Mechanical Properties of Oxygen Multilayers on Graphite

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We have used a high-resolution, high-stability, graphite-fiber oscillator to measure properties of oxygen films adsorbed on graphite. We show that the bulk triple temperature is the wetting temperature. The observation of a transition from solid to liquid in the saturated film at a well-defined temperature below the bulk triple temperature is in accord with the prediction of a Potts lattice-gas model of adsorbed systems.

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While the subject of adsorbed film growth is quite old, it has recently received increased attention because understanding of the phenomenon of wetting has advanced considerably.

Two types of wetting behavior are relevant here, the first being "type 1." A substrate-adsorbate system displays type-1 film growth if, at constant temperature, the film thickness increases monotonically with increasing pressure, becoming infinitely thick (and therefore "completely wet") at the coexistence pressure, at which it is in equilibrium with the appropriate bulk phase. In "type-2" behavior the film thickness is finite to just below the coexistence pressure. (The film is "incompletely wet.") At coexistence bulk material forms. The present experiment addresses the situation in which the wetting properties of the system change abruptly at the triple temperature, T_3. The transition from type-2 to type-1 behavior in this manner permits us to identify T_3 as the "wetting temperature."

Adsorption isotherm measurements can straightforwardly indicate how film thickness depends on ambient pressure. The usual approach involves the introduction into a cell packed with a high-specific-area substrate of known amounts of gas. Equilibrium pressure is determined by a device located outside the experimental cryostat. Unfortunately, two problems with this technique make it unsuitable for the present purpose, which is the study of film growth at temperatures both above and below the bulk triple temperature: Firstly, at high coverages capillary condensation must occur in the tortuous geometry of the substrate. Secondly, equilibration and determination of the pressure of the vapor immediately above the substrate become very questionable at temperatures below the bulk triple temperature.

In order to avoid the above-mentioned problems and still use the desirable substrate, graphite, we have developed a graphite-fiber oscillator. The shift in resonant frequency of the oscillator is proportional to the mass of gas adsorbed on it, provided that the addition of the film does not cause a change in the effective tension or stiffness of the oscillator. In some situations, however, there certainly is a tension or stiffness change and this can provide useful information. We should expect that both capillary condensation and equilibration problems would be minimized in our experiment. The exterior of the fibers is basal-plane graphite (the plane wrapping cylindrically around the fiber). While the fibers used[1] in the present experiments are heat treated at temperatures lower than those which would produce large substrate coherence lengths, homogeneity of the substrate is indicated by the presence of two "steps" in many of our isotherms. Further, scanning electron micrographs show firstly that the surface does not have any features which could lead to capillary condensation and secondly that the substrate coherence length is probably a few nanometers. The surface area of a fiber determined from isotherms agrees well (within 15%) with that appropriate to a solid cylinder of the dimensions of the fiber and confirms that the fibers are not porous. The fibers, typically 10 μm in diameter, are incorporated in a bridge circuit and vibrate at about 10 kHz in a magnetic field of about 0.1 T when driven by an alternating current. A resonant condition is maintained by incorporation of the bridge into a phase-locked-loop circuit. At present, frequency stability corresponds to a mass change on the order of 1% of a liquid monolayer during an experimental run and resolution is on the order of 0.1% of a liquid monolayer.

Our interest in the growth of adsorbed solid films from the vapor leads us to compare here data which we have taken above the triple temperature, T_3, with that taken below. Most usually we have performed measurements of $\Delta\nu_0$, the resonant frequency shift, versus P, the ambient pressure, while maintaining T constant to within ±5 mK. Now, $\Delta\nu_0/\nu_0 = (\Delta S/S - \Delta m/m)/2$ in the small-displacement, linear approximation, where $\Delta S/S$ and $\Delta m/m$ are the fractional changes in stress[2] and mass per unit length for the fiber as gas is adsorbed. We believe that the $\Delta S/S$ term vanishes for fluid films. Flexing and stretching of the fiber will cause a minute circumferential flow of the fluid which relieves stress within the film. [While we cannot easily test the frequency dependence of this effect we are satisfied that there is no obvious breakdown of the mechanism with increasing amplitude of vibration up to 1 μm (10 times our operating amplitude).] In a solid film, on the other hand, circumferential flow is not possible and the $\Delta S/S$ term contributes to $\Delta\nu_0/\nu_0$.

The growth of a structureless film should, in the case that the film completely wets the substrate, be described by the relation $d = [(kT/\alpha)\ln(P_0'/P)]^x$, where d is the film thickness, P_0' is the "virtual" pressure at which the thickness would diverge, and α characterizes the strength of the substrate-adsorbate attraction.[3] If the attraction is of the van der Waals type, the potential falling off with increasing distance, z, from the substrate as z^{-3}, then $x = -\frac{1}{3}$. We have measured isotherms at temperatures between 44 and 57 K in order to test whether or not this exponent is applicable to film growth above *and* below the oxygen bulk triple temperature $T_3 = 54.34$ K.

We find that oxygen films are not completely wet below T_3; that is, a typical isotherm reaches only a finite thickness at P_0, the bulk-solid–gas coexistence pressure. The P_0' values at which the film would become infinitely thick are obtained from fits to the isotherm expression. They appear to lie above the sublimation curve and approach this as T approaches T_3. When the fitting is performed over approximately the last 20% of the pressure range, the exponent values plotted in Fig. 1 are obtained. One sees that the values for isotherms taken at greater than T_3 are in good agreement with the van der Waals value of $-\frac{1}{3}$. However, the values corresponding to temperatures below T_3 are of mean value -0.53 (and may actually be slightly dependent on temperature).

In order to check the validity of our results regarding the exponent x, we have performed the following experiment: After saturating the cell at 50 K with gas (i.e., ensuring that bulk oxygen will be present in parts of the cell) we incrementally raised the temperature from 50 to 56 K. In so doing we maintained equilibrium conditions for coexistence of the adsorbed film with saturated vapor. Typical data are shown in Fig. 2. One sees that the coverage diverges as T_3, but falls to a finite value above T_3. Our tentative explanation for the latter phenomenon is that a truly liquid film cannot be arbitrarily thick because it is necessary to allow for the effect of gravity. (It would thus be interesting to perform these measurements with a vertical fiber.) One can show that if T_3 is the wetting temperature, as the data clearly indicate, the saturation thickness dependence should be described by $d = A[(T_3 - T)/T_3]^x$, where x is the same exponent as that in the pressure-dependence relation provided that $T_3 - T \ll T_3$. Fitting our data by this relation for five runs (using two different fibers) as shown in Fig. 3, we find that the mean value of x is -0.63. While the agreement with the value obtained from isotherms is only fair, it is again quite clear that the value of $-\frac{1}{3}$ is not appropriate to the regime below T_3.

Krim, Dash, and Suzanne[3] used a quartz microbalance to study the wetting behavior of several adsorbed gas films on gold. They consider their films to be "liquidlike" below T_3 and find that $x = -\frac{1}{3}$ below T_3 on the basis of measurement of saturation coverages for various isotherms. Clearly, there is a discrepancy between our data and that of Krim, Dash, and Suzanne. However, it should be noted that they fitted their data for $(T_3 - T)/T_3$ between 0.8% and 30%. We, on the other hand, fitted ours between 0.16% and 1.5%, believing that this is the valid region in which to perform this procedure. (If we "force" fits to our data in the reduced temperature range from 1.5% to 10% we obtain an exponent value of -0.4.)

Before drawing conclusions from the difference observed in our experiment between values of x mea-

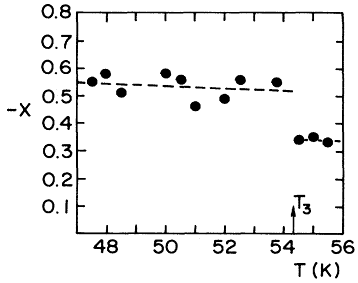

FIG. 1. Values of exponent x for temperature range 47 to 56 K.

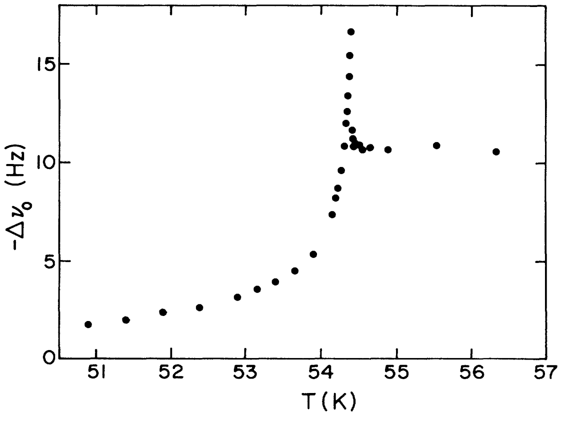

FIG. 2. $\Delta\nu_0$ at saturation vs T. Shift above T_3 corresponds to 46 liquid monolayers. The two highest temperature points are the end points of *individual* isotherms, taken as a check on our "sweep" technique.

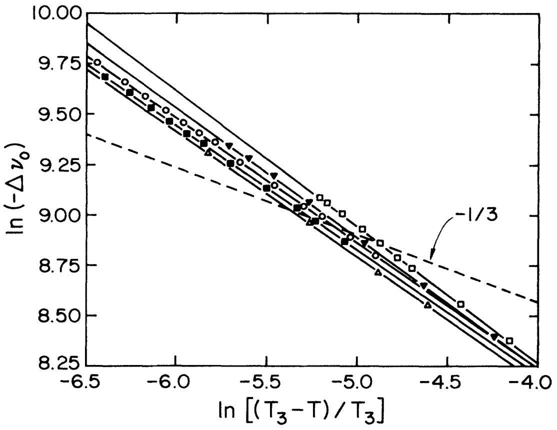

FIG. 3. Fits to $\Delta\nu_0$ at saturation vs T data for five runs. The $-\frac{1}{3}$ exponent line is shown for comparison.

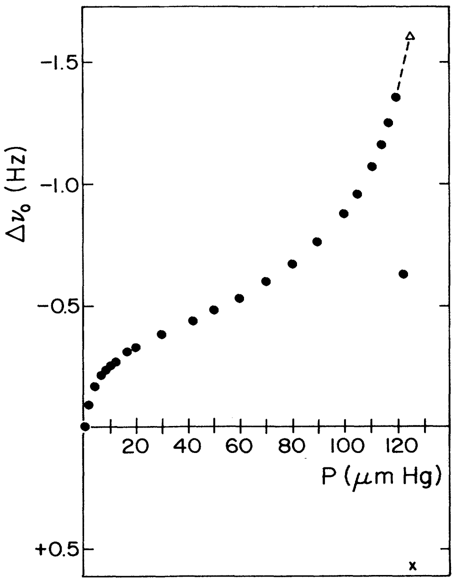

FIG. 4. Frequency shift vs pressure at 48.50 K. The open triangle indicates the $\Delta\nu_0$ value obtained by extrapolation from lower pressures to P_0. The cross indicates the measured $\Delta\nu_0$ at saturation.

sured above and below T_3 we must consider whether it could be explained as an experimental artifact: The shapes of isotherms cannot be greatly distorted by the contribution due to the additional "hydrodynamic" mass of gas surrounding the fiber because this is small and pressure independent. (This can be shown to be true in the pressure regime studied by calculation of the viscous penetration depth and estimation of the mass of bulk gas dragged by the fiber.) Further, any such effect would change only gradually with P or T, but the value of x changes abruptly at T_3. We would not expect a $\Delta S/S$ contribution to $\Delta\nu_0/\nu_0$ to be significant—*above 49 K* (see below).

The sensitivity of our technique to film stress provides us with rather compelling evidence that the saturated film is a solid below 49 K but melts at this temperature, forming the nonwet liquid film to which the data of Figs. 2 and 3 pertain. Figure 4 shows an isotherm taken at 48.5 K. Below 49 K, as the films reach saturation all isotherms show a fairly abrupt positive frequency shift, a clear indication of stress increase associated with the adsorbed film. There is no such shift for isotherms taken above 49 K. It is for this reason that we believe that a $\Delta S/S$ contribution is not likely to explain the value $x = -0.53$ for $T < T_3$. (In future experiments we shall measure the frequency shifts for two fibers under different tensions, from which we can obtain truly decoupled values of $\Delta m/m$ and $\Delta S/S$.) The evidence that the film is liquid above and below T_3 renders yet more remarkable the difference in exponent values. However, we note that the metastable overshoot in Fig. 2 below T_3 is evidence that the two liquid states must be structurally distinguishable.

Ebner[4] has performed a Monte Carlo analysis of a Potts lattice-gas model which, in contrast to an Ising model, allows *three* bulk phases. It is therefore a particularly appropriate model for study of the phase diagram of adsorbed gases near the bulk triple point. Ebner found that at low temperatures the film is solid and completely wet at saturation. However, this film melts along a first-order phase boundary which lies below T_3 for all coverages. Hence a liquid film which does not completely wet the substrate is predicted to exist between the film melting temperature and T_3. Such a situation is also envisaged by Pandit and Fisher,[5] who argue on general, model-independent grounds.

We think that our results are consistent with a slightly modified version of Ebner's phase diagram. To see this, consider Fig. 5, which shows the maximum negative frequency shifts (extrapolated to P_0 in the case of data taken below 49 K) and the positive shifts below 49 K. One expects, from knowledge of the low-coverage phase diagram,[6,7] that a two-dimensional oxygen film would be liquid above 40 K. The existence of abrupt positive shifts in $\Delta\nu$ at saturation for $T < 49$ K indicates that, while the unsaturated film is indeed liquid, the saturated film, or some large fraction thereof, is solid. It seems most probable that the film undergoes a freezing transition as it saturates and the solid coverage is therefore equal to that of the liquid just below saturation (triangles in Fig. 5). The solid film is not completely wet. Its appearance at saturation might be viewed as preventing the liquid film from reaching the thickness one obtains by analytically continuing the nonwet film thickness

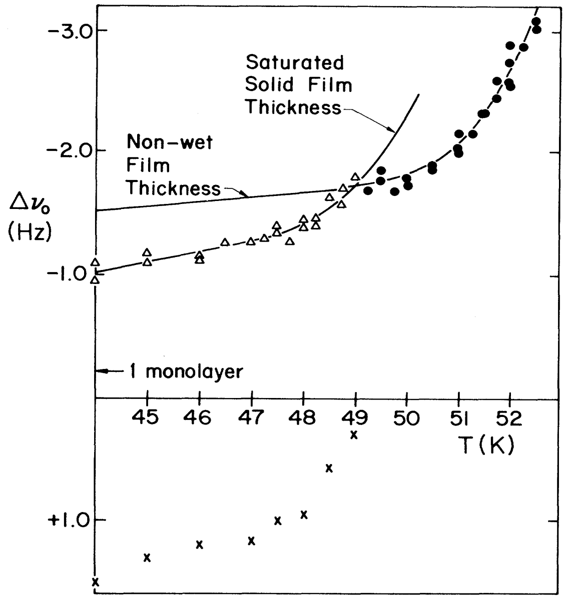

FIG. 5. "End points" for temperatures between 44 and 52.5 K. Triangles indicate $\Delta\nu_0$ values obtained by extrapolation from lower pressures to $P_0(T)$ ($T \leqslant 49$ K). Crosses indicate the measured $\Delta\nu_0$ at saturation ($T \leqslant 49$ K). Circles indicate the measured $\Delta\nu_0$ at saturation ($T \geqslant 49$ K).

curve below 49 K. Above 49 K even the saturated film is liquid and there is therefore no positive shift upon reaching of saturation.

In previous work[7] in which the magnetic susceptibility and heat capacity of oxygen films adsorbed on exfoliated graphite were measured, anomalies in both quantities were seen at 47 K. While we should remember that the films in those experiments were always unsaturated, it is possible that the presence of microscopically distributed, capillary-condensed oxygen could create a situation in which effects related to those of the present work might be seen. The 47-K features and the 49-K transition of the present work are well removed from any other known features of film or bulk oxygen—we would be rather surprised if they were not connected.

Preliminary investigations of both nitrogen and argon have shown that there is a positive frequency shift for both gases upon reaching of saturation, which for argon, is absent in a range of about 2 K below its triple temperature. (The nitrogen behavior suggests that the solid film may persist to a temperature very close to its triple temperature.) These results are consistent with the Potts-model prediction which gives a liquid-film temperature range dependent on a coupling strength. This strength involves the ratio T_c/T_3, where T_c is the bulk critical temperature and T_3 the corresponding triple temperature. Oxygen, it should be noted, has an unusually large value for this ratio. We expect that our technique as extended in the two-fiber experiments will enable us to study more precisely a number of gases and make quantitative comparisons between the melting and wetting properties of these.

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[1] The fibers were of the "Thornel" type, manufactured by Union Carbide.

[2] In the present context we are not attempting to distinguish between tensional and stiffness effects in connection with the film and therefore use the noncommittal description, "stress."

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