Surface Dynamics using Coherent X-rays: X-ray Photon Correlation Spectroscopy

The new method of x-ray photon correlation spectroscopy (XPCS) [1] is developed recently for probing the dynamics of surface height fluctuations as a function of lateral length scale. Measurements were performed on supported polystyrene (PS) films of thicknesses varying from 84 to 333 nm at temperatures above the PS glass transition temperature. Within a range of wave vectors spanning $10^{-3}$ to $10^{-2}$ nm$^{-1}$, good agreement is found between the measured surface dynamics and the theory of overdamped thermal capillary waves on thin films. Quantitatively, the data can be accounted for using the viscosity of bulk PS.

The third generation synchrotron sources show many new possibilities for research with x-ray beams that are several orders of magnitude brighter than have been available previously. One of the most exciting opportunities is to investigate the dynamics of condensed matter on molecular length scales using XPCS. This emerging technique applies the principles of dynamic light scattering in the x-ray regime. The short wavelength and slow time scales characteristic of XPCS extend the phase space accessible to scattering studies beyond some restrictions by light and neutron. The motivation of this work was the fact although the surface modes of viscoelastic liquid films were predicted [2] to be strongly overdamped modes with relaxation times determined by viscosity, surface tension, film thickness, and wavenumber, there had been no experimental tests of how these theories might apply to thin films, and particularly to thin polymer films. This question is especially interesting in the context of recent experiments of indicating that the glass transition temperature near surface is lower than in the bulk [3]. We introduced XPCS to study surface and thin film dynamics using a reflection geometry, where the x-ray beam impinges on the sample at grazing incidence.

The XPCS experiments were performed at beam line 8-ID at the Advanced Photon Source (APS) in Argonne National Laboratory, USA and employed monochromatic radiation with an x-ray energy of 7.66 keV. The schematic diagram is shown in Fig. 1. We have characterized the surface dynamics of supported polystyrene (PS) films as a function of lateral length scale, film thickness, and temperature. The results of this study were reported in Ref. 4.

The experimental geometry is illustrated schematically in Fig. 2. By arranging for the x-ray incidence angle to lie below the critical angle for total external reflection, we were able to restrict the x-ray penetration into the film to a depth of 9 nm, far less than any of the film thicknesses studied here. Thus, scattering from the film-substrate interface is negligible, and only fluctuations of the polymer/vacuum interface are probed. Moreover, with x-rays it is possible to access larger in-plane wavevectors than can be easily achieved with optical methods. This makes it possible to avoid complications due to the van der Waals interaction with the substrate for thin films.
Fig. 1. Experimental setup in beamline 8-ID in the Advanced Photon Source.

Fig. 2. The schematic reflectivity geometry in XPCS.

The best fit relaxation time constants as a function of in-plane wavevectors for different film thicknesses at several temperatures were extracted from the intensity autocorrelation function. From excellent agreement between the experimental results and the theory for the time dependence of surface height relaxations, as well as for the wavevector, film thickness, and temperature in a viscous liquid, we obtained the viscosity of PS films. Evidently bulk and film viscosities are identical within error bars. On the basis of these data, together with a supplementary calculation of the capillary wave relaxation times for inhomogeneous thin films, we can give a limit of thickness and viscosity of the surface layer if it exists. Our measurements provide an important constraint on theories seeking to elucidate the temperature and depth dependence of the viscosity near a polymer surface.

These first results demonstrate that surface XPCS is an exciting new research opportunity to study the dynamics of all kinds of surface fluctuations and fluctuations within films.