Influence of Surface Melting Characteristics on the Wetting Behavior of Solid Adsorbed Films

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Surface melting is in principle a widespread phenomenon and has recently been observed for physisorbed films on graphite and magnesium oxide substrates. Neutron diffraction studies of oxygen films adsorbed on graphite have revealed a logarithmic temperature dependence for the quantity of fluid present in the surface melting regime and have confirmed a close link between film melting and wetting properties. These studies also suggest that multiple transitions from incomplete to complete wetting may be present, each occurring at a bulk triple point. Preliminary investigations of bulk oxygen indicate that its surface melting behavior may be quite distinct from that of the film phase.

I. Introduction

The wetting behavior of a film adsorbed on a solid substrate is an important issue in surface science concerning a wide range of fundamental and applied problems. Wetting behavior falls into two general categories. In systems which exhibit complete wetting, the film thickens monotonically as the vapor pressure surrounding the substrate increases. Incomplete wetting refers to a material that, as the pressure increases, forms only a thin film, which coexists with bulk droplets or crystallites. Continuous transitions from incomplete to complete wetting at bulk triple points $T_c$ are extremely common. Arguments for the occurrence of continuous triple point wetting suggest that a metastable extension of the bulk liquid–vapor coexistence line persists into the bulk solid regime at temperatures below $T_c$. This would require that the film (or film surface) melt at temperatures lower than $T_c$ and would imply that surface melting is present whenever a triple point wetting transition occurs.

Premelting on any surface, be it that of a film, 3D crystal, or otherwise, is itself based on broad thermodynamic grounds and is predicted to occur whenever the solid phase is wetted by its own liquid phase. Although for many years this behavior was believed to be widespread; it has only recently been confirmed by experiments on three-dimensional (3D) lead crystals and physisorbed films on graphite and magnesium oxide substrates.

The temperature dependence of the thickness of the surface-melted layer is of great interest. This information allows understanding of the mechanisms which control both surface melting and 3D melting. Theories which assume short-range interactions predict a logarithmic dependence, while long-range interactions produce a power law dependence. Not all experiments on adsorbed films have revealed the same temperature dependence. Oxygen films on graphite which are 2–4 layers thick and thin methane films on magnesium oxide show a logarithmic temperature dependence, while studies of 20–40-layer-thick argon films indicate a power law dependence for the melted layer thickness. One suggested reason for this discrepancy is that the argon films are dominated by long-range interactions while the relative thinness of the oxygen and methane films induces a logarithmic temperature dependence. If so, a crossover from logarithmic to power law behavior is expected as the adsorbed film thickens. Such behavior has recently been observed both experimentally and theoretically. We therefore anticipate that a study of surface melting in thick oxygen films or bulk oxygen should reveal a power law dependence. We describe here such a study of the surface melting of bulk oxygen adsorbed on graphite, beginning with a summary of the results obtained for oxygen films.

II. Surface Melting of Adsorbed Oxygen Films

A. Experimental Details. The neutron-scattering measurements were performed at Grenoble’s Institut Laue-Langevin (ILL) on the D1b beam line operating in the elastic mode. The wavelength of the incident neutrons is $2.517 \AA$. Elastically scattered neutrons were collected within the range $0.07-0.86 \AA^{-1}$. The overlayer diffraction patterns were obtained by subtracting off the background due to the bare graphite. The substrate consisted of a 8 g of Papyex exfoliated graphite, with a density of 0.1 g/cm$^3$ and having a surface area estimated to be 36 m$^2$/g. Surface coverage was calibrated with respect to that of a $\sqrt{3} \times \sqrt{3}$ registered monolayer phase (0.645 mol/Å$^2$) of methane. 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. The experiments were carried out between 34.5 and 54.5 K, and for coverages ranging from 0.24 to 0.9 mol/Å$^2$, the equivalent of 2–8 solid layers (density 0.11 mol/Å$^2$) or 3–12 liquid layers (density 0.075 mol/Å$^2$).

B. Analysis and Results. Figure 1 shows the scans recorded at a surface coverage of 0.32 mol/Å$^2$. The scan at 49.5 K has been recorded well below the bulk triple point.

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Figure 1. Diffraction scans recorded at a surface coverage of 0.32 mol/Å². Bulk γ peaks are observed at $T = 46.5$ K. Too little of the bulk γ phase is present at 49.5 K to be observed in the diffraction scan.

point, yet it reveals a fluid-phase film. The scans between 41.5 and 46.5 K have been recorded in the surface-melted-film regime. All of the surface-melted-film scans show evidence of a compound film phase, indicated by the superposition of solidlike peaks with a fluid film background.

The scattering intensity at $Q = 2.0$ Å⁻¹ is due only to the solid film phase and is well away from any oleic acid or 3D solid peak. We employ the intensity at this point to estimate the quantity of fluid film present in each of the surface-melted-film scans and then subtract the fluid film portion so as to reveal the line shape of the solid component. The resulting scans (for total surface coverages of both 0.24 and 0.32 mol/Å², excepting 0.32 mol/Å² at 46.5 K), including our best fit, are shown in Figure 2. For reference, we also include a scan recorded in the 2D solid regime at 0.24 mol/Å² and 34.5 K (Figure 2b).

To determine the structure of the underlying solid, the diffraction data were fit by following a method described previously in great detail. Multilayer line shapes were obtained by assuming the surface monolayer line shape is modified by a structure factor, which describes multilayer interference effects. For each possible molecular stacking arrangement (AA, AB, ABA, or ABC), the multilayer line shape has a well-defined characteristic functional form. It is the ordered arrangement of molecules in a given stacking sequence, along with the in-plane structure, that provides the characteristic shape of the multilayer diffraction pattern.

The best fit to the data corresponded to O₂ molecules oriented perpendicularly to the substrate and arranged in equilateral triangles within the planes. The solid component of the film grew in an ABC stacking arrangement with lattice parameters quite close to that of the 3D β phase of oxygen. This rhombohedral phase is stable between 24 and 43.8 K and consists of an ABC stacking arrangement with 3.76 Å between the individual planes of molecules. The results are summarized in Table I and are in excellent agreement with recent computer simulations of oxygen on graphite. The complete details of the fit are published elsewhere. As the temperature increases from 40 to 48 K, the quantity of liquid increases. Assuming the liquid density to be 0.075 mol/Å² per layer, the surface-melted liquid layer thickness, $n_0$, is well described by

$$n_0 = 12.9 - 4.70 \ln (54.4 - T)$$

(1)

Table 1. Film Characteristics in the Surface Melting Regime

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>34.5</th>
<th>39.5</th>
<th>44.5</th>
<th>41.5</th>
<th>44.5</th>
<th>46.5</th>
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<td>$n_0$, mol/Å²</td>
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<td>0.24</td>
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<td>0.32</td>
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<tr>
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<td>0.062</td>
<td>0.145</td>
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<td>$n_2$, mol/Å²</td>
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<td>0.075</td>
<td>0.258</td>
<td>0.175</td>
<td>0.08</td>
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<td>$n_3$, layers</td>
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<td>2.2</td>
<td>0.83</td>
<td>1.93</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>$n_4$, layers</td>
<td>2.19</td>
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<td>0.72</td>
<td>2.28</td>
<td>1.63</td>
<td>0.75</td>
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</table>

Figure 3a shows the number of liquid layers for coverages of 0.24 mol/Å² (diamonds) and 0.32 mol/Å² (squares) along with our best fit to the data, eq. 1. The cross at 48 ± 1 K and four liquid layers corresponds to the “feature” reported in heat capacity studies and microbalance studies at 47 K and microbalance studies at 49 K. We associate this feature with the high-temperature limit of the surface melting regime. The cross at 39 ± 1 K and 0 liquid layers corresponds to the low-temperature limit of the “fluid II” regime reported

in X-ray diffraction studies. Our study does not allow us to determine whether the surface melting is occurring in a continuous or layer-by-layer manner. Throughout the surface melting regime $n_l$ is within experimental error of an integer number of layers, suggestive of layer-by-layer melting. The evidence is, however, far from conclusive.

Figure 3b shows $n_l$ plotted as a function of $\ln (T_l - T)$. The dashed curve shows the best fit to the data and is not linear. The dotted line shows the expected behavior if the data were to follow the power law $n_l \propto (T_l - T)^{-1/3}$. The logarithmic temperature dependence is preferred over the power law behavior.

No film phase occurs, which is similar to 3D $\gamma$ oxygen, the bulk phase which is stable between 43.8 and 54.4 K. We conclude that both the $\beta$ phase and the liquid phase wet graphite more strongly than $\gamma$ oxygen. Complete wetting by the $\gamma$ phase is therefore prevented. This is apparently due to the attractive nature of the substrate, and a preference for the higher density $\beta$ phase results. The results are quite suggestive that multiple wetting transitions may be present. If the $\beta$ phase indeed wets graphite, then a transition to incomplete wetting would occur at the $\beta-\gamma$ triple point (43.8 K). A transition from incomplete to complete wetting is known to occur at the $\gamma$-liquid triple point (54.4 K). The 46.5 K scan in Figure 1 is suggestive of this possibility. At this temperature, bulk $\gamma$ peaks are present and show coexistence with a surface-melted-film phase. This behavior is indicative of incomplete wetting. No bulk $\gamma$ peaks are observed at either higher or lower temperatures. This shows that thicker film phases are able to form at both higher and lower temperatures, since the surface coverage is a constant throughout Figure 1.

Incomplete wetting by the oxygen films near the melting point prevents the study of surface melting in thick adsorbed films. It does not, however, prevent study of the

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Figure 3. (a) Number of liquid layers as a function of $\ln (T_l - T)$ for coverages of $0.24 \text{ mol} / \text{Å}^2$ (diamonds) and $0.32 \text{ mol} / \text{Å}^2$ (squares) layers, respectively. The solid line corresponds to the best logarithmic fit to the data, eq 1. Crosses denote the beginning and end of the surface-melted regime, as determined in previous studies (see text).19,20 (b) $n_l$ as a function of $\ln (T_l - T)$ for coverages of $0.24 \text{ mol} / \text{Å}^2$ (diamonds) and $0.32 \text{ mol} / \text{Å}^2$ (squares) layers, respectively. The dashed line corresponds to the best logarithmic fit to the data. The dotted line corresponds to a power law with exponent $-1/3$.

Figure 4. Bulk diffraction scans recorded at an equivalent film coverage of $20 \sqrt{2} \times \sqrt{2}$ registered monolayers. The solid lines are the best fits to the data. Arrows indicate the 3D $\gamma$ oxygen (210) and (211) diffraction peak positions, respectively. (a) 50.3 K, $n_l = 0.93 \text{ mol} / \text{Å}^2$, $n_h = 0.35 \text{ mol} / \text{Å}^2$; (b) 52.0 K, $n_l = 0.99 \text{ mol} / \text{Å}^2$, $n_h = 0.29 \text{ mol} / \text{Å}^2$; (c) 53.5 K, $n_l = 1.11 \text{ mol} / \text{Å}^2$, $n_h = 0.17 \text{ mol} / \text{Å}^2$; (d) 54.3 K, $n_l = 1.26 \text{ mol} / \text{Å}^2$, $n_h = 0.02 \text{ mol} / \text{Å}^2$; (e) 55.0 K, $n_l = 1.28 \text{ mol} / \text{Å}^2$. The surface melting behavior of the bulk $\gamma$ crystals, which form when oxygen is introduced to the cell at the saturated bulk vapor pressure. Such a study is described in the next section.

III. Surface Melting of Bulk Oxygen

A. Experimental Details. Neutron diffraction measurements on bulk $O_2$ were performed at the high flux beam reactor of Brookhaven National Laboratory (BNL) beam line H5 operating in the elastic mode. The instrumental resolution was 0.0123 Å$^{-1}$ half peak width at half maximum intensity (hwmi), and the incident neutron wavelength was 1.651 Å. Data were collected over the range 1.94–2.40 Å$^{-1}$. The vermicular graphite (Union Carbide GTA grade) substrate was loaded into a thin-walled aluminum sample cell mounted to a closed cycle helium refrigerator. The $O_2$ was condensed at approximately 60 K and then cooled to the desired temperature. Diffraction scans were recorded at coverages ranging from 3 to about 20 $\sqrt{2} \times \sqrt{2}$ registered monolayers. Surface coverage was calibrated by matching the liquid-phase normalized integrated diffraction intensity of the ILL data to that of the BNL data in the region of overlap and then extrapolating to higher coverage, assuming the integrated diffraction intensity to be proportional to surface coverage.

B. Analysis and Results. Figure 4 shows the diffraction scans recorded in the range 50.3–55 K at an equivalent film coverage of $20 \sqrt{2} \times \sqrt{2}$ registered monolayers (1.28 mol / Å$^2$). The scans were recorded above 50 K in order to avoid complications due to 2D solid peaks. (The 2D solid has completely melted at or below 49 K.) The scans taken throughout this temperature range are indicative of a 3D solid (sharp, narrow diffraction peaks) coexisting with a fluid phase (broad Lorentzian back-
Table II. Bulk Surface Melting Characteristics

<table>
<thead>
<tr>
<th>$T$, K</th>
<th>50.3</th>
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<td>$d_{200}$, Å</td>
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<td>525</td>
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<td>546</td>
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<tr>
<td>$G_1$, Å⁻¹</td>
<td>0.36</td>
<td>0.34</td>
<td>0.36</td>
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<td>0.36</td>
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</table>

*Quantity of fluid on the portion of the substrate not covered by oxygen crystallites. The oxygen crystallites cover a maximum of 3% of the available surface area for adsorption. $\mu_1$ and $G_1$ are the liquid peak position and full width at half maximum, respectively.

Figure 5. (a) Quantity of liquid as a function of $\ln (T_i - T)$ for bulk oxygen (20 $\sqrt{3} \times \sqrt{3}$ registered monolayers). Boxes correspond to $n_i$ (melted) given in Table II. The solid line is the best logarithmic fit to the data. (b) $n_1$ as a function of $\ln (T_i - T)$ for bulk oxygen. The solid line is the best power law fit to the data, which provides an exponent of $-1/18$.

We employ the quantity of liquid attributable to bulk surface melting as a rough gauge of the thickness of the surface-melted layer. In contrast to the results for oxygen films, there is no close preference between the logarithmic (Figure 5a) or power law (Figure 5b) behaviors. Without information on the size and shape of the crystallites, we are unable to carry out a more definitive analysis.

IV. Discussion

Our studies have confirmed a close link between the triple point wetting transition and surface melting. Indeed, it stands to reason that if the surface free energy of the substrate–film combination can be lowered by the presence of an adsorbed liquid film below $T_i$ (triple point wetting), then the solid phase of the adsorbate might also be wetted by its own liquid (surface melting). The converse does not appear to be the case. Complete wetting by a solid adsorbed film precludes the occurrence of a triple point wetting transition yet does not appear to preclude surface melting, as evidenced by the Ar/graphite system.

The $O_2$/graphite triple point wetting transition has facilitated our studies of surface melting in the film phase. Unfortunately, it has greatly complicated our studies of surface melting in bulk oxygen. We have obtained evidence that surface melting does indeed occur, and it appears to be quite distinct from that observed for the film phase. Nonetheless, the presence of the graphite substrate and the film-phase wetting transition and the lack of precise knowledge concerning crystallite size and geometry prevent us from distinguishing between a logarithmic or power law temperature dependence. Such information could ideally be obtained by employing a substrate solid oxygen was known to wet or by studying bulk oxygen in the absence of any substrate.

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Registry No. $O_2$, 7782-44-7; graphite, 7782-42-5.