Surface Melting and Roughening of Adsorbed Argon Films

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Argon multilayers adsorbed on graphite display heat-capacity anomalies attributed to surface roughening and surface melting. Melting begins 3° or 4° below the triple point, producing strong peaks with power-law risers $\sim(T_t-T)^{-r}$, $r=1.35\pm0.03$. The exponent and the thickness dependence of peak temperature agree with the theory of surface melting under long-range forces. Rounded anomalies at $\sim0.8T_t$ are identified with roughening transitions. The two types of anomalies are well separated, indicating that melting and roughening are distinct forms of surface disorder.

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Surface roughening and surface melting are possible forms of disorder that may occur at crystal-vapor interfaces below the triple-point temperature T_t of the bulk solid.[1,2] The basic ideas date from many years ago and theoretical work is now quite extensive, but few definitive experiments have been performed, and several important questions remain. For example, the effects of material properties on the transition temperatures and other characteristics of the transitions are largely unknown; moreover, it is still an open question whether the onset of surface melting can be distinguished from progressive roughening. The experimental results reported here bear on each of these issues.

Adsorbed multilayers offer several advantages for the study of surface effects, particularly high sensitivity, chemical purity, and precision thickness control. Unfortunately, surface effects in very thin films can be complicated by adsorption forces, finite thickness, and wetting phenomena,[3-5] but as discussed below, their experimental effects may be estimated through the evolution of film properties with thickness.

We chose Ar/graphite, since Ar is one of the few adsorbates that can form thick uniform incommensurate solid films on graphite.[6,7] The Ar was deposited in a thin-walled copper cell containing 12 g of exfoliated graphite foam, in a calorimeter previously employed for monolayers.[8] Temperatures were determined by Pt resistance thermometry, with sensitivity better than 1 mK. Thermal relaxation times τ_{int} within the cell are quite short relative to τ_{ext} between the cell and its surroundings: Examples for the empty cell are $\tau_{\text{int}}\sim6$ and $\tau_{\text{ext}}\sim$ several hours. Typical heat pulses produced temperature rises of 0.15–0.25 K. Heat capacity was calculated by least-squares linear approximations to the post-heat period over time intervals $10\tau_{\text{int}}<t<33\tau_{\text{int}}$. We studied thirteen films, with thickness range $2<L<13$ layers, at $60\text{ K}<T<90\text{ K}$, prepared with purified Ar; after adsorption, each was annealed by warming above T_t, then slowly cooled. The coverages were corrected for desorption, with use of vapor pressures and isosteric heats of Ar/graphite films of one to three layers,[9] and of bulk Ar[10] for thicker films. The quoted thicknesses are scaled from the coverages, one layer corresponding to the first step of a 78-K isotherm. We calibrated the thermometer's absolute scale *in situ* at the triple point of "bulk" Ar, actually a forty-layer-thick film. Its melting peak provided a sharp fiducial signal, which we identified with the published[10] value $T_t=83.810$ K.

The data show many thickness-dependent features, particularly complex in the thinner films, where discrete layer phenomena are evident. The few-layer results will be reported elsewhere. We focus here on the thicker range, where a strong peak develops near T_t. Figure 1 presents data for samples with $L>5$. Each shows a gradual rise, beginning at ~80 K, to a maximum at $T_p<T_t$. In the thicker films the peaks are asymmetric, being steeper at $T>T_p$. The peak height grows and T_p increases with L. The peak of the "bulk" sample is impressively high ($C/Nk>350$) and narrow, but has the same type of asymmetry seen at lower coverage. The peaks evidently tend toward a normal first-order melting transition with increasing thickness. In the following, we first analyze the data for premelting and then compare with theory. Other aspects of the results are discussed later.

If premelting occurs, there is a range of T in which the films are partially liquid and solid, with the liquid presumably in the form of a coating over the solid. The heat capacity will have terms due to the liquid and solid fractions and the progressive conversion from solid to liquid. In thick samples, the phases are relatively homogeneous, except for gradients close to the interfaces, but these variations and the substrate field may be important in very thin films. If finite thickness, interfacial, and gradient effects are expressed as a lumped correction δC the heat capacity at constant total N is the sum

$$C=N_sc_s+N_lc_l+T\Delta s(dN_l/dT)+\delta C, \qquad (1)$$

where N_l,N_s and c_l,c_s are the populations and specific heats of uniform phases. The terms due to premelting should be distinguishable from the rest by their T depen-

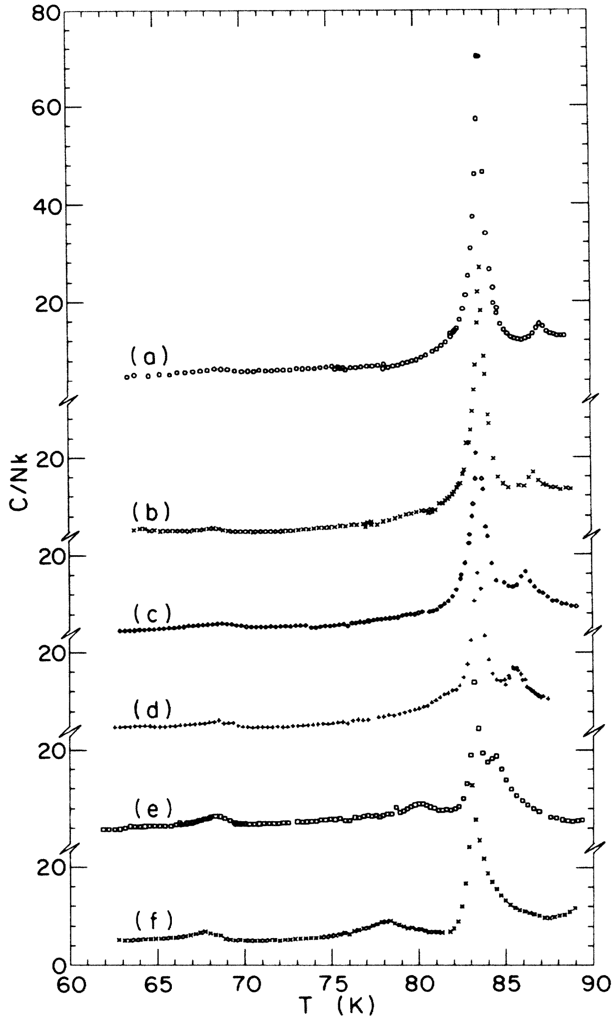

FIG. 1. Specific heat of Ar/graphite films, corrected for desorption. Thicknesses in layers at 83 K are (a) 10.5, (b) 8.9, (c) 8.0, (d) 7.1, (e) 6.2, and (f) 5.3. The rises beginning at ~80 K are attributed to surface melting, and the weak anomalies at 68 K to surface roughening. The sharp cusps above 83 K seems to be due to the melting of a compressed monolayer next to the substrate.

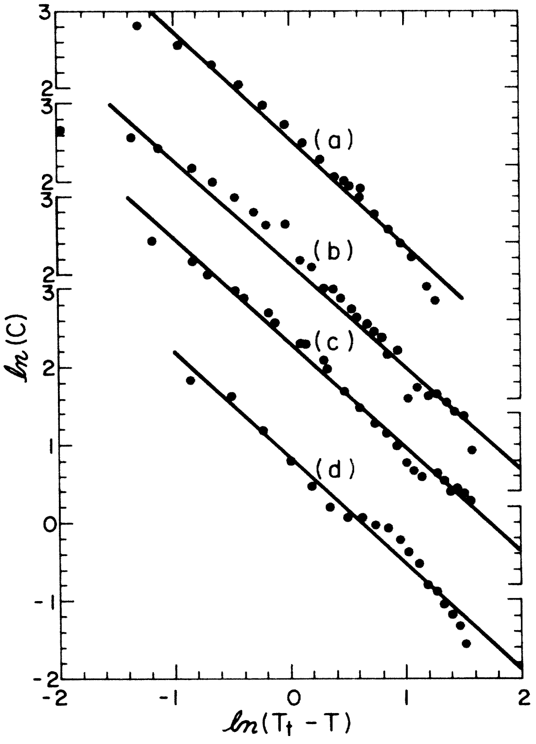

FIG. 2. Background-corrected heat capacities of the four thickest films, vs relative temperature. The empirical exponents r are (a) 1.38, (b) 1.32, (c) 1.33, and (d) 1.35. Letters refer to the same thicknesses as in Fig. 1.

dence: N_l and dN_l/dT vary with the difference $\Delta T = (T_t - T)$, while the remaining "background" is a function of T. In the limit of infinite thickness N_l is presumed to diverge as $\Delta T \rightarrow 0$; hence premelting should tend to dominate C near T_t. The data are consistent with this picture. Since the rises extend over only a few kelvins, the nonsingular background can be approximated by a linear extrapolation from lower temperature, as $A + BT$. We show the background-corrected data of the four thickest films as a function of ΔT in Fig. 2. The films exhibit power-law behavior, $(\Delta T)^{-r}$, over about one decade in ΔT. There is no obvious trend of r with thickness, and the values are quite close: The average $r = 1.35 \pm 0.03$. The measured exponents are increased slightly because of the finite heating intervals: The corrected value for the limit of zero heating width is lower by 1.3%.

The empirical power law represents two terms in C, proportional to N_l and dN_l/dT; if Eq. (1) is correct, the experimental exponent should vary with T. The absence of a pronounced variation is due to the limited range of ΔT and the dominance of the term involving dN_l/dT. With bulk values for the coefficients in Eq. (1), the term in N_l contributes no more than 6% to the total. Assuming Eq. (1), we estimated the exponents of the separate contributions from the average r: The results are 1.36 and 0.36. The uncertainties in this calculation are quite small since C is almost entirely a result of the derivative term alone. Another source of error is the background subtraction: We believe that it adds no more than ± 0.02 to the uncertainty. With these corrections, our best estimate of the exponent for dN_l/dT is 1.36 ± 0.05. This agrees with the theoretical result $\frac{4}{3}$ for surface melting of van der Waals solids. We outline the theory using a phenomenological argument first given by Kristensen and Cotterill.[11]

If a solid is wetted by its melt liquid, its free energy at $T < T_t$ can be lowered by "premelting," i.e., by conversion of a thin coating to liquid, replacing the solid-vapor coefficient γ_{sv} by the smaller sum $\gamma_{lv} + \gamma_{ls}$. The change

δF_{surf} depends on L_l. For forces varying as the inverse cube of the distance between interfaces, $\delta F_{\text{surf}} = A(\gamma_{lv} + \gamma_{ls} - \gamma_{sv})(1 - \text{const}L_l^{-2})$. There is also an increase δF_m due to solid-liquid conversion, proportional to L_l. Minimizing $\delta F_{\text{surf}} + \delta F_m$ with respect to L_l establishes the equilibrium thickness of liquid. Its variation with T arises from δF_m, which is zero at T_t and increases at lower T. Expanding δF_m in powers of ΔT, the first-order result finds L_l diverges as $(\Delta T)^{-1/3}$. The exponent of ΔT depends on the specific type of interactions between interfaces; for short-range forces, where δF_{surf} varies exponentially with L_l, one obtains $L_l \sim |\ln(\Delta T)|$.[12,13] The Ar data agree with the predicted power law and exponent for van der Waals systems; logarithmic dependence is well outside the measurement.

Two previous experiments are especially relevant here. Direct measurements of Pb surfaces indicated logarithmic dependence of L_l on ΔT.[14] It is possible that the interactions in Pb and Ar are different, but the authors of the Pb study admit that their T scale is uncertain, hence further experiments seem necessary to be sure of the distinction. A recent calorimetric study of methane-graphite found wetting and dewetting transitions but no evident premelting near the triple point.[15] In other aspects this system is rather similar to Ar/graphite; hence its very different behavior is puzzling and extremely interesting.

Finite film thickness appears to have no significant effect on the exponent, but the monotonic drift of T_p toward T_t can be understood as a simple effect of finite thickness. The trend is shown in Fig. 3, which superposes the specific heats near T_t of several samples. The data are enclosed in a common envelope, but each curve drops away at some temperature T_p which increases with L. This can be understood as follows. As melting proceeds, the thickness of liquid increases rapidly as T approaches T_t, until its progress is truncated by reaching the substrate interface. If there is a highly compressed thin solid layer next to the substrate, the truncation occurs before the entire film is melted, i.e., at some finite value L_0. Since C is dominated by the term involving dN_l/dT, truncation causes a strong drop in C. Thus, we expect that the T_p's should follow a power law involving the same exponent as that determined for N_l:

$$L - L_0 \sim (T_t - T_p)^{-0.36}. \tag{2}$$

Figure 4 shows that the peak temperatures do obey Eq. (2), with exponent -0.35 and L_0 corresponding to one layer.

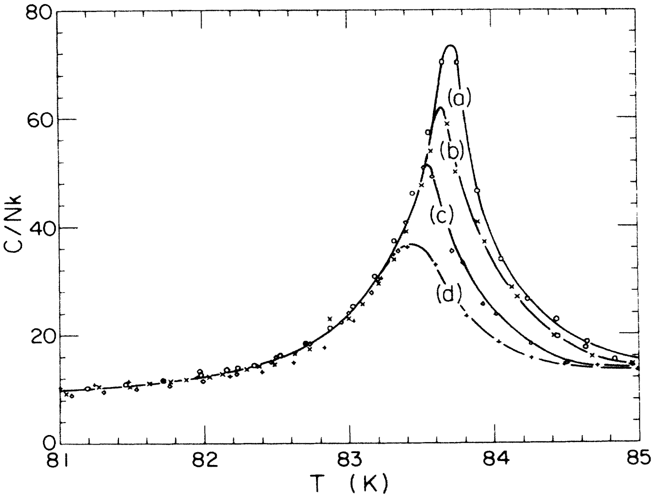

FIG. 3. Expanded melting regions, showing the common envelope and the progression of the peak temperatures with increasing thickness.

The empirical value for L_0 indicates that a single layer closest to the substrate has a melting temperature appreciably different from the others. This in turn suggests that it is the melting of this single layer that causes the small peak at $T > T_t$. Its shift to higher T in thicker films may be due to compression.

All of the films in Fig. 1 show weak, rounded anomalies centered at 68 K. Changes of thickness have little effect on their temperature, shape, or absolute magnitude; hence they are probably associated with the vapor interface. A possible cause is surface roughening; further evidence supports the hypothesis. Roughening temperatures T_R are approximately equal to $0.8T_t$ for dense faces of simple bulk systems, as deduced from the growth of van der Waals crystals[16] and molecular-dynamics simulations[17]: Our Ar multilayer peaks are at $0.8T_t$. Roughening transitions in multilayers must be affected by finite thickness, but T_R is expected to be independent of substrate potential.[4] Roughening transitions have been observed in adsorbed films by the disappearance of sharp layer steps in vapor pressure isotherms: in Ar/CdCl$_2$, $T_R \sim 0.8T_t$,[18] and in methane/graphite, $T_R \sim 0.85T_t$.[7] Roughening is predicted to be a

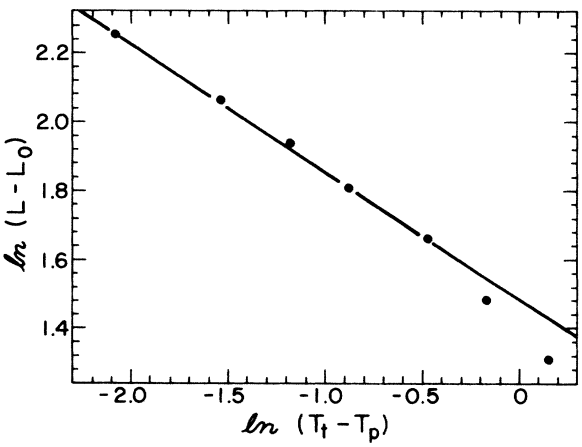

FIG. 4. Variation of peak temperature T_p on thickness, showing that $(T_t - T_p)$ varies as a power law with thickness.

continuous transition of the same class as the Kosterlitz–Thouless planar model, producing a nonuniversal rounded specific-heat anomaly below T_R.[1] Thus, our experimental anomalies may be intrinsically rounded rather than heterogeneity-broadened sharp peaks, and the actual transition temperatures may be somewhat above 68 K. The existence of roughening, with T_R lower than the start of surface melting, can explain why we see no evidence of layering in the melting regime. Nevertheless, the anomalies are well separated from the premelting regime, evidence that a rough solid and liquid surface are qualitatively distinct.

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