CPP 13: Poster: Interfaces and Thin Films

Time: Tuesday 18:15–20:45 Location: Poster A

CPP 13.1 Tue 18:15 Poster A

Critical Adsorption of Polymers with Different Architecture — •Olga Mironova[1] and Jens-Uwe Sommer[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden e. V., Dresden, Germany — [2]TUD, Dresden, Germany

In order to understand the role of the chain architecture for the adsorption properties of polymers, we simulate polymer systems using the bond-fluctuation model (BFM). End-grafted polymers at an adsorbing surface are considered under good solvent conditions and we analyzed our results using scaling arguments. Suggestion, that adsorption properties of polymers, such as critical energy of adsorption and crossover exponent, for instance, can differ between molecules with the same molecular weight, but with different architectures, can be used as basis in separation technique (Liquid chromatography at the critical condition-mass spectrometry) of such molecules. We consider molecules with three different types of architecture: linear, star-shaped and hyperbranched. It was found that critical parameters for 4-arms star-shaped polymers and linear chains are very close to each other. To determine the critical parameters for hyperbranched polymers ensemble averages over many realizations of the branching topology is necessary. Variations of the branching probability gives access to experiments on hyperbranched polymers.

CPP 13.2 Tue 18:15 Poster A

Influence of charge density on bilayer bending rigidity in lipid vesicles: a combined dynamic light scattering and neutron spin-echo study — •Beate-Annette Brüning[1], Ralf Stehle[1,2], Peter Falus[3], and Bela Farago[3] — [1]Helmholtz Zentrum Berlin, Hahn-Meitner Platz 1, 14109 Berlin, Germany — [2]Universität Bayreuth, Postfach 10 12 51, 95440 Bayreuth, Germany — [3]Institut Laue-Langevin, B.P. 156, 6 rue Jules Horowitz, 38042 Grenoble, France

We report a combined dynamic light scattering and neutron spin-echo study on vesicles composed of the uncharged helper lipid DMPC and the cationic lipid DOTAP. Mechanical properties of a model membrane and the corresponding fluctuation dynamics can be tuned by changing composition. We compare the bilayer undulation dynamics in lipid vesicles composed of DMPC/DOTAP to vesicles composed of DMPC and the also uncharged reference lipid DOPC. We find, that on the local scale, lipid headgroup composition and charge change the vesicle fluctuations less than acyl chain packing inhomogenities between the composite lipids. We discuss this result on the basis of domain formation in the lipid mixtures containing charged (DMPC/DOTAP) and uncharged reference lipid (DMPC/DOPC). First, we investigate lipid vesicle size and mass diffusion using dynamic light scattering, then we study collective bilayer undulations and bulk diffusion on two distinct time scales around 25ns and 150ns, using neutron spin-echo spectroscopy. Finally, we estimate bilayer bending rigidities κ_B for the charged and uncharged lipid vesicles.

CPP 13.3 Tue 18:15 Poster A

Monte-Carlo Simulation of Compatibilization by Network-Building and Catalytic Interface Reactions in Two-Component Injection Molding — •Andreas John, Jürgen Nagel, and Gert Heinrich — Leibniz Institut für Polymerforschung Dresden e. V., Hohe Strasse 6, 01069 Dresden

Adhesion of immiscible polymers during two-component injection molding can be improved by transreactions of properly functionalized molecules in situ by exploitation of the thermal energy of the melts.To investigate these processes, we performed Monte-Carlo (MC) simulations based on the three-dimensional coarse-grained Bond Fluctuation Model (BFM) including a thermal interaction potential in r<=sqrt(6) with energy eps=0.1kBT. We compared a simple Split type reaction, which is capable of network-forming, with a catalytic interface reactive process both exhibiting different values of activation energy. The main process of the catalytic reaction system is identical to the simple Split reaction as described previously, but now a reactive monomer creating process is prefixed. For the reacting systems different physical properties like consumption, radius of gyration, concentration profiles or the distribution of the degree of polymerization were calculated as a function of time. Additionally, several functions for the description of the adhesive strength on the molecular level were adopted and calculated depending on reaction type, activation energy and degree of consumption, respectively. From the results, those chemical reaction types were deduced, which should be most suitable for compatibilization intentions in two-component injection molding.

CPP 13.4 Tue 18:15 Poster A

Molecular Dynamics of Miscible Polymer Blend Thin Films — •Huajie Yin and Andreas Schönhals — BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

Molecular dynamics of Polystyrene (PS), Poly(vinyl methyl ether) (PVME) and their blend (PS/PVME) confined in thin film geometry have been studied by mean of broadband dielectric spectroscopy (BDS). No thickness dependence of PS segmental dynamics was observed down to 14 nm. For pure PVME, three relaxation processes (Alpha,Beta and Gamma) were observed. The Arrhenius plots of the Beta and Gamma processes have activation energy of 38.3 kJ/mol and 20.5 kJ/mol, respectively. The relaxation rate of the Alpha process is well described by the Vogel-Fulcher-Tamman (VFT) equation. Thin films of PS/PVME polymer blend in the weight ratio of 25/75 have been investigated for different thicknesses. The broadening of the Alpha-relaxation peak for the polymer blend was observed, the intensity of which increases with the temperatures. The glassy dynamics of the polymer blend thin films are independent of the layer thickness under study.

CPP 13.5 Tue 18:15 Poster A

Implementation of super-structures on mesoporous titania films via soft embossing — •Gregory D. Tainter, Martin A. Niedermeier, and Peter Müller-Buschbaum — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str.1, 85748 Garching, Germany

Metal oxide thin films are the subject of numerous studies due to their potential as photoactive layers, e.g. in photocatalysis and photovoltaics. Using diblock copolymer scaffolds to control the morphologies of mesoporous titania films has been shown to be effective in improving the specific area of such films. The benefits of super-structuring have been successfully demonstrated in the past. A light trapping effect can lead to enhanced absorption in the film which is a highly desirable property for optoelectronic devices.[1]

In this work, hybrid polymer/titania films are prepared via a sol-gel route. The diblock copolymer poly(styrene - block - ethylene oxide) is used to create a mesoporous titania structure through good-poor solvent induced phase separation. The results of soft embossing such hybrid films with varying pressures and temperatures are investigated using optical microscopy, atomic force microscopy and scanning electron microscopy. The optical properties are probed with UV/Vis spectroscopy.

[1] Niggemann et al., Physica status solidi. A 205 12, 2862 (2008)

CPP 13.6 Tue 18:15 Poster A

Electrodeposition of porous ZnO in the presence of sodium dodecylbenzene sulfonate (NaDBS) as structure-directing agent — •Magnus Schäfer, Max Beu, and Derck Schlettwein — Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-Ring 16, D-35392 Gießen

ZnO was electrodeposited on fluorine-doped tin oxide (FTO) on glass using an aqueous $ZnCl_2$-solution as electrolyte, heated up to 70°C. A constant voltage of $-1060mV$ vs. a $Ag/AgCl$ reference electrode was used for the deposition. To form a porous ZnO-layer, $sodiumdodecylbenzenesulfonate(NaDBS)$ was added as structure-directing agent to the electrolyte. After the deposition the $NaDBS$ was desorbed from the ZnO electrodes. The influence of $NaDBS$ on the porous structure and on the morphology of ZnO was studied. The subsequent adsorption of organic dyes as sensitizers to the porous zinc oxide layers and their characteristics in dye-sensitized solar cells was tested to analyze the suitability of the porous ZnO matrix as electrode material.

CPP 13.7 Tue 18:15 Poster A

Competing Ordering Processes at Liquid Crystal Surfaces Laden with Semifluorinated Alkane Molecules — •Xunda

Feng[1], Ahmed Mourran[2], Martin Möller[2], and Christian Bahr[1] — [1]Max-Planck-Institute for Dynamics and Self-Organization, Göttingen, Germany — [2]Institute for Technical and Macromolecular Chemistry, RWTH Aachen, Germany

We present an ellipsometric study of the interface between isotropic liquid crystals (LCs) and air in the vicinity of the nematic – isotropic and smectic-*A* – isotropic transition. The LCs are doped with a small amount of the semifluorinated alkane $C_{18}H_{37}$–$C_{12}F_{25}$ ($H_{18}F_{12}$) which forms a Gibbs film (GF) at the LC/air interface. Our measurements elucidate the interplay between the nematic or smectic surface order at the isotropic LC/air interface and a structural phase transition in a GF on the same interface.

GFs of $H_{18}F_{12}$ on normal alkanes are known to exhibit a transition from a dilute state at higher temperatures to a dense state at lower temperatures. Our results indicate that the same transition takes place in GFs formed on the isotropic LCs. The transition temperature can be tuned by controlling the $H_{18}F_{12}$ concentration in the bulk LC phase. When the transition takes place in the temperature range in which a molecular thin smectic or nematic film exists at the isotropic LC/air interface, the smectic surface order is destroyed while the nematic surface order is affected by a change of the orientation of the LC molecules. The ellipsometric data indicate that both behaviors result from a change of the anchoring condition of the LC molecules in contact with the GF.

CPP 13.8 Tue 18:15 Poster A

Stimuli-responsive layer-by-layer films containing block copolymer micelles — •Inna Dewald[1], Julia Gensel[1], Johann Erath[1], Eva Betthausen[2], Axel H.E. Müller[2], and Andreas Fery[1] — [1]1Physical Chemistry II, University of Bayreuth, 95440, Germany — [2]Macromolecular Chemistry II, University of Bayreuth, 95440, Germany

We report on a novel approach for the design of stimuli-responsive thin films based on the incorporation of charged core-shell-corona micelles consisting of a hydrophobic core, a pH-responsive shell and a permanently charged cationic corona. [1,2] The films were produced using the layer-by-layer technique. Thereby the micelles were electrostatically self-assembled in an alternating manner using a strong anion as binding partner. Our results reveal that the assemblies exhibit fully reversible swelling transition due to pH-response of the weak polyelectrolyte middle block. The swelling behavior shows a strong dependence on solution pH and bilayer number. In order to characterize the multilayer films and analyze their pH-dependent behavior methods such as ellipsometry and atomic force microscopy were used. Measurements for both methods were performed on air as well as in liquid resulting in an up to ten-fold increase of the film thickness compared to the dry thickness. The films capacity of reversible swelling due to changes of solution pH makes our multilayer films excellent candidates for future applications in e.g. drug delivery with controlled release mechanism.

[1] E. Betthausen et al., Soft Matter, 2011, 7, 8880

[2] J. Gensel et al., Soft Matter, 2011, 7, 11144

CPP 13.9 Tue 18:15 Poster A

In Situ Growth Studies of N-Alkanes on Silica with Real-Time X-Ray Methods — •Christopher Weber[1], Christian Frank[2], Wolfram Leitenberger[3], Frank Schreiber[2], and Stefan Kowarik[1] — [1]Institut für Physik, Humboldt Universität zu Berlin, 12489 Berlin — [2]Institut für angewandte Physik, Universität Tübingen, 72076 Tübingen — [3]Institut für Physik, Universität Potsdam, 14476 Potsdam-Golm

We use n-alkanes as a model system to study how the chain-length of molecules influences thin film growth. Because of their insulating properties n-alkanes also have attracted some technological attention. Recently they have been used with great success to improve the performance of an organic field effect transistor. Real-time x-ray methods combined with theoretical models allow us to monitor the growth process in situ, determine changes of the growth modes and follow the roughening of the films. Grazing Incidence X-ray Diffraction allowes to find also some chain-length dependency within the final film structures.

CPP 13.10 Tue 18:15 Poster A

Wetting of solid surfaces by microemulsions — •Stefan Wellert[1], Samantha Micciulla[1], Roland Steitz[2], Regine von Klitzing[1], and Thomas Hellweg[3] — [1]TU Berlin, Str. d. 17. Juni 124, 10623 Berlin, Germany — [2]Helmholtz Center Berlin, Hahn-Meitner Platz 1, 14109 Berlin, Germany — [3]University of Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany

The increasing use of bio-inspired surfactants in microemulsions leads to an increasing interest in these thermodynamically stable self-assembled structures of oil, water and amphiphiles. Although the interaction between such microemulsions and solid surfaces is essential for many desired functionalities, only few is known about local structure and dynamics of a microemulsion in the vicinity of a solid surface. In particular, the influence of surface hydrophobicity, surfactant adsorption, bending elasticity of the amphiphilic interface and related properties have to be investigated in future studies. We used different methods to investigate the interaction of microemulsions with solid surfaces. Measurements of wetting properties at hydrophilic, partially hydrophobic and hydrophobic surfaces were combined with scattering methods resolving the structure of the microemulsion at the various solid surfaces. The resulting structural parameters and the observed dynamics in the vicinity of surfaces are compared to the corresponding results measured in the bulk phase with the undisturbed volume phase structure.

CPP 13.11 Tue 18:15 Poster A

Deformation and Buckling of Elastic Capsules — •Sebastian Knoche and Jan Kierfeld — TU Dortmund

We investigate the deformation behavior of soft elastic capsules. Based on nonlinear shell theory, a theoretical model for liquid filled capsules hanging from a capillary in a pendant drop geometry is developed, and shape equations are derived.

Their deformation behavior upon (a) changing gravity forces (by changing the phase contrast between liquids) and (b) reducing capsule volume is analyzed numerically. In case (a), the capsule stretches and sags and in case (b) we find a rich bifurcation behavior between buckled shapes; the preferred configurations are deduced from a least-energy principle. Based on theoretical results we develop a fitting procedure which allows us to extract the elastic moduli of the capsule membrane from experimental data.

We use similar methods to analyze the buckling behavior of spherical capsules upon reduction of the capsule volume. By preventing self-intersection for strongly reduced volume, we obtain a complete picture of the buckling process and can follow the transition from the undeformed configuration into the fully buckled state.

CPP 13.12 Tue 18:15 Poster A

Microfabrication and characterization of stress-reduced YSZ membranes — •Florian Kuhl, Markus Piechotka, Torsten Henning, Daniel Reppin, Peter J. Klar, and Bruno K. Meyer — I. Physikalisches Institut, Justus Liebig University, Heinrich-Buff-Ring 16, 35392 Giessen

The oxygen conductor YSZ (Yttria-stabilized-zirconia) is a material often used as electrolyte for solid oxide fuell cells. To achieve a higher packing density and to optimize the currents it is necessary to miniaturize the fuel cell components, especially to reduce the thickness of the solid electrolyte. Another application of very thin YSZ films may be their utilization as ion source. Si wafers were locally pre-thinned by photolithography and crystallographic etching to provide pre-thinned areas on which the YSZ thin film was deposited by RF sputtering. Free standing membranes were created by wet chemical etching of the thinned portions of the wafer using a variety of masking patterns defined by electron beam lithography and optimized to reduce stress induced cracking. Since the growth of the YSZ is not completely free of stress, membrane crack issues were observable. We show how the fabrication influences the stress of the sputtered YSZ. For characterization of the fabricated membranes we used light- and laser microscopy as well as SEM and AFM. Additionally, we applied Raman mapping to see how the stress of the YSZ membranes changes the behavior of the Raman modes.

CPP 13.13 Tue 18:15 Poster A

The interplay of structure and molecular dynamics in confinement of block copolymer meso-phases in thin layers — Markus Fuchs, •Martin Tress, Emmanuel Mapesa, and Friedrich Kremer — Universität Leipzig, Leipzig

Broadband Dielectric Spectroscopy (BDS) in combination with X-ray scattering is applied to investigate the molecular dynamics and the meso-phase morphology of the block copolymer system poly(isoprene-b-styrene) confined to thin layers. For the isoprene block, BDS enables one to study the segmental dynamics, taking place on a length scale of ~0.5 nm, and chain dynamics, which cover length scales of tens of nanometers, separately at the same time. Different compositions of the block copolymer are selected according to their particular meso-phase structure and thin layers are deposited onto recently developed nano-structured electrode arrangements for the BDS measurements. By that, and the complementary structural investigations by X-ray scattering, the interplay of the meso-phase structure and the molecular dynamics on different length scales is examined.

CPP 13.14 Tue 18:15 Poster A

Phase diagram of a diblock copolymer film in an electric field in the strong segregation limit — •Michael Harrach[1], Marianne Heckmann[1], Tiago Peixoto[2], and Barbara Drossel[1] — [1]Institut für Festkörperphysik, TU Darmstadt — [2]Institut für Theoretische Physik, Universität Bremen

We obtain phase diagrams for a thin film of diblock copolymers in an electric field at low temperatures in the strong-segregation limit. In this limit, the system consists of pure A and B domains, and the contributions to the free energy are due to interfacial and polymer stretching effects. We assign different dielectric constants to the two types of domains and evaluate the free energy for different types of phases that are composed of lamellar and cylindrical components, which may be deformed. We consider a two-dimensional system, assuming translational invariance in the third dimension, and periodic boundary conditions in the direction parallel to the condensator plates, between which the polymer film is confined. Specific three dimensional morphologies are considered as well. Phase diagrams are shown as function of film thickness and electric field. Results are presented for a ratio of permittivites of 1:5, for three volume fractions of monomers and four differing field strengths.

CPP 13.15 Tue 18:15 Poster A

Evidence of elastic behaviour of a distorted monolayer — •Uli Langer and Thomas M. Fischer — Uni Bayreuth, Bayreuth, Germany

In our experiment we spread carboxilic particles with a diameter of 100 nm at the air/water interface where they form a monolayer with two phases. Adding nickel nanowires we can excess a shear force by using an external static magnetic field. The nanowires reorient when the external field is switched between x- and y-direction. Located in the denser phase they deform the nearby domains of the less dense phase. While most of the domains start relaxing immediately after the torque was applied some keep their distorted shape until the nanowires are flipped back to their original position.

We computed several physical properties of the monolayer including the line tension λ between the phases, the viscosity η of the denser phase, the pressure difference $\Delta\pi$ between the two phases, and the force density profile acting on a distorted domain.

CPP 13.16 Tue 18:15 Poster A

Interfacial effects on single dye dynamics in ultrathin liquid films and in nanopores — •Fabian Meier, Daniela Täuber, and Christian von Borczyskowski — nanoMA, TU-Chemnitz, Institut für Physik

Nanopores have gained importance as filters in industrial and environmental applications. Thereby interactions of guest molecules are of interest, and thus have led to ongoing research. Here we use single molecule methods to explore the dynamics of dye molecules within nanopores and ultrathin liquid films [1,2] on differently treated silica surfaces. In contrast to ensemble methods, we thereby gain information on a local sub-micron scale. This allows us to draw conclusions on diffusion coefficients and physio-chemical binding affinities depending on the chemical structure of participating molecules and solid surfaces.

[1] D. Täuber, C. von Borczyskowski et al: Diff. Fund. J. 11 (2009) 76.

[2] D. Täuber, Dissertation, TU Chemnitz, 2011.

CPP 13.17 Tue 18:15 Poster A

Increased sorption of water investigating ultrathin polyvinylacetate films — •Heiko Huth and Christoph Schick — Universität Rostock, Institut für Physik, Wismarsche Straße 43-45, 18051 Rostock

Calorimetry is known as a very powerful tool for the characterization of a wide variety of materials and their transitions. There is an ongoing interest in improving the technique in order to achieve high sensitivity and precision. As one example there is thin film ac calorimetry able to measure in the nanometer range [1]. There is also an increasing interest in thin films and small sample sizes from a technological point of view. As these applications often include the presence of water the controlled humidity is used as a new parameter in addition to temperature for calorimetry. Also for biolgical samples as proteins for example there is an interest to measured under controlled humidity [2].

We show a new setup to measure heat capacity of thin films and samples under controlled humidity. As a first example thin films of polyvinylacetate are measured where a large influence of humidity on the glass transition is known from literature. In comparison to bulk samples the glass transition temperature is not changed while an increased sorption of water is observed measuring ultrathin films.

[1] Huth, H., Minakov, A. A., Schick, C., J. Polym. Sci. B Polym. Phys. 44 2996 (2006).

[2] Svanidze, A. V., H. Huth, et al. Applied Physics Letters 95 (26): 263702 (2009).

CPP 13.18 Tue 18:15 Poster A

Functionalization of silicon oxide nanopatterns by selective binding of fluorescent molecules — •Thomas Baumgärtel[1], Christian von Borczyskowski[1], and Harald Graaf[2] — [1]Center of Nanostructured Materials and Analytics, Institut für Physik, TU Chemnitz, 09107 Chemnitz, Germany — [2]FB 10, Institut für Chemie, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Local anodic oxidation (LAO) of alkyl-terminated silicon is a neat way for generating nanostructures with lateral dimensions below 100 nm and a height of a few nm. One of the remaining challenges is to give those structures a desired functionality in order to build more complex systems. Functionalization can be achieved via different methods such as electrostatic or covalent binding of optically active materials (e.g. molecules or nanoparticles). Here we report on the selective binding of dye molecules to LAO nanostructures and their investigation by means of temporally and spectrally resolved fluorescence microscopy. The spectra of bound perylene dyes have only little similarity to the monomer spectrum, are strongly red-shifted and the radiative transition is characterized by a higher lifetime of the excited state. This can be understood in terms of an oligomer formation of the dyes bound to the nanostructure similar to thin films or stacks of perylene derivatives. Fluorescein dyes that are bound covalently to the oxide on the other hand exhibit a spectrum which is quite similar to the monomer spectrum except of a slight red-shift caused by the different environment. Both systems may be promising candidates for chemically well-defined optically functional nanodevices on semiconductor surfaces.

CPP 13.19 Tue 18:15 Poster A

Mineralisation of iron oxides under lipid monolayers studied by x-ray scattering experiments — •Steffen Bieder[1], Florian Wieland[1], Patrick Degen[2], Michael Paulus[1], Martin Schroer[1], Johannes Möller[1], Christoph Sahle[1], Ralph Wagner[3], Heinz Rehage[2], and Metin Tolan[1] — [1]Fakultät Physik/DELTA, TU Dortmund, Maria-Goeppert-Mayer-Str. 2, D-44227 Dortmund — [2]Physikalische Chemie II, TU Dortmund, Otto-Hahn-Str. 6, D-44227 Dortmund — [3]Fakultät Physik, Bergische Universität Wuppertal, Gaußstr. 20, D-42097 Wuppertal

Composite materials formed by nature show a hierarchically organized and complex structure. The biomineralization processes in living organisms are controlled by proteins and the environment where the process takes place, e.g., the cell interia or the surface of membranes. We studied the mineralization of iron oxide in-situ at the aqueous solution/air interface. As a model system for membranes in living cells we used Langmuir layers consisting of lipids with differently charged headgroups in order to investigate the influence of electrostatic interactions on the mineralization process. The adsorption of iron oxide at the monolayers was observed by grazing incidence diffraction (GID) and extended x-ray absorption fine structure (EXAFS) spectroscopy. We also studied the mineralization with x-ray reflectivity (XRR) experiments at the liquid-liquid interface. The extracted data show an agglomeration of iron oxides at the monolayers. The formation of the growing iron oxides were similar to the formation of lepidocrocite and goethite.

CPP 13.20 Tue 18:15 Poster A

Surface Properties of Catanionic Mixtures — •Heiko Fauser, Martin Uhlig, and Regine v. Klitzing — Stranski-Laboratorium, Department of Chemistry, TU Berlin, Straße des 17. Juni 124 D-10623 Berlin, Germany

Mixtures of oppositely charged surfactants show a strong synergism.

It allows reducing the required amount of surfactant, which makes catanionic surfactant mixtures eco-friendly. Thus, these mixtures are of great interest for a broad field of applications like detergency, oil recovery, food technology and drug delivery. Furthermore, foam stability can be increased with these mixtures, since the formation of surface active complexes and aggregates strongly increases the adsorption at liquid-air interfaces.

Literature shows that mixtures of surfactants with unequal chain length have different surface properties in comparison to mixtures with equal chain length. Thus, the focus of our study is on the influence of the surfactant alkyl chain length on the foam properties. In our work catanionic mixtures from two widely used surfactant types, sodium alkyl sulfates and quarternary alkylammonium bromides are investigated. To describe the adsorption of the aggregates at the liquid-air interface both the surface tension and the surface elasticity of mixtures with both matching chain length and mismatching chain length are investigated. Studies about the correlation between adsorbed amount of surfactants, interactions in thin foam films, foam ability and foam stability are in progress.

CPP 13.21 Tue 18:15 Poster A

The role of the solid/liquid interface on the dewetting process of thin polystyrene films — •Mischa Klos[1], Matthias Lessel[1], Oliver Bäumchen[1,2], and Karin Jacobs[1] — [1]Saarland University, Experimental Physics, D-66041 Saarbrücken — [2]Dept. of Physics & Astronomy, McMaster University, 1280 Main St. W, Hamilton, Canada, L8S 4M1

The continuing miniaturization of microfluidic devices causes a growing importance of the solid/liquid interface for the flow dynamics. Our experiments probe slippage using the dewetting process of thin polymer films on hydrophobic substrates. As hydrophobic coatings we use amorphous polymers (AF1600, AF2400) and different types of highly ordered self-assembled silane monolayers on top of ultraflat silicon substrates. Polystyrene (PS) of low molecular weight shows slip lengths between several hundreds of nanometers and even micrometers on silane surfaces [1], whereas on AF1600 nearly no slip is observable. However, slip can be induced by increasing the molecular weight of the PS [2]. Recent studies using scattering techniques showed an ordering effect of PS at the solid/liquid interface depending on the structure of the substrate [3]. Will the situation change if, instead of PS, polymethyl methacrylate (PMMA) is used? To probe the influence of the polymers composition on slippage, we show very first results of the dewetting dynamics of PMMA on AF2400.

[1] R. Fetzer, et. al., Europhys. Let., 75, no. 4, 638 (2006) [2] O. Bäumchen, et al., PRL, 103, 247801 (2009) [3] P. Gutfreund, et. al., arxiv.org 1104.0868v1 (2011, April 5)

CPP 13.22 Tue 18:15 Poster A

Adsorption of supercritical fluids on solids — Sebastian Holz, •Julia Nase, Michael Paulus, Christian Sternemann, Thorsten Brenner, and Metin Tolan — Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund

Adsorption at interfaces is critical for many processes in nature, as formation of gas hydrates, catalysis, or industrial applications like water purification. The formation of an adsorption layer enhances the gas offer significantly and is thus of importance for transport and exchange processes at membranes and interfaces in nature. More than 100 models have been established to describe the various types of adsorption isotherms. Supercritical adsorption, however, is far less understood, though this phenomenon has been known for some time now. It has tremendous importance in industrial applications like high pressure gas storage systems, Supercritical Fluid Chromatography (SFC), and polymer processing. So far, supercritical adsorption was investigated indirectly by volumetric and gravimetric methods in highly porous systems. However, the solid-gas interface with a possible restructuration of the molecules has never been directly measured. The exact density profile along the surface normal can be determined by x-ray reflectometry, a reliable and well adapted technique to determine interfacial structures. We report on results concerning the adsorption of supercritical carbon dioxide on a silicium wafer. Adsorption isotherms below the critical point are compared to the near critical ($T < T_\mathrm{C} + 10\mathrm{K}$) and the over critical regime ($T > T_\mathrm{C} + 10\mathrm{K}$).

CPP 13.23 Tue 18:15 Poster A

Freezing single molecule dynamics on interfaces and in polymers — •Felix Schmieder, Stefan Krause, and Christian von Borczyskowski — Fakultät für Naturwissenschaften, Technische Universität Chemnitz, D-09107 Chemnitz

During the past decade, probing nano-scale fluctuations within materials by single molecule spectroscopy (SMS) has become a common method. As the observed emission spectra, fluorescence lifetime and polarization are always a result of intramolecular processes and environmental interactions, it is necessary to exactly know about the photophysics of the probe molecules. We report on the freezing of molecular dynamics of quasi-free molecules on surfaces upon lowering of temperature and embedding into a poly(methyl methacrylate) (PMMA) polymer. This has been investigated by measuring heterogeneous line broadening and spectral diffusion of fluorescence emission spectra by means of time dependent SMS using a home-built confocal laser scanning microscope. Thereby changes of optical transition energies could be observed as a result of both intramolecular changes of conformation and dynamics induced externally by the polymer matrix.

CPP 13.24 Tue 18:15 Poster A

Swelling of Polyelectrolyte Multilayers in Ionic Liquid — Nagma Parveen[1,2] and •Monika Schönhoff[1] — [1]Institute of Physical Chemistry, University of Muenster, Corrensstr. 28/30, D-48149 Muenster, Germany — [2]NRW Graduate School of Chemistry, University of Muenster, Wilhelm-Klemm-Str. 10, D-48149 Muenster, Germany

Their controlled thickness and high mechanical stability make Polyelectrolyte Multilayers (PEM) promising ion conducting membranes. Suitable electrolyte solvents could possibly enhance the ionic conductivity for application in Li batteries. Here, the swelling of PEM with Ionic Liquid (IL) is investigated by Quartz Crystal Microbalance (QCM-D). PEM films are prepared with different combinations of polyelectrolyte, employing PSS/PAH, and PSS/PDADMAC. 1-Hexyl-3-methyimidazolium chloride is used here as a room temperature ionic liquid (RTIL). An enhancement of mass coverage and dissipation is found for films in contact with solutions of IL, suggesting incorporation of IL into the films, accompanied by film swelling. The swelling increases linearly with IL concentration. It is reversible at low IL concentrations, while at higher concentrations irreversible film decomposition occurs. The incorporation can be attributed rather to hydrophobic than to ionic interactions, since PDADMAC-containing films swell more strongly. Generally, the overall swelling can be decomposed into a fast and a slow process of IL uptake and chain reorganisation, respectively. Reversibility and stablility limits of PEM in IL solutions are established by these data.

CPP 13.25 Tue 18:15 Poster A

Frequency Response of Polymer Films Made from a Precursor Colloidal Monolayer on a Nanomechanical Cantilever — Ting Liu[1], Sascha Pihan[1], Marcel Roth[1], Markus Retsch[1], Ulrich Jonas[3], Jochen Stefan Gutmann[2], Kaloian Koynov[1], •Hans-Jürgen Butt[1], and Rüdiger Berger[1] — [1]Max-Planck-Institut für Polymerforschung, Mainz, Germany — [2]Institut für Physikalische Chemie, Universität Duisburg-Essen, Essen, Germany — [3]BOMC Laboratory, FORTH IESL, Heraklion, Greece

Nanomechanical cantilevers (NMC) were used for the characterization of the film formation process and the mechanical properties of colloidal monolayers made from polystyrene (PS). Closely packed hexagonal monolayers of colloids with diameters ranging from 400 nm to 800 nm were prepared at the air water interface and then transferred in a controlled way on the surface on NMC. The film formation process upon annealing of the monolayer was investigated by measuring the resonance frequency of the NMC (≈12 kHz). Upon heating of noncrosslinked PS colloids we could identify two transition temperatures. The first transition resulted from the merging of polymer colloids into a film. This transition temperature at 147 ± 3°C remained constant for subsequent heating cycles. We attributed this transition temperature to the glass transition temperature Tg of PS which was confirmed by dynamic mechanical thermal analysis (DMTA) and using the time temperature superposition principle. The second transition temperature (175 ± 3°C) was associated to the end of the film formation process and was measured only for the first heating cycle.

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Fabrication of carbon nanomembranes by helium ion beam lithography — •Xianghui Zhang, Henning Vieker, André Beyer, and Armin Gölzhäuser — Fäkultät für Physik, Universität Bielefeld, Postfach 10 01 31, 33501, Germany

A scanning helium-ion microscope (HIM) can be employed as an imaging and metrology tool for nanotechnology. In addition, the helium ion beam is capable of creating nano-sized patterns and it can perform ion milling as commonly done in a focused ion beam (FIB) system. It is known that aromatic self-assembled monolayers (SAMs) can be cross-linked due to electron irradiation and form mechanically stable carbon nanomembranes (CNMs). Here we use a helium ion beam as direct writing tool to cross-link 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) SAMs with arbitrary patterns. The cross-linked SAMs were transferred to either silicon substrates with an oxide layer for optical characterization or transmission electron microscopy (TEM) grids for preparing free-standing CNMs. The required dose for the complete cross-linking with helium ions is quite similar to that with electrons. To determine the feature resolution limit, we prepared dot arrays of CNMs at various doses and 5 nm feature sizes have been achieved. The proximity effect and the sample damage on the nano-scale patterns were also investigated. Furthermore, we use the ion beam to form nanopores in the CNM with an attainable feature size of 5 nm.

CPP 13.27 Tue 18:15 Poster A

Switching properties and orientation of dichroic fluorescent dyes in a nematic liquid crystal — •Clemens Göhler, Harald Graaf, and Christian von Borczyskowski — TU Chemnitz, Institut für Physik

In a liquid crystal cell (LC-cell), the direction of the nematic phase director can be varied by applying an electric field [1]. It is also known that dichroic dye molecules may align with their long molecular axis parallel to the director. While illuminating the LC-cell, fluorescence emission intensity will change due to the applied field and the angle between the dye long molecular axis and its transition dipole moment [2]. By using both principles, a LC-cell with field induced colour switching should be realizable.

We investigate dye molecules that show shape anisotropy caused by long alkyl chains. Thus we manage both a collinear and perpendicular alignment to the transition dipole moment. Using (polarized) fluorescence emission spectroscopy the orientation and order parameter of the dyes within the nematic liquid crystal is determined.

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[2] Heilmeier, G.H, Zanoni, L.A.: Appl. Phys. Letters 13, 91 (1968)

CPP 13.28 Tue 18:15 Poster A

Morphology and rupture forces of liquid gallium immobilized on different surfaces — •Frank Lawrenz[1], Nikolai Severin[2], Jürgen P. Rabe[2], Christiane A. Helm[1], and Stephan Block[3] — [1]Institut für Physik, Ernst-Moritz-Arndt Universität, Felix-Hausdorff-Str. 6, D-17487 Greifswald, Germany — [2]Department of Physics, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany — [3]ZIK HIKE - Zentrum für Innovationskompetenz Humorale Immunreaktionen bei kardiovaskulären Erkrankungen, Fleischmannstr. 42 - 44, D-17487 Greifswald, Germany

Liquid gallium is immobilized on mica, silicon and silica surfaces at 50 °C. AFM tapping mode imaging shows that gallium drops (micrometer-sized) as well as extended layers with nm-thickness and very low roughnesses are formed. Relatively large forces (on the order of several 10 nN) have to be applied to immerse a silicon tip (curvature radius around 10 nm) into the micrometer-sized gallium droplets. The forces exhibit many rupture events. The distribution of the rupture length is very broad and has a maximum at around 0.25 nm. It is most likely, that (solid) sheets of amorphous gallium oxide is formed at the air/liquid interface of gallium drops. These sheets interact with the AFM tip leading to the observed rupture events. Moreover, they are transferred during the preparation procedure to the surface forming the flat layers with nm-thickness.

CPP 13.29 Tue 18:15 Poster A

Interactions of Radical Oxygen Species with Phosphatidylcholine Monolayers and Liposomes — •Andreas Gröning[1], Heiko Ahrens[1], Frank Lawrenz[1], Thomas Ortmann[1], Gerald Brezesinski[2], Fritz Scholz[3], Doris Vollmer[4], and Christiane A. Helm[1] — [1]Institut für Physik, Uni Greifswald, 17487 Greifswald, Germany — [2]MPI KGF, 14476 Potsdam, Germany — [3]Institut für Biochemie, Uni Greifswald, 17487 Greifswald, Germany — [4]MPI P, Ackermannweg 10, 55128 Mainz, Germany

The reaction of phosphatidylcholines with hydroxyl radicals is investigated. The radicals are produced by the Fenton reaction. The radical concentration is varied. For DPPC monolayers a decrease in the lateral pressure is used as a measure of the efficiency of the radical attack. Combining isotherms and X-ray diffraction we find that the monolayer can be compressed to smaller molecular areas, with a reduced tilt angle of the alkyl chains. Consistent with this observation IRRAS experiments indicate a partial cleavage of the head group leading to a reduced head group size. X-ray reflectivity demonstrates Fe^{2+} binding to the head group. Fluorescence microscopy during the radical attack shows that new domains in the condensed phase nucleate immediately.

Furthermore, DMPC liposomes are investigated with differential scanning calorimetry. With increasing radical concentration, the alkyl chain melting transition is shifted to higher temperatures. Summarising, we observe solidification for both monolayers and liposomes which we attribute to a preferential radical attack on the hydrophilic head group region, followed by Fe^{2+} binding.

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Can we correlate residual stresses in ultrathin polymer films with a high surface mobility? — •Mithun Chowdhury[1], Paul Freyberg[1], and Günter Reiter[1,2] — [1]Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, 79104, Freiburg, Germany — [2]Freiburg Institute for Advanced Studies (FRIAS), 79104, Freiburg, Germany.

The fabrication process of a thin polymer film, involving the transition from a solution to a glass, is believed to have an impact on film properties, often related to poorly entangled out-of-equilibrium chain conformations and corresponding residual stresses caused by rapid solvent loss. Physical ageing of polymer films, at temperatures below the glass transition was found to lead to a progressive decay in dewetted hole size (indicative of a decreasing residual stress), in a close to exponential fashion with ageing time, defining a characteristic relaxation time. Relaxation times are largely in agreement with some earlier reports based on surface sensitive techniques for thin polymer films. This is indeed surprising as dewetting cannot be considered as a surface sensitive probe. Moreover, temperature dependence of the relaxation time of residual stresses, above the glass transition of the polymer can be obtained from the evolution of the shape of the dewetting rim. Relaxation times in that region are much faster with a significant deviation from the bulk polymer. Our results certainly invoke the possibility to explain the faster relaxation dynamics in thin films and its deviation from the bulk, also in terms of residual stresses induced from the film preparation stage.

CPP 13.31 Tue 18:15 Poster A

Modification of wrinkled surfaces through defects — •Patrick Wünnemann[1], Marco Phillip Schürings[1], Felix Plamper[2], Andrij Pich[3], and Alexander Böker[1] — [1]DWI an der RWTH Aachen, Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen, D-52056 Aachen, Germany — [2]IPC an der RWTH Aachen, Lehrstuhl für Physikalische Chemie, RWTH Aachen, D-52056 Aachen, Germany — [3]DWI an der RWTH Aachen, Funktionale und Interaktive Polymere, RWTH Aachen, D-52056 Aachen, Germany

We verify the effects of defects introduced to soft Poly(dimethylsiloxane) (PDMS) substrates through the formation of wrinkle structures to develop new patterns of wrinkled surfaces. These stress induced disruptions lead to star-like wrinkled sufaces on the nanoscale. Next to the effects of single defects we investigate wrinkled structures in the area between adjacent defects. First description of the domains, the wavelength and the induced pattern in the vicinity of the nanodefects are characterized by scanning force microscopy (SFM). The focus of our work is the correlation between wavelength and thickness of the oxidized PDMS-surface and the applied strain. Compared to other systems these defects are more likely to be fabricated by lithographic methods. We further study the possible use as a template for the two-dimensional arrangement of soft matter particles.

CPP 13.32 Tue 18:15 Poster A

Phase transitions of Polypeptides in confined geometries — •Renate Reiter[1], Frédéric Wintzenrith[2], and Günter Reiter[1] — [1]Physikalisches Institut, Universität Freiburg, Germany — [2]Ecole Polytechnique, France

Poly-γ-benzly-glutamte (PBLG) is a synthetic polypeptide which can adopt α-helical conformation in aprotic solvents and thus forms rigid rods with flexible side chains. The experimentally observed phase diagram in organic solvents corresponds well to the theoretical one of Flory which predicts a coexistence region of isotropic, liquid crystalline and network phases. Networks were observed experimentally by cooling the isotropic phase to the transition temperature followed by quenching.

We demonstrate that quasi two dimensional network like structures are obtained by preparing Langmuir films of PBLG from helicogenic solvent. With this technique molecules are confined to the air water interface and changing the molecular density via movable barriers allows inducing phase transitions which appear as discontinuities in the isotherms. BAM and AFM micrographs reveal fibrils and networks directly on the water surface and in films transferred to solid substrates. Unusual hysteric and relaxation behavior of the isotherms are observed and discussed. A correlation between morphological changes and phase transitions is targeted.

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Controlling Colloidal Self-Assembly with Gradient Wrinkle Substrates in Combinatorial Experiments — Stephanie Hiltl, Jens Oltmans, and •Alexander Böker — DWI an der RWTH Aachen e.V., Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen, D-52056 Aachen, Germany

We prepare wrinkle gradients in oxidized top layers on elastic poly(dimethylsiloxane) (PDMS) substrates covering several millimeters of the sample. While the amplitude of the gradient structure ranges from 7-230 nm, the wavelength spans several hundred nanometers (250-900 nm). Crucial for the gradient preparation is partial shielding of the PDMS sample during plasma oxidation. We take advantage of the newly developed surface geometry for combinatorial experiments regarding the assembly of microgels as a model particle system. By variation of the ratio of particle radius vs. wrinkle wavelength, we scan and optimize the influence of the wrinkle dimensions on particle shape, particle-sample interaction and the particle assembly in a single experiment.

CPP 13.34 Tue 18:15 Poster A

Modelling surfactant covered films - thermodynamic reformulation and extension of the hydrodynamic evolution equations — •Uwe Thiele[1], Andrew J. Archer[1], and Plapp Mathis[2] — [1]Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK — [2]Physique de la Matiere Condensee, Ecole Polytechnique, CNRS, 91128 Palaiseau, France

We propose several models that describe the dynamics of liquid films that are covered by a relatively large concentration of insoluble surfactant. First, we briefly review the 'classical' hydrodynamic form of the coupled evolution equations for film height and surfactant concentration that are well established for small concentrations. Then we re-formulate the basic model as a gradient dynamics based on an underlying free energy functional that accounts for wettability and capillarity. Based on this re-formulation in the framework of non-equilibrium thermodynamics, we propose extensions of the basic hydrodynamic model that account for (i) nonlinear equations of state, (ii) surfactant-dependent wettability, (iii) surfactant phase transitions, and (iv) substrate-mediated condensation. In passing we discuss important differences to models found in the literature.

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CPP 13.35 Tue 18:15 Poster A

Layer thickness homogeneity determination via Rutherford backscattering in helium-ion microscopy — •Henning Vieker, Karsten Rott, André Beyer, Günter Reiss, and Armin Gölzhäuser — University Bielefeld, Faculty of Physics, Germany

The recently developed helium-ion microscope allows remarkable surface resolution with the secondary-electron (SE) detector. Simultaneously, backscattered ions can be detected that allow imaging with a substantially higher elemental contrast. This Rutherford backscattered (RBS) ion contrast depends mainly on the elemental composition of the investigated sample surface. The escape depth of RBS ions is much larger than for secondary electrons. Thus whole layers with a wide range of thicknesses will contribute to a RBS ion image, whereas the SE image is far more surface sensitive, i.e. insensitive to buried parts under the sample surface.

In this contribution we examine RBS ion imaging as tool to characterize thickness variations of layered samples with well defined compositions. In a model example the homogeneity of gold layers on silicon substrates is investigated. Achievable spatial resolutions as well as the possibilities in using a reference sample to measure layer thicknesses will be addressed.

CPP 13.36 Tue 18:15 Poster A

Site specific electronic structure of electron doped SrTiO$_3$ and SrTiO$_3$ /LaAlO$_3$ interfaces — •Christoph Schlueter[1], Tien-Lin Lee[2], Carmela Aruta[3], and Jörg Zegenehagen[1] — [1]ESRF,Grenoble, France — [2]Diamond Light Source Ltd, Didcot, UK — [3]CNR-SPIN, Naples, Italy

A quasi-2dimensional electron gas is formed at the interface of the insulation oxides SrTiO3 (STO) and LaAlO3 (LAO). Despite significant research efforts the origin of the conductivity is still heavily discussed. This electron gas is expected to occupy states up to the Fermi level.

We present results of hard X-ray photoelectron spectroscopy (HAXPES) measurements on the STO/LAO hetero structures in comparison to electron doped single crystalline STO samples. Additional information is added by combining HAXPES with the site specific X-ray standing wave effect. This gives the possibility to decompose the spectra into the relative contributions from different lattice sites. Hence, coherent and incoherent (delocalized/localized) states close to the Fermi level can be distinguished. The obtained spectra show a partial filling of Ti d-bands, crossing the Fermi level. Oxygen deficient samples exhibit an additional incoherent peak +1.3eV below the Fermi level. For the hetero structures we identified carriers at the Fermi level from the conductive interface region and give experimental evidence of partial filling of Ti 3d bands and the presence of the oxygen vacancy related incoherent peak.