High Resolution Studies of Surface Freezing in Alkanes

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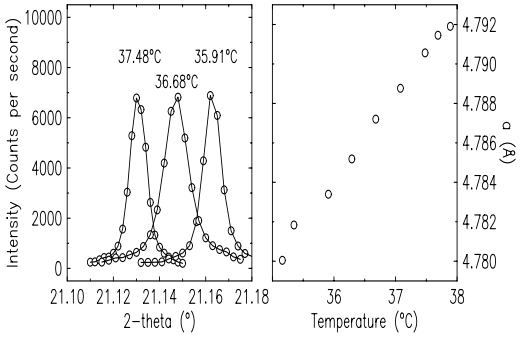
Introduction

Surface freezing occurs in n-alkanes and other chain molecules where an ordered monolayer forms a few degrees above the melting/freezing temperature. The structure of the monolayer has been investigated with x-ray reflectivity and grazing incidence diffraction (GID) and its thermodynamics with temperature dependent surface tension measurements. The surface frozen monolayers of the n-alkanes have been shown to have a structure and entropy similar to that of the hexagonal rotator phase which occurs in bulk n-alkanes. Prior GID measurements were performed using a low in-plane resolution, and thus the extent of the in-plane positional order was not determined very accurately. Also, while the surface tension was found to vary substantially across the ≈ 3°C range of the surface phase, no structural variation were observed with the previous lower resolution measurements.

Results

At ID 9B, we carried out GID measurements using the recently commissioned CMC liquid surface spectrometer which utilized a Ge(111) analyzer. Combined with the high brightness of the APS, high resolution GID measurements from the frozen monolayer were possible. The resolution limited GID peaks showed that the surface ordered monolayer indeed has at least quasi-long-range positional order. The high resolution also allowed us to measure the variation in the peak position across this rather small temperature range, thus determining the coefficient of thermal expansion, $(dA/dT)/A = 1.8 \times 10^{-3}/$ °C, comparable to that of the bulk hexagonal rotator phase.



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