



## Workshop 5

### Scattering from Liquid Surfaces and Interfaces

#### X-ray Studies of the Interface between Two Polar Liquids: Neat and with Electrolytes

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The interfacial distribution of ions at liquid interfaces is important for many processes of scientific and industrial interest. X-ray reflectivity is used to probe the interface between two polar liquids both with and without dissolved electrolytes. The measured width of the neat nitrobenzene/water interface differs from predictions by standard capillary wave theory with a progressively smaller deviation with increasing temperature. Computer simulations suggest the presence of both molecular layering and dipole ordering parallel to the interface. Either layering or a bending rigidity, which may result from dipole ordering, can explain the measured widths. Addition of the electrolytes TBABr to the water and TBATPB to the nitrobenzene induces an electrostatic potential across the interface. For larger potential (fixed by the electrolyte concentration), the electrolyte distribution differs from the Gouy-Chapman prediction. Deviations from this classical theory are also measured in studies of the interface between an aqueous solution of  $\text{BaCl}_2$  and a nitrobenzene solution of TBATPB. In this case, the electrostatic interfacial potential is varied externally. Electrolyte distributions that fit these data will be discussed.

#### Molecular Dynamics of the Liquid-Liquid Interface

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Over the last decade, numerous molecular dynamics simulations have suggested that the interface between two immiscible liquids is molecularly sharp and dynamically rough. The dynamic roughness can be described as molecular-sized protrusions of one liquid into the other with a size distribution that approximately follows capillary wave theory down to the bulk correlation length. We show that this dynamic roughness has important implications for hydrogen bond dynamics. Other things being equal, the hydrogen bond lifetime lengthens as the degree of roughness increases. We discuss the implications of these and other surface characteristics to ion hydration and transport at the interface.

## **Organic-Template-Directed Growth of Inorganic Films: Epitaxy and Reconstruction without UHV**

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Langmuir monolayers floating on aqueous solutions can be used as templates for the nucleation of inorganic minerals. Such nucleation is analogous to biomineralization and may ultimately provide new ways to control the growth of inorganic materials and thin films. This talk will describe our *in situ* x-ray scattering studies of the soft-hard interface during nucleation. We find a variety of phenomena familiar in studies of inorganic surfaces, but previously seen only when the surfaces are kept very clean either electrochemically or in UHV. Implications for “real” biomineralization will be discussed.

## **Mineralization at a Monolayer: Questions about Structure and Answers about Kinetics**

E. DiMasi

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Liquid-surface x-ray scattering is an important and still under-utilized tool for examining mineralizing interfaces, which can be studied to gain insight into the fascinating process of biomineralization. One 15-year-old school of thought regarding stereochemical registry of minerals at Langmuir films has now been disproven by x-ray techniques. Instead, kinetics has been shown to play the predominant role in the nucleation of calcium carbonate. More recent research has followed two slightly distinct approaches. In one, systems are engineered to increase the role of the interface as a structural template for crystallization. This talk will focus upon a second approach, which is to investigate kinetics in further detail, including the existence of amorphous precursor phases in  $\text{CaCO}_3$  mineralization. Technical aspects discussed along the way will include the challenges of data collection and the modeling of large surfactant molecules in reasonable ways.

## **Thermal Capillary Fluctuations from Liquid Surfaces: Surface Structure and Surface Tension**

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The effect of long-wavelength thermally excited capillary fluctuations on x-ray scattering from liquid surfaces will be reviewed in the context of efforts to measure effects associated with short-wavelength fluctuations. We will argue that the properties of long-wavelength fluctuations are sufficiently well understood that their effects on the reflectivity from the liquid surfaces can be quantitatively removed in order to measure the intrinsic form factor. We will show that, although water and liquid potassium have similar surface tensions, the surface form factor for water does not display surface-induced layering like that observed for potassium. Furthermore, the form factor of potassium is essentially identical to that of metals like gallium and indium, whose surface tension is nearly an order of magnitude larger [1, 2]. Finally we will show recently observed examples of anomalous surface form factors for liquid Sn and for two eutectic mixtures that are promising candidates for Pb-free solders,  $\text{Bi}_{43}\text{Sn}_{57}$  and  $\text{Au}_{80.5}\text{Si}_{19.5}$  [3, 4].

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- [3] O.G. Shpyrko, A.Y. Grigoriev, R. Streitel, D. Pontoni, P.S. Pershan, M. Deutsch, and B.M. Ocko, "Atomic-scale surface demixing in a eutectic liquid BiSn alloy," submitted (2005).
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## Langmuir Films on the Liquid Mercury Surface

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The structure and phase behavior of organic monolayers on surfaces depends sensitively on the details of the molecular interactions. Liquid subsurfaces (water, mercury and alkanes) provide the possibility of investigating fundamental aspects of thin organic films, in the absence of strong substrate interactions, such as those for self-assembled-monolayers on Au(111). Results will be presented for thiols, fatty acids, alcohols, and alkanes on liquid mercury.

For octadecanethiol monolayers on liquid Hg surfaces, the structure evolves with increasing coverage from a laterally disordered phase of surface-parallel molecules to an ordered rotator phases of surface-normal molecules. For the latter, an abrupt transition is found at  $19 \text{ \AA}^2/\text{molecule}$  from a rectangular packing of molecules tilted by  $27^\circ$  in the nearest-neighbor direction to a hexagonal unit cell of untilted molecules. The unit cell of the tilted phase is centered for the chains and noncentered for the headgroups. The thiol headgroups associate in pairs with a single Hg atom, and the bonds form long-range orientational order. The different order of thiols on Au(111) and on Hg highlights the subphase's role in determining the overlayer's structure. Recent results of organic monolayers, sandwiched between silicon and mercury, will also be presented.

Self-assembly of organic films on a liquid metal, O.M. Magnussen, B. M. Ocko, M.D. Deutsch, M.J. Regan, P.S. Pershan, D.A. Abernathy, G. Grubel, and J.F. Legrand, *Nature* **384**, 250-152 (1996).

Structure of a Langmuir film on a liquid metal surface, H. Kraack, B. Ocko, P. Pershan, and M. Deutsch, *Science* **298**, 1404 (2002).

Langmuir films of normal-alkanes on the surface of liquid mercury, H. Kraack, B. Ocko, P. Pershan, E. Sloutskin, and M. Deutsch. *J. Chem. Phys.* **119**, 10339 (2003).

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Crystalline phases of alkyl-thiol monolayers on liquid mercury, B.M. Ocko, H. Kraack, P. Pershan, E. Sloutskin, L. Tamam, and M. Deutsch. *Phys. Rev. Lett.* **94**, 017802 (2005).

Direct Structural Observation of a Molecular Junction using High-Energy X-ray Reflectometry, M. Lefenfed, J. Baumert, E. Sloutskin, P. Pershan, M. Deutsch, C. Nuckolls, and B. M. Ocko (submitted to *Nanoletters*)

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## **Diffuse Scattering from the Liquid-Vapor Interfaces of Pure Metals and Alloys**

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I will review recent experimental studies of diffuse x-ray scattering from the liquid-vapor interfaces of Ga and dilute binary alloys of Bi, Tl and Pb in Ga. The data will be used to examine aspects of the Mecke-Dietrich theory of the wavelength dependence of the liquid-vapor interfacial tension as applied to liquid metals. Differences between the character of the diffuse scattering from the liquid-vapor interface of Ga and from the liquid-vapor interfaces of Bi, Tl and Pb in Ga will be discussed, and a new mode of excitation of the surfaces of such binary alloys, that does not appear in the pure liquid case, with a model that represents the diffuse scattering, will be postulated.

## **Studies of Fluctuations on Thin Films of Polymer Melts**

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Studies of surface (capillary wave) fluctuations on polymer films using the techniques of x-ray scattering have yielded a number of intriguing results over the last few years and indicate that, unlike the surfaces of simple liquids, the dynamics of polymer surfaces and interfaces need to be understood in greater detail. In particular, issues such as interaction with the substrate, chain-entanglement effects, and the approach to the glass transition all affect the dynamics at the surface. We shall review some recent results on polystyrene films of different thicknesses and at different temperatures obtained from studies of off-specular diffuse (static) scattering (which measures the static height-height correlation function) and also using the relatively new technique of x-ray photon correlation spectroscopy (XPCS), which is the analogue of dynamical light scattering and measures the dynamical height-height correlation function. Both these techniques extend the lateral length-scales that can be probed to at least an order of magnitude smaller than those observable with light scattering. We shall discuss to what extent these results can be described by the ordinary capillary wave theory for liquid surfaces.

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## **Dynamics in Confined Polymer Films**

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Viscosity measurements of ultrathin polymer films were performed using three different complementary techniques. The results from all three methods were consistent with each other and indicated that proximity to surfaces produces a significant increase in the viscosity. A similar increase is also observed when interacting nanoparticles are used. An open question still remains as to the time scale of the different methods. For example, when techniques that rely on dewetting velocities are used, shear thinning may be a factor, whereas, when diffusion

measurements are performed, only the zero shear viscosity is probed. Correlated x-ray reflection on the other hand, can yield information as a function of shear rate, as well as proximity to the surface. The effects of planar surfaces can then be compared to more complicated structures, such as nanoparticles of different aspect ratios.

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### **Cholesterol/Phospholipid Interactions: Evidence of Ordering and Displacement of Cholesterol by Alcohol**

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One of the models for the interaction of cholesterol with phospholipids predicts the existence of stoichiometric complexes. The phase diagrams of these cholesterol-lipid mixtures exhibit two distinct humps along with a sharp cusp, pointing to a particular stoichiometry for possible lipid/cholesterol complex formation. It has been hypothesized that mixtures with cholesterol content greater than that at the cusp leads to the presence of reactive cholesterol monomers. To test this cholesterol monomer hypothesis, we have examined how the presence of alcohol alters the lipid/cholesterol phase diagram. Although binary mixtures of lipid and alcohol do not exhibit any mixing/demixing line like lipid/cholesterol mixtures, lipid/cholesterol/alcohol systems in which various mole fractions of cholesterol are replaced by alcohol reproduce the identical phase diagram as the lipid/cholesterol system, with the cusp position unaltered. We have also examined the uptake of cholesterol by beta-cyclodextrin in both binary and ternary systems. Our results indicate that the uptake of cholesterol is large in the ternary system as long as the total mole fraction of cholesterol and alcohol exceed that given by the cusp. This suggests that alcohol interacts more strongly with lipids and displaces cholesterol in the process. By so doing, the presence of alcohol results in the production of free cholesterol monomers even when the actual cholesterol content is low. We have also used grazing incidence x-ray diffraction techniques on these binary and ternary mixtures and have observed the presence of a broad Bragg peak, indicative of the formation of an ordered phase with short-ranged order. These peaks are very different from the ordering of single-component lipid or binary mixtures of lipid in the absence of cholesterol. Our results indicate the existence of crystalline order, with coherence length of several molecular dimensions, in mixed lipid/cholesterol systems.

## **X-ray Scattering Studies of Amphiphilic 4-Helix Bundle Peptides Vectorially Oriented at Soft Interfaces**

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Amphiphilic 4-helix bundle peptides have been designed to incorporate both biological and non-biological cofactors. An ensemble of these peptide-cofactor complexes, vectorially oriented at a soft interface between polar and nonpolar media, can provide for the translation of their designed molecular function into a macroscopic material property of the interface. Such amphiphilic 4-helix bundle peptides can also serve as model integral membrane proteins for vectorial incorporation into a lipid bilayer providing a molecular laboratory for the detailed study of structure-function correlations, for example, the mechanism by which anesthetic binding to a designed cavity within its hydrophilic domain modulates the ion-channel activity of its hydrophobic domain. Detailed structural studies of these amphiphilic peptides within such non-crystalline ensembles can be performed utilizing an essential combination of x-ray scattering, neutron scattering, and molecular dynamics simulation techniques. In particular, resonance and nonresonance x-ray reflectivity and grazing-incidence x-ray diffraction can provide key structural information.

## **Poisson-Boltzmann Model Predictions for Monovalent Ions near Charged Planar Interfaces versus Experimental Data**

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Surface-sensitive synchrotron x-ray studies have been used to determine the distribution of monovalent counterions ( $\text{Cs}^+$ ) near planar charged interfaces, formed by spreading dihexadecylphosphate (DHDP) at the air/solution (CsI) interface, with lateral charge-density of one electronic charge per DHDP molecule. Combined analysis of x-ray reflectivity measurements taken at the Cs  $L_{\text{III}}$  electron binding energy (5012 eV) and off resonance (16200 eV) at various bulk concentrations, yields the distribution profile of the adsorbed  $\text{Cs}^+$  counterions. Our results show that the number of counterions ( $\text{Cs}^+$ ) in the region near the interface increases with bulk salt concentration as a power law, in disagreement with predictions from simple and modified Poisson-Boltzmann models. Implications of our results for theoretical models and for some thermodynamical observables will be discussed.