

CPP 2: Interfaces and Thin Films I (joint session with DECHEMA and VDI)

The session is a joint session with ProcessNet "Grenzflächenbestimmte Systeme und Prozesse" of DECHEMA and VDI.

Organizers: Thomas Danner (BASF), Leo Nick (DECHEMA) and Regine v. Klitzing.

Time: Monday 9:30–13:30

Location: H40

Invited Talk

CPP 2.1 Mon 9:30 H40
Langmuir monolayers as physical models in bio- and nanosciences — •HELMUTH MÖHWALD and GERALD BREZESINSKY — Max-Planck-Inst. of Colloids and Interfaces, 14424 Potsdam

Monolayers of amphiphilic molecules on water surfaces are on one hand excellent models to study ordering processes in 2 dimensions on a flexible and amorphous substrate, on the other hand they may serve as biophysical models to study processes at membrane surfaces. A plethora of techniques has been developed in the past to study the films in detail, the most important ones X-Ray diffraction, reflection and fluorescence and FTIR spectroscopy. - Polyoxometallates as most defined inorganic clusters with high application potential in catalysis and optics can be coupled with hydrocarbon chains, and ordering of the system at an interface is physically interesting in view of the competitive interactions of the clusters and the chains. - Peptides can arrange at interfaces leading to changes of secondary structures. These can be modeled theoretically including their additionally interactions with ions. one can thus contribute to processes that are involved in various diseases like Alzheimer's. - Sugars are important for recognition processes in biology, and many of these processes occur at membrane surfaces. Thus studies of their arrangement at interfaces are most welcome. It will be shown that they can form a strong crystalline hydrogen bonded network, and if these molecules are coupled to aliphatic chains the competition between chain and sugar ordering can be won by the latter. the resulting structure is again in agreement with molecular dynamics simulations.

CPP 2.2 Mon 10:00 H40
The influence of compressed gases on lipid monolayers — FRIEDERIKE GIEBEL, •JULIA NASE, MICHAEL PAULUS, STEFFEN BIEDER, IRENA KIESEL, and METIN TOLAN — Fakultät Physik/DELTA, TU Dortmund, 44221, Dortmund, Germany

An intact cell membrane is essential for the correct functionality of cells in the human body. Depending on their solubility and size, gas molecules can cross the cell barrier by diffusion through the membrane. Thus, the question of how diverse harmful substances can modify membranes is of eminent importance for the understanding of basic mechanisms of malfunctions. To reduce the complexity of the bilayer and gain access to more basic mechanisms, simple lipid monolayers are a well-established model system. These so-called Langmuir layers are formed at the water-gas interface if certain lipids are applied carefully to the water surface.

We investigated the influence of diverse pressurized gases on the structure of a lipid monolayer using high-energy synchrotron radiation at ID10 of ESRF. The vertical structure of the interface was determined via x-ray reflectivity measurements, whereas changes in the lateral structure were detected from GID measurements. We observed an adsorption of gas molecules on the lipid layer. A change in the film structure was evident in the presence of gas, and the Langmuir film remained stable.

CPP 2.3 Mon 10:15 H40
Protein Adsorption at the Electrified Air-Water Interface: Implications on Foam Stability — •BJÖRN BRAUNSCHWEIG, KATHRIN ENGELHARDT, and WOLFGANG PEUKERT — University of Erlangen-Nuremberg, Institute of Particle Technology (LFG), Germany

The interfacial structure of ions, water molecules and surface active proteins as well as their tendency to form foam stabilizing networks can considerably influence and control macroscopic properties of foamy dairy products. The molecular structure and composition of adjacent electric double layers are, however, not yet fully understood on a molecular level. We have applied vibrational sum-frequency generation (SFG) as an inherently interfacial specific probe that provides information on composition and conformation of interfacial layers. In particular, we have addressed the adsorption of bovine serum albumin (BSA) at air-water interfaces and show pH depending charging and electric field-induced polar ordering of interfacial molecules such

as H₂O and BSA. Varying the bulk pH of protein dilutions, changes the SFG intensity of vibrational bands due to interfacial H₂O dramatically while much weaker changes in the protein related Amide I and carboxylate R-COO⁻ bands are observed. Using the intensity of OH vibrational bands as a measure of the interfacial electric field, we have determined the isoelectric point of interfacial BSA. Based on the molecular level information from our SFG and ellipsometric measurements we can link the microscopic properties of BSA at the air-water interface with macroscopic properties such as the stability of BSA foams.

CPP 2.4 Mon 10:30 H40
Nanoparticle-induced permeability of lipid bilayer membranes — SERGEY POGODIN¹, •MARCO WERNER^{2,3}, JENS-UWE SOMMER^{2,3}, and VLADIMIR A. BAULIN^{4,5} — ¹Institut Català d'Investigació Química, Tarragona, Spain — ²Leibniz-Institut für Polymerforschung Dresden, Germany — ³Technische Universität Dresden, Germany — ⁴Universitat Rovira i Virgili, Tarragona, Spain — ⁵ICREA, Barcelona, Spain

Using lattice Monte Carlo simulations with explicit solvent we investigate interactions of nanoparticles with self-assembled bilayer membranes as function of nanoparticle hydrophobicity and heterogeneity of amphiphilic site distribution. Our simulation results indicate, that there is an adsorption transition for nanoparticles at the model membrane for intermediate values of nanoparticle hydrophobicity, where the effective repulsions from solvent- and lipid tail environments are balanced. Close to this transition, we observe a significant frequency increase of nanoparticle translocations through the bilayer as well as an increased bilayer permeability for solvent. Depending on nanoparticle concentration we observe clustering of homogeneous nanoparticles to larger agglomerates perturbing the membrane on a larger scale. Amphiphilic nanoparticles as used in our study do not agglomerate and show an enhanced localization at the bilayer surface as compared to homogeneous nanoparticles.

CPP 2.5 Mon 10:45 H40
Messung des Transfermassenstroms nanoskaliger Partikeln über die Grenzfläche gegensätzlich polarer Flüssigkeiten — •PHILIPP GRIMM¹, JACQUELINE ERLER², URS A. PEUKER² und HANS-JOACHIM SCHMID¹ — ¹Universität Paderborn — ²TU Bergakademie Freiberg

Nanoskalige Organosole werden häufig als Nanokomposite oder im Bereich der Beschichtungstechnologie eingesetzt. Die Synthese der Partikeln findet üblicherweise in wässriger Umgebung statt, was jedoch zu Agglomeration und somit zum Verlust der spezifischen Eigenschaften (z.B. Superparamagnetismus) führt.

Als Transferapparat kommt hierbei eine Einzeltropfensäule zum Einsatz. Das Hauptaugenmerk liegt darin, den Transfermassenstrom in Abhängigkeit der Parameter Grenzflächengröße, Verweilzeit und Tensid- zu Partikelmasse messtechnisch zu erfassen.

Hierzu wird ein neuartiger Aufbau vorgestellt, der die Messung der relevanten Größen mittels Röntgenabsorption ermöglicht. Dieses ist notwendig, da das Stoffsystem bedingt durch Streuung keine optische Zugänglichkeit der Tropfeneigenschaften bietet. Die Röntgenstrahlung durchstrahlt hierbei die Einzeltropfensäule und trifft auf eine CCD-Zeilenkamera, die erlaubt es die Einzeltropfengröße sowie -geschwindigkeit messtechnisch zugänglich zu machen. Die Zeilenkamera wurde mit einer entsprechenden Optik ausgestattet um den relevanten Wellenlängenbereich zugänglich zu machen. Es lassen sich zeitliche Auflösungen im ms-Bereich realisieren.

CPP 2.6 Mon 11:00 H40
Grenzflächeneffekte: Gezielte Nutzung zur Herstellung von Nanopartikeln in Miniemulsionen — •MARION WINKELMANN¹, REINHARD MILLER² und HEIKE P. SCHUCHMANN¹ — ¹Karlsruher Institut für Technologie, Lebensmittelverfahrenstechnik — ²Max-Planck-Institut für Kolloid- und Grenzflächenforschung

In dem vorgestellten Miniemulsionsverfahren wird zunächst eine W/O-Miniemulsion hergestellt und dabei ein wasserlöslicher Reaktand in

der Dispersphase vorgelegt. Danach wird die Miniemulsion mit einem amphiphilen Reaktanden versetzt, der über die von Emulgator belegte Grenzfläche in die Miniemulsionstropfen diffundiert und damit die Partikelbildung durch eine Fällungsreaktion auslöst. Unsere Ergebnisse zeigen, dass die Anwesenheit von Emulgator an der Flüssig/Flüssig-Grenzfläche den Stoffübergang aus der öligen in die wässrige Phase beeinflusst. Entscheidend ist zusätzlich, ob die Grenzfläche belegt oder zunächst unbelegt von Emulgator ist. Liegt eine belegte Grenzfläche vor, wie für die Gewährleistung der Emulsionsstabilität erforderlich, so adsorbiert vergleichsweise weniger Reaktand an die Grenzfläche. Stehen hingegen Reaktand und Emulgator in direkter Konkurrenz um die unbelegte Grenzfläche, befindet sich anteilmäßig mehr Reaktand in der Grenzfläche. Die Grenzflächenbelegung wird somit nicht nur von den Adsorptions- und Desorptionseigenschaften des Reaktanden beeinflusst, sondern auch durch die Prozessführung. Die Prozessführung beeinflusst demnach maßgeblich die Partikelbildung durch Fällung in Miniemulsionen mit. Im Vortrag wird auch gezeigt, wie sich dies auf die resultierende Partikelgröße des gefällten Produkts auswirkt.

15 min. break

CPP 2.7 Mon 11:30 H40

Interfacial roughening and breakup of thin liquid films — ●MARKUS GROSS — ICAMS, Ruhr-Universität Bochum, Germany

A fluid interface in equilibrium is characterised by the presence of thermally excited capillary waves. However, in many cases, such as in phase-separation processes under shear or in pattern-forming systems, interfaces are initially not in equilibrium and it takes a certain time during which the interfaces roughens to reach its equilibrium state. Employing an effective Langevin formalism and simulations of the full fluctuating hydrodynamic equations, we first discuss the different dynamic universality classes of fluid interfacial roughening. Besides being a theoretically interesting non-equilibrium growth phenomenon, interfacial roughness has also important repercussions on the stability of thin films or liquid domains: if the surface tension is low, interfaces fluctuate violently and a breakup of the domain can result. So far, film breakup has typically been studied assuming the dominance of disjoining pressure. Here, we focus on the purely fluctuation-dominated regime, where the breakup is a "rare event" and effects of disjoining pressure are negligible at all times except close to the breakup.

CPP 2.8 Mon 11:45 H40

Between soap bubbles and vesicles: Dynamics of smectic bubbles — ●KATHRIN MAY, KIRSTEN HARTH, TORSTEN TRITTEL, and RALF STANNARIUS — Institute of Experimental Physics, Faculty of Natural Sciences, Otto von Guericke University Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

Smectic bubbles are ideal model systems to study thin closed liquid membranes. A preparation technique for these meniscus-free smectic bubbles is presented. The initially oblong-shaped bubbles perform shape transformations towards the equilibrium sphere shape with minimum surface. The monitoring of these processes is done by optical high-speed imaging. Their shape transformations, especially the changes of the surface area, are analyzed and their dynamic characteristics are compared to classical soap bubbles and vesicles. Small submillimeter bubbles can be studied under normal gravity laboratory conditions. Larger bubbles have been investigated during parabolic flights, which provide a 22 s microgravity phase.

CPP 2.9 Mon 12:00 H40

Structure formation at μ - structured liquid/gas interfaces — ●HANS-GEORG BRAUN, RENE HENSEL, and ANDRE ZAMITH-CARDOSO — Leibniz Institute of Polymer Research Dresden - Max Bergmann Center of Biomaterials, D-01069 Dresden, Germany

Application of microheterogeneous surfaces easily prepared by soft-lithographic patterning techniques has provided deep insights into interfacial processes such as wetting or dewetting, nucleation at patterned solid/liquid interfaces. Much less is known about the formation of microstructured liquid/gas interfaces and their influence on interfacial self-organization processes. This contribution focuses on

- the preparation, surface modification and interfacial stability of floating microstructured polymer membranes by PRINT
- the interfacial stabilization of aqueous liquids by encapsulation in microparticles in so called Liquid marbles and the pH triggered self-organization of peptides into ultrathin gel layers at the liquid/gas interface into these liquid marbles.

c) Finally the interfacial formation of floating calciumcarbonate rafts at the liquid / air interface will be discussed.

- 1) R. Hensel and H.-G. Braun, *Soft Matter* 2012,8, 5293
- 2) H.-G. Braun, A. Zamith-Cardoso, *Colloids and Surfaces: B Biointerfaces*, 2012, 97, 43-50

CPP 2.10 Mon 12:15 H40

Imaging of carbon nanomembranes and graphene with helium-ion microscopy — ●ANDRÉ BEYER, HENNING VIEKER, ANNIKA WILLUNAT, NILS-EIKE WEBER, MATTHIAS BÜENFELD, ANDREAS WINTER, XIANGHUI ZHANG, MIN AI, ANDREY TURCHANIN, and ARMIN GÖLZHÄUSER — Physics of Supramolecular Systems, University of Bielefeld, 33615 Bielefeld, Germany

We present a helium-ion microscopy (HIM) study of carbon nanomembranes (CNMs) and graphene. CNMs are extremely thin (~ 1 nm) nanolayers consisting only of surface-near atoms. They are made via cross-linking of self-assembled monolayers (SAMs) with large-area exposures of electrons, photons or helium ions and subsequent transfer to suitable substrates. In this contribution we demonstrate that imaging of CNMs with HIM is an effective way of their characterization due to the high surface sensitivity of HIM. Patterned radiation exposures allow the fabrication of perforated nanomembranes, e.g. nanosieves. Another way of generating nanopores in homogeneous CNMs is to irradiate them with slow highly charged ions. Imaging such perforated CNMs with HIM yields high signal-to-noise ratios as well as low sample damage. Annealing of CNMs at high temperatures in vacuum transforms them into graphene. HIM images of graphene from SAMs are compared with CVD grown graphene. Capabilities of HIM imaging of freestanding CNMs and graphene will be discussed.

CPP 2.11 Mon 12:30 H40

Structure of nano-phase separated monomolecularly thick water-ethanol layers confined between graphene and mica — ●NIKOLAI SEVERIN, VITALIJ SCENEV, PHILIPP LANGE, IGOR M. SOKOLOV, and JÜRGEN P. RABE — Department of Physics, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

Understanding and control of liquids confined to the nano-scale is of wide interest, e.g., for molecular assays and synthesis to be performed on small scales. We report in-situ scanning force microscopy imaging of graphenes replicating nano-phase separated ethanol-water monomolecular films on an atomically flat mica surface. Graphenes conform to the film topography bending at the boundaries between domains of water and the larger ethanol molecules. The lateral size of molecular domains becomes larger with the graphene thickness, which we attribute to the graphene bending energy. Ethanol and water molecules have been demonstrated to dope graphene negatively and positively, respectively [1]. Consequently, we account for stabilization of the heterogeneity by the counteraction of electrostatic repulsion of the doped charges and line tension controlled by the bending energy of the graphene layers. 1. Schedin, F., et al., *Nature Materials*, 6 (2007) 652.

CPP 2.12 Mon 12:45 H40

Gas permeation through PDMS membranes covered by 2D carbon nanomembranes (CNMs) — ●MIN AI¹, SERGEY SHISHATSKIY², JAN WIND², ANDRÉ BEYER¹, NILS MELLECH¹, ANDREAS WINTER¹, HENNING VIEKER¹, JUN QIU³, and ARMIN GÖLZHÄUSER¹ — ¹Physics of Supramolecular Systems of Surfaces, Bielefeld University — ²Institute of Polymer Research, Helmholtz-Zentrum Geesthacht — ³DSM, The Netherlands

Polymeric ultra-thin films are promising candidates to be used as components in miniaturized electronic, medical or energy devices. In this contribution, we report the fabrication of ultra-thin (~ 1 or 3 nm) carbon nanomembranes (CNMs). Organic self-assembled monolayers were irradiated by electrons, leading to a two-dimensional cross-linked CNM through dehydrogenation and recombination mechanisms [1]. The 1-nm- or 3-nm-thick CNMs with an area of 1.2 square centimeters were then transferred onto polydimethylsiloxane (PDMS) composite membranes. The CNM-PDMS membranes were analyzed by XPS, SFM and Helium Ion Microscopy. Gas permeances of H₂, He, CO₂, O₂, N₂, Ar, CH₄, C₂H₆ were measured using "constant volume variable pressure" technique. The new CNM-PDMS composite membranes exhibited significantly lower permeances for all the gases than the PDMS composite membrane and different gas selectivities from the PDMS membrane.

[1] A. Turchanin, D. Käfer, M. El-Desawy, Ch. Wöll, G. Witte, A. Gölzhäuser, *Langmuir* 25, 7342 (2009).

CPP 2.13 Mon 13:00 H40

Living polymer system in contact with a solid substrate.

— •DEWEN SUN and MARCUS MÜLLER — Institut für Theoretische Physik der Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077, Göttingen, Niedersachsen, Deutschland

Systems, in which polymerization takes place under the condition of chemical equilibrium between polymers and their respective monomers are termed "living polymer systems". The reversible bonding gives rise to a chain length polydispersity in these complex polymer fluids. Using computer simulation of a soft, coarse-grained model, we investigate how the presence of a solid substrate influences the behavior of living polymer system in the narrow interface between a solid substrate and a polymer melt and in the wider interphase region. We observe that the contact with a solid substrate in a film geometry alters the local mean molecular weight and the local molecular weight distribution and we discuss the changes as a function of the scission energy.

CPP 2.14 Mon 13:15 H40

Fast formation of roughness correlation in thin spray-coated polystyrene homopolymer film

— •JAN PERLICH, ADELIN BUFFET, MATTHIAS SCHWARTZKOPF, GERD HERZOG, BERIT HEIDMANN, STEPHAN V. ROTH, and RAINER GEHRKE — Deutsches Elektronen-

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Thin polymer films form smooth films with correlated interfaces, so-called conformal roughness, under suitable preparation conditions in dependence of the polymer characteristics [1,2]. The directed replication of the substrate features to a certain cut-off length is highly desirable. Hence, insight into the formation process is required. We present the fabrication of such a thin film of a polystyrene homopolymer via spray-coating. The spray-coating process is monitored in situ real-time by microbeam grazing incidence small angle X-ray scattering (microbeam-GISAXS) performed at the synchrotron beamline P03 (MiNaXS) of PETRA III (DESY) in Hamburg [3]. The dedicated in situ setup provides a time resolution in the millisecond regime enabling the observation of the fast formation of roughness correlation in the thin film upon drying of the polystyrene homopolymer solution. The recorded scattering signals reveal the information to extract the evolution of the correlation and cut-off lengths as well as the corresponding time constants in the formation process.

[1] P. Müller-Buschbaum et al., *Macromolecules* 31 (1998) 3686.

[2] J. S. Gutmann et al., *Physica B* 283 (2000) 40.

[3] A. Buffet et al., *J. Synchrotron Rad.* 19 (2012) 647.