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Keywords: total reflection X-ray fluorescence, dynamical theory of X-ray diffraction, Darwin profile

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Micro and quick reflectometry with high-energy white synchrotron X-rays

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X-ray reflectivity is sensitive to slight structural changes along the depth of layered materials in the order of sub-nanometers or even smaller. This property is extremely promising for the observation of buried layers and interfaces of multilayered thin films. So far, the method looks at quite wide area (mm²~cm²) and requires typically 20min~1h for one measurement. Here we report the instrumentation for upgrading the technique to give it a much higher spatial resolution with very quick measurement. The experiment has been done with high-energy white synchrotron beam ranging up to 100 keV, at BL28B2, SPring-8. Parallel small beam of 17micron(H) x 5.5micron(V) has been formed by several pairs of thick blade of tungsten. The data have been taken by a silicon drift detector as X-ray reflection spectra. One can analyze inhomogeneous layered thin films with around 20 micron resolution, and even scanning has become possible. Figure shows the results of the line scan of a patterned sample which has Cu, Cr and Au layer on the same substrate. Further experimental details and results will be presented.

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Keywords: grazing incidence, microbeam analysis, energy-dispersive analysis

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Melting behavior of substrate-free polystyrene surfaces studied by X-ray reflectivity

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Glass transition, melting and solidification in the surface region of polystyrene (PS) were observed by surface-sensitive X-ray reflectivity (XR). Unlike the studies reported, in which ultrathin layers with several nm thick had been prepared by the spin coating method on flat substrates, we used the surface of bulk PS with several mm thick. The reason why we adopt such a PS surface is to reveal the kinetics and dynamics of glass-forming polymers on the surface without any effect from the substrates. Not a few results on physical properties on thermal behaviors of glass-forming polymer surfaces would severely be affected by the physical and chemical properties of substrates, and by residual solvents. A lump of solvent-free PS (glass transition temperature: ca. 373 K) melted on a Si (100) wafer at 450 K in low vacuum for 6 hours was cooled down

to the room temperature with a cooling rate of 1 K/min. Then, the PS was removed from the Si to obtain the flat surface of PS with 2 cm X 2 cm in area and 2 mm thick. The surface of PS was found to be extraordinary flat; the root-mean-square roughness of the surface was fitted to be 1 nm by XR measured at room temperature, which was also confirmed by AFM. XR at various temperatures up to 400 K is now undertaken to obtain the temperature dependence of surface roughness, height-height correlation function, and electron density of the novel PS surface.

Keywords: melting, surfaces, X-ray reflectivity

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Time-resolved X-ray reflectivity investigation of lysozyme adsorption at the air-water interface

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X-ray reflection measurements of a globular protein adsorbed at the air-water interface was demonstrated using recently developed liquid interface reflectometer at SPring-8. The reflectometer equipped with two-dimensional hybrid pixel array detector, PILATUS, achieved only 1 sec, having enormous potential for quick measurements. A globular protein, lysozyme (LSZ) was injected into a phosphate buffer solution. The reflectivities shown in Fig.1 were measured under non-equilibrium condition, 4 sec after the protein injection. The time required each measurement was 150 sec. A broad peak observed in R/R_F moves towards small q_z, suggesting that the thickness of protein layer becomes thicker during adsorption. More details will be discussed.

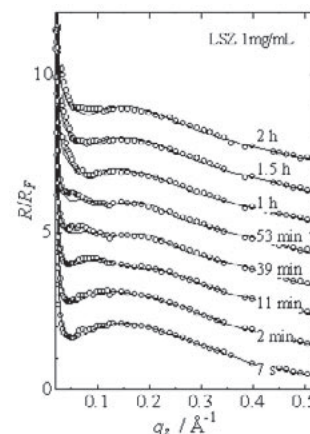


Fig. 1 Time-resolved X-ray reflection measurements of Lysozyme (LSZ) adsorption at the air/water interface

Keywords: X-ray reflectivity, protein unfolding, SPring-8

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Resonance shear measurement on liquid crystal confined between solid surfaces under electric field

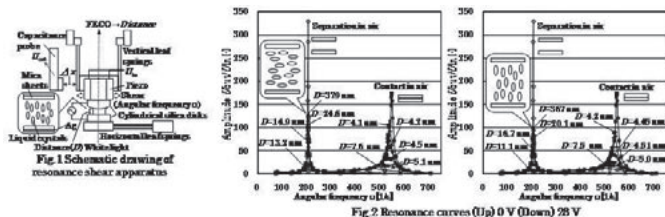
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It is known that the properties of liquids confined in the nanometer scale spaces are quite different from those of bulk liquids due to the structuring. We developed a resonance shear measurement¹⁾

which can monitor the rheological properties of liquids between two surfaces as a function of surface separation distance (D) from μm to contact with nm resolution. In this study, we investigated the rheological properties of a liquid crystal, 4-cyano-4'-hexylbiphenyl (6CB), under the electric field which induces the orientational change of 6CB. Resonance curves were obtained by measuring the amplitude of shear as a function of angular frequency. Polarizing microscopy confirmed that 6CB was in the planar orientation between mica surfaces without electric field, and in the homeotropic orientation under the electric field (28 V, 1 kHz). The viscosity of 6CB was larger for the case of 0 V than the case of 28 V at 370-14 nm, which agreed with Miesowicz viscosity. Below $D=14$ nm, the viscosity increased similarly both at 0 V and 28 V, indicating the same orientation of 6CB under confinement.

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Keywords: liquid crystal, orientation, rheology

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Pressure-induced structural changes of liquid As, Sb, and IV-VI compounds

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Pressure-induced structural transformations have recently been attracting a lots of attentions. For example, the finding of pressure-induced first-order phase transition in fluid Phosphorous is very interesting in that it showed a possibility of a novel border which separates one fluid phase from another. We investigated the structure of heavier group V elements As and Sb, and IV-VI compounds such as GeS, GeSe, GeTe, PbSe, PbTe, SnSe, SnTe, in liquid phase, by high-temperature high-pressure X-ray diffraction. The intermediate-range structure of liquid As and GeSe was found to change by pressure; we suggest a change from two- to three-dimensional structure. We also found that R2/R1 (the ratio of the second peak position to the first of the pair distribution function) approaches root two with compression. This result show that the bond angle 90 degree is preferred in a certain pressure range. Interestingly this ratio R2/R1 was found to change its pressure dependence when it passes root two. This indicates that further compression causes another structure. For liquid Sb and SnTe, the structure at ambient pressure has been conventionally assigned to a SC-like structure. However we found that the structure is not SC-like in low pressures, and our results suggest a considerable covalency in the bonds. With compression, the structure factor S(Q) showed a similar change to each other for these two liquids, and we found a hump in S(Q) (which is next to the first peak) rapidly and sharply changes at a certain pressure range. The overview of the pressure-induced structural changes for liquid

group-V (and IV-VI compounds) will be given in the presentation, and systematic results and differences from crystalline pressure sequences will be shown.

Keywords: liquid structure, energy-dispersive X-ray diffraction, liquid alloys

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Low resolution structure of synthetic melanin aggregates in aqueous solutions and organic solvents

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In an effort to find out details of the melanin fundamental structural unit, a great amount of information has been gathered using several techniques. The local short range order of the melanin molecular clusters has been described as consisting of five to seven 5,6-indolequinone units, arranged in planes which are pi-stacked with a spacing of 0.34 nm. Typical cluster size is 1.5-2.0 nm in lateral dimensions and 1.0 nm; in height. Nonetheless, structural details and dimensions of the aggregates are still not clearly defined and experiments did not answer the key question concerning the identification of the fundamental melanin protomolecule. More recently, small angle scattering of X-rays (SAXS) and neutrons (SANS) were performed. Several authors used these techniques, which are well designed to study macromolecules in solution to find details of melanin-copper ions interaction as well as chemical bleaching effects. A diversity of aggregated structures were proposed for these nanoscaled particles based on size and apparent shape. In this presentation we report the results of SAXS experiments performed with melanin synthesized from L-dopa and L-tyrosine in organic solvents, which were reported to be very effective for thin film formation. Water-based synthetic melanin was also studied for comparison purposes, since molecular aggregation behavior is known to vary with the route used for the synthesis. Reliable data was obtained for the water-based and DMSO dispersions. Data analysis was performed by conventional IFT methods and the overall shape and dimensional parameters of the melanin particles were obtained. Using ab-initio calculations, a low resolution 3D model is proposed for the basic melanin particle in aqueous media and DMSO. Sponsorship: CNPq, LNLS

Keywords: biologically important substances, SAXS, melanine

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Long period structure in D₂O/3-methylpyridine induced by adding salt or ionic surfactant

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The binary mixture of water and 3-methylpyridine, which shows