

Observation of a Prewetting Transition during Surface Melting of Caprolactam

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The surface-induced melting of the close-packed (100) face of the anisotropic molecular crystal caprolactam has been studied using x-ray reflectivity. A thin-to-thick film prewetting transition is observed at about 13 K below the bulk melting point. Only above this transition does the thickness of the quasiliquid layer increase continuously with temperature. We speculate that initially the surface melting proceeds via layering transitions.

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The experimental observation of a quasiliquid film wetting the solid-vapor interface below the melting temperature T_M [1-5] has confirmed the old idea that the surface initiates the melting of a solid. Theoretically surface melting can be regarded as the wetting of the solid by the melt [5,6] and can result in either the quasiliquid film thickness remaining finite (incomplete wetting) or diverging (complete wetting) as the temperature approaches T_M . In the latter case the divergence is governed by the range of the dominant interactions in the system. While long-range van der Waals interactions result in the thickness increasing as $(T_M - T)^{-1/3}$, short-range interactions result in a logarithmic divergence. Experimentally incomplete wetting has been observed in Ge(111) [7] and Pb(001) [8]. Complete wetting with a logarithmic divergence has been observed in Pb(110) [1], Al(110) [2], the (001) and (010) faces of biphenyl [3] while a power-law divergence has been observed in multilayers of Ar and Ne adsorbed on graphite [4,5]. A crossover from a logarithmic to a power-law growth regime has also been observed in some cases [1,3-5]. In all these systems the film thickness was found to increase continuously with temperature. In this Letter we present an x-ray reflectivity study of the surface melting of the close-packed (100) face of caprolactam where a fundamentally different growth of the quasiliquid layer thickness is observed. In this system the quasiliquid film thickness is found to increase discontinuously from 25 to 56 Å at 13 K below T_M . This large jump is attributed to a theoretically predicted thin-to-thick prewetting transition [6,9,10]. Moreover, the available data also suggest that initially the surface melting proceeds via single-layer jumps in the film thickness (layering transitions).

Caprolactam ($C_6H_{11}ON$) crystallizes below $T_M = 342.3$ K into a monoclinic $C2/c$ structure having lattice parameters $a = 19.28$ Å, $b = 7.78$ Å, $c = 9.57$ Å, and $\beta = 112.39^\circ$ and four dimerized molecules per unit cell [11]. The dimers in the crystal, shown in Fig. 1, are arranged such that their major axis subtends an angle of 67° with respect to the (100) surface. The separation of the dimers along the surface normal is 8.91 Å. A crystal measuring about $10 \times 6 \times 3$ mm³ was grown from a solution of high-purity caprolactam and a toluene-xylene

mixture [12]. The crystal was mounted into a snugly fitting recess in an aluminum block on the inner stage of a leak-tight two-stage sample holder and held in place by two steel tabs. To prevent excessive vaporization from the crystal the outer stage was loaded with caprolactam powder. The sample holder was then evacuated and filled with dry nitrogen. Initially a smooth surface was obtained by the desorption of a number of surface layers. During the measurements both stages were resistively heated to the same temperature as measured by Pt-100 resistors embedded in them. The accuracy of the relative sample temperature was estimated to be 10 mK. The absolute surface temperature was calibrated to an accuracy of 0.1 K by monitoring the (200) Bragg peak intensity as the crystal was melted at the end of the experiment [for this crystal structure the (100) reflection is forbidden].

The x-ray reflectivity experiments, which probe the density profile normal to the surface, were carried out on a triple axis spectrometer with a 15-kW rotating anode source and a graphite monochromator which was used to select Cu $K\alpha$ radiation ($k = 2\pi/\lambda = 4.08$ Å⁻¹). The x-ray spot size of 0.2 mm in the horizontal scattering plane and 3 mm in the vertical was set using slits close to the sample. With this spot size the entire sample is illuminated below $Q = 0.159$ Å⁻¹, where $Q = 2k \sin\theta$ is the wavevector transfer and θ the grazing angle of incidence. The angular divergence of the incident beam was 30×170 mdeg (horizontal \times vertical) and the angular acceptance

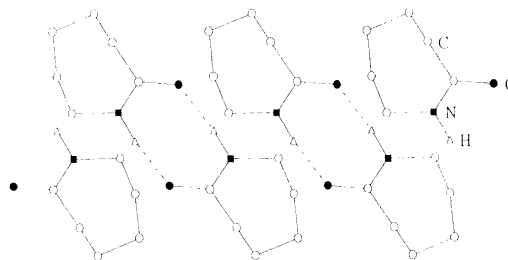


FIG. 1. Side view of the top layer of the (100) face of caprolactam. The surface is at the top of the figure. H atoms are only shown in the hydrogen bonds between N and O atoms of the monomers.

of the detector was set using 0.5×3 mm slits 475 mm from the sample. The x-ray measurements were made during different sample heating and cooling cycles. At each temperature the sample was allowed to equilibrate for an hour before a transverse scan of the specular beam at $Q = 0.107 \text{ \AA}^{-1}$ was measured. The specularly reflected intensity and the background intensity, at a sample offset of 250 mdeg, were then measured in the range $Q = 0.08$ to 0.285 \AA^{-1} . At Q values below 0.08 \AA^{-1} additional scattering from the sample mounting was observed while above 0.285 \AA^{-1} the reflected signal was essentially that due to background. All scans showed a weak (200) Bragg peak at $Q = 0.235 \text{ \AA}^{-1}$ due to beam contamination with $\lambda/3$ from bremsstrahlung. This peak was excluded from the subsequent data analysis. The transverse half width at half maximum (HWHM) of the specular beam was found to span the range from 30 to 100 mdeg during a typical sample heating or cooling cycle. However, during the final heating cycle a power failure resulted in a sudden decrease in temperature from 327.7 to 300 K. Upon heating back to 327.7 K the HWHM was found to have increased from 80 to about 150 mdeg. In spite of these changes in the HWHM the fits to the reflectivity data, to be described below, were found to result in the same interfacial separation.

To analyze the reflectivity data quantitatively both a one-interface and a two-interface model were used. Taking only a solid-vapor interface into account and assuming an error function for the density profile, the reflected intensity for $Q \gg Q_c$ is given by [13,14]

$$I(Q) = I_0 R_F(Q) \exp(-\sigma_1^2 Q^2). \quad (1)$$

Here σ_1 is the roughness of the solid-vapor interface while the Fresnel reflectivity is given by $R_F(Q) = (Q_c/2Q)^4$, where $Q_c = 0.0226 \text{ \AA}^{-1}$ is the critical wave vector of total reflection for solid caprolactam. The parameter I_0 is used to match the absolute reflectivity to the measured intensity. In the second model it is assumed that there is a region having a thickness l and density ρ_L between the solid and vapor. The reflectivity in this model follows

$$I(Q) = I_0 R_F(Q) |(\rho_L/\rho_S) \exp(-\sigma_1^2 Q^2/2) + (1 - \rho_L/\rho_S) \times \exp(-\sigma_2^2 Q^2/2) \exp(-iQl)|^2, \quad (2)$$

where σ_2 is the roughness of the second interface. The scattered intensity then shows oscillations with a period $2\pi/l$ and an amplitude proportional to the density difference $\rho_S - \rho_L$. Least-squares fits were made by Eqs. (1) and (2) convoluted with the instrumental resolution function and with the measured background added. In these fits the data were corrected for sample illumination below $Q = 0.159 \text{ \AA}^{-1}$. For the single-interface model I_0 and σ_1 were used as fitting parameters; in the case of the two-interface model I_0 , σ_1 , and l . Although the density difference between solid and liquid caprolactam at T_M is

7%, the data around 334 K do indicate a difference of around 12% which decreases with increasing temperature. Such a change in the density difference was also found in x-ray reflectivity experiments on the surface melting of Pb(110) [14]. Since using this difference as a free parameter did not change the interfacial separation and as the relative fitting errors in this parameter were large, $1 - \rho_L/\rho_S$ was fixed at 0.07. As the fits were also found to be insensitive to changes in the second interfacial roughness between 1 and 5 \AA , σ_2 was kept fixed at 1 \AA . The factor I_0 had to be used as a free parameter for each fit as changes in the transverse HWHM resulted in a change in the fraction of the scattered beam accepted by the detector. In all cases $1/I_0$ was found to track these changes in the transverse width.

Some typical reflectivity scans and the fits to the two models are shown in Fig. 2. All the data and fits shown have been corrected for the background, divided by the Fresnel reflectivity, and normalized to the same factor. As can be seen in Fig. 2, the data at 306.2 K are well reproduced by the one-interface model. At this temperature, the film thickness in the two-interface model is essentially zero leading in both models to reduced chi squared values of $\chi^2 \approx 0.8$ and an interfacial roughness of around 2 \AA . As the temperature is increased to 324.2 K the two-interface model with a film thickness of 22 \AA gives a better fit with $\chi^2 \approx 0.7$ compared to 1.7 for one interface. Both models show the roughness increasing to 4 \AA . Oscillations in the data are clearly seen at 334.2 K and lead to $l \approx 58 \text{ \AA}$. The χ^2 of 8 for the one-interface model is about 3 times that for two interfaces and the interfacial roughness in both models is about 3 \AA . The period of the oscillations decreases as the temperature is increased to 338.9 K corresponding to an increase in the thickness to 70 \AA . The interfacial roughness also increased to 5 \AA . This increasing roughness of the interface made it impossible to acquire data above 339 K.

The separation of the two interfaces is shown as a function of temperature in Fig. 3. Initially, as the temperature is increased above 323 K, the film thickness increases to around 25 \AA . Upon heating the crystal to between 326 and 330 K the thickness jumps from 25 to 56 \AA . Repeated cycling through the thin-to-thick film transition region indicates considerable hysteresis in the transition with no intermediate film thicknesses being detected. Above the transition the film thickness increases smoothly as the temperature approaches T_M . The nature of the divergence could not be determined from the present set of data.

Apart from surface melting the origin of the observed surface film could in principle be due to solid-state effects such as multilayer lattice expansion or molecular tilt. However, such large solid-state effects propagating 50–60 \AA into the bulk would appear unlikely on close-packed surfaces. Evidence for a quasiliquid layer was also obtained from earlier experiments where the sample was ei-

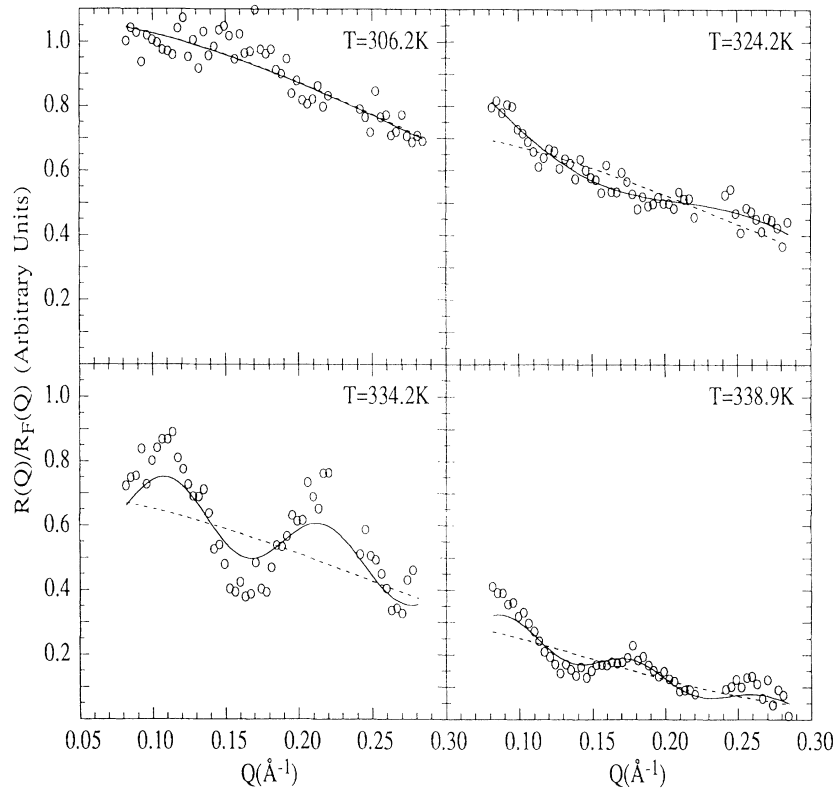


FIG. 2. Typical reflectivity scans and fits to the one-interface (dashed line) and two-interface model (full line).

ther fixed with a high-temperature glue or held down loosely by steel tabs. Under these conditions a dramatic increase in the mobility of the crystal with motor movements was observed above 330 K. When the crystals were glued on, the sample was even found to slide off the

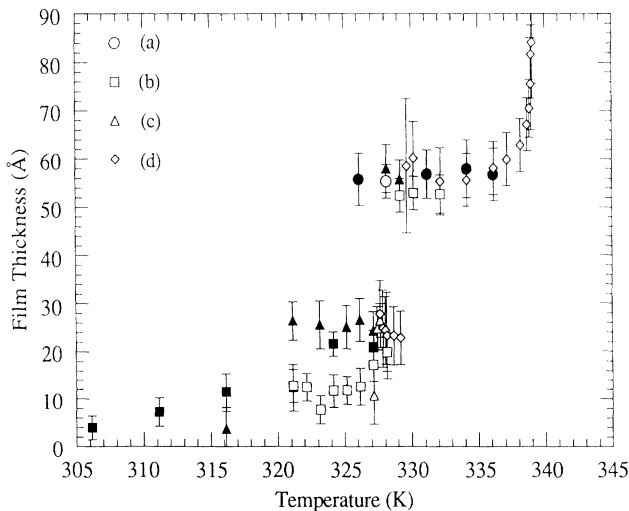


FIG. 3. Thickness of the quasiliquid layer as a function of temperature. Also shown is the order, (a)–(d), in which the data were taken with open (solid) symbols for scans with increasing (decreasing) temperature. Error bars indicate a two-fold increase in χ^2 .

mounting. Additionally the transverse HWHM of the specular beam which typically increased from 30–50 mdeg at 320 K to 100 mdeg at 328 K dropped back to 30–50 mdeg at 330 K. This decrease in the transverse width with increasing temperature again indicates a high mobility of the surface molecules due to a quasiliquid layer at the interface. Finally at the end of the experiment the concentration of organic impurities in the crystal was analyzed to be < 10 ppm; the molar concentration of water was found to be 1.2×10^{-3} . This concentration of water would result in a melting point depression of only 0.08 K [15]. To explain our data in terms of a melting point depression due to the surface segregation of impurities requires a 100-fold increase in the surface concentration of water which is extremely unlikely under the experimental conditions. We therefore conclude that the presence of two interfaces is due to surface melting of the crystal.

In terms of surface melting the quasiliquid thickness appears to increase via a first-order thin-to-thick film prewetting transition above which the thickness increases smoothly with temperature. Such a transition requires a competition between two terms in the surface free energy which impose different length scales on the film thickness. This can occur when the short-range interactions oppose surface melting while the long-range component favors surface melting [9]. The thickness-dependent terms in the surface free energy per unit area are then given by

$$V_1(l) = L_M(1 - T/T_M)l + b \exp(-2l/\xi_b) + W/l^2, \quad (3)$$

where L_M is the latent heat of melting per unit volume, ξ_b is the correlation length in the bulk liquid, and W is the Hamaker constant. The free energy cost of maintaining a liquid below the triple point is accounted for by the first term. Ordering in the liquid due to short-range interactions is represented by the second term while the final term is due to van der Waals interactions. With this potential a prewetting transition would occur if $b < 0$, $W > 0$, and $|b| < W$. This would, however, result in a jump in the film thickness from zero to a finite value above which the thickness diverges as a power law. Without the addition of higher-order terms for the short-range interactions this model does not explain the observed jump from 25 to 56 Å.

An alternate explanation, which takes into account the exponentially decaying smectic ordering induced in a liquid layer by interfaces, has recently been pointed out by Chernov and Mikheev [10]. Such a smectic ordering has been observed at the isotropic liquid-vapor interface of highly anisotropic (liquid crystalline) molecular systems [16]. In the case of surface melting this smectic ordering results in an additional damped oscillatory contribution to the interfacial free energy. The surface free energy is then given by

$$V_2(l) = V_1(l) - a \cos(2\pi l/d) \exp(-l/\xi_b), \quad (4)$$

where d is the periodicity of the short-range order in the bulk liquid and $a, b, W > 0$. This additional term, expected to be important on close-packed faces where the short-range order periodicity in the bulk liquid matches that of the crystal, is thought to result in the incomplete wetting of Ge(111) [7] and Pb(001) [8]. In the case of the (100) face of caprolactam crystal growth experiments indicate a smooth crystal-melt interface [17] which will add to the importance of this term. This theory predicts that as the temperature is initially increased towards T_M the thickness increases by a succession of first-order layering transitions where the thickness jumps by d in units of Å. As the film thickens the long-range interactions drive a prewetting transition from k layers to $k+n$ layers where $n \geq 1$. Above this transition the film enters a region where capillary waves, which are suppressed at low film thicknesses, result in the roughening of the liquid-vapor interface. This destroys the smectic layering and consequently washes out the oscillatory interaction resulting in a continuous increase in the thickness with temperature. Since the parameters entering the theory are not known for caprolactam, we cannot make a quantitative comparison with the data. However, below the prewetting transition the data are clustered around 11–12 and 25 Å and exhibit the hysteresis expected of a first-order transition. These thicknesses might correspond to the first two layering transitions. We speculate that at 329 K the long-range interaction drives a prewetting transition from two to five layers, and thus is responsible for the observed jump in the quasiliquid layer thickness. In agree-

ment with this theory only above this transition does the film thickness increase smoothly with temperature. Further experiments to establish the layering transition more firmly, and to determine the nature of the increase in thickness above the prewetting transition, are in progress.

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