorobenzene).[3] In the presentation, recent AFM studies on the C-F$\cdots$F-C halogen bonding,[4] mechanical properties of conjugated polymers [5] and on-surface chemical reaction will be present.

[1] L. Gross et al., *Scienc* **325**, 1110 (2009).
[2] S. Kawai et al., *ACS Nano* **7**, 9098 (2013).
[3] N. Moll et al., *Nano Letters* **14**, 6127 (2014).
[4] S. Kawai et al., *ACS Nano* **9**, 2574 (2015).
[5] S. Kawai et al., *Proc. Natl. Acad. Sci. USA* **111**, 3968 (2014).

Trapping, reacting and switching molecules on metal supported h-BN monolayer

O. Gröning[1] T. Dienel[1] L. Liu[1] R. Widmer[1] M. Ianuzzi[2]

[1]Empa, Materials Science and Technology
[2]University of Zurich

In the last 25 years the field of molecular surface science has seen a tremendous development partly enabled by the wide spread use of Scanning Tunneling Microscopy (STM) in addition to other surface analytical tools. This development has yielded the assembly of highly complex supramolecular networks and covalently coupled 1D and 2D nanostructures, which have a high potential to serve as active components in future molecular electronic devices. However the overwhelming majority of studies in this respect have been carried out on metallic substrates, where the novel electronic, optic and magnetic properties of the produced nanostructures can be strongly altered or even quenched by hybridization effects. In this regard metal supported ultra-thin insulating films are ideal substrates to solve this problem, yet still allowing surface analytical methods like STM, STS, LEED and photoemission spectroscopy to be used for the investigation. In our presentation we will discuss the possibly of using metal supported monolayer hexagonal boron nitride (h-BN) as substrates to investigate the chemical and electronic properties of organic molecules adsorbed on them. We will review how the choice of the single crystalline metallic substrate can influence the properties of the h-BN layer in view of superstructures, which modulate the topography and the surface potential. Particularly we discuss the origin of the single molecules templating of phthalocyanine (PC) molecules on the h-BN/Rh(111) so-called önanomeshö surface from an experimental and theoretical perspective[1]. In a second part we will Ullmann type of reactions, i.e. radical formation by dehalogenation and subsequent covalent coupling have become essential in the synthesis of novel graphene derived nanostructures, such as graphene nanoribbons[2] or porous graphene[3]. We will discuss in the adsorption, dehalogenation and coupling of the molecular precursor -hexaiodocyclohexa-m-phenylene (CHP) form porous graphene[3]. We will emphasize the role of specific radical-surface interactions governing the dehalogenation sequence and stability of partially dehalogenated derivatives of the CHP. It turns out that the h-BN is not acting as an inert bystander to the dehalogenation reaction but on the contrary very strongly alters it in an anisotropic way[4]. Finally we will show that the h-BN/Rh(111) can be used to investigate charging phenomena of individual molecules. We will discuss the chase of field induced charging of MnPC on h-BN/Rh(111) and relate the variations in switching behavior of the molecules to shifts in the HOMO level position, which in turn is influences by the adsorption configuration of the molecule to the substrate.

[1] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A.P. Seitsonen, M. Saleh, X. Feng, K. Möllen, R. Fasel, *Nature* **466**, 470 (2010).
[2] M. Bieri, M.T. Nguyen, O. Grüning, J. Cai, M. Treier, K. Aüt-Mansour, P. Ruffieux, C.A. Pignedoli, D. Passerone, M. Kastler, K. Móllen, R. Fasel, *JACS* **132**, 16669 (2010).
[3] M. Iannuzzi, F. Tran, R. Widmer, T. Dienel, K. Radican, Y. Ding, J. Hutter, O. Gréning, *Phys. Chem. Chem. Phys.* **16**, 12374 (2014).
[4] . T. Dienel, J. Gømez-Døaz, A. P. Seitsonen, R. Widmer, M. Iannuzzi, K. Radican, H. Sachdev, K. Møllen, J. Hutter, and O. Gr—ning, *ACS Nano* **8**, 6571 (2014).

Electronic states in ultra-narrow metallic armchair graphene nanoribbons

A. Kimouche[1] R. Drost[1] S. Halonen[1] P. Joensuu[1] M. Ervasti[1] A. Harju[1]
P. Liljeroth[1]
[1]Aalto University School of Science, PO Box 15100, 00076 Aalto, Finland

Graphene nanoribbons (GNRs) are a new class of materials that have promising applications in next-generation nanoelectronic, photonic and spintronic devices [1]. GNRs have been predicted to show interesting electronic properties that depend strongly on their width and edge structure [2]. Therefore, precise structural control is essential to reproducibly obtain GNRs with desired properties. However, the required precision cannot be achieved by the predominant top-down approaches, including lithography of graphene sheet or the unzipping of carbon nanotubes. Recently, bottom-up synthesis using molecular precursors has been shown to provide precise control over the width and edge geometry of the ribbon [3]. By changing the monomer design, the fabrication of a wide range of different GNRs can be achieved with engineered chemical and electronic properties. The zigzag GNRs [4] possess a localized edge state and are predicted to be metallic whereas armchair GNRs can be meta llic or semiconducting depending on their width.

We have focused on armchair GNRs of width N=5. This family of GNRs with the widths of N= 3m+2 (m is an integer), are predicted to be metallic within a nearest-neighbor tight-binding model. While more accurate calculations predict a presence of a bandgap, it should remain much smaller than in armchair GNRs with other widths (N=3m or N=3m+1). We have investigated how the electronic band gap and orbital structure of short GNR segments vary as a function of their length using low-temperature scanning probe techniques [5]. Scanning tunneling spectroscopy shows that N=5 ribbon can have bandgaps below 500 meV, which is much less than in the wider N=7 GNRs belonging to the N=3m+1 family. We have performed first principle calculations to support our experimental STS data and to identify fingerprints in the dI/dV maps. This allows detailed understanding of the length-dependent properties of these ultra-narrow GNRs, which is important for their potential use as interconnects in nanoelec tronic circuits or in transistor structures.

[1] 1. Li, X,; Wang, x,; Zhang, L,; Lee, S,; Dai, H, *Science* **319**, 1229 (2008).
[2] 2. Son, Y.W,; Cohen, M. l,; Louie, S. G, *Phys Rev Lett* **97**, 216803 (2006).
[3] 3. Cai, J,; Ruffieux, P,; Jaafar, R,; Bieri, M,; Braun, T,; Blankenburg, S,; Muoth, M,; Seitsonen, A. P,; Saleh, M,; Freng, X,; Mullen, K,; Fasel, R, *Nature* **466**, 470 (2010).
[4] 4. Nakada, K,; Fujita, M, *Phys Rev B* **54**, 17954 (1996).

[5] Kimouche, A; Drost, R; Halonen, S; Joensuu, P; Ervasti, M; Harju, A & Liljeroth, P , *In preparation* **vol**, pp (2015).

Creating nanoporous graphene with swift heavy ions

E. H. Åhlgren[1] A. A. Leino[1] A. V. Krasheninnikov[2] F. Djurabekova[1]
K. Nordlund[1] J. Kotakoski[3,1]
[1]University of Helsinki, Department of Physics, Helsinki, Finland
[2]Aalto University, Department of Applied Physics, Espoo, Finland
[3]University of Vienna, Department of Physics, Austria

Controllable modification of nanoscale materials can be achieved by irradiating the sample with energetic ions. Swift heavy ions (energy in the MeV range) on graphene have been studied only for a short time in a few experimental studies[1,2]. We present results on highly controllable defect production in suspended single layer graphene samples with swift heavy ions. The study comprises of an experimental ion irradiation study with Raman spectroscopy analysis, two-temperature molecular dynamics simulations including both the ionic and electronic subsystems, and density functional theory calculations of the specific electronic heat capacity for graphene with different charge states. The Raman mapping shows an increase in the defect size for increasing stopping power of the ion. This is also seen in the simulations, where the high energy irradiation creates cylindrical defects in the membrane. The diameter of the pores vary from few nm's up to hundreds of nm's. The dia meter of the defects can be controlled with the stopping power of the ion. Controllable modification of the atomic structure of graphene opens a way for patterning suspended samples for application purposes, such as creating porous graphene membranes for highly sensitive sensors and filters.

[1] S. Akcöltekin , H. Bukowska , T. Peters, O. Osmani, I. Monnet, I. Alzaher, B. Ban d'Etat, H. Lebius, M. Schleberger, *Appl. Phys. Lett.* **98**, 103103 (2011).
[2] O. Ochedowski, S. Akcöltekin, B. Ban d'Etat, H. Lebius, M. Schleberger, *Nucl. Inst. and Meth. in Phys. Res. B* **314**, 18 (2013).

Amorphization of Graphene at the micrometer-scale by electron irradiation

S. Hummel[1] J. Kotakoski[1] G. Argentero[1] J. C. Meyer[1]

[1]Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria

An experimental study on the amorphization of Monolayer Graphene [1,2] by means of electron irradiation at 200kV is being presented. While electron bombardment of graphene at 200kV leads to drilling of big holes in the membrane at 300K, heating up the sample during irradiation drastically reduces the formation of holes while still allows for creation of a sufficient amount of defects. Employing aberration-corrected scanning transmission electron microscopy at 60kV, we performed ring statistics, i.e. collecting the number of different polygons in the lattice and relate it to the electron dose used for irradiation. Furthermore, enhanced attraction of impurities (Si) by the defects has been observed which leads to possible applications of amorphized graphene, e.g. gas sensors

[1] Jani Kotakoski, Arkady V. Krasheninnikov, Ute Kaiser and Jannik C. Meyer, *Physical Review Letters* **106**, 105505 (2011).
[2] Franz R. Eder, Jani Kotakoski, Ute Kaiser and Jannik C. Meyer, *Scientific Reports* **4**, 4060 (2014).

Thursday 11.06.2015

			chair: Groening
9:00	-	9:40	**Sloan** HRTEM, DFT modeling and Raman Spectroscopy of Extreme Nanowires within Single Walled Carbon Nanotubes
9:40	-	10:20	**Arenal** Heteroatomic and Functionalized Carbon Nanotubes: Atomic Configuration Studies via Spatially-Resolved EELS
10:20	-	10:40	Booth In operando nanopatterning of 2D devices in the transmission electron microscope
10:40	-	11:00	Dienel Atomically resolved connectivity in graphene nanostructure junctions
11:00	-	11:40	*Coffee*
			chair: Arenal
11:40	-	12:20	**Ramasse** A new era in scanning transmission electron microscopy: from single-atom defect engineering and characterisation to vibrational spectroscopy
12:20	-	12:40	Temirov Scanning Quantum Dot Microscopy
12:40	-	13:00	Schulz Many-body transitions in a single molecule visualized by scanning tunneling microscopy
13:00	-	14:00	*Lunch*
			chair: Komsa
14:00	-	14:40	**Ternes** Engineering of Spin and Magnetic Anisotropy of CoH complexes on BN/Rh(111)
14:40	-	15:00	Hlawacek Helium Ion Microscopy of atomic steps and surface reconstruction
15:00	-	15:10	*Closing*

HRTEM, DFT modeling and Raman Spectroscopy of Extreme Nanowires within Single Walled Carbon Nanotubes

J. Sloan[1] D. C. Smith[2] J. H. Spencer[2] L. P. McDonnell[2] H. Trewhitt[1]
R. J. Kashtiban[1] E. Faulques[3] E. Bichoutskaia[4]
[1]Department of Physics, University of Warwick, Coventry CV4 7AL, UK
[2]School of Physics and Astronomy, University of Southampton, SO17 1BJ, UK
[3]University of Nantes CNRS, UMR6502, F-44322 Nantes, France.
[4]School of Chemistry, University of Nottingham, NG7 2RD, UK

Extreme nanowires formed by filling the central pore of single walled carbon nanotubes (SWCNTs) have extreme diameters and thus extreme properties. In some instances the extreme confinement causes entirely new crystalline forms not observed in bulk and these structures are investigated by high performance electron microscopy (i.e. hardware corrected HRTEM and exit wave reconstruction (EWR)). Until recently, there has been only limited research into the physical properties of these extreme nanowires. While there has been a significant effort in terms of revealing the physical properties of, for example, KI and HgTe extreme nanowires in SWCNTs by density functional theory (DFT) [1,2] there are few experimental studies besides imaging. A significant impetus towards new studies in these materials has been given by the observation that under beam irradiation or induced strain, some materials undergo significant 'phase change' behaviour [3,4,5] We report here investigatio ns into two new systems, SWCNT embedded SnSe [5] which undergoes band gap expansion, as well as shear induced phase change behaviour in SWCNTs with diameters >1.4 nm and also experimental studies into two-atom thick SWCNT-embedded HgTe extreme nanowires. Raman spectra have been measured for ensembles of bundled filled tubes for excitation photon energies in the ranges 3.39 to 2.61 eV and 1.82 to 1.26 eV for Raman shifts down to 25 cm^{-1} and sample temperatures in the range 4-300K. All of the evidence support the hypothesis that the observed Raman features are not attributable to single walled carbon nanotubes, but instead to the HgTe nanowires. The observed additional features are due to four distinct phonons, with energies 47, 51, 94 and 115 cm^{-1} respectively, plus their overtones and combinations [6].

[1] E. L. Sceats, J. Green, S. Reich, *Phys. Rev. B* **73**, 125441/1-11 (2006).
[2] R. Carter, J. Sloan, A. Vlandas, M. L. H. Green, A. I. Kirkland, R. R. Meyer, J. L. Hutchison, P. J. D. Lindan, G. Lin, J. Harding, *Phys. Rev. Lett.* **96**, 215501/1-4 (2006).
[3] C. E. Giusca, V. Stolojan, J. Sloan, F. Börrnert, H. Shiozawa, K. Sader, M. H. Rümmeli, B. Büchner, S. R. P. Silva, *Nano Lett.* **13**, 4020 (2013).
[4] J. Sloan, A. I. Kirkland, J. L. Hutchison, M. L. H. Green, *Comptes Rend. Phys.* **4**, 1063 (2003).
[5] R. Carter, M. Suyetin, S. Lister, M. A. Dyson, H. Trewhitt, S. Goel, Z. Liu, K. Suenaga, C. Giusca, R. J. Kashtiban, J. L. Hutchison, J. C. Dore, G. R. Bell, E. Bichoutskaia, *Dalton Trans.* **43**, 7391 (2014).

[6] J. H. Spencer, J. M. Nesbitt, H. Trewhitt, R. J. Kashtiban, G. R. Bell, V. G. Ivanov, E. Faulques, J. Sloan, D. C. Smith, *ACS Nano* **8**, 9044 (2014).

Heteroatomic and Functionalized Carbon Nanotubes: Atomic Configuration Studies via Spatially-Resolved EELS

R. Arenal[1,2]

[1]Laboratorio de Microscopias Avanzadas, Instituto de Nanociencia de Aragón, Universidad de Zaragoza, 50018 Zaragoza, Spain.
[2]ARAID Foundation, 50018 Zaragoza, Spain.

The modification of the atomic configuration of pristine carbon nanotubes (NTs) via the incorporation of heteroatoms (B, N or BN) or via the surface functionalization is a perfect way of control their opto-electronic properties [1-5]. However, it is worth noting that a very detailed analysis of this atomic configuration and concentration of the different species of these heteroatomic/functionalized nanotubes is highly required in order to determine their impact on the electronic/optoelectronic properties of the NTs. In this sense, transmission electron microscopy (TEM) is an essential tool to perform such studies [1-5]. In particular, spatially-resolved electron energy loss spectroscopy (SR-EELS), developed in an aberration-corrected TEM (having access to a close to 1 angstrom electron probe), is the most powerful technique to achieve these goals.

In this communication, we present a detailed study of the atomic configuration of different kinds of heteroatomic (CNx, BxCyNz) and functionalized single-walled NTs via SR- EELS [3-5]. We have examined the different chemical species present in the NTs, determined their average concentration as well as their spatial distribution within the walls and studied their chemical environment and bonding.

The research leading to these results has received funding from the EU under Grant Agreement 312483-ESTEEM2, from the EU under Grant Agreement 604391-Graphene Flagship, from the Spanish Ministerio Economia y Competitividad (FIS2013-46159-C3-3-P) and from the EU under the Marie Curie Grant Agreement 642742 - Enabling Excellence.

[1] R. Arenal, X. Blase, A. Loiseau, *Advances in Physics* **59**, 101 (2010).
[2] P. Ayala, R. Arenal, A. Rubio, A. Loiseau, T. Pichler, *Rev. Mod. Phys.* **82**, 1843 (2010).
[3] R. Arenal, K. March, C.P. Ewels, X. Rocquefelte, M. Kociak, A. Loiseau, O. Stéphan, *Nano Lett.* **14**, 5509 (2014).
[4] R. Arenal, L. Alvarez, S. Campidelli, R. Le Parc, J.-L. Bantignies, *Submitted* -, - (2015).
[5] R. Wang, A. Lopez-Bezanilla, A. Masseboeuf, M. Monthioux, R. Arenal, *Submitted* -, - (2015).

In operando nanopatterning of 2D devices in the transmission electron microscope

T. J. Booth[1] J. D. Thomsen[1] F. Pizzocchero[1] C. B. Gade[1] A. Cagliani[1] I. Yidliz[1] P. Bøggild[1]
[1] DTU Nanotech

The impact of defects and nanoscale structures on the electronic properties of 2D materials is of critical importance for the development of technologies based on these exciting materials. The electron beam of the transmission electron microscope and residual or deliberately introduced gas environments provides exciting opportunities to study the impact of the atomic scale structure of these materials - a function of their production and application in real systems — at the same time as measuring their electronic properties.

Here we discuss the use of a new microfabricated multiterminal electron microscopy support chip and attendant techniques for building 2D devices on such systems, and describe our initial results on the correlation of electronic properties in such systems with their structure in operando. In particular, we will discuss recent observations of the sensitivity of transport properties to lattice mismatch angle in artificial incommensurate (twisted) bilayer stacks of graphene.

Atomically resolved connectivity in graphene nanostructure junctions

T. Dienel[1] S. Kawai[2,3] H. Soede[1] P. Ruffieux[1] R. Fasel[1] O. Groening[1]

[1]nanotech@surfaces Lab, Empa - Swiss Federal Laboratories for Materials Science,
Ueberlandstrasse 129, CH-8600 Duebendorf, Switzerland
[2]Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland
[3]PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Japan

The controlled nanostructuring of two-dimensional materials will become a key technology for the application of these novel materials in future electronic devices. The nanoscale fabrication is furthest developed for graphene. Only recently, the fabrication of ultranarrow graphene nanoribbons (GNRs) was demonstrated by surface-catalyzed reactions of suitably designed precursor molecules [1,2]. Such GNRs can be covalently joined to fabricate larger units create contacts (junctions) [2] and heterojunctions [3,4]. The junctions exhibit complex bond topologies, which influence the electronic properties of the connected GNRs. In this context scanning probe microscopy plays an important role in the investigation of the involved on-surface reactions and the characterization of their products. Standard scanning tunneling microscopy (STM) however can come at its limits when it comes down to elucidating these structures with ultimate ”bond resolution”. Here, we report on the structural characterization of junctions between atomically well-defined armchair GNRs, characterized by an armchair structure along the edge and 7 rows of carbon atom pairs across the ribbon width (7-AGNR) by means of low-temperature, non-contact atomic force microscopy (nc-AFM). We combine simultaneously acquired frequency-shift and tunneling current maps with tight binding (TB) simulations for a comprehensive characterization of the atomic connectivity in the GNR junctions. The careful comparison between the experimental AFM/STM data and the TB simulation of the local density of states allows a determination of the bond configuration in the GNR junction region with single bond precision.

[1] L. Grill et al., *Nature Nanotech.* **2**, 687 (2007).
[2] J. Cai et al., *Nature* **466**, 470 (2010).
[3] J. Cai et al., *Nature Nanotech.* **9**, 2014 (896).
[4] Y.-C. Chen et al., *Nature Nanotech.* **10**, 2015 (156).

A new era in scanning transmission electron microscopy: from single-atom defect engineering and characterisation to vibrational spectroscopy

Q. M. Ramasse[1] D. M. Kepaptsoglou[1] F. S. Hage[1] C. R. Seabourne[2]
T. Hadcastle[2] T. Susi[2] J. Kotakoski[3] U. Bangert[4] A. J. Scott[3]
[1]SuperSTEM Laboratory, SciTech Daresbury Campus, Keckwick Lane, Daresbury WA4 4AD, U.K.
[2]Institute for Materials Research, SCAPE, University of Leeds, Leeds LS2 9JT, U.K.
[3]Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria
[4]Department of Physics and Energy, University of Limerick, Limerick, Ireland

Modern aberration-corrected scanning transmission electron microscopes (STEMs) have been optimised to provide improved data collection ability and greater flexibility even at low acceleration voltages, spurring what could be arguably described as a new era in nano-scale materials characterisation. A wealth of complementary analytical signals is now available from a single experiment: when combining chemically-sensitive Z-contrast and bright field STEM imaging, 2D chemical mapping using analytical techniques such as electron energy loss spectroscopy (EELS) together with advanced image analysis, it is for instance possible to fully characterise minute chemical variations around nano-scale defects in complex oxide structures. These in turn are related to accurately measured atomic displacements and to the electronic properties of the material determined through theroretical calculations [1]. These developments were also a great benefit to the field of two-dimensional m aterials such as graphene. By reducing the acceleration voltage to overcome knock-on damage limitations, these structures can be imaged directly at atomic resolution, revealing for instance the successful low-energy ion implantation of single N or B dopants in graphene, a technique widely used by the semiconductor industry and with the potential to revolutionize graphene technology [2]. Furthermore, the sensitivity of EELS of is such that it possible to study how these atoms bond to one another: subtle differences in EELS fine structure can help distinguish unambiguously between tri- and tetravalent bonding configurations of single Si contaminants in graphene [2], while ab initio calculations are used simulate experimental spectra and to rationalize the experiments [3,4]. These otherwise 'gentle' STEM observation conditions can also be precisely tailored to engineer and modify defects in 2-dimensional materials: the electron beam can thus drive the diffusion of substitutiona l Si dopants through graphene, one atomic jump at a time [5]. There are further exciting times ahead, with the advent of ultra-high energy resolution monochromators, which are boosting the resolution of STEM-EELS into the sub 10meV range and are now opening the door to vibrational and phonon spectroscopy at unprecedentedly high spatial resolution [6].

[1] I. MacLaren and Q.M. Ramasse, *International Materials Review* **59**, 115 (2014).
[2] U. Bangert, W. Pierce, D.M. Kepaptsoglou et al., *Nano Letters* **13**, 4902 (2013).
[3] Q.M. Ramasse, C.R. Seabourne, D.M. Kepaptsoglou et al., *Nano Letters* **13**, 3936 (2013).
[4] D.M. Kepaptsoglou, T. Hardcastle, C.R. Seabourne et al., *Nature Communications* Submitted (2015).
[5] T. Susi, J. Kotakoski, D. Kepaptsoglou et al., *Physical Review Letters* **113**, 115501 (2014).
[6] Q.M. Ramasse, F.S. Hage, J. Yates et al., *Microscopy and Microanalysis* Submitted (2015).

Scanning Quantum Dot Microscopy

R. Temirov[1] C. Wagner[1] M. Green[1] P. Leinen[1] T. Deilmann[2] P. Krüger[2]
M. Rohlfing[2] F. S. Tautz[1]

[1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany
[2]Institut für Festkörpertheorie, Westfalische Wilhelms-Universität Münster, 48149 Münster, Germany

Interactions between atomic and molecular objects are to a large extent defined by the nanoscaleelectrostatic potentials which these objects produce.Consequently, a tool for nanometre scale imaging and quantification of local electrostatic fields could help in many areas of nanoscience research. In this contribution we introduce a scanning probe technique that for the first time enables truly three-dimensional imaging of local electrostatic potential fields with subnanometreresolution. Registering single electron charging events of a molecular quantum dot attached to the tip of a tuning fork atomic force microscope operated at 5 K, we quantitatively measure theäquadrupole field of a single molecule and the dipole field of a single metal adatom, both adsorbed on a clean metal surface. Because of its high sensitivity, the technique can record electrostatic potentials at large distances from their sources, which above all should help to image complex samples wi th increased surface roughness.

Many-body transitions in a single molecule visualized by scanning tunneling microscopy

F. Schulz[1] M. Ijäs[1] R. Drost[1] S. K. Hämäläinen[1] A. Harju[1] A. P. Seitsonen[2]
P. Liljeroth[1]

[1]Department of Applied Physics, Aalto University School of Science, Espoo, Finland
[2]École Normale Supérieure, Départment de Chimie, Paris, France

Scanning tunneling spectroscopy (STS) of molecular systems is usually interpreted in terms of single-particle electronic transitions [1]. A prominent exception is the Kondo effect [2], a many-body state resulting from the interaction of an unpaired molecular spin with the conduction electrons of a metallic substrate. However, the Kondo effect is a property of the coupled molecule-substrate system and does not correspond to an intrinsic many-body state of the molecule. Probing excited states in single molecules by STS, we demonstrate many-body effects arising purely from electronic states confined in the molecule.

Cobalt phthalocyanine (CoPC) molecules deposited onto monolayer hexagonal boron nitride (h-BN) on Ir(111) [3] allows to carry out STS on molecules that are initially in different charge states [4]: A moiré superstructure formed by h-BN on Ir(111) results in a periodic modulation of the local work function and CoPC adsorbing either in a neutral or negatively charged ground state. The observed molecular resonances are inconsistent with the single-particle interpretation of tunneling spectroscopy. Instead, combining time-dependent density functional theory calculations with STS wave function maps, we show that they can be understood as a series of many-body excitations of the different ground states of the molecule [5].

[1] F. Albrecht et al., *J. Am. Chem. Soc.* **135**, 9200 (2013).
[2] I. Fernandez-Torrente et al., *Phys. Rev. Lett.* **101**, 217203 (2008).
[3] F. Schulz et al., *Phys. Rev. B* **89**, 235429 (2014).
[4] F. Schulz et al., *ACS Nano* **7**, 11121 (2013).
[5] F. Schulz et al., *Nature Phys.* **11**, 229 (2015).

Engineering of Spin and Magnetic Anisotropy of CoH complexes on BN/Rh(111)

M. Ternes[1] P. Jacobson[1] T. Herden[1] M. Muenks[1] G. Laskin[1] O. Brovko[2]
V. Stepanyuk[2] K. Kern[1]
[1]Max-Planck Institute for Solid State Research, Stuttgart
[2]Max Planck Institute of Microstructure Physics, Halle

Single molecule magnets and single spin centers can be individually addressed when coupled to contacts forming an electrical junction. In order to control and engineer the magnetism of quantum devices, it is necessary to quantify how the structural and chemical environment of the junction affects the spin center. Metrics such as coordination number or symmetry provide a simple method to quantify the local environment, but neglect the many-body interactions of an impurity spin when coupled to contacts [1]. Here, we utilize a highly corrugated hexagonal boron nitride (h-BN) monolayer [2] to mediate the coupling between a cobalt spin in CoHx (x=1,2) complexes and the metal contact. While the hydrogen atoms control the total effective spin, the corrugation is found to smoothly tune the Kondo exchange interaction between the spin and the underlying metal. Using scanning tunneling microscopy and spectroscopy together with a transport model which includes higher-order scat tering effects [3], we quantitatively demonstrate how the Kondo exchange interaction mimics chemical tailoring and changes the magnetic anisotropy.

[1] Oberg, J. C. et al., *Nature Nanotechnology* **9**, 64 (2013).
[2] Herden, T., Ternes, M. & Kern, K., *Nano Lett.* **14**, 3623 (2014).
[3] Zhang, Y.-H. et al., *Nature Communications* **4**, 2110 (2013).

Helium Ion Microscopy of atomic steps and surface reconstruction

G. Hlawacek[1,2] M. Jankovski[1] R. van Gastel[1] H. Wormeester[1] H. Zandvliet[1] B. Poelsema[1]

[1] Helmholtz-Zentrum Dresden - Rossendorf, Institute for Ion Beam Physics and Materials Research, Bautzner Landstr. 400, 01328 Dresden, Germany
[2] Physics of Interfaces and Nanomaterials, University of Twente, PO Box 217 7500 AE Enschede, The Netherlands

Helium Ion Microscopy (HIM) [1] is well known for its exceptional imaging and nanofabrication capabilities. HIM has an unprecedented surface sensitivity, and channeling can be utilized to maximise the signal to noise ratio. We demonstrate the resolving power of the technique using a thin (2 ML) silver layer on Pt(111). The obtained HIM results are compared to results obtained by low energy electron microscopy, spot profile analysis low energy electron diffraction (SPA-LEED), and atomic force microscopy phase contrast. In HIM single atom layer high steps can be visualized as a result of a work function change—across the otherwise atomically flat terraces—of only $\approx$20 meV. By utilizing the dechanneling contrast mechanism [2] also the surface reconstruction of this thin surface layer can be revealed. We find a threefold periodic structure of channeling (fcc stacking) and dechanneling (hcp stacking) areas. The periodicity—measured along the $\langle\bar{1}\bar{1}2\rangle$ surface direction—of this structure is 5.8 nm. This is in excellent agreement with values obtained by SPA-LEED [3].

[1] Gregor Hlawacek, Vasilisa Veligura, Raoul van Gastel, and Bene Poelsema, *J. Vac. Sci. Technol. B* **32**, 020801 (2014).
[2] Gregor Hlawacek, Vasilisa Veligura, Stefan Lorbek, Tijs F. Mocking, Antony George, Raoul van Gastel, Harold J. W. Zandvliet, and Bene Poelsema, *Beilstein J. Nanotechnol.* **3**, 507 (2012).
[3] Maciej Jankowski, Herbert Wormeester, Harold J. W. Zandvliet, and Bene Poelsema, *Phys. Rev. B* **89**, 235402 (2014).

Posters

Sergey Bozhko
DFT modeling of electronic growth of Pb nanoislands on Si(557) surfaces

Luca Camilli
Atomically thin films as protective coatings

Eero Holmstrom
$SrTiO_3$-H_2O interface from first-principles molecular dynamics

Bora Karasulu
First-Principles Investigation of Platinum Atomic Layer Deposition on Graphene Line Defects

Andrei Ksenz
Charge-transfer induced rotation of C_{60} molecules on the WO2/W(110) surface

Philipp Leinen
3D visual feedback during molecular manipulation

Peter Liljeroth
Zigzag interfaces between graphene and hexagonal boron nitride

Tomasz Pabisiak
DFT+U studies of different terminations of iron oxide surfaces

Bernhard Reischl
Simulation of AFM imaging of surfaces with defects in solution

Hagen Söngen
The solid-liquid interface: Probing charges on insulators with KPFM

Edward William Tait
Linear Scaling Density Functional Theory for the Study of Defective Oxide Nanomaterials

Holly Tetlow
DFT Calculations of Processes in Early Stage Graphene Growth

Joachim Dahl Thomsen
Micro-Fabricated Platform with Electrical Connections for In-situ Environmental TEM Characterization of Graphene

Milica Todorovic
Combining DFT with scanning probe microscopy to explore organic/inorganic interfaces for photovoltaic applications

Lianheng Tong
Introduction to CP2K, a first principles electronic structure simulation package

John Tracey
Modular Python Virtual Atomic Force Microscopy (PyVAFM)

Liujiang Zhou
Black Phosphorus (BP) Interfaced with TiO_2 (110) Surface: An Novel Photovoltaic Heterojunction

Lidija Zivanovic
Hydrophobic properties of clay minerals investigated using molecular simulations

DFT modeling of electronic growth of Pb nanoislands on Si(557) surfaces

S. I. Bozhko[1] A. S. Ksenz[1,2] A. M. Ionov[1]

[1]Institute of Solid State Physics RAS, Chernogolovka, 142432, Moscow district, Russia
[2]Moscow State University(FFPI), 119991, Russia

The Pb-islands growth on a clean vicinal Si(557) surface at room temperature has been studied using Scanning Tunneling Microscopy. We observed anisotropic tilted wedge-shaped Pb-islands to grow following the Stransky-Krastanov scenario. The elongation of the islands along the step edges of Si is associated with the anisotropic potential of the vicinal template. It was demonstrated that the growth of tilted Pb bulk islands is accompanied by their separation into layers which is clearly observed in the STM images as a slab-like stacking morphology, and also appearing from the statistical analysis. The single layer preferable thickness in the slab-like stacking like structure was found to be 2nm, which corresponds to 7 Pb monolayers. Using DFT simulations, we argue that such growth mode is realized due to minimization of the electron energy owing to quantum confinement inside of created quantum wells. The quantum wells are generated by plain defects between slab-like layers. It was shown that a twin boundary is one of the most favorable candidates for plain defects separated Pb layers. DFT simulation support that preferable position for Pb atom during growth of the 8th layer is hcp i.e. twinning boundary creation. The growth mechanism can be explained in the framework of the electronic growth model including the interfacial strain and twin boundary formation.

Atomically thin films as protective coatings

L. Camilli[1] A. C. Stoot[1] F. Yu[1] P. Bøggild[1]

[1]Danish Technical University

Proving that monolayer graphene membrane is impermeable to standard gases including helium triggered an intense research towards the usage of graphene-based film as an anti-corrosion coating. [1] However, the effectiveness of chemical vapor deposited graphene as a protective coating is still subject to debate and controversy. Indeed, cracks or wrinkles in the graphene film open up windows for localized corrosion, which may progress underneath the graphene itself. [2, 3] In our work, we explore how to improve the intrinsic limitations of graphene-based coatings — i.e., to limit the effect of wrinkles and other imperfections of the graphene film. In addition, we discuss also the potential of other 2D dimensional materials and their combination as protective coatings.

[1] JS Bunch et al., *Nano Letters* **8**, 2458 (2008).
[2] I. Wlasny et al., *Applied Physics Letters* **102**, 111601 (2013).
[3] Y. H. Zhang et al., *Applied Physics Letters* **104**, 143110 (2014).

$SrTiO_3$-H_2O interface from first-principles molecular dynamics

E. Holmström[1] S. Kawasaki[2] P. Spijker[1] H. Onishi[3] M. Lippmaa[2] A. S. Foster[1]
[1]Department of Applied Physics, Aalto University School of Science
[2]Institute for Solid State Physics, University of Tokyo
[3]Chemistry Department, Kobe University

Strontium titanate ($SrTiO_3$) is a promising photocatalyst for hydrogen production through water-splitting. In order to realize this technological potential, a robust and detailed understanding of the $SrTiO_3$-H_2O interface is necessary. Using density functional theory molecular dynamics simulations, we model this solid-liquid interface at room temperature using various levels of H_2O coverage. We present results on the atomic and electronic structure as well as the vibrational properties of the system. Finally, we link our results to molecular dynamics simulations based on a classical force field and use these to provide an extensive model of water hydration on different $SrTiO_3$ surface reconstructions - this is compared directly to high resolution atomic force microscopy images in water.

First-Principles Investigation of Platinum Atomic Layer Deposition on Graphene Line Defects

B. Karasulu[1] W. Kessels[1] A. A. Bol[1]

[1]Eindhoven University of Technology, Department of Applied Physics, De Zaale, 5612 AZ Eindhoven, the Netherlands

Graphene, an atomically thick two-dimensional monolayer of sp^2-bonded carbons, has emerged as one of the most promising materials of modern nanoelectronics due to its exceptional electrical, mechanical, and optical properties, e.g. high carrier mobility, stability, strength and tunable optical absorption. Superior features of graphene are typically deteriorated by defects within the perfect hexagonal crystalline structure of graphene, introduced during growth, transfer or processing procedures. These defects, however, help activate an otherwise chemically inert graphene surface by altering the electronic structure of a pristine graphene, which stimulates functionalization by and trapping of for example transition-metals on these sites [1]. Recently, Kim et al. [2] achieved to deposit Pt layers selectively on graphene's one-dimensional (1D) defects, grain-boundaries (GBs), folds and cracks, using atomic layer deposition (ALD) techniques, that is deemed to for m a basis for high-performance hydrogen gas sensors at room temperature. For Pt ALD, Kim et al. utilized the commonly-used precursor, methylcyclopentadienyltrimethyl-platinum ($MeCpPtMe_3$) and air as co-reactant, whereas several other precursors and co-reactants have also been reported to work with other substrates [3].

An in-depth understanding of the underlying mechanism of Pt ALD would be vital in optimizing the ALD process and ultimately achieving deposition of closed Pt films on graphene surfaces. Two distinct mechanisms using $MeCpPtMe_3$ (as outlined in Ref. [4,5] and Ref. [6]) have, hitherto, been proposed to explain the stoichiometry in half-reactions based on a collection of experimental data (see Ref. [7] and references therein). These two mechanisms differ mainly in terms of intermediate species and saturation factors, whereas both require chemisorbed oxygen on the target surface prior to ALD. The lack of a conclusive experimental study regarding the chemical mechanism calls for molecular-level simulations of the ALD process. Considering the latter, in the current study we performed an elaborate first-principles investigation of the Pt ALD on graphene GBs using density functional theory (DFT). In this presentation, discussions will concentrate on the feasibility of two proposed mechanisms and the reactivity of different sites on graphene GBs.

[1] F. Banhart, J. Kotakoski, and A. V. Krasheninnikov, *ACS Nano* **5**, 26-41 (2011).

[2] K. Kim, H.-B.-R. Lee, R. W. Johnson, J. T. Tanskanen, N. Liu, M.-G. Kim, C. Pang, C. Ahn, S. F. Bent, and Z. Bao, *Nat. Comm.* **5**, 1-9 (2014).
[3] J. Hämäläinen, M. Ritala, and M. Leskelä, *Chem. Mater.* **26**, 786-801 (2014).
[4] T. Aaltonen, A. Rahtu, M. Ritala, and M. Leskelaä, *Electrochem. Solid-State Lett* **6**, C130 (2003).
[5] W. M. M. Kessels, H. C. M. Knoops, S. A. F. Dielissen, A. J. M. MacKus, and M. C. M. van De Sanden, *Appl. Phys. Lett.* **95**, 13-16 (2009).
[6] A. J. M. MacKus, N. Leick, L. Baker, and W. M. M. Kessels, *Chem. Mater.* **24**, 1752-1761 (2012).
[7] S. M. Geyer, R. Methaapanon, B. Shong, P. A. Pianetta, and S. F. Bent, *J. Phys. Chem. Lett.* **4**, 176-179 (2012).

Charge-transfer induced rotation of C_{60} molecules on the WO2/W(110) surface

A. Ksenz [1] S. Bozhko [1] O. Lübben [2] K. Radican[2] V. Semenov [1] E. Levchenko[1] I. Shvets [2]

[1]Institute of Solid State Physics, Russian Academy of Sciences - Chernogolovka (Russian federation)

[2]Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), School of Physics, Trinity College Dublin - Dublin (Ireland)

Understanding of molecular switching between different charge states is crucial to further progress in molecule-based nano-electronic devices. Scanning tunneling microscopy (STM) is one of the most promising techniques for imaging of prototype molecular devices and testing their properties. We employed scanning tunnelling microscopy to study the structure of ultrathin molecular layer C_{60} film grown on the WO2/W(110) surface and reveal a correlation between charge state of a individual C_{60} molecule and it orientation. Tunnelling junction based on individual C_{60} molecule is stable below temperature of kinetic rotational transition of 220K [1] when all molecules are static. However, in the temperature range of 220–260 K some isolated molecules switch between high- and normal- conductance states. At high temperatures the molecules rotate continuously so fast that no "blinking" is observed and all molecules appear as perfect spheres [2]. High-conductance state arises due to charging of the C_{60}, which causes changes in the local density of electron states near Fermi level and consequently a variation in tunnelling current. Using density functional theory calculations, these states were suggested to be: charge-neutral C_{60}; negatively charged $C_{60}{}^{-}$, which has accepted an electron. Such molecules appear in STM topography as flashing nano-bulbs on the surface. Switching of the molecule conductance state is accompanied by change of molecule orbital structure detected in STM topography that proves change of orientation of the molecule during switching. Molecular movement accompanies the molecule's switching between these states; as the molecule rotates, it exchanges charge with the substrate, gaining or loosing an electron.

[1] Sergey I. Bozhko et.al., *Phys. Rev. B.* **84**, 195412 (2011).
[2] Sergey A. Krasnikov et.al., *Nano Res.* **4(2)**, 194–203 (2011).

3D visual feedback during molecular manipulation

P. Leinen[1,2] M. F. B. Green[1,2] T. Esat[1,2] C. Wagner[1,2] F. S. Tautz[1,2]
R. Temirov[1,2]

[1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany
[2]JARA-Fundamentals of Future Information Technology

The scanning probe microscope is the tool of choice for the manipulation of single molecules on surfaces. With increased molecular complexity the number of degrees of freedom of such systems increases likewise. The respective high-dimensional potential energy surfaces call for the use of customized tip-trajectories for successful manipulation. Here, we present an intuitive approach to the task of SPM-based manipulation of large organic molecules. In brief, we connect a motion tracking and a 3D visualization device to a low-temperature non-contact atomic force microscope / scanning tunneling microscope (nc-AFM/STM). As a proof of principle application we demonstrate the controlled removal of single molecules from a monolayer of 3,4,9,10-perylene-tetracarboxylicdianhydride (PTCDA). The mutual hydrogen bonds in such a layer can only be broken if a specific tip-trajectory is used [1]. The motion tracker allows to find such a trajectory within minutes in a trial and error approach. Using immersive 3D virtual reality goggles we provide the experimenter with a visualization of the current or the frequency shift as well as previous tip trajectories and thus allow a systematic search by selective variation.

[1] M. F. B. Green, T. Esat, C. Wagner, P. Leinen, A. Grätsch, F. S. Tautz, and R. Temirov, *Beilstein J. Nanotechnol.* 5, 1926 (2014).

Zigzag interfaces between graphene and hexagonal boron nitride

R. Drost[1] S. Kezilebieke[1] M. Ervasti[2] S. K. Hämäläinen[1] F. Schulz[1] A. Harju[2] P. Liljeroth[1]

[1]Department of Applied Physics, Aalto University School of Science, PO Box 15100, 00076 Aalto, Finland
[2]COMP Centre of Excellence, Department of Applied Physics, Aalto University School of Science, PO Box 11100, 00076 Aalto, Finland

In addition to the exciting bulk properties of graphene, the edges of this two dimensional crystal host localised states that have been proposed to be used in spin- and valleytronic applications: Using the spin degree of freedom of the electron or the valley degree of freedom inherent to the honeycomb crystal structure of graphene to transmit and process information. Despite the intense theoretical attention, the zigzag (ZZ) graphene edge state has remained largely unexplored experimentally due to the difficulty of preparing clean ZZ edges without reconstructions or chemical functional groups that could destroy the edge properties.

We show that this problem can be overcome by passivating the graphene edge with hexagonal boron-nitride (BN), a wide band gap insulator isostructural to graphene. This prevents uncontrolled chemical functionalisation of the graphene edge while preserving the edge state in the band gap of the insulator. We use the ZZ edges of epitaxial graphene on a metal substrate as a template for h-BN growth to produce ZZ-oriented graphene - BN interfaces [1,2]. Using low temperature scanning tunnelling microscopy and spectroscopy, we demonstrate the existence of a localised electronic state on the ZZ oriented graphene-BN interfaces. We complement these experiments with tight binding and density functional theory (DFT) calculations. Our results demonstrate that the ZZ-terminated, atomically sharp interfaces between graphene and hexagonal boron nitride are an experimentally realizable, chemically stable model systems for graphene ZZ edges, which host localized electronic states similar to th ose on the pristine graphene ZZ edge.

[1] R. Drost, A. Uppstu, F. Schulz, S.K. Hämäläinen, M. Ervasti, A. Harju, P. Liljeroth, *Nano Lett.* **14**, 5128 (2014).
[2] R. Drost, S. Kezilebieke, M. Ervasti, Sampsa K. Hämäläinen, F. Schulz, A. Harju, P. Liljeroth, *submitted* (2015).

DFT+U studies of different terminations of iron oxide surfaces

T. Pabisiak[1] A. Kiejna[1]
[1]Institute of Experimental Physics, University of Wroclaw

The surface properties of the two most common and stable iron oxide phases, hematite (α-Fe_2O_3) and magnetite (Fe_3O_4), attract a lot of interest because of their important role in a variety of applications. Iron oxides are also considered as efficient support for catalytic applications. In order to understand the reactivity of iron oxide surfaces and adsorbate structures thereon a more complete information about the structural and electronic properties of different oxide terminations is needed. The detailed structure of hematite (0001) and magnetite (111) iron oxide surfaces is thus, both of fundamental interest and of crucial meaning, in understanding the reactivity of the surfaces with respect to different adsorbates [1-3], and the induced surface reconstruction [4]. From the experimental point of view the complex structure of these systems make them very challenging for study, and often may lead to different interpretation. For example the struc ture of the reconstructed surface of so called *biphase* termination is still not fully understood and various models for this reconstruction were proposed. The DFT results can provide the detailed description of oxide structure at atomic level, but must be verified by measurements obtained in real regime of temperature and pressures. In this work the properties of various terminations of the α-Fe_2O_3(0001) surface are studied with the spin-polarized density functional theory accounting for the effect of strong on-site Coulomb correlations (DFT+U). The resulting structures are applied to simulate STM images, in order to compare them with experimental findings. Work supported by the National Science Center (NCN), Poland (Grant No. 2012/07/B/ST3/03009).

[1] A. Kiejna, T. Pabisiak, *J. Phys: Cond. Mat.* **24**, 095003 (2012).
[2] A. Kiejna, T. Ossowski, T. Pabisiak, *Phys. Rev. B* **85**, 125414 (2012).
[3] T. Pabisiak and A. Kiejna, *J. Chem. Phys.* **141**, 134707 (2014).
[4] A. Kiejna and T. Pabisiak, *J. Phys. Chem. C* **117**, 24339 (2013).

Simulation of AFM imaging of surfaces with defects in solution

B. Reischl[1] A. L. Rohl[1]

[1]Nanochemistry Research Institute, Curtin University

We investigate the imaging mechanism of defects in crystal surfaces in solution in atomic force microscopy (AFM), by comparing experimental AFM images and atomistic simulations of the imaging process for several systems such as Calcite ($CaCO_3$), Gibbsite ($Al(OH)_3$), or Barite ($BaSO_4$) surfaces in solution. The AFM is the only instrument available to image surfaces in solution and their hydration layers with atomic resolution in *real space*, and the potential to study the atomistic processes involved in crystal growth and dissolution, as well as the mechanism by which growth modifiers affect these processes. Understanding the role of the AFM tip in the imaging process further opens the door for new ways to use the AFM as a tool in *crystal engineering*, the controlled design and manipulation of crystals (both organic and inorganic) in solution.

The solid-liquid interface: Probing charges on insulators with KPFM

H. Söngen[1,2] P. Rahe[3] J. L. Neff[2] R. Bechstein[2] A. Kühnle[2]

[1]Graduate School of Excellence "Materials Science in Mainz", Mainz, 55128, Germany
[2]Institut für Physikalische Chemie, Johannes Gutenberg Universität Mainz, Mainz, 55128, Germany
[3]Department of Physics and Astronomy, The University of Nottingham, Nottingham NG7 2RD, UK

Knowledge on the distribution of ions at the solid-liquid interface is crucial to understand many fundamental processes like the self-assembly of molecules in the liquid environment.

We report on the implementation of a Kelvin Probe Force Microscopy (KPFM) setup for the study of charges at solid-liquid interfaces. In particular, we discuss how to transfer the open-loop KPFM approach described in [1] to measurements on insulating materials in liquids.

For the purpose of quantitatively determining the charge density beneath the cantilever tip, a model for the KPFM signals is needed. We explore a classical electrostatic model [2,3] and its applicability for measurements in liquids. Furthermore, we clarify how to distinguish the contribution by localized charges from the contact potential difference caused by the metallic back electrode.

[1] Kobayashi, N.; Asakawa, H.; Fukuma, T., *Rev. Sci. Instrum.* **81**, 123705 (2010).
[2] Kantorovich, L. N.; Livshits, A. I.; Stoneham, M., *J. Phys. Condens. Matter* **12**, 795 (2000).
[3] Rahe, P.; Neff, J. L. , *Phys. Rev. B* **91**, 085424 (2015).

Linear Scaling Density Functional Theory for the Study of Defective Oxide Nanomaterials

E. W. Tait[1] N. Hine[2] C. Ducati[3]

[1]University of Cambridge, Department of Physics, Theory of Condensed Matter Group and NanoDTC
[2]University of Warwick, Department of Physics, Theory Group
[3]University of Cambridge, Department of Materials Science, Electron Microscopy Group

Transition metal oxides already enjoy a great many industrial uses: for example titanium dioxide is found in paints and as a food additive. However, TiO_2 also has interesting optical properties, both in photo-voltaic and photo-catalytic situations. Exploitation of these optical properties relies on being able to characterise the material accurately. Identifying and controlling defects, particularly at surfaces, is a major challenge. To assist in defect identification we are developing methods to simulate electron energy loss spectra (EELS) using the ONETEP linear scaling DFT code[1]. The large system sizes which can be studied with LS-DFT enable spectra of realistic defect structures and whole nanoparticles to be simulated, so comparisons to experimental spectra can be made.

[1] C.K. Skylaris, P. D. Haynes, A. A. Mostofi, M. C. Payne, *Journal of Chemical Physics* 122, 084119 (2005).

DFT Calculations of Processes in Early Stage Graphene Growth

J. Posthuma de Boer[1] A. Baraldi[1] D. Vvendsky[1] I. Ford[1] L. Kantorovich[1]
[1]King's College London

Graphene has attracted a large amount of interest due to its properties that make it suitable for a variety of applications. For many of these potential uses the graphene needs to be produced in large quantities and with high quality. This may be possible using epitaxial growth, where graphene is grown on a transition metal surface by depositing hydrocarbon molecules at high temperatures (>1000K).

One particular method of epitaxial graphene growth, temperature programmed growth (TPG), has successfully been used to grow graphene islands [1]. In this method hydrocarbon molecules are deposited onto a transition metal surface at room temperature and then the temperature is increased in order to facilitate the thermal decomposition of the hydrocarbons and lead to the formation of graphene flakes. It is widely believed that during the thermal decomposition the molecules lose their H atoms to form carbon species on the surface which act as the precursors for graphene growth [2]. However the mechanism behind this including whether there is any dependence on the initial species is not understood.

To investigate this we have examined the reaction processes when ethylene is adsorbed onto an Ir(111) surface using DFT-based nudged elastic band calculations. All possible dehydrogenation, hydrogenation and isomeristion reactions involved in the decomposition of the initial molecule to form adsorbed carbon were included in this scheme. In addition breaking of the carbon-carbon bond was considered. The energy barriers for each reaction have been used in rate equations to determine the species evolution on the surface. This evolution is in good agreement with the species identified during recent XPS experiments. Our results, coupled with the new experimental insight, suggest that the decomposition process is not as originally thought [2], during which the carbon-carbon bond is broken, leading to the production of C monomers.

[1] J. Coraux, A. T. N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie, F. J. M. zu Heringdorf, R. van Gastel, B. Poelsema, T. Michely, *New J. Phys.* **11**, 023006 (2009).
[2] S. Lizzit, A. Baraldi, *Catalysis Today* **154**, 68 (2010).

Micro-Fabricated Platform with Electrical Connections for In-situ Environmental TEM Characterization of Graphene

J. D. Thomsen[1] C. Gade[1] P. Bøggild[1] T. J. Booth[1]
[1]DTU Nanotech

Transmission electron microscopy is a characterization tool able to obtain atomic scale resolution, but can also be used to nanopattern graphene. We have designed a micro-fabricated silicon platform with on-chip heating and electrical contacts for in-situ environmental TEM characterization and modification of graphene. We will present the basic TEM platform characteristics and well as the first measurements of suspended in-situ patterned graphene and interflake conductance between stacked graphene layers.

Combining DFT with scanning probe microscopy to explore organic/inorganic interfaces for photovoltaic applications

M. Todorovic[1,2] C. Moreno[3,4] O. Stetsovych[5,4] T. K. Shimizu[4] O. Custance[4]
R. Perez[2]

[1]Aalto University, P.O. Box 11100, Aalto, 00076, Finland
[2]Universidad Autonoma de Madrid, Madrid, 28049, Spain
[3]Catalan Institute of Nanoscience and Nanotechnology, Bellaterra, 08193, Spain
[4]National Institute for Materials Science, Tsukuba, 305-0047, Japan
[5]Institute of Physics of the Czech Academy of Science, Prague 6, 16200, Czech Republic

Promising candidates for future organic solar cell and transistor devices include complex nanoscale structures, with thin films of organic molecules and metal oxides layered between metallic electrodes. Identifying the atomic arrangement at the organic/inorganic boundary is key to understanding the electronic and excitonic properties at the interface and evaluating technological potential.

We employ density-functional theory (DFT) techniques in combination with scanning probe microscopy (NC-AFM/STM) imaging of pentacene monolayers on the (101) surface of $\mathrm{TiO_2}$ anatase to gain insight into how these prototype optoelectronic materials interact. DFT simulations were used to determine the AFM/STM imaging mode of the surface [1]. Aided by experimental images, we identified the preferential attachment site and geometry for isolated pentacene molecules and the key molecule-oxide interactions. In continuation, we explored the geometry of pentacene monolayers on the $\mathrm{TiO_2}$ surface at high coverage. We found the pentacene thin film arrangement different from the organic solid packing geometry, with molecules re-oriented by strong molecule-substrate interactions. Electronic structure analysis of this organic/inorganic interface revealed that molecular orbitals of pentacene introduce localised electronic states into the band gap of the $\mathrm{TiO_2}$ anatase substrate, which may add to device functionality.

[1] O. Stetsovych, M. Todorovic et al., *Nat. Commun.* accepted (2015).

Introduction to CP2K, a first principles electronic structure simulation package

L. Tong[1]

[1]King's College London

Density functional theory (DFT) based ab initio simulations provide good approximation to electron charge densities on surfaces and has been widely used to reproduce scanning tunneling microscopy (STM) images observed experimentally. This provides us with valuable insight into the detailed electronic structure of the sample, and is extremely important for the correct interpretation of the experimental images.

CP2K (www.cp2k.org) is an open-source program for molecular dynamics simulation, best known for its implementation of the Quickstep (Gaussian and Plane Waves, GPW) linear-scaling Density Functional Theory (DFT) method [1]. It also provides a wide range of capabilities beyond the basic DFT, allowing calculations using classical forcefield potentials, semi-empirical methods, hybrid functionals and Møller-Plesset 2nd order perturbation theory (MP2).

In this presentation, I will give a general overview of the CP2K package and demonstrate how it can be used to generate STM images. We will consider two polyantryl molecules—intermediate molecules formed during the manufacturing of a long armchair graphene nano ribbon [2]—which have different terminations, and show how a simple change in termination (1 vs. 2 hydrogens) can change the state structure completely.

I will also highlight the recent work of implementing the Filtered Matrix Diagonalisation method in CP2K. Filtered diagonalisation [3] allows the run-time construction of a contracted basis set which is fully optimised for the system configuration, at every energy minimisation step. As the main bottle-neck in a DFT calculation is the diagonalisation of the Kohn-Sham matrix and it is a $\mathcal{O}(N)$ process, the filter method reduces the matrix size and can therefore significantly reduce computation time for large systems while still maintaining accuracy. I will demonstrate how the filtered diagonalisation method is useful for STM simulations on metallic surfaces, where the use of direct diagonalisation of the Kohn-Sham matrix is preferred over other iterative energy minimisation methods, and where a large system size is important.

[1] VandeVondele et al., *Comput. Phys. Commun.* **167**, 103 (2005).
[2] Talirz et al., *J. Am. Chem. Soc.* **135**, 2060 (2013).
[3] Rayson et al., *Phys. Rev. B* **80**, 205104 (2009).

Modular Python Virtual Atomic Force Microscopy (PyVAFM)

J. Tracey[1] F. F. Canova[2] D. Gao[3] A. S. Foster[1] B. Reischl[4]

[1]COMP, Department of Applied Physics, Aalto University, Otakaari 1, FI-00076 Aalto, Finland
[2]Aalto Science Institute, Aalto School of Science, PO Box 15500, FI-00076, Aalto, Finland
[3]Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom
[4]Nanochemistry Research Institute, Curtin University, GPO Box U1987, WA 6845, Perth, Australia.

In both scientific and industrial associations atomic force microscopy is extensively used for such applications as nanomanipulation or investigating chemical reactions on a surface. Atomic force microscopy has several modes of operation for imaging surfaces, one such method is FM-AFM. In this technique the tip will experience a force caused by surface interactions and hence alter the frequency of the cantilever as it scans across the surface. By examining the change in frequency over the surface it is possible to obtain an intensity pattern. The link between physical surface topography and experimental data can be can be difficult to interpret, hence a common method is to use detailed simulations. Although this is not a trivial task since such experiments contain many electronic components that can contribute to the inaccuracy of a signal for example the acquisition time of the PLL.

Majority of AFM simulators focus on simulating one specific setup, hence it has been one of the goals of this project to construct a modular AFM simulator that is open source, well documented and is capable of being expanded upon with relative ease. This software is being developed using a Python interface to allow ease of use when creating input files as well as the added flexibility that a Python script is capable of. The philosophy of the PyVAFM (Python virtual atomic force microscope) is to allow any electrical component to be created and added. An individual component is referred to as a ”circuit”. A ”circuit” is simple a piece of code that describes some physical process for example a low pass filter. By connecting several ”circuits” together any experimental setup can be constructed and simulated. It is possible to add your own ”circuits” allowing for researchers to create unique setups that contain elements not included as standard with the PyVAFM.

In this work the basic design and philosophy of the PyVAFM is presented along with some characteristic examples: atomic resolution of ionic surfaces in vacuum and liquid; comparison of AM- and FM-AFM modes for imaging calcite in liquid.

Black Phosphorus (BP) Interfaced with TiO_2 (110) Surface: An Novel Photovoltaic Heterojunction

L. Zhou[1] L. Kou[2] G. Shan[3] T. Frauenheim[1] S. Smith[2]

[1] Bremen Center for Computational Materials Science, University of Bremen, Am Falturm 1, 28359 Bremen, Germany
[2] Integrated Materials Design Centre (IMDC), School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia
[3] Department of Physics and Materials Science and Centre for Functional Photonics (CFP), City University of Hong Kong (Hong Kong SAR)

Two-dimensional (2D) crystals, such as graphene, boron nitride, molybdenum disulphide, with extraordinary properties impact greatly future electronic technologies. Monolayer black phosphorus (BP, denoted as phosphorene), a single layer of phosphorus arranged in a hexagonal puckered lattice,showing extraordinary functional properties, including its highly anisotropic effective masses, high electron mobility (≈1000 cm2=V·s),a direct band gap around 2.0 eV, realize graphene's potential without graphene's weaknesses in optoelectronic devices.Constructing such van der Waals vertical hetero structures or in-plane hetero-structure hybrids is an alternative way to modulate the optoelectronic device properties at atomistic and quantum scale. As for phosphorene-based hetero-structures, experimental black phosphorus (BP)-based hetero-structures have been reported, mainly focusing on BP-MoS_2 [2]and BP-TiO_2 surface. Despite the rare numbers of experimental attempts , predictive theoretical studies have been conducted widely, such graphene-BP interface, bilayer phosphorene/AlxC photo-voltaic device. Due to their suitable band alignment, these studies motivate us to explore the optoelectronic properties and charge dynamics of BP-based hetero-structures as a photo-voltaic device. Here,we constructure a serials of Type-II heterostructures based on pure monolayer or bilayer BP and therir B- and N-doped deritives interfaced with TiO2 (110) face. These heterojunctions show a promisting application in excitonic solar cell with high efficiency of exciton separation and high PCEs in a tunable range, within which the phosphorene and its doped deritives are serived as the donor materials and the TiO2 (110) as the acceptor material.

[1] 7. Qiao, J., Kong, X., Hu, Z.-X., Yang, F. & Ji, W, *Nat. Commun.* **5**, 4475 (2014).
[2] Deng, Yexin, Zhe Luo, Nathan J. Conrad, Han Liu, Yongji Gong, Sina Najmaei, Pulickel M. Ajayan, Jun Lou, Xianfan Xu, and Peide D. Ye, *ACS Nano* **8**, 8292–99 (2014).
[3] Uk Lee, Hyun, Soon Chang Lee, Jonghan Won, Byung-Chul Son, Saehae Choi, Yooseok Kim, So Young Park, Hee-Sik Kim, Young-Chul Lee, and Jouhahn Lee., *Scientific Reports* **5**, 8691 (2015).

Hydrophobic properties of clay minerals investigated using molecular simulations

L. Zivanovic[1] P. Spijker[1] K. Kobayashi[2] A. Foster[1]

[1]COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland
[2]Department of Electronic Science and Engineering, Kyoto University, Kyoto, Japan

A natural occurring material composed primarily of fine-grained minerals is commonly referred to as a clay mineral. Most of them are sheet silicates(phyllosilicates) and are important industrial minerals. Examples include aluminum silicate minerals such as kaolinite, pyrophyllite and muscovite, as well as the corresponding magnesium silicate minerals, antigorite, talc and phlogopite.

Recent Non-Contact Atomic Force Microscopy (NC-AFM) measurements on several clay minerals (e.g., hydrotalcite and phlogopite) in a liquid environment show strong hydrophilic and hydrophobic regions. In order to better understand the molecular process that give rise to the hydrophobic properties of these clay minerals, we investigated the same systems using molecular dynamics (MD) simulations and the ClayFF force field [1]. In systems with mixed hydrophobicity (e.g., clinochlore) the NC-AFM measurement show interesting transition regions and using the same MD methodology we assess how these regions are formed.

As in the case of previously obtained results for the mica-water interface [2], the water near the interface is strongly ordered. However, the type of order and the strength of the water binding to the surface depends strongly on the type of clay and the substrate surface charge. In all cases our MD models are in good qualitative agreement with the NC-AFM measurements. We also compare our results to free energy simulations including an explicit tip model to gain even deeper insight into the imaging mechanism and hydrophobic properties of the clay minerals.

[1] R.T. Cygan, et al., *J. Phys. Chem. B* **108**, 1255 (2004).
[2] M. Ricci, et al.,, *Nat Commun.* **5**, 4400 (2014).

Participants

Arenal Raul	Spain	arenal@unizar.es
Booth Timothy	Denmark	tim.booth@nanotech.dtu.dk
Bozhko Sergey	Russia	bozhko@issp.ac.ru
Camilli Luca	Denmark	lcam@nanotech.dtu.dk
Dienel Thomas	Switzerland	thomas.dienel@empa.ch
Federici Canova Filippo	Finland	filippo.federici@aalto.fi
Foster Adam	Finland	adam.foster@aalto.fi
Fukuma Takeshi	Japan	fukuma@staff.kanazawa-u.ac.jp
Grutter Peter	Canada	grutter@physics.mcgill.ca
Gröning Oliver	Switzerland	oliver.groening@empa.ch
Hlawacek Gregor	Germany	g.hlawacek@hzdr.de
Holmstrom Eero	Finland	eero.holmstrom@aalto.fi
Hornekaer Liv	Denmark	liv@phys.au.dk
Hummel Stefan	Austria	stefan.hummel@univie.ac.at
Hynninen Teemu	Finland	teemu.hynninen@utu.fi
Kantorovich Lev	United Kingdom	lev.kantorovitch@kcl.ac.uk
Karasulu Bora	Netherlands	b.karasulu@tue.nl
Kawai Shigeki	Switzerland	shigeki.kawai@unibas.ch
Kimouche Amina	Finland	amina.kimouche@aalto.fi
Komsa Hannu-Pekka	Finland	hannu-pekka.komsa@aalto.fi
Krasheninnikov Arkady	Finland	arkady.krasheninnikov@aalto.fi
Ksenz Andrei	Russian Federation	anksser92@mail.ru
Kühnle Angelika	Germany	kuehnle@uni-mainz.de
Leinen Philipp	Germany	p.leinen@fz-juelich.de
Liljeroth Peter	Finland	peter.liljeroth@aalto.fi
Loukonen Ville	Finland	ville.loukonen@aalto.fi
Onishi Hiroshi	Japan	oni@kobe-u.ac.jp
Pabisiak Tomasz	Poland	pabi@ifd.uni.wroc.pl
Ramasse Quentin	UK	qmramasse@superstem.org
Reischl Bernhard	Australia	bernhard.reischl@curtin.edu.au
Schulz Fabian	Finland	fabian.schulz@aalto.fi
Sloan Jeremy	United Kingdom	j.sloan@warwick.ac.uk
Spijker Peter	Finland	peter.spijker@aalto.fi
Stocker Matthias	Germany	matthias.stocker@uni-ulm.de
Söngen Hagen	Germany	soengen@uni-mainz.de
Tait Edward William	United Kingdom	ewt23@cam.ac.uk
Temirov Ruslan	Germany	r.temirov@fz-juelich.de
Ternes Markus	Germany	m.ternes@fkf.mpg.de
Tetlow Holly	UK	holly.tetlow@kcl.ac.uk
Thomsen Joachim Dahl	Denmark	jdth@nanotech.dtu.dk

Todorovic Milica	Finland	milica.todorovic@aalto.fi
Tong Lianheng	United Kingdom	lianheng.tong@kcl.ac.uk
Tracey John	Finland	john.tracey@aalto.fi
Voitchovsky Kislon	UK	kislon.voitchovsky@durham.ac.uk
Yazyev Oleg	Switzerland	oleg.yazyev@epfl.ch
Zhou Liujiang	Germany	liujiang86@gmail.com
Zivanovic Lidija	Finland	lidija.zivanovic@aalto.fi
Åhlgren Harriet	Finland	ahlgren.harriet@gmail.com

Index