

## CPP 47: Fluids and Interfaces I

Time: Wednesday 16:15–18:15

Location: ZEU 255

## Invited Talk

CPP 47.1 Wed 16:15 ZEU 255

**Hard science with soft spheres: learning from foams and emulsions** — •WIEBKE DRENCKHAN-ANDREATTA — Institut Charles Sadron, CNRS UPR22, Srasbourg, France

Who has not marvelled at the delicate organisation of bubbles floating on top of a beer or a bathtub? Or similarly, of oil drops hovering on the surface of a soup or a vinaigrette? Under gravity, those soft and frictionless bubbles and drops snuggle neatly together, creating sphere-type packings where the influence of gravity is small, and polyhedral packings, where the influence of gravity is important.

Being able to understand and to predict these packings has challenged physicists and mathematicians alike; and their close collaboration has brought forward an increasingly deep understanding of the intriguing features that characterise the packing procedures and the final structure of foams and emulsions.

Building on these advances, physical chemists are now joining this subject. The necessity of stabilising foams or emulsions with interfacially active agents (soap-like molecules, block-copolymers, particles,...), provides a vast playground to tune (and to understand) the interactions of these soft spheres via specific modifications of their surfaces: How do the interactions change if the bubbles/drops are covered by a visco-elastic skin? How to they pack if this skin creates non-negligible friction? And what if these spheres are adhesive?

In this presentation I will give an overview of the state of the art of this interdisciplinary field in bridging historical aspects with recent findings.

CPP 47.2 Wed 16:45 ZEU 255

**The role of aggregates in the stabilization of protein foams** — •MANUELA E. RICHERT and BJÖRN BRAUNSCHWEIG — Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

Native and fluorescein isothiocyanate (FITC) labelled bovine serum albumin (BSA) were used to investigate the role of protein aggregates in the stabilization of aqueous protein foams through structure-property relations that reach from the molecular to the macroscopic scale. Protein modified air/water interfaces, which are ubiquitous in aqueous foam, were studied with tensiometry and vibrational sum-frequency generation (SFG). At the air/water interface, SFG and tensiometry provide information on coverage and the net charging state of the interface and thus information on the isoelectric point (IEP) of labelled and native BSA proteins at the air/water interface is gained. At the interfacial IEP a reversal of the phase of OH stretching bands from interfacial H<sub>2</sub>O molecules is observed in SFG spectra and corresponds to a minimum in the surface tension. The latter can be attributed to the formation of protein aggregates at the interface which promotes macroscopic foam stability. Using confocal fluorescence microscopy aggregates of labelled proteins are found to be predominantly located inside foam lamella where they possibly form a gel-like network and thus cause non-DLVO like interactions.

CPP 47.3 Wed 17:00 ZEU 255

**Ultra-thin Polymer Films at the Air/Water Interface: Lateral and vertical structure of poly (butyl acrylate) during compression** — •CHRISTIAN APPEL and BERND STÜHN — Institut für Festkörperphysik, Technische Universität Darmstadt, D-64289 Darmstadt, Germany

The behaviour of poly (butyl acrylate), PBA, spread readily at the a/w interface is well studied. It forms stable films that become elastic at high surface pressures (20–30 mN/m).<sup>[1]</sup> We prepare Langmuir monolayers of PBA and the diblock copolymer poly(ethylene glycol)-PBA with different molecular weights from 5 kg/mol to 20 kg/mol. The PEG block acts as a small hydrophilic anchor ( $N_M < 10$ ).

We perform in-situ Brewster-Angle-Microscopy (BAM) and in-situ X-Ray reflectometry (XRR) to get a thorough understanding of the film structure. For the dilute and semi-dilute regime the surface pressure and coverage follows the expected scaling laws. In the concentrated regime there is a transition from a continuous water-free monolayer to a more complex structure. At first in the semi-dilute regime, XRR and BAM show a single monolayer structure of the film. During the compression to the concentrated regime the lateral structure of the film changes to 2D-disks of PBA within the monolayer. This

is complementarily observed by XRR (Yoneda peak and off-specular intensity) and BAM. Hysteresis experiments indicate that a part of the monolayer is irreversible deformed within the concentrated regime.

<sup>[1]</sup> K. Witte et al., *Macromolecules* 43, 2990–3003 (2010)

CPP 47.4 Wed 17:15 ZEU 255

**Influence of Surfactant Chain Length on the Interfacial Structure and Properties of Surfactant/Polyelectrolyte Mixtures** — •FELIX SCHULZE-ZACHAU and BJÖRN BRAUNSCHWEIG — Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany

Mixtures of poly(sodium 4-styrenesulfonate) (NaPSS) polyelectrolytes and 0.1 mM alkyltrimethylammonium bromides C<sub>16</sub>TAB, C<sub>14</sub>TAB and C<sub>12</sub>TAB surfactants were studied at the air/water interface with tensiometry, ellipsometry and vibrational SFG spectroscopy as a function of PSS concentration. In addition, macroscopic foams from these mixtures were studied in order to relate the interfacial molecular structure and its charging state to foam stability.  $\zeta$ -potential and turbidity measurements were done to investigate charge and equilibrium states of the respective systems in the bulk solution. The chemical potential of the surfactants to bind to PSS increases with their chain length, which results in different interfacial structures. For C<sub>16</sub>TAB, charge neutralization in the bulk and at the interface is observed close to equimolar concentrations and leads to bulk solutions that are far outside the thermodynamic equilibrium. Here, hydrophobic complexes aggregate and precipitate for C<sub>16</sub>TAB while binding to PSS is much weaker for C<sub>14</sub>TAB and C<sub>12</sub>TAB where no precipitation is observed. In case of C<sub>16</sub>TAB/PSS mixtures, SFG spectra indicate a phase shift of the water molecules that is indicative for a charge reversal at the interface at 0.09 mM. Complementary methods indicate a depletion of complexes from the interface when this point of zero charge is crossed.

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**Tuning protein adsorption using multivalent ions** — •MADELEINE FRIES<sup>1</sup>, FRANK SCHREIBER<sup>1</sup>, FAJUN ZHANG<sup>1</sup>, ALEXANDER HINDERHOFER<sup>1</sup>, ROBERT JACOBS<sup>2</sup>, and MAXIMILIAN SKODA<sup>3</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — <sup>2</sup>Chemistry Research Laboratory, University of Oxford, Oxford, OX1 3TA, United Kingdom — <sup>3</sup>Rutherford-Appleton Laboratory, ISIS Facility, Didcot, OX11 0QX, United Kingdom

We studied protein (bovine serum albumin, BSA) adsorption at the solid-liquid interface tuned by trivalent ions ( $Y^{3+}$ ) using ellipsometry, neutron reflectivity and quartz-crystal microbalance. We find re-entrant behavior of the interface adsorption, which increases upon approaching  $c^*$  and decreases above  $c^{**}$ , where  $c^*$  and  $c^{**}$  are the corresponding critical concentrations marking the region of the re-entrant condensation behavior in the bulk. We thus manage to relate the rich bulk phase behavior, which also features liquid-liquid phase separation and new pathways to crystallization [1] discussed in terms of an ion-activated attractive patch model [2], to the interface adsorption behavior. In addition to the general challenge of connecting bulk and interface behavior, our work has implications for, inter alia, nucleation at interfaces.

[1] Zhang, F. et. al, *Physical Review Letters* 2008, 101 (14), 148101.

[2] Roosen-Runge, F.; Zhang, F.; Schreiber, F.; Roth, R., *Scientific reports* 2014, 4, 7016.

CPP 47.6 Wed 17:45 ZEU 255

**Solvent Extraction: Structure of the Liquid-Liquid Interface Containing a Diamide Ligand** — •ERNESTO SCOPPOLA<sup>1</sup>, ERIK WATKINS<sup>2</sup>, RICHARD CAMPBELL<sup>3</sup>, OLEG KONOVALOV<sup>4</sup>, LUC GIRARD<sup>5</sup>, IGNACIO RODRIGUEZ-LOUREIRO<sup>1</sup>, JEAN-FRANÇOIS DUFRÈCHE<sup>5</sup>, GEOFFROY FERRU<sup>6</sup>, GIOVANNA FRAGNETO<sup>3</sup>, EMANUEL SCHNECK<sup>1</sup>, and OLIVIER DIAT<sup>5</sup> — <sup>1</sup>Max Planck Institut of Colloids and Interfaces, Potsdam, Germany — <sup>2</sup>LANL, Los Alamos, USA — <sup>3</sup>ILL, Grenoble, France — <sup>4</sup>ESRF Grenoble, France — <sup>5</sup>ICSM, Bag-nols sur Cèze Cedex, France — <sup>6</sup>ANL, Lemont, USA

Knowledge of the (supra)molecular structure of an interface that contains amphiphilic ligand molecules is necessary for a full understanding of ion transfer during solvent extraction. Even if molecular dynamics simulations already yield some insight in the molecular configurations in solution, hardly any experimental data giving access to distributions

of both ligands and ions at the liquid\*liquid interface exist. Here, the combined application of X-ray and neutron reflectometry represents a milestone in the deduction of the interfacial structure and potential with respect to different lipophilic ligands. It is also shown that neutron reflectometry can specifically reveal the ion distribution at the interface when neutron absorption and neutron-induced gamma-fluorescence are analyzed. To this end we show that hard trivalent cations can be repelled or attracted by the ligand-enriched interface depending on the nature of the ligand. References: 1.Scoppola E et al. (2016) Solvent Extraction: Structure of the Liquid-Liquid interface containing a Diamide ligand. *Angewandte Chemie International Edition* 55 (32), 9326.

CPP 47.7 Wed 18:00 ZEU 255

**Light-switchable molecules at planar fluid interfaces** — ●JOSUA GRAWITTER and HOLGER STARK — Institut für Theoretische Physik, Technische Universität Berlin, 10623 Berlin, Germany

Surfactants are part of many self-assembled structures in soft matter, from biological membranes to liquid foams. Especially promising are surfactants which change shape under illumination, so-called *photosensitive surfactants*, because their isomer densities can locally be manipulated with light.

We study their dynamics at a planar fluid interface using a coarse-grained theory for a surfactant mixture, which follows previous research on surfactant-driven droplets [1, 2]. The theory takes into account light-switching, surfactant adsorption, diffusion, mean field interactions, and advection due to Marangoni flow, which is initiated by gradients in surface tension. We present an exact solution of the incompressible Stokes flow for two immiscible fluids with an arbitrary field of surface tension at a planar interface. Using our theory we calculate the dynamic profiles of photosensitive surfactants driven by spots of light with intensities either constant in time or oscillating.

[1] M. Schmitt and H. Stark, *Europhys. Lett.* **101**, 44008 (2013).

[2] M. Schmitt and H. Stark, *Phys. Fluids* **28**, 012106 (2016).