

**MS89 STRUCTURAL CHARACTERIZATION OF CONTROLLED SOLID-LIQUID INTERFACES****Chairpersons:** José Martín-Gago, Giovanna Fragneto**MS89.30.1***Acta Cryst.* (2005). A61, C113**Neutron Reflection from Complex Layers Adsorbed at the Solid/Aqueous Interface****Robert K. Thomas**, *Physical and Theoretical Chemistry Laboratory, University of Oxford*. E-mail: robert.thomas@chemistry.oxford.ac.uk

Neutron reflection gives information about structure of a layer normal to an interface and also about composition. Adsorption at solid/aqueous interfaces often leads to bilayer and more complicated structures with thicknesses in the range 20-100 Å. This is the range of optimum sensitivity of the neutron technique. Given also that isotopic labelling may be used to discriminate the different components within a mixture or within a molecule, the technique is uniquely sensitive to complex structures at these interfaces. Examples of the application of neutron reflection to bilayers, bilayer mixtures and to the evolution of structure during enzyme attack of the bilayer will be given.

**Keywords:** neutron reflection, interfaces, applications of neutron reflection**MS89.30.2***Acta Cryst.* (2005). A61, C113**Self Assembled Thiols Monolayers on Au(111) Surfaces: Structure Defects and Dynamics****Roberto C. Salvarezza**, *Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA) Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina*. E-mail: robsalva@inifta.unlp.edu.ar

Alkanethiolate self-assembled monolayers (SAMs) on metals, particularly alkanethiolates on Au, Ag and Cu have attracted considerable scientific and technological attention because they provide a route to control corrosion, wetting and wear properties of metal surfaces, they serve to anchor different functional groups used as chemical and biochemical sensors, they are used as building blocks in nano-devices for electronics, and they are promising candidates as surface active agents in new nano/microfabrication methods. Two-dimensional alkanethiolate SAMs result from the self-assembly of molecules on a metal surface by simple adsorption from the vapor or liquid phases. The control of SAMs quality is a crucial point in many technological applications of SAMs. Here we discuss surface structures, adsorption sites, defects and dynamics of alkanethiolate and sulfur adlayers formed on Au(111) substrates. By using in situ and ex situ STM combined with AES, XPS, and SXRD a detailed picture at the molecular levels of these fascinating two-dimensional structures is presented.

**Keywords:** surfaces, defects, dynamics**MS89.30.3***Acta Cryst.* (2005). A61, C113**Fluctuations of a Single floating Lipid Bilayer: a Specular and Off-specular Reflectivity Study****Thierry Charitat**<sup>a</sup>, Jean Daillant<sup>b</sup>, Edith Bellet-Amalric<sup>c</sup>, Alan Braslau<sup>d</sup>, Giovanna Fragneto<sup>e</sup>, François Graner<sup>f</sup>, Serge Mora<sup>d</sup>, François Rieutord<sup>h</sup>, Barry Stidder<sup>c</sup>, <sup>a</sup>ICS-Université Louis Pasteur, Strasbourg, France. <sup>b</sup>LIONS-CEA, Saclay, France. <sup>c</sup>DRFMC-CEA, Grenoble, France. <sup>d</sup>SPEC-CEA, Saclay, France. <sup>e</sup>Institut Laue Langevin, Grenoble, France. E-mail: charitat@ics.u-strasbg.fr

We have recently succeeded in preparing samples consisting of a homogeneous lipid bilayer (di-acyl phosphocholines, with 16 to 20 carbons per chain), floating near an identical bilayer deposited on the surface of a silicon single crystal.

I will first present a neutron specular reflectivity study of the temperature effect on such a floating bilayer. We determine both average and r.m.s. positions of the floating bilayer and observe a large increase of the water layer spacing. I will present an interpretation of this effect in terms of competition between the interbilayer potential

and membrane fluctuations leading to an estimation of bending rigidity of the bilayer.

In the second part, I will present recent off-specular x-ray reflectivity results. We measure for the first time the fluctuation spectrum in submicrometric range on a single fluctuating bilayer leading to the determination of three main physical quantities which govern the bilayer height fluctuations: bending modulus, surface tension and wall attraction potential.

[1] Charitat T., Bellet-Amalric E., Fragneto G., Graner F. *Eur. Phys. J. B*, 1999, **8**, 583. [2] Fragneto G., Charitat T., Bellet-Amalric E., Cubitt R., Graner F. *Langmuir* 2003, **19**, 7695. [3] Daillant J., Fragneto G., Charitat T., Bellet-Amalric E., Cubitt R., Graner F. *submitted to PNAS* 02/2005.

**Keywords:** membrane structure, X-ray neutron reflectivity, X-ray diffuse scattering**MS89.30.4***Acta Cryst.* (2005). A61, C113**The New Distributions of Water Molecules at Ni(111)-2x2-O and Cu(111) Electrode Interfaces****Masatoki Ito**<sup>a</sup>, Masashi Nakamura<sup>b</sup>, <sup>a</sup>Department of Chemistry, Keio University, <sup>b</sup>Chiba University, Japan. E-mail: masatoki@chem.keio.ac.jp

[I] The structures of a monomeric water molecule adsorbed on  $p(2 \times 2)$ -Ni(111)-O surface were determined by difference Fourier calculations (unique reflection intensities observed are 120(140K) and 80(25K)). At temperatures of 25 K, water molecules chemisorb predominantly at  $2 \times 2$  oxygen atom sites, forming an OH---O<sub>ad</sub> ( $2 \times 2$ ) hydrogen bond. A  $2 \times 2$  oxygen atom (O<sub>ad</sub>) is surrounded by one to three monomeric water molecules, which take statistically disordered positions with threefold symmetry. At temperatures of 140 K, monomeric water molecules occupy a top site of Ni atoms via an oxygen lone pair and are stabilized as a singleton molecule on the surface with a distance of 0.2241(22) nm.

[II] Further, we report surface X-ray scattering measurements result of the water distribution perpendicular to a Cu(111) electrode in 0.05M H<sub>2</sub>SO<sub>4</sub> solution at -0.40V (vs, NHE). The new water phase on Cu(111) was found with a space group, P3m1, a=b=0.31 nm, c=0.63 nm, Z=3, ρ=1.62(g/cm<sup>3</sup>). The important features of the water distribution are (1) the network structure is a simple closest pack type and not a honeycomb or a diamond-like structure, (2) oxygen positions of water molecules show continuous disordering in time and space (fluctuating), (3) configuration around oxygen is not a tetrahedral but a three (or six) coordination. Proton (electron) transfer across water double layer could be facilitated by flipping of water molecule toward the electrode surface.

**Keywords:** water adsorption, water double layers, new water structure**MS89.30.5***Acta Cryst.* (2005). A61, C113-C114**Structural Dynamics of the Competing Forces of Light and Matter****Jens Wenzel Andreasen**<sup>a</sup>, Dag Werner Breiby<sup>a</sup>, Sonja Rosenlund Hansen<sup>a</sup>, P.S. Ramanujam<sup>b</sup>, Martin Drews<sup>a</sup>, Martin Meedom Nielsen<sup>a</sup>. <sup>a</sup>Danish Polymer Centre, Risø National Laboratory. <sup>b</sup>Optics and Plasma Research Department, Risø National Laboratory, Denmark. E-mail: jens.wenzel.andreasen@risoe.dk

The microstructure of azobenzene-based and azobenzene dyedoped liquid crystals deposited on pre-aligned polymer surfaces has been studied by grazing incidence X-ray diffraction (GIXRD) at the HASYLAB synchrotron facility and by optical measurements. It is demonstrated that a high degree of in-plane (azimuthal) orientation is induced by the alignment layer.

Irradiating the sample with a laser induces trans-cis isomerisation of the azobenzene. This provides a torque when the polarisation direction of the laser light is at an angle to the alignment layer orientation, causing a re-orientation of the liquid crystal structure, directly observable by GIXRD. When the laser light is switched off, the structure re-aligns with the alignment layer during a relaxation period of several minutes. This has been observed with different kinds

of liquid crystals on several types of alignment layers.

The results provide direct evidence for the structural dynamics responsible for laser-induced anisotropy as observed by polarisation holography [1], and gives an intriguing insight into the interaction of forces acting on liquid crystal molecular arrangements.

[1] Berg R.H., Hvilsted S., Ramanujam P.S., *Nature*, 1996, **383**, 505.

**Keywords:** liquid crystals, laser-induced alignment, grazing incidence X-ray diffraction

#### MS90 APPLYING NON-CRYSTALLOGRAPHIC ALGORITHMS TO CRYSTALLOGRAPHY

**Chairpersons:** Ralf W. Grosse-Kunstleve, Maryjane Tremayne

##### MS90.30.1

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##### Cluster Analysis in Crystallography

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Cluster analysis is a well established tool in statistics, but one that is used surprisingly little in crystallography despite its considerable potential. We have established its use in several diverse areas of crystallography, in particular:

1. Pattern matching in powder X-ray diffraction: High throughput screening experiments designed to search for polymorphs and salts of drug candidates use PXRD to characterize the results, and this produces large quantities of data. We show how pattern matching methods based on appropriate correlation coefficients can be used in conjunction with clustering calculations to classify patterns automatically [1,2].

2. Databases: Database searching using the Cambridge Structural Database (CSD) [3] can produce thousands of 'hits' if a simple fragment is used, and as a result processing and interpreting the results becomes a considerable task. Cluster analysis using dendrograms, metric multidimensional scaling and suitable visualization tools can reduce the workload to a few hours of computer time with minimal user intervention.

3. Indexing powder patterns: In difficult indexing problems, it is possible to produce a large number of potential unit cells with figures of merit that are only marginally useful. Cluster analysis can be useful here, especially when self-organizing maps are utilised.

[1] Gilmore C.J., Barr G., Paisley J., *J. Appl. Cryst.*, 2004, **37**, 231-242. [2] Barr G., Dong W., Gilmore C.J., *J. Appl. Cryst.*, 2004, **37**, 243-252. [3] Allen F.H., Motherwell W.D.S., *Acta Cryst.*, 2002, B58, 407-422.

**Keywords:** cluster analysis, pattern matching, databases

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##### Crystal Structures from Powder X-ray Diffraction using Genetic Algorithms

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Contemporary advances of direct space strategies in solving crystal structures directly from powder X-ray diffraction data [1,2], and in particular, the success of the Genetic Algorithm method [3], have opened up a whole area of research which has hitherto been inaccessible even as recent as fifteen years ago. Applications to the study of synthetic products *in situ*, as well as the tackling of structural problems which have the complexity of more than one molecule in the asymmetric unit, are now at the forefront of these techniques. In addition to tackling such new challenges, structure solution strategies employing other analytical or computational methods have become a natural complement alongside the X-ray diffraction data. For example, multi-component molecular co-crystals have been prepared by an *in situ* solid state grinding process, yet have been solved using a combination of powder X-ray diffraction and solid state NMR techniques [4]. Moreover, the collection and assessment of reliable

powder diffraction intensity prior to structure solution calculations is an avenue of study that shows considerable promise [5].

[1] Harris K.D.M., Tremayne M., Lightfoot P., Bruce P.G., *J. Am. Chem. Soc.*, 1994, **116**, 3543. [2] Harris K.D.M., Tremayne M., Kariuki B.M., *Angew. Chemie Int. Ed.*, 2001, **40**, 1626. [3] Kariuki B.M., Serrano-González H., Johnston R.L., Harris K.D.M., *Chem. Phys. Lett.*, 1997, **280**, 189. [4] Cheung E.Y., Kitchin S.J., Harris K.D.M., Imai Y., Tajima N., Kuroda R., *J. Am. Chem. Soc.*, 2003, **125**, 14658. [5] Cheung E.Y., Foxman B.M., Harris K.D.M., *Crystall Growth and Design*, 2003, **3**, 705.

**Keywords:** diffraction data, powder diffraction, X-ray crystallography of organic compounds

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##### Powders, Prediction and Epitaxy: Applications of Differential Evolution

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Differential evolution (DE) is a robust and efficient global optimization algorithm based on evolutionary principles, which has been applied to a wide range of problems [1]. It shares the attractive features of other evolutionary algorithms but has a simpler implementation and fewer user defined control parameters enabling a greater insight into the control of the optimization process to be achieved.

Direct space methods of structure determination from powder diffraction is a field of rapid growth due to a number of computational and experimental developments [2, 3]. DE has been successfully applied to the determination of a number of organic and inorganic molecular structures from laboratory powder data.

The DE algorithm has also been applied to the prediction of crystal structures and epitaxial interfaces of organic crystals. In both cases, the lattice energy of the trial packing is calculated by an appropriate force field and then minimized by the DE algorithm. Utilization of a Beowulf cluster enables optimization of the DE algorithm control parameter to be performed in parallel.

In this talk, I will discuss these applications of DE with particular attention to the optimization of the performance of the algorithm, while highlighting areas of potential improvement and future developments.

[1] Price K.V., Storn R.M., Lampinen J.A., *Differential Evolution: A Practical Approach to Global Optimization*, Springer-Verlag, London, 2005. [2] Harris K.D.M., Tremayne M., Kariuki B.M., *Angew. Chem. Int. Ed.*, 2001, **40**, 1626. [3] David W.I.F., Shankland K., McCusker L., Baerlocher C. (Eds.), *Structure Determination from Powder Diffraction Data*, Oxford University Press, Oxford, UK, 2002.

**Keywords:** optimization algorithms, ab-initio powder structure determination, epitaxy

##### MS90.30.4

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##### Refinement when Amplitudes aren't enough: Real-Space, H-Bonding & Electrostatics

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Methodological improvements have reduced, but not eliminated over-fitting in macromolecular structure refinement. It is well known that over-fitting depends on freedom in the atomic model compared to the quality and quantity of the experimental data. The latter depends on resolution – 3 Å usually being considered the minimum.

Our goal is to improve the robustness of refinements at resolutions that are at best marginal, by using fully the available data, or by adding stereochemical restraints to the model freedom. Real-space refinement is most advantageous when model-independent phases can be used as additional data. The local nature of the refinement eliminates the over-fitting due to compensating errors that occurs in reciprocal-space where all atoms depend on all data points. Atomic density functions that rigorously incorporate resolution limits allow