

CPP 14: Interfaces and Thin Films I

Time: Monday 15:00–17:45

Location: C 264

CPP 14.1 Mon 15:00 C 264

Permittivity at Liquid-Liquid Interfaces: An Iterative Reaction Field Approach — ●DAVID EGGER, KARSTEN REUTER, and CHRISTOPH SCHEURER — TU München

Realistic models for catalytic reactions at liquid-liquid interfaces require a profound knowledge of the electrostatic properties in the vicinity of the solvated catalytic complex. For polar fluids like water, these properties as described by the static dielectric constant, ϵ , can be related to thermal equilibrium fluctuations of the polarization at zero field. The Kirkwood-Fröhlich (KF) approach usually applied in the derivation of such formulas faces two major difficulties: First, correlated polarization fluctuations are long-range and subject to slow convergence, making KF expensive in simulations. Second, the difficulty of the electrostatic boundary value problem one needs to solve in a KF ansatz increases with the systems' complexity. In this contribution, we present a possible alternative procedure, following the reaction field approach described by Neumann for cubic and spherical sample shapes [1]. Exploiting the constant reaction field of oblate spheroidal dielectric bodies immersed in continuum dielectrics, we present an iterative method to calculate a spatially resolved ϵ from cavities of different shape and volume, avoiding difficulties with geometry-induced boundary conditions in the electrostatic description. Gaussian error regression is further applied to drive down statistical errors, exploiting the presupposed continuity of the dielectric tensor field. Results are discussed for water bulk and water-dichloroethane interfacial systems.

[1] M. Neumann, Mol. Phys. 50, 841 (1983).

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On the Origins of the Charging of Water at the Air-Water Interface — ●EMILIANO POLI¹, ALI HASSANALI¹, and HIMANSHU MISHRA² — ¹The Abdus Salam International Centre for Theoretical Physics (ictp), Trieste, Italy — ²King Abdullah University of Science and Technology Thuwal, Saudi Arabia

Aqueous interfaces are ubiquitous in nature and technological applications. Numerous physical, chemical and engineering processes occur at interfaces involving water and hydrophobic surfaces. Despite long study, many issues still remain controversial regarding the properties of water at hydrophobic interfaces. One particular interface in this regard that has received a lot of attention is the air-water interface. In particular, the origin of the surface charge of water, remains elusive.

In this work we investigate the electronic properties of the air-water interface using state-of-the-art linear scaling DFT methods allowing us to model systems consisting of over thousands of atoms. We examine how the dipole and quadrupole moments of water change near the interface as well as how charge transfer between layers is rooted in topological properties of the water network such as coordination defects and water wires. The role of both classical electrostatics and quantum mechanical effects like charge transfer and exchange, are examined with respect to the affinity of protons and hydroxide ions for the surface of water.

Finally these results are discussed within the broader framework of water near hydrophobic interfaces such as oil, proteins and hydrophobic polymers.

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Monitoring the Swelling Behavior of PEDOT:PSS Electrodes under High Humidity Conditions — ●LORENZ BIESSMANN¹, LUCAS PHILIPP KREUZER¹, TOBIAS WIDMANN¹, NURI HOHN¹, JEAN-FRANÇOIS MOULIN², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — ²HZG at MLZ, 85748 Garching

One main advantage of organic electronics is the enabling of building flexible electronic devices. The polymer mixture poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) offers good electrical conductivity, transparency and inherent flexibility, which makes it to a promising alternative to rigid and brittle transparent electrodes like indium tin oxide (ITO). By different treatment methods it is possible to adjust the conductivity and work function of PEDOT:PSS to its desired requirements. The hygroscopic behavior of the PSS component yields a high potential for water uptake of the PEDOT:PSS. This is known to have a negative influence on its electronic conductivity. Furthermore, an increasing film thickness due to water

uptake may lead to mechanical stress on the other functional layers in the organic device. Hence, we investigate the PEDOT:PSS thin films regarding their swelling behavior under high humidity conditions, using in-situ time of flight neutron reflectivity (TOF-NR) measurements. Two commonly used PEDOT:PSS treatments are compared to pristine PEDOT:PSS. We observe a strong dependence of water uptake and thickness evolution on the type of PEDOT:PSS treatment.

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Controlling Adhesion and Friction on Cyclodextrin Assemblies — ●JOHANNA BLASS^{1,2}, MARCEL ALBRECHT³, GERHARD WENZ³, and ROLAND BENNEWITZ^{1,2} — ¹INM - Leibniz-Institute for New Materials, Campus D2 2, Saarland University, 66123 Saarbrücken, Germany — ²Physics Department, Saarland University, Campus D2 2, Saarland University, 66123 Saarbrücken, Germany — ³Organic Macromolecular Chemistry, Campus C4 2, Saarland University, 66123 Saarbrücken, Germany

Controlling and understanding adhesive interactions on the molecular scale is one of the main challenges in the field of nanotechnology. We developed a new surface functionalization based on assemblies of cyclodextrin molecules to control adhesive forces and study the molecular mechanisms underlying dynamic effects of adhesion and friction. The dynamics of the molecular system were studied with respect to multivalency effects, single bond kinetics and flexibility of the attachment. By varying the compliance of the surface attachment, the relation between adhesion and friction and their dynamic rupture characteristics can be tuned. The rupture force of single bonds in thermodynamic equilibrium increases proportional to the square root of the force probe stiffness and is not determined by the stiffness of the molecular linker. The applicability of the surface functionalization was demonstrated when attaching cyclodextrin molecules onto stiff polymers to bridge the surface roughness of real contacts. Active control of adhesion and friction was achieved using photosensitive connector molecules which are sensitive to external light stimuli.

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Multivalent-Ion-Activated Protein Reflecting Bulk Reentrant Behavior — ●MADELEINE FRIES¹, DANIEL STOPPER², MICHAL K. BRAUN¹, ALEXANDER HINDERHOFER¹, FAJUN ZHANG¹, ROBERT M. J. JACOBS³, MAXIMILIAN W. A. SKODA⁴, HENDRIK HANSEN-GOOS², ROLAND ROTH², and FRANK SCHREIBER¹ — ¹Institute for Applied Physics, University of Tübingen — ²Institute for Theoretical Physics, University of Tübingen — ³Department for Chemistry, Chemistry Research Laboratory, University of Oxford, UK — ⁴Rutherford-Appleton Laboratory, ISIS Facility, Didcot, UK

Protein adsorption at the solid-liquid interface is an important phenomenon that often can be observed as a first step in biological processes. Despite its inherent importance, still relatively little is known about the underlying microscopic mechanisms. Here, using multivalent ions, we demonstrate the control of the interactions and the corresponding adsorption of net-negatively charged proteins (BSA) at an interface (SiO₂) by ellipsometry. We show that the reentrant condensation observed within the rich *bulk* [1] phase behavior of the system featuring a nonmonotonic dependence of the second virial coefficient on salt concentration c_s is reflected in an intriguing way in the protein adsorption $d(c_s)$ at the *interface*. Our findings are successfully described and understood by a model of ion-activated patchy interactions within the framework of classical density functional theory. In addition to the general challenge of connecting bulk and interface behavior, our work has implications for, *inter alia*, nucleation at interfaces [2].

[1] Fries et al, PRL (2017); [2] Zhang et al, PRL (2008).

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Specific Ion Effects of Nd³⁺ on the Structure and the Charging State of β -Lactoglobulin Adsorption Layers — MANUELA RICHERT and ●BJÖRN BRAUNSCHWEIG — Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

The influence of Nd³⁺ cations on β -Lactoglobulin (BLG) at air/water interfaces was investigated as a function of NdCl₃ concentration at a constant protein concentration of 15 μ M. In addition, we studied the proteins' bulk charging state with ζ -potential measurements and ob-

serve a complete reversal of the ζ -potential from -40 to +25 mV at low and high $c(\text{NdCl}_3)$, respectively. The zero net charging in the bulk is observed between 25 and 50 μM NdCl_3 , which is linked to a low colloidal stability. At the air/water interface, vibrational sum-frequency generation (SFG) shows a minimum in intensity of O-H stretching bands and a 180° phase change of the latter bands. We attribute these observations to a change in the net orientation of interfacial water molecules. The extreme charge screening of Nd^{3+} ions leads to a reduction of electrostatic repulsive forces and thus to a higher surface excess of BLG. As a result, the equilibrium surface tension decreases from 57 to 50 mN/m when the NdCl_3 concentration is increased to 200 μM . Foams show substantial changes in mean bubble size, stability and foamability as a function of NdCl_3 concentration. We relate these observations to changes in electrostatic disjoining pressure at low and intermediate $c(\text{NdCl}_3)$ until interfacial BLG aggregates lead to non-DLVO stabilization of the foams.

15 min. break

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Electronically coupled two-dimensional assembly of Cu2-xS nanocrystals for selective vapor sensing applications — ●SONAM MAITI^{1,2}, SANTANU MAITI², YVONNE JOSEPH³, ANDREAS WOLF⁴, DIRK DORFS⁴, FRANK SCHREIBER², and MARCUS SCHEELE¹ — ¹Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen, Germany — ²Institute of Applied Physics, University of Tuebingen, Tübingen, Germany — ³TU Bergakademie Freiberg, Freiberg, Germany — ⁴Leibniz Universität Hannover, Hannover, Germany

The fabrication of two dimensional (2D) ordered nanocrystal (NC) superlattice films with unique physical properties has remained a challenge for years [1,2]. Here, we demonstrate a novel method to prepare electronically coupled, monolayered films of Cu_{2-x}S NCs with the organic semiconductor molecule TACuPh, which exhibits fascinating charge carrier transport and optical properties. A systematic temperature dependence of the conductivity of the film is studied over a wide range of temperatures. The results indicate that charge carrier transport is governed by 2D variable range hopping (VRH) in the temperature range (280-30K) and changes from Mott VRH to Efros-Shklovskii VRH below 60 K. The high conductivity is attributed to better interparticle coupling by virtue of TACuPh, which is also evident from GISAXS. Finally, the films show good sensing performance towards 4-methyl-2-pentanone and toluene vapors at 0% relative humidity [3]. [1] X. Huang et al. *Adv. Mater.* 2014, 26, 2185. [2] M. Scheele et al. *PCCP*, 2005, 17, 97. [3] Y. Joseph et al. *Sensor Actuat B*, 2004, 98.

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Silicon surface functionalization towards biosensing via free standing Si-OH bonds on a non-oxidized surface — ●JESSICA HÄNISCH¹, KARSTEN HINRICHS², and JÖRG RAPPICH¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Kekuléstraße 5, 12489 Berlin (Germany) — ²Leibniz-Institut für Analytische Wissenschaften - ISAS - e. V., ISAS-Berlin, Schwarzschildstraße 8, 12489 Berlin, Germany

Silicon (Si) is widely used as a substrate material for the fabrication of biosensor devices.[1] In the most cases, the starting point of the surface functionalization are the surface hydroxyl groups present on the native oxide layer of the Si. The hydroxyl groups can be easily coupled with a huge variety of different silane molecules, depending on the desired functionalities. However, the present oxide layer between the surface functionalization and the bulk Si has some disadvantages like a high defect density and a lower transconductance.[2][3][4] To overcome

these downsides, we developed a synthetic pathway, with which single standing and highly stable hydroxyl groups directly bound to the Si surface can be obtained, which has not been achieved before. The hydroxyl groups were further functionalized to obtain a surface ready for immobilization reactions. [1] N.S.K. Gunda, M. Singh, L. Norman, K. Kaur, S.K. Mitra, *Appl. Surf. Sci.* 2014, 305, 522. [2] H. Haick, P. T. Hurley, A. I. Hochbaum, P. Yang, N. S. Lewis, *J. Am. Chem. Soc.* 2006, 128, 8990. [3] Y. Cui, Z. Zhong, D. Wang, W. U. Wang, C. M. Lieber, *Nano Lett.* 2003, 3, 149. [4] O. Assad, H. Haick, 2008 IEEE International Symposium on Industrial Electronics, 2040.

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Unexpected behavior of thin PVME/PS blend films investigated by specific heat spectroscopy — ●PAULINA SZYMONIAK, SHERIF MADKOUR, and ANDREAS SCHÖNHALS — BAM Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin (Germany)

The structure and molecular dynamics of thin polymer films are of topical interest of soft matter-physics. Commonly, spatial structural heterogeneities of 1D confined thin films (surface, bulk-like and adsorbed layer), are expected to alter the glassy dynamics, compared to the bulk. Here, Specific Heat Spectroscopy (SHS) was used to investigate the glassy dynamics of thin films of an asymmetric miscible PVME/PS 25/75 wt% blend. SHS measurements showed a non-monotonous thickness dependence of the dynamic T_g, on the contrary to the previously investigated PVME/PS 50/50 wt% [1]. For PVME/PS 25/75 wt% thin films (> 30 nm), due to the presence of PVME-rich adsorbed and surface layers, the bulk-like layer experienced a thickness dependent increase of PS concentration. This led to a systematic increase of dynamic T_g. Further decrease of the film thickness (< 30 nm) resulted in a decrease of dynamic T_g, ascribed to the influence of the surface layer, which has a high molecular mobility. This is the first study, which shows deviations of dynamic T_g of thin films, compared to the bulk, resulting from the counterbalance of the influence of the surface and adsorbed layer [2,3]. [1] Yin, H. et al. *Macromolecules* 2015, 48, 4936. [2] Madkour, S. et al. *J. Chem. Phys.* 2017, 146, 203321. [3] Madkour, S. et al. *ACS Macro Lett.* 2017, 6, 1156.

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Preparation and Characterization of Pentacene Thin Films on SiC Graphene — ●MARTIN HODAS¹, PETER SIFFALOVIC², GIULIANO DUVA¹, BERTHOLD REISZ¹, MICHAL BODIK², PETER NADAZDY², ALEXANDER HINDERHOFER¹, ALEXANDER GERLACH¹, EVA MAJKOVA², and FRANK SCHREIBER¹ — ¹Universität Tübingen, Germany — ²Slovak Academy of Sciences, Slovakia

We report on the results of thin pentacene deposition on epitaxially grown graphene on SiC, focusing on growth kinetics, molecular orientation, structure and lattice parameters of pentacene on defect-free graphene. Epitaxially grown graphene on SiC possesses a high-quality crystal structure, essentially without grain boundaries. Pentacene thin films exhibit high structural order and relatively high field-effect mobility. The optical and electronic properties of pentacene are highly anisotropic. The films have been monitored in-situ with real-time X-ray scattering techniques (GISAXS, GIWAXS), ex-situ with atomic force microscopy (AFM) and polarized Raman measurements. Epitaxial growth of pentacene on graphene yields a lying-down molecular assembly that shows a six-fold symmetry with respect to graphene crystallographic orientation[1]. Surprisingly, the theoretical position of the 001 diffraction peak for the single crystal phase matches our thin film measurements. Temporal evolution of R_g reveals maximum value at 60 nm for 3 different substrate temperatures (320, 330, 350K).

[1] L. Wi Hyoung et al. Surface-Directed Molecular Assembly of Pentacene on Monolayer Graphene for High-Performance Organic Transistors. *JACS* 2011, (133), 4447.