

Triple-Point Wetting and Surface Melting of Oxygen Films Adsorbed on Graphite

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Neutron-diffraction experiments on multilayer oxygen films on graphite have been carried out between 30 and 55 K. A compound solid-liquid film is observed in the range 40–48 K, exhibiting properties consistent with surface melting. The quantity of liquid in this range varies as $\ln(T_i - T)$. This behavior ceases when the thickness of the liquid component reaches that of the film itself, giving rise to the “metastable liquid” phase of the triple-point wetting process.

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Wetting behavior of a film on a solid substrate falls into two general categories.¹ In systems which exhibit complete wetting, the film thickens monotonically as pressure increases, and remains uniform and flat up to macroscopic dimensions. In systems which exhibit incomplete wetting, the film remains uniform only up to some finite thickness: All additional material goes to form droplets or crystallites of the bulk phase. Wetting behavior is in general temperature dependent and the system may undergo a transition from incomplete to complete wetting at the wetting temperature T_w . Essentially all wetting transitions observed to date occur at bulk triple points.² This connection between melting and wetting phenomena has been considered by Pandit and Fisher³ who suggests a variety of scenarios for the triple-point wetting process, several of which include a compound film phase. We report here a neutron-diffraction study of the triple-point wetting transition of oxygen films on graphite showing the existence of a compound film phase and a direct link between surface melting and wetting phenomena.

Arguments for the occurrence of continuous triple-point wetting suggest that a metastable extension of the bulk liquid-vapor coexistence line persists into the region of bulk solid phase at temperatures below the triple point T_i .⁴ Complete wetting of the liquid that would normally have occurred on this boundary is prevented by abrupt formation of solid crystals as the bulk solid-vapor coexistence line is reached. This argument therefore asserts that the film melting transition occurs well below T_i , the bulk solid-liquid-vapor triple point. Our motivation for the present work was to probe this phenomenological explanation of triple-point wetting by investigation of the structure of multilayer films at temperatures just below the bulk triple point. Of the many systems which exhibit triple-point wetting, we selected oxygen on graphite on the basis of experimental convenience and the extensive literature available on monolayer and multilayer oxygen films.^{5–13}

Figure 1 shows the phase diagram for this system, based on Refs. 5–13 and the present work. Surface coverage is expressed in units of molecules per square angstrom, with a 2D solid bilayer corresponding to roughly $0.22 \text{ molecule}/\text{\AA}^2$. Solid oxygen incompletely wets graphite and below 39 K, 2D solid films coexist with the bulk phase. With increasing temperature, progressively thicker films are able to form and a transition to complete wetting occurs at 54.4 K, the bulk triple point.¹⁴ Film fluid phases are observed well below T_i , consistent with the conjecture proposed above for triple-point wetting. The “fluid-I” phase observed above 47–49 K is similar to bulk liquid oxygen. Prior to the present work, the nature of the “fluid-II” phase occurring between 39 and 48 K remained in doubt: Heiney *et al.*⁵ observed a fluid in this regime but suspected the presence of an “unobserved solid” on the basis of x-ray diffraction measurements. A recent study of oxygen adsorption on an oscillating graphite fiber¹¹ suggested that

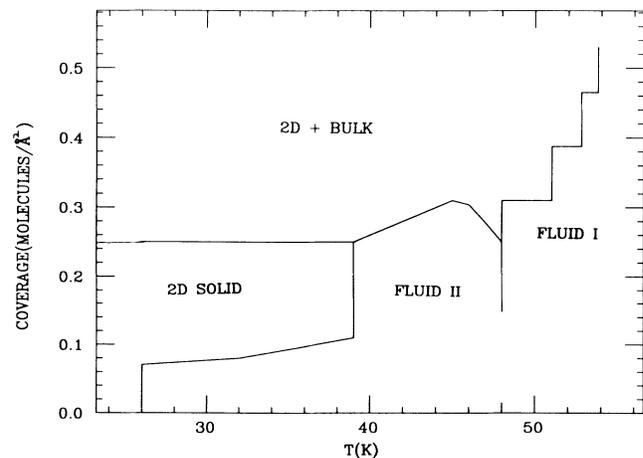


FIG. 1. Phase diagram for oxygen on graphite (Refs. 5–13 and this work).

the films in this regime were solid at coexistence and melted at 49 K. In this Letter we present definitive neutron-diffraction data revealing the fluid-II phase to be a compound solid-liquid film. In addition we will argue that this phase results from surface melting of the adsorbed film and is a precursor to the triple-point wetting transition.

Our measurements were carried out on 1.36 g of Papyex of exfoliated graphite, density 0.1 g/cm^3 and having a surface area estimated to be $36 \text{ m}^2/\text{g}$. This sample was roughly one-tenth as dense as that ordinarily employed in diffraction studies so as to minimize condensation of oxygen into capillaries and crevices, and its mosaic spread was estimated to be 66° (full width at half maximum). The plane of scattering was parallel to the planes of the graphite chips, corresponding to the average basal-plane orientation of the crystallites. Surface coverage was calibrated with respect to that of a $\sqrt{3} \times \sqrt{3}$ registered monolayer phase ($0.064 \text{ molecule/\AA}^2$). The oxygen was condensed at 55 K and then slowly cooled to the temperature of interest. Annealing after cooling produced no change in the observed diffraction scans. Our measurements were carried out between 34.5 and 54.5

K, and for coverages ranging from 0.24 to 0.9 molecule/ \AA^2 , the equivalent of 3 to 12 liquid layers.

Figure 2 shows three scans carried out within the fluid-I regime at surface coverages of 0.24 and 0.32 molecule/ \AA^2 . Peaks near $Q = 1.85$ and 2.55 \AA^{-1} correspond to imperfect subtraction of the graphite substrate and aluminum sample-cell background signals. Scans (a) and (b) were carried out below T_t , while scan (c) was recorded at a temperature slightly above T_t . All are essentially identical, and the shape and position of the diffraction pattern are those expected for a fluid with the spacing of bulk liquid oxygen.⁷ This result is consistent with earlier studies and the conjecture for triple-point wetting.

Figure 3 shows scans which were carried out within the fluid-II regime. All show evidence of a compound film phase, indicated by the superposition of solidlike peaks with a fluid-I background. We thus confirm the existence of the "unobserved solid" suspected by Heiney *et al.*⁵ Although two-phase coexistence is observed, fluid

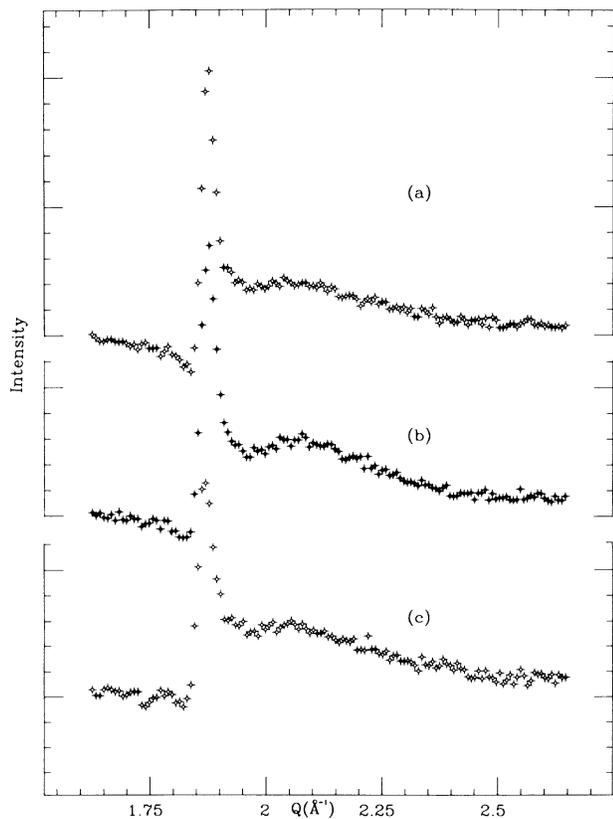


FIG. 2. Diffraction scans recorded in the fluid-I regime. (a) 0.24 molecule/ \AA^2 at 49.5 K. (b) 0.32 molecule/ \AA^2 at 49.5 K. (c) 0.32 molecule/ \AA^2 at 54.5 K.

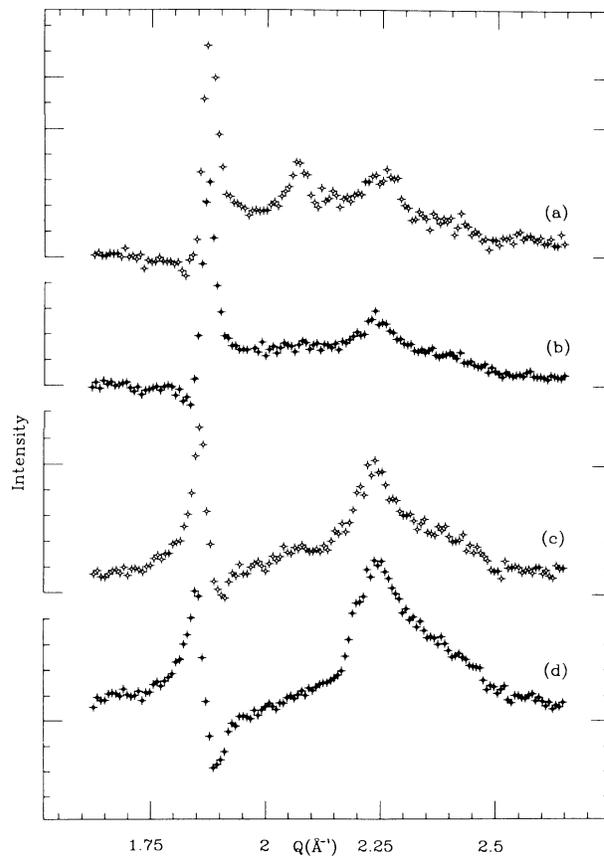


FIG. 3. Diffraction scans recorded in the fluid-II regime. (a) 0.32 molecule/ \AA^2 at 46.5 K. (b) 0.24 molecule/ \AA^2 at 44.5 K. (c) 0.32 molecule/ \AA^2 at 44.5 K. (d) 0.32 molecule/ \AA^2 at 41.5 K.

II occurs over too large a temperature span to correspond to first-order film melting. A second possibility is that the solid peaks observed in the fluid-II regime correspond to condensation of bulk solid crystallites. Such peaks for the solid γ phase are indeed observed in scans (a) and (c) at $Q=2.05 \text{ \AA}^{-1}$, but serve only to confirm the occurrence of incomplete wetting. All other peaks show no correspondence to the bulk γ phase.

The scattering intensity near $Q=2.0 \text{ \AA}^{-1}$ is essentially due to the fluid-I phase, well away from any film or 3D solid peak. We employed the scattering intensity at this point to gauge the quantity of liquid present in each of the fluid-II scans. We then subtracted that amount of liquid [via direct numerical subtraction of fractions of scans (a) and (b) in Fig. 2] from each fluid-II scan so as to probe the nature of the solid component. Several of the resulting scans are shown in Fig. 4. For reference, we have included a scan taken within the ζ 2D solid regime at $0.24 \text{ molecule/\AA}^2$ [Fig. 4(a)]. We note a striking similarity between the solid component of fluid-II and diffraction scans recorded for true solid monolayers and bilayers.¹⁰ It is likely, therefore, that fluid II is composed of fluid I atop a solid underlayer with the ζ or η structure described in detail in earlier studies. We reserve precise determination of these structures for future work and so present no line fits to the data.

Zhu and Dash¹⁵ have studied surface melting in the

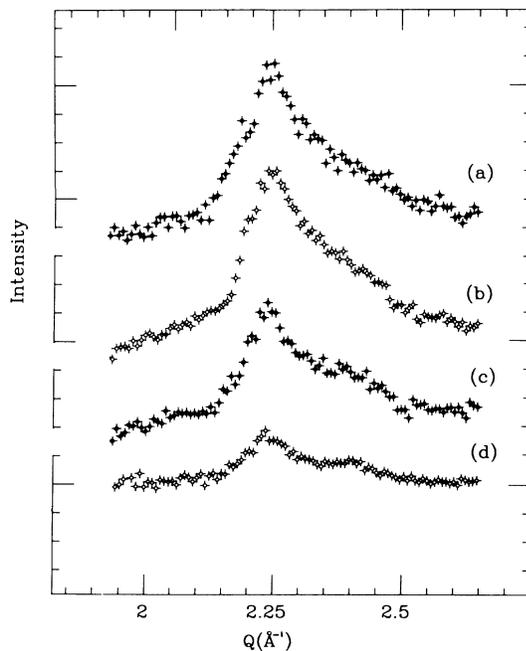


FIG. 4. Diffraction scans of the solid component of fluid II. (a) $0.24 \text{ molecule/\AA}^2$ at 34.5 K (ζ solid regime). (b) $0.32 \text{ molecule/\AA}^2$ at 41.5 K (liquid subtracted). (c) $0.32 \text{ molecule/\AA}^2$ at 44.5 K (liquid subtracted). (d) $0.24 \text{ molecule/\AA}^2$ at 44.5 K (liquid subtracted).

system Ar/graphite via heat-capacity measurements and have observed a power-law dependence for the melted-surface layer. In contrast, our data for oxygen films exhibit a logarithmic dependence on temperature. In Fig. 5 we plot the dependence of the intensity of the liquid component of fluid II (measured near $Q=2.0 \text{ \AA}^{-1}$) versus $\ln(T_i - T)$ for our measurements which were carried out at coverages of 0.24 and $0.32 \text{ molecule/\AA}^2$. With the exception of $0.24 \text{ molecule/\AA}^2$ at 44.5 K , these scans were carried out at bulk coexistence, as indicated by small quantities of 3D solid, and by extrapolation of the third- and fourth-layer condensation lines reported in Ref. 12. Also plotted is the fluid-I film thickness at bulk coexistence deduced from the adsorption-isotherm measurements of Drir and Hess. We are unable to explain the difference in the temperature dependence between the argon and oxygen films. There are, however, major differences between the two systems: Argon films completely wet graphite and were substantially thicker than the oxygen films studied here. In addition, argon films appear to exhibit solid-liquid stratification above T_i , whereas oxygen films melt entirely at a temperature well below T_i . The logarithmic dependence of the liquid component of fluid II is consistent with that predicted by Lipowsky¹⁶ for surface melting in semi-infinite systems with short-range forces. Short-ranged forces may dominate here on account of the very limited film thicknesses

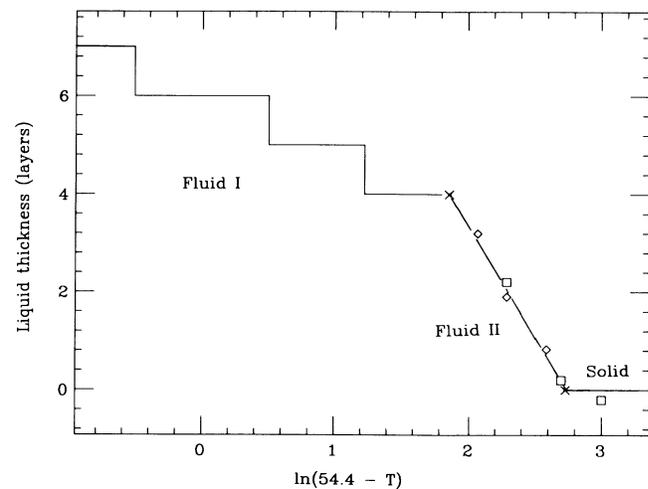


FIG. 5. Quantity of liquid present vs $\ln(T_i - T)$. "Staircase" solid line from Ref. 12. Solid line at zero liquid thickness is the 2D solid regime (Fig. 1). Lozenges at $(2.07, 3.2)$, $(2.29, 1.9)$, and $(2.59, 0.83)$ recorded at surface coverage $0.32 \text{ molecule/\AA}^2$ along bulk coexistence line. Squares at $(2.29, 2.2)$, $(2.70, 0.2)$, and $(3.0, -0.2)$ recorded at surface coverage $0.24 \text{ molecule/\AA}^2$. The lowest two temperatures are estimated to be at bulk coexistence. The highest-temperature point was recorded at $P/P_0=0.82$. Crosses at $(2.73, 0)$ and $(1.86, 4)$ denote the beginning and end of the fluid-II regime, as determined in previous studies.

involved. With the assumption that surface melting is indeed occurring, between 47 and 48 K the thickness of the melted surface layer reaches that of the film itself and a new regime (fluid I) is encountered.

In summary, we observe a compound film in the fluid-II regime of oxygen on graphite similar to that suggested by Pandit and Fisher. The solid component of this film displays diffraction patterns essentially identical to those of true solid monolayers and bilayers (Fig. 4). There is strong evidence that the fluid-II phase occurs on account of surface melting of the film, commencing between 35 and 40 K (in the same vicinity that monolayer melting occurs). The quantity of liquid observed increases as $\ln(T_f - T)$, consistent with surface-melting predictions for short-ranged interactions. Between 47 and 48 K, the thickness of the "surface-melted" component reaches that of the film itself, marking the end of the fluid-II regime (Fig. 5). Above 47–48 K, only liquid films can occur, thus explaining the "metastable liquid" phase of the triple-point wetting process.

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