Small-angle X-ray Scattering:
Binary Fluid Universal Adsorption Surface Scaling Functions

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Introduction

In critical binary fluid mixtures where the surface tension difference between the two components is large, the component with the lowest surface tension preferentially adsorbs at the liquid-vapor surface. The variation of the local volume fraction as a function of depth into the liquid is governed by specific universal surface scaling functions, as described by scaling theory. In experiments, B.M. Law and collaborators [1, 2] have compared the theoretical predictions from scaling theory with the results of ellipsometry measurements for a number of different binary fluids. These experiments measured an integral over the density profile, where, from the temperature variation of the ellipticity, a measure of the shape of the universal adsorption scaling function describing the variation in composition near the surface could be determined. In order to perform further detailed tests of these scaling predictions, we have performed x-ray specular reflectivity from the surface of a binary fluid of dodecane and tetra-bromoethane at its critical composition.

Methods and Materials

The sample cell consisted of a chemically resistant, glass-etched Pyrex® tray inside a two-staged oven composed of a resistively heated inner stage and a water-cooled outer stage. Thermal gradients over the length of the cell are <1 mK/cm. The liquid sample overfills the Pyrex tray such that the specular reflected x-ray beam from the liquid-vapor surface could be directly measured through Kapton® entry and exit windows. To minimize sample beam damage, the sample was periodically topped off *in situ*; the liquid overflowed the glass tray, refreshing the liquid-vapor surface. The critical temperature T_c of the sample was determined by measuring the temperature at which spinodal decomposition occurs, which allowed T_c to be determined to within ~30 mK. (A more accurate measure of T_c, although possible, was not required because much of the x-ray structure was found to occur far from T_c.) The binary fluid was always kept above its critical temperature of 37.5°C in order to avoid phase separation.

The unique size requirements of the temperature-controlled cell were accommodated by CMC-CAT's sector 9 liquid spectrometer, which has both an incident beam and detector rotating arm assembly designed to maintain the stability of the sample chamber during scans.

Results

X-ray reflectivity data were recorded for Q's up to 3 nm^{-1}, at temperatures above a T_c of 1°, 2°, 5°, 10°, 15°, 25°, and 30°C. Figure 1 displays the measured reflected intensity R normalized to the reflectivity R_f that would be predicted for a perfectly flat interface of a liquid with a uniform density equal to the bulk composition. The curves of R/R_f display a steep initial falloff whose width in Q increases with increasing temperature. In addition, the curves show a maximum at around 1 to 2 nm^{-1}, which appears to move out to larger Q and decrease in intensity as the temperature is increased. In addition, oscillations are observed for several temperatures at ~0.3 to 0.4 Q, or immediately above the critical angle with a period of around 200 nm.
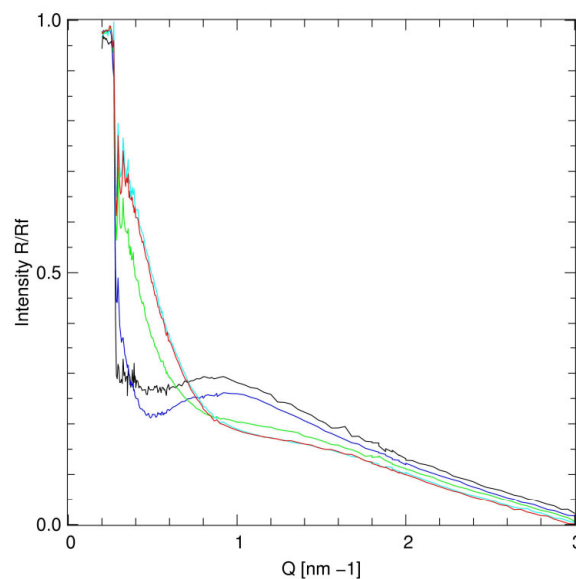

FIG. 1. Measured values of R/R_f at various temperatures. Black $(T - T_c) = 1$ °C, blue $(T - T_c) = 5$ °C, green $(T - T_c) = 10$ °C, cyan $(T - T_c) = 25$ °C, red $(T - T_c) = 30$ °C.

Discussion

In the limit of the first Born approximation, the shape of the R/R_f curves should scale with Q as a function of reduced temperature, assuming that the structure is due to a scaling function. The feature corresponding to the initial falloff displays apparent scaling but does not fall entirely within the region of scattering where the first Born approximation is valid. The maximum at larger Q does not appear to show scaling with reduced temperature. Additional comparisons between theory and experimental results are still in progress.

Acknowledgments

References

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[2] J.-H.J. Cho and B.M. Law, Phys. Rev. Lett. **86**, 2070 (2001).