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Multilayer adsorption of oxygen on graphite near the triple point

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Using an ellipsometric technique, we have observed layer-by-layer adsorption isotherms of oxygen on a small patch of a single cleaved surface of highly oriented pyrolitic graphite. As many as nine steps are seen. The overall features are characteristic of wetting at the triple point ($T_3 = 54.35$ K): Below T_3, bulk crystallite formation preempts film growth after a limited number of layers. Above T_3, the film grows to a thickness equivalent to about 40 layers. However, indications of bulk droplets appear above about 12 layers. Our results suggest not quite complete wetting even by the liquid phase.

There has been recent theoretical[1] and experimental[2–12] interest in wetting behavior in physisorption systems. It has been known for some time that solid krypton and xenon wet graphite;[2] that is, a solid film is believed to grow layer by layer with increasing vapor pressure into the bulk solid phase. Other systems, including ethylene[3–5] or oxygen[6–11] on graphite, or various adsorbates on gold,[12] seem to exhibit complete wetting by liquid but not by solid adsorbate, so that there is a wetting transition at the triple point. In these cases the film is liquid on either side of the bulk triple temperature T_3, but below T_3 three-dimensional crystallites can coexist with a liquid film of finite thickness, each having lower chemical potential than the three-dimensional liquid, so that thicker films are preempted. This limiting thickness should diverge as the temperature approaches T_3 from below.[13,9]

For ethylene and oxygen on graphite, the two-dimensional critical temperatures of at least the first few layers are above T_3. Therefore, adsorption isotherms in the vicinity of the triple point will be stepped due to first-order condensation in successive layers. The simplest theoretical model for a stepped isotherm is the Frankel-Halsey-Hill (FHH) isotherm,[14] which will be discussed below. Adsorption isotherms on exfoliated graphite or powder substrates are generally limited to four or five layers before capillary condensation. In addition, high uniformity of the substrate potential is required to observe higher steps, otherwise the free energy difference between successive layers will quickly become less than the difference in binding energy over different patches, washing out layering.[15] Previous studies addressing wetting have often been limited to four[3,4,6] or even two[9,12] resolved steps.

In this paper we report isotherms of oxygen[16] adsorbed on highly oriented pyrolytic graphite (HOPG)[17] in the neighborhood of the triple point of bulk oxygen. We measure coverage of adsorbate by a phase-modulation ellipsometric technique.[18] Quentel, Rickard, and Kern[19] have demonstrated the usefulness of this method in multilayer physisorption. This technique uses only a small patch (0.2×0.1 mm in the present experiment) of a single cleaved surface of substrate, thus avoiding the problem of capillary condensation, while allowing use of a surface of superior uniformity. The primary signal from our ellipsometer is the amplitude I_1 of the output at the modulation frequency (50 kHz), which is proportional to coverage, for low coverages. In addition, the dc output I_0 is a measure of the average reflectance of the surface, and decreases with the appearance on the surface of droplets or crystallites which scatter light out of the specular beam.

The graphite sample is clamped to a copper mount, which is connected to a closed-cycle refrigerator and is electronically temperature regulated. This mount is brazed to a reentrant tube in the wall of a stainless steel vacuum cell, which also contains two windows for ellipsometry. The cell is maintained at a temperature a few degrees warmer than the sample, and is connected to room temperature and to the ion pump system by a 3 cm diameter tube and a room-temperature bakable valve. Gas is admitted through a leak valve and the pressure in the cell is measured by a capacitance diaphragm gauge operated at the cell temperature. It is convenient to manipulate the pressure in the valved-off cell by adjusting the temperature of a copper baffle, which can be colder or warmer than the sample mount. Temperatures are measured with platinum thermometers, with absolute calibration estimated to be uncertain by ± 0.3 K and resolution ± 1 mK. The HOPG sample was baked in flowing argon gas at 500 °C, then cleaved in air with a razor blade immediately before installing in the cell and evacuating. The sample was then baked *in situ* at 300 °C for several hours, at which time the pressure at the ion pump was about 10^{-9} Torr.

Adsorption of the first layer is observed only once each run, during initial filling of the cell. Thereafter the pressure is raised by slowly warming the baffle until bulk adsorbate is distilled to the sample, and then lowered by cooling the baffle, until the third or the second layer is removed from the sample. Figure 1 shows an isotherm at 57 K, beginning after one layer and extending to saturation. The higher coverage portion is expanded in the inset. This temperature is above the bulk oxygen triple point ($T_3 = 54.35$ K), but below the two-dimensional critical temperatures of the first several layers (≈ 61 K).[6] Steps are seen, corresponding to condensation of successive layers, up to the eighth or ninth. The higher steps may be washed out because the substrate does not induce

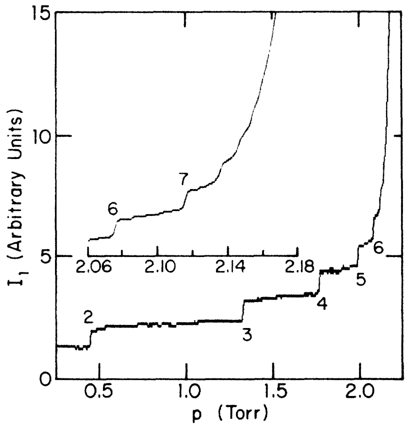

FIG. 1. Ellipsometric adsorption isotherm for oxygen on graphite at $T=57$ K (raw data). The quantity I_1 is proportional to coverage. The inset is a part of the same curve, with an expanded abscissa.

layering to this distance, although surface nonuniformity or the rate of pressure ramping (typically 1 mTorr/sec) could contribute. In all of our isotherms above T_3, the film continued to grow to a thickness equivalent to about 40 layers. Traces of droplet formation appear at about 12 layers and attenuate I_0 by about 3% at 40 layers. There follows a rapid transition to a macroscopically rough state, in which about 40% of the light is diffusely scattered and the I_1 signal is offset, probably due to loss of coherence between reflections from the upper and lower surfaces of the oxygen layer. Termination of film growth at about 40 layers and coexistence with droplets, indicated by scattering, make it appear that liquid oxygen barely fails to wet HOPG. A similar limiting thickness was reported in Ref. 9 in their Fig. 2.

Because of compliance of the temperature regulator, and also thermal impedance between the sample surface and the thermometer, the sample does not remain exactly isothermal, especially during condensation and evaporation of bulk adsorbate. To correct for this, the pressure is normalized to the saturated vapor pressure $p_s(T)$, evaluated at the actual surface temperature inferred from analysis of the thermometer readings. Normalized pressures at the steps are read from plots of I_1 versus p/p_s. The temperature offset during deposition of layers is small, requiring a correction of up to a few percent in pressure. On the evaporation side the corrections can be substantial, as the steps occur while the sample mount is recovering from cooling due to evaporation of bulk condensate. The correction procedure removes most of the resulting hysteresis. However, we use only data from the condensation side for analysis.

A set of isotherms recorded during condensation is shown in Fig. 2. The abscissa for each isotherm has been further normalized by a factor p_s/p_0, where p_0 is the pressure at infinite thickness, extrapolated from the observed steps according to the FHH relation, Eq. (2), below. This is done to put on an equal footing the isotherms taken above and below the triple point, where p_s corresponds to different bulk phases. Isotherms A—E have features characteristic of all recorded below T_3, notably the following: At saturation, I_1 began to fluctuate without increasing beyond a limited number of layers, while I_0 dropped to less than 1% of its initial value, except in cases where the excursion into saturation was slight. Isotherms F—J have the previously described characteristics for temperatures above T_3. From the normalized pressure at the nth step, we calculate the chemical potential difference

$$\mu_n - \mu_0 = k_B T \ln(p_n/p_0) , \tag{1}$$

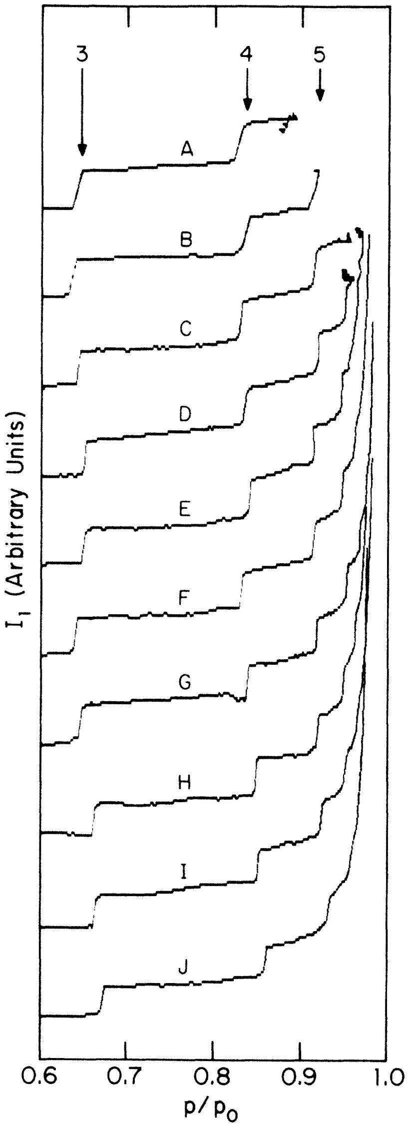

FIG. 2. Oxygen coverage versus normalized pressure along several isotherms: $A=50.05$ K, $B=51.10$ K, $C=52.15$ K, $D=53.24$ K, $E=54.34$ K (below T_3); $F=54.39$ K, $G=56.13$ K, $H=57.17$ K, $I=58.29$ K, $J=60.17$ K (above T_3). The curves are offset vertically. The normalization parameter p_0 is the extrapolated pressure for infinite coverage. Arrows indicate the approximate locations of third, fourth, and fifth layer condensation. Curves A—E terminate with bulk crystallite formation, whereas curves F—J would extend far off scale vertically if not truncated.

and plot this difference for steps $n=3$–7 as a function of temperature in Fig. 3. Also shown is the bulk liquid or solid phase, corresponding to p_s/p_0. The dashed lines are least-squares fits to the step loci. The negative slope of a layer line is equal, by a Maxwell relation, to the partial entropy (in units of k_B) in that layer, relative to the reference state. For the third layer, the partial entropy relative to bulk liquid is $(+0.21\pm0.21)k_B$, where most of the uncertainty is from the bulk liquid line. For the higher layers this difference is closer to zero. This similarity of the film and liquid entropies is not surprising, as the second layer is known to melt near 36 K.[10] It is apparent from Fig. 3 that only a limited number of layers are found below T_3 because the region of chemical potential in which the higher layers would exist is preempted by the three-dimensional solid.

We now ask what information is contained in the magnitude of the chemical potential at which the steps occur. The difference $\mu_n-\mu_L$ (subscript L refers to bulk liquid) includes the attractive potential seen by a molecule in the nth layer due to the graphite substrate, minus the potential from the same region if the graphite were replaced by liquid oxygen, plus the change in free energy associated with any difference in the structure of the film from that of bulk liquid. The FHH model is based on the hypothesis that there is no contribution from a difference in structure, and the difference in potential is of the van der Waals form, varying as the inverse cube of the distance from the interface. Thus,

$$\mu_n-\mu_0=\Delta V=-\alpha d^{-x}n^{-x}\ , \qquad (2)$$

where $x=3$, α is the van der Waals coefficient, and all layers are assumed to have equal thickness d. We have made linear least-squares fits of μ_n versus n^{-3} for each isotherm, starting at $n=3$, from which we obtain $\alpha d^{-3}/k_B=-650\pm20$ K. In those cases in which our isotherms extended to the second step ($\mu_2\approx-85k_B$), that step also falls nearly on the same line.

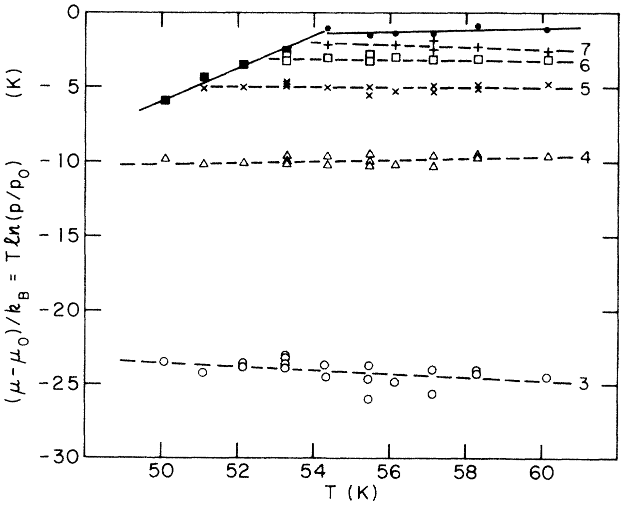

FIG. 3. Chemical potential at layer condensation versus temperature for 19 isotherms. Different symbols are used for each layer, which is identified at the right end. Dashed lines are fits to the points for each layer. The solid circles indicate the appearance of bulk liquid (averaged over repeated isotherms, for clarity) and solid squares indicate the formation of bulk solid. The solid lines are fit to these data. As in Fig. 2, the reference chemical potential (μ_0) is extrapolated from the measured layers to $n\rightarrow\infty$ using Eq. (2) with $x=3$.

Bartosch and Gregory[9] have recently reported adsorption isotherms for oxygen on graphite, obtained by an innovative inertial loading technique, in which they find the exponent x drops abruptly from 3 above T_3 to about 1.9 below. We do not confirm this dramatic jump (indeed, it would imply a drastic modification of the phase diagram in Fig. 3), but we do find deviations from the inverse cube law. This is evident already in the fact that μ_L at which liquid droplets appear is consistently below μ_0 by about (1.0 K)k_B. These would coincide if the FHH assumptions hold and there is complete wetting by the liquid. Below saturation, we find a thickness equivalent to 12 layers where about 9 are expected by extrapolation as n^{-3} from the observed steps. This deviation is in the direction corresponding to $x>3$, and is opposite to the artifact which would arise if condensation were producing significant heating at this point.

We have made least-squares fits of Eq. (2) to our isotherm steps, allowing x as well as α and μ_0 to vary.[20] The resulting best exponents, using all of the available steps from $n=3$–7, are shown as points in Fig. 4. (When the second step is also included, it forces an exponent closer to 3.) The temperature dependence found for the exponent x can be attributed partly to a change in the relative spacing of the steps (i.e., different slopes for different steps in Fig. 3) and partly to the fact that more steps are included above T_3. These higher steps are closer together than predicted by FHH. A possible interpretation is that there is a structural contribution to the energy difference, perhaps associated with layering, which is decreasing with increasing thickness, with significant change in the range $n=5$–7 as well as higher. The failure of the film to grow beyond 40 layers may be due to this same energy, which

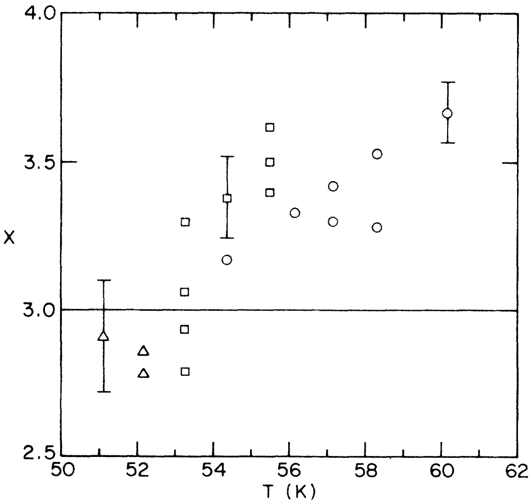

FIG. 4. Exponent, for each isotherm, which gives the best fit of Eq. (2) to the layer chemical potentials. The symbols indicate which steps were measured: Triangles indicate 3, 4, and 5; squares indicate 3–6; circles indicate 3–7.

will prevent wetting if it exceeds the substrate potential at some thickness.[21] The coexistence of droplets with a range of film thicknesses may reflect nonuniformity of the substrate potential ($\delta V/k_B \approx 0.4$ K over a few per cent of the surface) or possibly the kinetics of breakup of a thicker-than-equilibrium film.

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[1] F. T. Gittes and M. Schick, Phys. Rev. B **30**, 209 (1984); C. Ebner, *ibid.* **28**, 2890 (1983); R. Pandit and M. E. Fisher, Phys. Rev. Lett. **51**, 1772 (1983); H. Nakanishi and M. E. Fisher, *ibid.* **49**, 1565 (1982); R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982); R. J. Muirhead, J. G. Dash, and J. Krim, *ibid.* **29**, 5074 (1984).

[2] A. Thomy and X. Duval, J. Chim. Phys. **66**, 1966 (1969); **67**, 286 (1970).

[3] J. Menaucourt, A. Thomy, and X. Duval, J. Phys. (Paris) Colloq. **38**, C4-195 (1977).

[4] I. C. Bassignana and Y. Larher, Surf. Sci. **147**, 48 (1984).

[5] S. G. J. Mochrie *et al.*, Phys. Rev. B **30**, 263 (1984); M. Sutton, S. G. J. Mochrie, and R. J. Birgeneau, Phys. Rev. Lett. **51**, 407 (1983).

[6] B. Gilquin, thesis, University of Nancy, 1979 (unpublished); B. Gilquin and Y. Larher, Surf. Sci. **75**, 703 (1978).

[7] M. Bienfait *et al.*, Phys. Rev. B **29**, 983 (1984).

[8] D. D. Awschalom, G. N. Lewis, and S. Gregory, Phys. Rev. Lett. **51**, 586 (1983).

[9] C. E. Bartosch and S. Gregory, Phys. Rev. Lett. **54**, 2513 (1985).

[10] S. G. J. Mochrie *et al.*, Surf. Sci. **138**, 599 (1984); P. A. Heiney *et al.*, *ibid.* **125**, 539 (1983); P. W. Stephens *et al.*, Phys. Rev. Lett. **45**, 1959 (1980).

[11] J. A. Venables, J. L. Sequin, J. Suzanne, and M. Bienfait, Surf. Sci. **145**, 345 (1984).

[12] J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. Lett. **52**, 640 (1984).

[13] R. Pandit and M. E. Fisher, Phys. Rev. Lett. **51**, 1772 (1983).

[14] See, for instance, W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford, 1974), pp. 238ff.

[15] J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975), pp. 237 and 238.

[16] Matheson research grade oxygen, 99.98% purity.

[17] HOPG is a product of Union Carbide Corp. We are indebted to J. G. Dash for part of a sample supplied to him by A. R. Moore.

[18] S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instrum. **40**, 761 (1969); R. C. O'Handley, D. K. Burge, S. N. Jasperson, and E. J. Ashley, Surf. Sci. **50**, 407 (1975).

[19] G. Quentel, J. M. Rickard, and R. Kern, Surf. Sci. **50**, 343 (1975); G. Quentel and R. Kern, J. Phys. (Paris) Colloq. **38**, C5-109 (1977).

[20] We can fit our steps about equally well with the three-parameter form $\mu_n - \mu_0 = -\alpha d^{-3}(n+x)^{-3}$. However, α then varies strongly in correlation with x so that the physical interpretation fails.

[21] A. D. Migone, J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. B **31**, 7643 (1985), report nonwetting of Ag and Au by liquid ^{4}He, although preceded by film thicknesses of ten layers and more.