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Positional order and thermal expansion of surface crystalline *N*-alkane monolayers

B. M. Ocko,[1] E. B. Sirota,[2] M. Deutsch,[3] E. DiMasi,[1] S. Coburn,[1] Joe Strzalka,[4] Songyan Zheng,[4] Andrey Tronin,[4]
Thomas Gog,[5] and Chitra Venkataraman[5]
[1]*Physics Department, Brookhaven National Laboratory, Upton, New York 11973*
[2]*ExxonMobil Research and Engineering Company, Route 22 East, Annandale, New Jersey 08801*
[3]*Department of Physics, Bar Ilan University, Ramat Gan 52900, Israel*
[4]*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
[5]*Complex Materials Consortium, Collaborative Access Team, Advanced Photon Source,*
Argonne National Laboratory, Argonne, Illinois 60439

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We report a high-resolution synchrotron grazing incidence x-ray diffraction measurement of a surface crystalline monolayer at the liquid-vapor interface of the *n*-alkane eicosane ($C_{20}H_{42}$) just above its melting temperature. The peak width of the surface monolayer rotator phase is shown to be resolution limited and implies positional correlations of at least $\sim 1\ \mu$m. The high resolution allowed determination of the temperature dependence of the peak position over the narrow (3 °C) temperature range of the surface crystal phase. The two-dimensional thermal expansion was determined to be $(dA/dT)/A = 1.8(\pm 0.1)\times 10^{-3}\,^{\circ}\mathrm{C}^{-1}$, which is comparable to the expansion in similar chain length bulk *n*-alkane rotator phases. Our data are consistent with the power-law shaped scattering tails expected from quasi-long-range order in two dimensions.

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Surface freezing occurs in *n*-alkanes [1] and other chain molecules [2–4], where an ordered monolayer forms at the surface of the melt a few degrees above the freezing temperature [1,5–7]. The high temperature ordered bulk phases of the *n*-alkanes are rotator phases, which are plastic crystals with three-dimensional long-range order of the molecules' centers of mass, but which lack long-range order with respect to the molecules' rotation about their long axes. The surface frozen monolayers of the *n*-alkanes exhibit a structure and entropy similar to that of the hexagonal rotator phase. The structure of the monolayer has been determined previously with x-ray reflectivity and grazing incidence diffraction [1,5], and its thermodynamics with temperature dependent surface tension measurements [6,7]. On the basis of those measurements, no structural variations within the monolayer phase were ascertained.

Previous grazing incidence diffraction (GID) measurements [1] were performed using a setup capable of only low in-plane resolution ($\Delta q_{\mathrm{res}} = 0.015\text{-Å}^{-1}$ full width at half maximum). The crystalline coherence length is given by the Debye-Scherer formula ($\xi = 0.9\times 2\pi/\Delta q$) where Δq is the line shape broadening in the absence of resolution effects. If the smallest resolvable Δq is Δq_{res} then coherence lengths greater than $0.9\times 2\pi/\Delta q_{\mathrm{res}}$ cannot be resolved. For the previous measurements, the maximum resolvable coherence length was about 400 Å. Furthermore, the absence of line shape information did not allow us to ascertain whether the lateral order was (quasi) long range or hexatic, nor could lattice properties, such as the thermal expansion coefficient of the monolayer be ascertained. While the surface tension was found to vary substantially across the ~3 °C range of the surface phase (see Fig. 1), no variations in the surface tension slope were observed. Since the temperature dependent slope of the surface tension gives the surface entropy change, its constant value suggests that no structural phase transitions occur within the surface frozen phase.

This paper describes GID measurements carried out with high in-plane resolution, made possible using third generation synchrotron sources. Our results demonstrate that the diffraction peaks are essentially resolution limited, implying that the domain size is at least on the order of 1 μm. The high resolution allowed us to measure very accurately the temperature variation in the GID peak position. The resulting coefficient of the thermal expansion is $(dA/dT)/A = 1.8\times 10^{-3}\,^{\circ}\mathrm{C}^{-1}$ where A is the molecular area. This value is comparable to the coefficient measured in the bulk R_{II} rotator phase.

The experiments were performed at the Complex Materials Collaborative Access Team (CMC) beamline ID-9B at the Advance Photon Source (APS) at Argonne National Laboratory using unfocused undulator radiation and a liquid nitrogen cooled Si(111) two bounce monochromator. Both the undulator and monochromator were set to provide radiation at 8.15 keV ($\lambda = 1.5212$ Å). The newly commissioned CMC liquid spectrometer utilized a Ge(111) crystal to tilt the beam downward at a grazing incident angle, $\alpha = 0.1°$, which is about 70% of the critical angle. The spectrometer outgoing

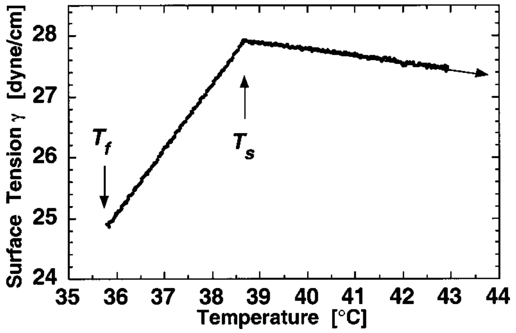

FIG. 1. Temperature dependence of the surface tension of C20 using the Wilhelmy plate method obtained using a different cell.

angle β, was also set at 0.1°, with a resolution width $\Delta\beta = 0.1°$. A Ge(111) crystal analyzer, mounted on the detector 2θ arm in a dispersive configuration, was used to provide excellent in-plane resolution with a direct beam width of $\Delta 2\theta = 0.0064°$ full width at half maximum (FWHM). Since minimal differences were observed in direct beam scans between the dispersive and nondispersive direct beam configurations, no finite energy bandwidth corrections were required. Including the effects of a finite $\Delta\beta$ provides a resolution width of 6.2×10^{-4} Å^{-1} FWHM at the scattering vector of $q \sim 1.5$ Å^{-1}, where the measurements were carried out. *N*-eicosane, $C_{20}H_{42}$ (abbreviation C20) was obtained from Aldrich, and used as obtained. The temperature controlled sample chamber for liquid surface reflectivity was described previously [1].

At the vapor interface of C20, a hexagonal rotator crystalline surface phase forms upon cooling below a temperature T_s, with the bulk remaining molten. At temperatures above T_s, the crystalline surface phase vanishes, and the bulk is terminated by an isotropic liquid surface. The bulk, on the other hand, crystallizes into a distorted rotator phase (R_I) at T_f that is about 3 °C below T_s. We note that the R_I phase is metastable with respect to forming the triclinic crystalline phase [8–10], a phase that is characteristic of the pure shorter even numbered carbon number *n*-alkanes.

The bulk and surface phase transition temperatures, along with information on the surface entropy, can be ascertained from surface tension measurements. In Fig. 1 we show the temperature dependence of the surface tension of C20 measured using the Wilhelmy plate technique [7]. The discontinuity in slope at $T_s = 38.7$ °C corresponds to the transition from an ordinary liquid surface to an ordered surface monolayer. The slope change $\Delta(d\gamma/dT) = 1.16$ dyn/(cm K) corresponds to the decreased entropy of an ordered surface compared to an ordinary liquid surface, and has been shown to correspond closely to the molar entropy change associated with the bulk rotator-liquid transition [11]. The surface tension can no longer be measured below the bulk freezing temperature, $T_f = 35.7$ °C.

Previous x-ray reflectivity measurements showed that the ordered monolayer of C20($T_f < T < T_s$) is 24.1 Å thick over the entire 3 °C temperature range, and without a noticeable temperature dependence [1,5]. This thickness corresponds closely to the calculated molecular length. The single in-plane reflection at $q \cong 1.516$ Å^{-1} indicates hexagonal packing. Bragg rod measurements showed that the elongated molecules are oriented normal to the surface, and are consistent with the thickness deduced from the reflectivity measurements [1,5].

In Fig. 2, we show grazing incidence in-plane 2θ scans [plotted as a function of $q = 4\pi\times\sin(2\theta/2)/\lambda$] of the hexagonal peak for three different temperatures. For the narrowest peaks, the width is very close to the resolution limit. A lower bound for the coherence length is obtained from the measured diffraction peak width $\Delta q = 0.0007$ Å^{-1}. This implies that correlated domains extend over a range greater than 9000 Å. We note that the small variations in the peak width did not change systematically with temperature. Rather, these variations are attributed to a small offset in the orientation of the surface crystallites from the Bragg condition.

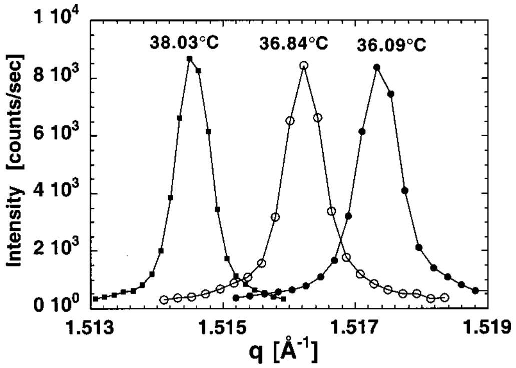

FIG. 2. Grazing incident scans at 38.03, 36.84, and 36.09 °C. The peaks are nearly resolution limited.

The peak positions in q are shown as a function of temperature in Fig. 3. A linear fit yields $q = 1.5676 - 0.001392(70)$ T, with T in °C and q in Å^{-1}. The area per molecule for a hexagonal lattice is given by $A = 8\pi^2/\sqrt{3q^2}$. The two-dimensional thermal expansion is thus $(dA/dT)/A = -2(dq/dT)/q = (1.8\pm0.1)\times10^{-3}$ °C^{-1}. This can be compared to values for bulk phases of the alkanes which are $\sim 1.3\times10^{-3}$ °C^{-1} for the R_{II} hexagonal rotator phase, $\sim 2.3\times10^{-3}$ °C^{-1} for the orthorhombic R_I rotator phase, and $\sim 5.3\times10^{-3}$ °C^{-1} for the orthorhombic herringbone crystal phase [12,13]. We see that the thermal expansion in the hexagonal rotator surface phase of C20 is comparable to the rotator phases of the other alkanes, and clearly much greater than the nonrotator crystal phases. It is, however, somewhat higher than that of the bulk hexagonal phase, lying between the values for the R_{II} and R_I bulk rotator phases.

For two-dimensional crystals, long wavelength fluctuations destroy the true long range order which is exhibited by ordinary three-dimensional crystals. A logarithmic decay of the correlation function leads to the well-known power-law form for the diffraction line shape characterized by an exponent η. For perfect crystalline alignment (single crystal) the intensity falls as $(\Delta q)^{\eta-2}$, whereas for random alignment (perfect powder) it falls as $(\Delta q)^{\eta-1}$ [14–17], where Δq is

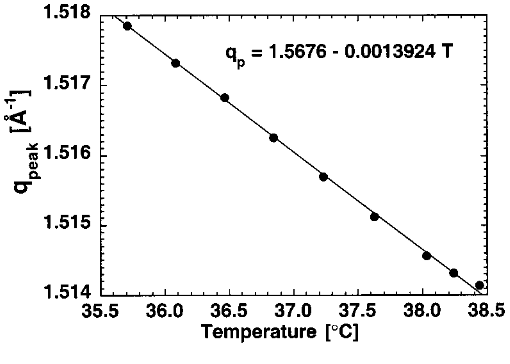

FIG. 3. The in-plane peak positions of the hexagonal phase, as a function of temperature. Here $q = 4\pi/\sqrt{3}a$, where a is the interparticle distance.

the longitudinal in-plane momentum transfer deviation from the peak. Our data exhibit such power-law tails with an alignment of macroscopic domains intermediate between a single crystal and a good powder. Thus, while the measured peak positions were reproducible regardless of the degree of alignment, the power-law tails exhibited some scatter with exponents ranging between -1.05 and -1.60. Since powder averaging decreases the apparent slope, the data are consistent with $\eta \leqslant 0.4$, comparable to the value of 0.5 obtained by Berge *et al.* for Langmuir films on water [15]. A more definitive measurement of the power-law line shape requires a systematic averaging over the azimuthal distribution.

We have shown that the surface frozen monolayer of C20 exhibits hexagonal order, with positional correlations extending over 1 μm. The coefficient of thermal expansion, extracted from the variation of the rotator phase lattice constant, is in reasonable agreement with that of the bulk rotator phase. In addition, the power-law line shape is consistent with the predicted quasi-long-range order. The power-law exponent may increase with decreasing temperature if the phase exhibits packing frustration [16–19].

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