Toward X-ray Interferometry of Unperturbed Ultrathin Organic/Bio-Organic Films at the Water-Air Interface

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Figure1: Schematic of an interferometry experiment can be performed either with either x-rays or neutrons. The much shorter absorption length for x-ray requires that the reflectivity experiment be performed with the typical "front-side" geometry. Here, the silicon surface of the wafer containing the underlying reference multilayer structure is alkylated with a hydroxy-terminated self-assembled monolayer. The resulting hydrophilic surface of the wafer is then raised to approach the hydrophilic surface of the Langmuir monolayer of the vectorially-oriented 4-helix bundle peptide to within 10-100Å (or more), sufficient to allow the intervening water layer to retain bulk-like properties. This close juxtaposition is sufficient to allow the incident x-rays or neutrons to be reflected by the Langmuir monolayer of the peptide and the underlying inorganic layers of the reference multilayer structure. In the manner described, the same Langmuir monolayer of the peptide can be investigated via both x-ray and neutron reflectivity, the phase problem rigorously solved in each case by interferometry.



Figure 2: The lower-left photo shows the Langmuir trough on the Liquid-Surface Spectrometer at Sector 9 at APS/ANL. The tilt & translation stages for positioning the reference multilayer substrate are located on the top of the trough canister (with the yellow Kapton windows), the positioning rod extends through the canister top into the sub-phase with the multilayer reference structure at the lower end of the rod located below the liquid surface in the trough (white teflon). An expanded view of the latter in the lower right photo shows the positioning rod and the upper surface of the silicon wafer containing the reference multilayer below the liquid surface prior to deposition and compression of a Langmuir monolayer of an amphiphile on the liquid surface



Figure 3: Upper: X-ray reflectivity data collected with the Liquid Surface Spectrometer at Sector 9 of the APS/ANL for a Ge/Si multilayer structure on the upper surface of a Si wafer before it was lowered into the aqueous subphase (black), a Langmuir monolayer of an amphiphilic α -helical bundle peptide spread on the surface of the subphase well above the wafer with the multilayer structure immersed in the subphase (blue), and from the peptide monolayer after the substrate was brought up through the subphase and into contact with the peptide monolayer at the interface (red). Lower: The corresponding Fresnel-normalized reflectivity data.



WHY should we care about this dramatic enhancement provided by interference with a reference structure???

- resonance x-ray reflectivity:
 - enhanced sensitivity to resonant atom in-plane density below ~ $1/20 \text{\AA}^2$ $1/40 \text{\AA}^2$
- improved spatial resolution:
 - for both x-ray & neutron reflectivity
- resonance neutron reflectivity (¹H vs. ²H):
 - enhanced sensitivity to ²H atom in-plane density below ~ 1/20Å²
 - increased number of ²H label positions in thin film profile simultaneously determined
- etc.?

Figure 4: Left-side: Reflectivity (top) and Fresnel-normalized reflectivity (bottom) with labels as for Figure 3. Right-side. Corresponding <u>gradient</u> electron density profiles derived by solving the phase problem via the box-refinement algorithm requiring no *a priori* assumptions (top). Model <u>absolute</u> electron density profiles fitting the gradient profiles to within the (Qz)_{max} truncation ripple (bottom).



Thoughts on "Consortium Building"

NIH Research Resource Model

FIVE KEY COMPONENTS

- A. <u>Core Research</u>: Cutting-edge instrumentation development (getting there & staying there!)
- **B.** <u>Collaborative Research</u>: Science "driving" Core development
- C. <u>Service Research</u>: Users "needing" developed instrumentation
- **D.** <u>Training</u>: Developing competent new users
- E. <u>Dissemination</u>: Attracting new users