Melting in Two Dimensions: The Ethylene-on-Graphite System

J. Z. Larese and L. Passell
Brookhaven National Laboratory, Upton, New York 11973

A. D. Heidemann and D. Richter
Institut Laue-Langevin, Grenoble, France

and

J. P. Wicksted
Oklahoma State University, Stillwater, Oklahoma 74078

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Elastic and quasielastic neutron-scattering results for the melting of submonolayer ethylene films on graphite are described and microscopic evidence is presented for a continuous melting transition. Comparisons are made with data for equivalent methane films and with molecular-dynamics simulations. Differences in melting behavior are attributed to different vacancy creation mechanisms in the films.

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Dislocation pairs, being much lower-energy defects in two than in three dimensions, are believed to have a profound effect on the stability of 2D solids. In fact, dislocation-pair unbinding[1] is thought to initiate a continuous melting process in which a bond-directionally ordered liquid first forms and then evolves, at a higher temperature, into an isotropic liquid phase. Whether it is the mechanism responsible for the melting of weakly bound, physisorbed solid films, however, is unclear. Evidence suggestive of bond-directional ordering has been seen in liquid-xenon films on both graphite[2] and silver[3] in a restricted coverage range. But—possibly because of peculiarities in the shape of the solid-liquid phase boundary—of the many physisorbed systems investigated to date, only one, ethylene on graphite, has been found to have a heat-capacity signature indicative of a continuous transition.[4]

The ethylene-on-graphite system is also unique in that both its structure and dynamics in the neighborhood of melting can be directly probed by elastic and quasielastic neutron scattering. Here we report the results of such a study and make comparisons with data for equivalent methane films in which melting is known from heat-capacity measurements to be a discontinuous transition.

At submonolayer coverages and low temperatures, methane (a pseudospherical molecule) forms a commensurate $\sqrt{3}\times\sqrt{3}$, orientationally disordered, triangular-lattice solid on graphite basal-plane surfaces. Isotropic rotational diffusion of the molecules begins below 30 K.[5] The film expands out of registry near 48 K and ultimately melts at 56.6 K.[6] At melting the nearest-neighbor distance is 4.31 Å. A sharp anomaly in the heat capacity (full width at half maximum 0.15 K) shows the melting transition to be a discontinuous, first-order, process.[7]

Ethylene (a planar molecule) forms, at low temperatures and all coverages below 0.84 monolayers, an incommensurate, orientationally ordered, centered-rectangular solid on graphite.[8] Molecular-dynamics simulations indicate that the molecules are aligned in a herringbone array in this phase and that their $C=C$ axes lie parallel to the film plane.[9] Above 30 K a simultaneous orientational disordering and structural transition sets in[8] and converts the film to an incommensurate, orientationally disordered, triangular-lattice solid which melts at 67.5 K. At melting the nearest-neighbor distance is 4.75 Å.

Both films melt from incommensurate, orientationally disordered, triangular-lattice solid phases expanded with respect to the substrate and in both cases the melting process is a transition from coexisting solid and vapor phases to coexisting liquid and vapor phases. Furthermore, the ratios of 2D to 3D melting temperatures (0.635 for methane, 0.650 for ethylene) are nearly identical and, at melting, the ratios of nearest-neighbor distances to van der Waals radii (1.9 for methane, 1.8 for ethylene at melting) are similar, indicating that molecular packing in the 2D solids is roughly the same. Nonetheless, their heat capacity peaks at melting (see the inset in Fig. 1) are very different: The ethylene peak is some 20 times broader than that of methane and has an area only a little more than half as large!

Surface heterogeneity is often invoked when broadening is observed in overlayer melting transitions. But heat-of-adsorption studies of methane in ethylene films on the same graphite substrate[10] show that about twice as many methane as ethylene molecules are adsorbed at sites with abnormally large surface binding (8% for methane versus 4.5% for ethylene) and yet there is no sign of broadening of the methane transition. Furthermore, no evidence of any upward shift in melting temperature (such as would be expected if the 2D solid were

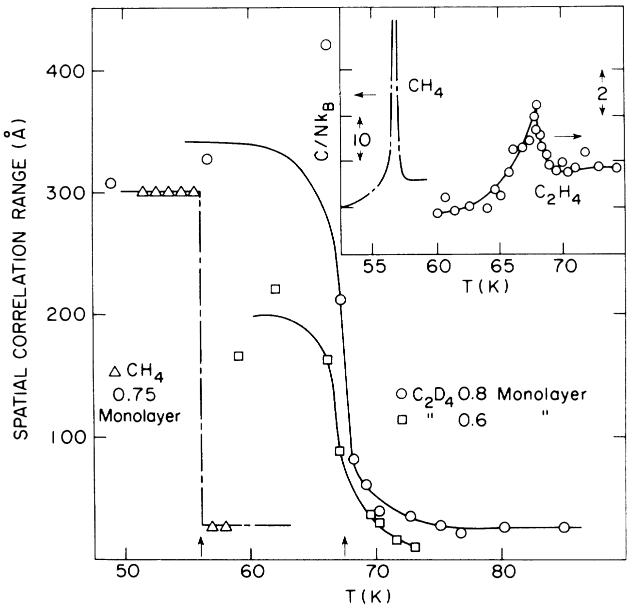

FIG. 1. Temperature dependence of the spatial correlation range in ethylene and methane submonolayer films observed on the same graphite substrate. Melting temperatures are identified by arrows. The heat-capacity profiles in the inset are from Refs. 4 and 7. None of the lines drawn through the data have any theoretical significance.

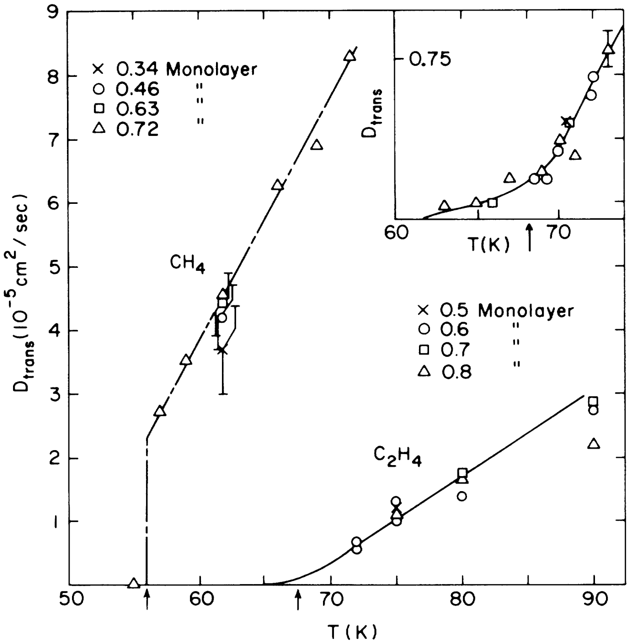

FIG. 2. Temperature dependence of the translational diffusion in submonolayer ethylene- and methane-on-graphite films. The methane data are from Ref. 12. Melting temperatures are identified by arrows. The lines drawn through the data have no theoretical significance.

stabilized by surface inhomogeneities) is found in the ethylene system even at coverages as low as 0.137 monolayer where approximately $\frac{1}{3}$ of the molecules are tightly bound.[11] The differences in melting behavior thus appear to arise from some inherent differences in the characteristics of the films themselves, not from the effects of substrate heterogeneity.

Our investigations were made with films adsorbed on a moderately compressed, exfoliated, crystalline-graphite powder substrate. Film and substrate scattering were separated by our taking the difference between counts with and without the adsorbant in the cell. Coverages were defined by nitrogen isotherms, unit coverage corresponding to one $\sqrt{3}\times\sqrt{3}$ registered monolayer. Two sets of neutron measurements were made: (i) At Brookhaven—using a triple-axis spectrometer operated in the elastic mode—we scanned the (10) diffraction profiles from deuterated methane and ethylene films between 54 and 85 K, fitted them by powder-averaged Lorentzian line shapes folded with the instrumental resolution, and thereby derived the temperature dependence of the spatial correlation range. We also studied the temperature dependence of the incoherent, elastic scattering from protonated ethylene films at fixed momentum transfers and used it to identify the onset of molecular rational motions. (ii) At the Institut Laue-Langevin—using the IN5 time-of-flight spectrometer—and at Brookhaven, we investigated the temperature dependence of the incoherent, quasielastic scattering from protonated ethylene films, fitted the observed spectral distributions by powder-averaged, resolution-convoluted cross sections [including both rotational and (jump) diffusional terms], and determined in this way the temperature dependence of the translational and rotational diffusive motions.

Figure 1 shows the temperature dependence of spatial correlations in the two systems. In the methane film the spatial correlation range drops abruptly, within 0.7% K, from a value characteristic of the 2D solid to one corresponding to the 2D liquid phase. Heat-capacity measurements[7] indicate that there is actually a discontinuous change in the methane film density at the phase boundary. The ethylene transition, on the other hand, is far more gradual: The loss of correlation takes place over a temperature interval of at least 6–8 K with no abrupt increase in the nearest-neighbor distance. This too is consistent with heat-capacity measurements,[4] which indicate a smooth and continuous change in the density of the film.

The translational diffusion data, plotted in Fig. 2, follow the same basic pattern. Coulomb, Bienfait, and Thore,[12] whose measurements of methane films are plotted in the figure, find that methane monolayers melt like 3D systems: Diffusion is undetectable in the solid below the melting transition, increases abruptly at melting, and then rises slowly and linearly with increasing temperature. Our observations of ethylene, however, show very different behavior. Translational diffusion starts slightly below the nominal melting temperature and—with no

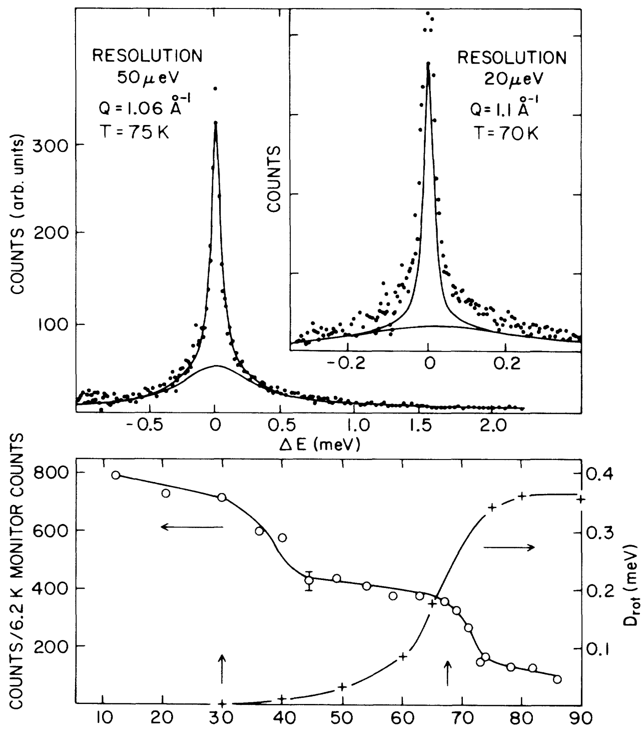

FIG. 3. Top: Comparison of low- and high-resolution scans of the quasielastic scattering from ethylene films. The solid lines are fits to the low-resolution data obtained with a 1.54-Å radius of rotation. Note the extra narrow component in the high-resolution spectrum. Bottom: Temperature dependence of the incoherent elastic scattering from a 0.6-monolayer ethylene-on-graphite film (open circles) observed at $Q=0.75$ Å^{-1}. The first drop at 30 K identifies the onset of rotations about axes normal to the film plane; the second at 67.5 K is the melting transition. The crosses are rotational diffusion rates derived from an incoherent, quasielastic scattering study of a similar film. The best fit to the data was obtained with a 1.54-Å radius of rotation. Neither solid line has any theoretical significance.

sign of a discontinuity at melting—increases smoothly with increasing temperature although at a much lower rate than in methane. There is little evidence of coverage dependence in either case which is not surprising since essentially all of the observed scattering derives from the liquid components of the films.

If we turn now to rotational motions, the data plotted as the open circles at the bottom of Fig. 3 show the temperature variation of the incoherent, elastically scattered intensity from a 0.6-monolayer ethylene film. The measurements were made with the scattering vector fixed at 0.75 Å^{-1} and with an energy resolution of about 50 μeV. Because the molecules in solid films are localized, rotational diffusive scattering has elastic as well as quasielastic components. As rotational motions are excited and rotational diffusion rates become more rapid, weight shifts from the elastic to the quasielastic part of the spectrum.[13] A drop in the incoherent elastic intensity from a solid can thus be used to identify the onset of rotational motions. Extrapolation of Moller and Klein's molecular-dynamics simulations[14] suggests that the molecules are primarily executing rotations about the $C=C$ axis at lower temperatures. The first drop in intensity at 30 K therefore probably marks the beginning of second-axis rotations, in this case rotations about an axis normal to the film plane. This identification correlates well with our observations of the loss of molecular orientational order at 30 K (Ref. 8) and with earlier observations of two-axis rotation deduced from the Q dependence of the incoherent, elastic scattering at 60 K.[13] It is also consistent with our quasielastic data (plotted as crosses at the bottom of the figure) which indicate the onset, above 30 K, of a rotation in which the effective radius of the scatterers (the four protons) is about 1.5 Å (the proton radius is 1.54 Å in the ethylene molecule). The second drop at 67 K is probably due mostly to the onset of translational diffusion at melting which makes all of the scattering quasielastic[13] and thus removes more of it from our 50-μeV window. Third-axis rotations may, however, also be a contributing factor since our highest-resolution, quasielastic data, displayed at the top of Fig. 3, show evidence of another, slower rotational motion near and above the melting transition, probably flipping motions related to the onset of isotropic rotational diffusion.

Comparing our results on ethylene films with the simulations of Ref. 14, we see that both indicate a gradual loss of spatial correlation occurring over a 6°–8° temperature interval (the same range as the heat-capacity measurements of Ref. 4) as well as a gradual increase in translational diffusion through the transition region. Agreement is less satisfactory where rotational motions are concerned. Both experiment and simulation show increased rotational diffusion above 30 K, but the neutron data identify the dominant rotational motion as one with a radius of about 1.5 Å while the simulations suggest that most of the temperature dependence is associated with $C=C$-axis rotational diffusion for which the radius is roughly half as large.

It is clear from the neutron measurements that the thermodynamic differences in the melting transitions of methane and ethylene on graphite stem from an underlying microscopic difference in the way the melting process occurs in the two films. What might this difference be? In Moller and Klein's simulations, ethylene melting seems to be triggered by molecular flipping. Noting that recent molecular-dynamics simulations[15] show that the dislocation pairs that appear near melting in 2D solids are primarily formed by lines of vacancies, we suggest that the difference in melting behavior arises from differences in the way vacancies are formed in the two films. In 2D solids three different vacancy-creation mechanisms are possible: (i) Molecules can leave the periphery of the solid, vacancies form and then diffuse into the interior; (ii) molecules can escape from the first layer and form a partial second layer; (iii) in solid films composed of nonspherical molecules with their long axes parallel to the film plane, the molecules can flip upright momentarily thereby reducing their local projected area and creating void spaces. How effective process (iii) is in a given film will obviously depend on the aspect ratio (A_r) of the molecules: For $A_r \approx 1$, this motion clearly has little effect, while if $A_r > 1$ flipping becomes an effective void-creating mechanism. Note, however, that if $A_r \gg 1$ flipping will require the breaking of surface bonds and will only occur as an adjunct of layer promotion.

Because methane molecules are effectively spherical, only the first two vacancy-creation mechanisms can operate in methane films. But an ethylene molecule upright on the surface covers only about 60% of the area it occupies when lying down and rotating about an axis normal to the film plane. Moreover, flipping can occur without breaking of surface bonds.

In neutron data, a 90° flipping motion would show up as an additional narrow component in the quasielastic scattering. In fact, we see such a component in the high-resolution quasielastic spectra of Fig. 3 and, although the relative intensity is somewhat greater than the 10% expected from the simulations, it suggests that flipping motions are taking place and could well be producing a more gradual drop in the local barriers to diffusion and thus a more continuous melting transition.

In summary, the differences in the heat-capacity signatures of methane and ethylene films on graphite at melting correlate well with differences in their microscopic behavior as observed with neutrons and with molecular-dynamics simulations. Our observations suggest that the mechanism of vacancy formation can affect the character of 2D melting transitions and that such factors as the shapes of the molecules in molecular films can play a role in overlayer melting processes.

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