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Freezing Transition of Monolayer Xenon on Graphite

P. A. Heiney and R. J. Birgeneau
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

G. S. Brown
Stanford Synchrotron Radiation Laboratory, Stanford, California 94304

and

P. M. Horn
IBM Research Center, Yorktown Heights, New York 10598

and

D. E. Moncton
Bell Laboratoratories, Murray Hill, New Jersey 07974

and

P. W. Stephens
Department of Physics, State University of New York, Stony Brook, New York 11794

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This paper reports a high-resolution synchrotron x-ray scattering study of the freezing transition as a function of temperature and chemical potential of the two-dimensional continuous-symmetry system monolayer xenon on graphite. It is found that for a coverage of 1.1 monolayers the transition is continuous to within the substrate-determined resolution with fluid correlation lengths exceeding 100 atomic spacings. Comparison is made with current theories of solidification in two dimensions.

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The nature of the fluid-solid transition of two-dimensional (2D) continuous-symmetry solids is at present a matter of considerable controversy. A theory due to Kosterlitz and Thouless (KT) suggests the possibility of a continuous melting transition mediated by dislocation unbinding.[1] Molecular-dynamics simulations of 2D solidification have, however, proven to be ambiguous.[2] Direct experimental measurements are therefore of considerable importance. Rare gases absorbed on graphite provide a particularly good experimental realization of 2D solids; both the adatom-adatom and the adatom-substrate interactions approximate simple Lennard-Jones potentials. Vapor-pressure isotherm[3] and x-ray measurements[4] show that *submonolayer* xenon physisorbed onto the (0001) surfaces of graphite has a gas-liquid-solid triple point and a *first-order* solidification transition to an incommensurate solid phase. However, the liquid-solid coexistence region becomes narrower with increasing temperature and coverage, suggesting that the transition could become second order in the coverage region of approximately one monolayer. Accordingly, we have carried out a high-resolution synchrotron x-ray scattering study of the freezing transition of xenon physisorbed on exfoiliated graphite with emphasis on the 1.1-monolayer coverage region.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory using the high-resolution x-ray diffraction spectrometer stationed on beam line VII which is equipped with a seven-pole wiggler. We used a high-resolution spectrometer configuration similar to that described previously.[5] The longitudinal resolution was 0.0003 Å^{-1} half width at half maximum (HWHM), much less than the substrate finite-size width of 0.0016 Å^{-1}. The use of a wiggler line in combination with improved mirror reflectivity improved our signal by a factor of 30 over previous adsorbed-gas synchrotron measurements.[5] The xenon-gas handling system and cryostat were as discussed previously.[4,5] For the substrate we used a $1.2\times 1.2\times 0.2$ cm^3 plate of Union Carbide *ZYX* exfoliated graphite, with the c axis, which is normal to the plate, in the scattering plane. At $T=112$ K, scans were carried out as a function of surface coverage near a coverage of 0.85 monolayers. At a coverage of 1.1 monolayers, temperature scans were carried out in a closed-cell configuration, so that both the chemical potential and surface density changed. At a constant temperature of 150 K, scans were taken as a function of vapor pressure. The closed-cell and constant-temperature runs crossed the liquid-solid phase boundary at approximately the same point.

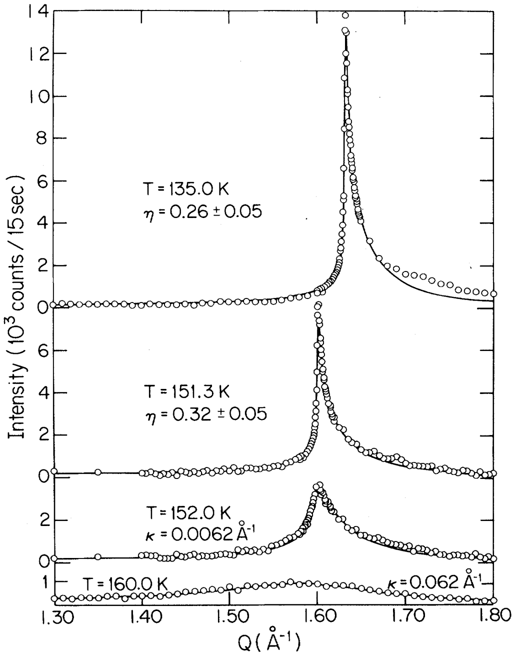

FIG. 1. Typical diffraction profiles from the closed-cell solidification runs. Empty-cell background, corrected for xenon x-ray absorption, has been subtracted. The solid lines are power-law and Lorentzian line shapes as discussed in the text.

Data from the closed-cell run are shown in Fig. 1. An empty-cell background, corrected for xenon absorption of the x rays, has been subtracted. Below $T\cong 140$ K, we see, in addition to a sharp (1,0) peak of the triangular structure at $Q=1.63$ Å^{-1}, an extra feature at $Q=1.7$ Å^{-1}, which appears to arise from substrate modulational effects.[4,5] This peak is not observable above 140 K because of the increased incommensurability. As the temperature is raised from 135 to 151.3 K the peak-to-wing intensity ratio decreases slightly. Above $T=151.6$ K, the linewidth is observed to increase rapidly and continuously, indicative of decreasing correlation lengths and a solid-fluid transition. The data taken versus chemical potential at constant temperature show equivalent features. One can characterize these changes quantitatively by fitting specific diffraction line shapes. In an infinite 2D continuous-symmetry solid it is believed[6] that the divergent long-wavelength fluctuations convert the solid-phase δ-function diffraction peaks at reciprocal-lattice points $\vec{G}$ to power-law singularities of the form

$$S(Q)\propto Q^{\eta-2}, \quad Q=|\vec{q}-\vec{G}| . \tag{1}$$

Here $\vec{q}$ is the scattered wave vector and η is a small positive number. In a finite system, the anticipated profile may, to a good approximation, be simply determined by convoluting Eq. (1) with the substrate shape function, which is well approximated by a Gaussian function[7] $R(Q) \propto \exp(-Q^2 \times L^2/4\pi)$ where L is the average crystallite size. Experiments on commensurate krypton on ZYX yield $L = 2000 \pm 300$ Å and this value is obtained for our sample as well. Using the analytic approximation of Dutta and Sinha[7] to this rounded power-law function, numerically averaged over planar orientation and vertical tilt, we generate the solid curves in Fig. 1 for $T = 135.0$ and 151.3 K. It is evident that the power-law singularity form for $S(Q)$ works very well. The errors on the exponent η are estimated systematic errors due to background subtraction, uncertainty in crystallite size, and correlation of fitting parameters.

The diffraction peaks in the solid phase are equally well described by a powder- and tilt-averaged Lorentzian convoluted with a Gaussian shape function corresponding to a finite size of 2000 Å,

$$S(Q) = C/(Q^2 + \kappa^2). \qquad (2)$$

Least-squares fits to this form yield an inverse correlation length κ of 0.0003 $Å^{-1}$ in the solid phase. For both the η power law and the Lorentzian line shapes, the finite crystallite function plays the role of a resolution function with HWHM of 0.0016 $Å^{-1}$; it turns out that η and κ are essentially determined by the ratio of the peak scattering amplitude to the wing scattering amplitude in the measured profiles. In order to differentiate between the two forms for $S(Q)$ we have also analyzed xenon-on-graphite data taken with a rotating-anode spectrometer,[4] with a resolution of 0.008 $Å^{-1}$ HWHM. These low-resolution scans yield the same values of η at equivalent temperatures within the error limits; however, the values of κ in the Lorentzian Eq. (2) are typically greater by a factor of 5. We regard this as strong support for the correctness of the power-law singularity form for $S(Q)$, with $\eta \cong 0.3$ at melting.

On the fluid side of the transition, the η line shape does not describe the data. If we assume oriented incommensurate droplets with exponential decay of positional correlations, we should obtain a Lorentzian scattering profile. Powder averaging over basal-plane orientation then yields a function which is approximately the square root of a Lorentzian.[4] In the data taken at $T = 112$ K, we observe diffraction peaks at coverages of 0.84 and 0.86 monolayer (absolute accuracy ± 5%) which can only be described as the sum of a sharp, finite-size limited Lorentzian peak with 0.00125 $Å^{-1}$ HWHM and a broad "fluid" peak with a 0.03-$Å^{-1}$ HWHM. This is consistent with vapor-pressure measurements which display a first-order solidification transition and liquid-solid coexistence in this temperature-coverage regime.[3] We emphasize that at this coverage the solid has about 8% vacancies; this may account for the first-order nature of the transition. However, in both the closed-cell and the $T = 150$ K chemical-potential runs, where the coverage at solidification is 1.1 monolayers, we observe a constant evolution of the correlation length from 10 Å to at least 500 Å, with no evidence for two-phase coexistence or hysteresis. In the constant-temperature data, taken as a function of chemical potential, we see no evidence of a discontinuous jump in correlation length as would be predicted for a first-order transition. The solid lines in Fig. 1 for $T = 152.00$ and 160.0 K are the results of least-squares fits to powder- and tilt-averaged Lorentzians. Figure 2 shows the fitted values of the inverse correlation length, peak scattering intensity, and peak position from the closed-cell run. The error bars around the inverse correlation-length values are estimates of the systematic error due to uncertainties in the subtracted empty-cell background. A variety of other experiments, particularly commensurate

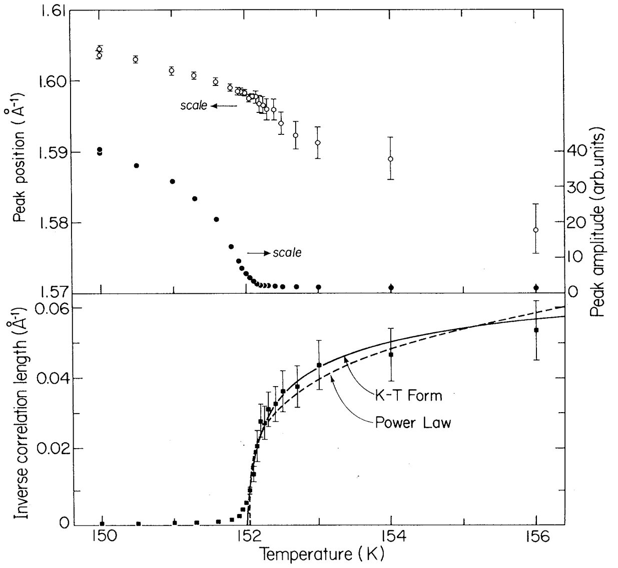

FIG. 2. Fitted peak amplitude, peak position, and inverse correlation length from Lorentzian line-shape analysis of closed-cell solidification run. The solid line is a fit of κ vs T by the KTNHY theoretical prediction. The dashed line is a power-law fit.

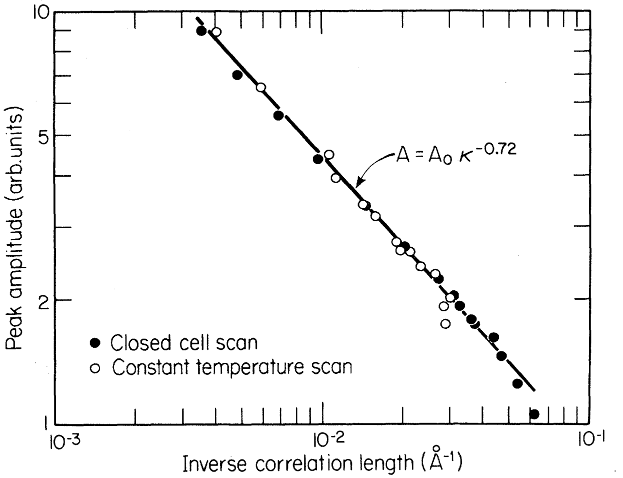

FIG. 3. Normalized peak scattering amplitude, corrected for vertical mosaic, vs inverse correlation length.

krypton melting,[4,5] have indicated that edge effects cause no pathologies on length scales less than 500 Å. Note that the peak position in the fluid phase is at $q = 1.58\ \mathrm{\AA}^{-1}$, quite far from the commensurate $\sqrt{3}\times\sqrt{3}\,R\ 30^\circ$ value of $1.70\ \mathrm{\AA}^{-1}$.

The exponent η in Eq. (1) also appears in the scaling of the peak scattering amplitude with inverse correlation length in the fluid critical region,[5] $S(\vec{G}) \propto \kappa^{\eta-2}$. In the present case, the intrinsic line shape has been powder averaged, changing the measured profile from a Lorentzian to the square root of a Lorentzian, that is, $S'(G) = (1/2\pi)\int d\varphi\, S(\vec{G}) \propto \kappa^{\eta-1}$. Figure 3 shows the normalized peak scattering amplitude, corrected for vertical mosaic, versus inverse correlation length for both the closed-cell and constant-temperature runs. The solid line is a fit by the $\kappa^{\eta-1}$ form with $\eta = 0.28 \pm 0.05$. This agrees to within the errors with the value $\eta = 0.32^{+0.08}_{-0.05}$ determined from the solid line shape at solidification, where the upper error limit arises primarily from our uncertainty in the exact location of T_c.

Our data are thus consistent with a continuous transition, with correlations in the fluid phase reaching at least 500 Å before finite-size effects, substrate interactions, or possibly a weak first-order transition play a role. The correlation length as a function of temperature may be fitted by the usual power-law form $\kappa = K_0 (T/T_c - 1)^\nu$. The dashed line in Fig. 2 shows the result of such a fit with $K_0 = 0.24\ \mathrm{\AA}^{-1}$, $T_c = 152.04$ K, and $\nu = 0.277$. The precise values of these parameters depend strongly on which points are included in the fit, and in particular ν could be as large as 0.5. The KT theory as developed by Nelson, Halperin, and Young (KTNHY) for the triangular floating solid predicts the very unusual form

$$\kappa = K_0 \exp[-B/(T - T_c)^\nu] \tag{3}$$

with ν varying between 0.3696. . . and 0.40 depending on the strength of the substrate orienting field. The solid line in Fig. 2 is a fit to Eq. (3) with ν fixed at 0.4; the parameters so obtained are $K_0 = 0.0818\ \mathrm{\AA}^{-1}$, $B = 0.643$, and $T_c = 152.00$ K. Equation (3) with these values describes the data quite well for $\xi = \kappa^{-1}$ less than 500 Å.

The KTNHY theory also predicts that the value of η at solidification should be between $\frac{1}{4}$ and $\frac{1}{3}$, with the exact value depending on the elastic constants. Our measurements give $\eta = 0.32^{+0.08}_{-0.05}$ as measured by the solid line shape and $\eta = 0.28 \pm 0.05$ as measured by the relation of peak scattering intensity to inverse correlation length in the fluid phase. In making comparisons of the results with those obtained using other techniques, such as molecular dynamics, it should be noted that the system of 1.1 monolayers of xenon absorbed on graphite differs somewhat from an "ideal" 2D continuous-symmetry solid. First, the substrate provides an orienting field; second, the film is in equilibrium with a 3D vapor; third, there is a small number of atoms on the second layer. We emphasize however that these effects do not change the essentially 2D nature of the phase transition.

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