

Why Do Vertical Steps Reappear in Adsorption Isotherms?

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On the basis of an extensive set of vapor pressure isotherm and diffraction measurements and computer simulations, we present a microscopic description of the mechanism responsible for the observations of Youn and Hess, *Phys. Rev. Lett.* **64**, 918 (1990), relating to the (reentrant) layering properties of argon-on-graphite films. In the neighborhood of 67 K (and for films more than one layer thick) a transition region exists where the outermost solid layer becomes liquid by a coverage driven process involving layer promotion. Once formed, the liquid layer can be "re" solidified by further increases in argon coverage. This advancing solid-liquid interface results in (re)appearance of vertical steps in the isotherms.

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For nearly a century, vapor-pressure isotherms have been used extensively to characterize the adsorption properties of many materials. The seminal work of Thomy and Duval [1] demonstrated that isotherms could be used successfully to characterize the thermodynamic properties of numerous physisorbed films on graphite. Such studies have provided fertile testing grounds for theories describing the phase transitions of two-dimensional matter, especially those associated with melting.

The recent ellipsometric coverage vapor-pressure measurements by Youn and Hess (YH) [2] to study the wetting properties of multilayer argon, xenon, and krypton films on graphite at constant temperature illustrate the difficulty of providing a microscopic understanding of the observations. At low temperatures they observed numerous (> 5) sharp, stepwise increases in the ellipsometry signals, indicating discrete, layer-by-layer growth of the films. Repeating these measurements at higher temperatures, they found that the number and "sharpness" of the isotherm steps decreased, presumably indicating the end of discrete layer-by-layer growth. This type of crossover in layering behavior has been described previously [3-5]. In the higher temperature regime, growth occurs by atoms filling several layers simultaneously rather than in a layer-by-layer fashion. The details of this process depend upon both the relative strengths of the atom-atom and atom-substrate interactions and the temperature. Such descriptions of film growth suggest that at sufficiently high temperatures all signs of discrete layer-by-layer growth should disappear; i.e., YH should eventually have lost all indications of sharp, stepwise adsorption. This is not, however, what occurred. They found that a further increase in temperature resulted in the reappearance of the stepwise behavior in the ellipsometry signals (albeit at a somewhat higher nominal surface coverage). YH referred to this phenomenon as "reentrant layering" but offered no explanation of the microscopic mechanism underlying the behavior they had observed. In this Letter, we wish to show that by combining a comprehensive set of computer simulations with adsorption isotherms and diffraction data it is possible to obtain a simple, physical picture of the microscopic be-

havior responsible for the reappearance of the isotherm steps.

Computer simulation studies have been used successfully in the past to describe the melting properties of multilayer argon-on-graphite films (at constant number N by varying the temperature T). In the present study, however, we are interested in holding T fixed and varying N . Since in vapor-pressure adsorption isotherm experiments the chemical potential is varied by increasing the number of adsorbate atoms, the grand canonical ensemble has been used in the past to simulate adsorption isotherms [6,7]. While these computer simulations proved to be satisfactory in describing the experimental isotherm data for coverages up to a monolayer, difficulties were encountered in trying to extend the studies beyond that point. We have chosen to use instead the canonical ensemble (constant N , V , and T), with the traditional Monte Carlo algorithm [8,9]. Configurations for the argon-on-graphite system were generated by systematically increasing the number of atoms from 2100 to 4200 at a fixed temperature. This corresponds to a coverage scale varying from two to four nominal atomic layers. At least fifteen different coverages were examined at each of the following temperatures: 25, 60, 65, 70, 75, 80, 90, and 110 K. Ensemble averages were calculated for the internal energy, 2D (two-dimensional) in-plane virial ($\langle \phi/NkT \rangle$, where ϕ is the spreading pressure, i th layer populations (N_i), 2D pair distribution functions ($G_i(r)$), and the vertical density profile. (Formulas for deriving these properties are available elsewhere [10-12].)

The corresponding-states scalable Lennard-Jones LJ(12,6) potential was used to model the adatom-adatom pairwise interaction together with a laterally invariant substrate holding potential given by the Steele $\Sigma(10,4)$ formula for the adatom-substrate interaction [13]. A rigid cylinder of 20σ fixed height (σ is the traditional LJ parameter) with a radius such that a 1050 atom monolayer would be uncompressed at 25 K was shown to define the system boundary conditions.

Figure 1 shows a representative selection of our argon-on-graphite vapor-pressure isotherm measurements. The details of the computer automated isotherm apparatus

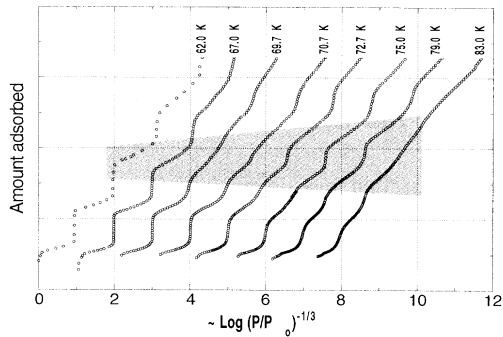


FIG. 1. Plots of selected volumetric isotherms for argon adsorbed on graphite. The origins of individual traces are displaced along the x axis by one unit for clarity. The shaded region indicates that portion of the isotherms discussed in the text.

have been presented elsewhere [14]. These data, using traditional volumetric techniques, provide an independent experimental confirmation of the ellipsometry results of YH and establish it as a reproducible phenomenon. Because of space restrictions we will limit further discussion to the reappearance of the third isotherm step (identified by the shaded portion of Fig. 1), since it is representative of the microscopic mechanisms responsible for what YH called "reentrant" behavior. It is important to note that the reappearance of vertical isotherm steps in the YH study and those shown in Fig. 1 occur at temperatures above the onset of layer-by-layer melting. Previous measurements [15–17] have shown that for argon-on-graphite films nominally thicker than two layers the melting of the uniform film takes place near 67 K. This suggests that a connection might exist between the high temperature layering properties of argon-on-graphite and the onset of atomic mobility.

Turning now to the computer simulations, Fig. 2 shows N_i for the 60 (a), 70 (b), and 75 K (c) computer isotherms. At 60 K both N_i and $G_i(r)$ (not shown) make it clear that the film growth is layer by layer with a narrow advancing solid-vapor interface; i.e., as the total number of atoms increases, the individual layer populations, N_i , increase monotonically with $N_i \gg N_{i+1}$ until the i th layer is completely filled.

At 70.7 K the vapor-pressure trace in Fig. 1 shows a gradual rise (nonvertical step) in the two-to-three layer regime followed by a very weak inflection point at higher coverages. What do the simulations show? At 70 K and a nominal coverage of 3.0 both the layer population [Fig. 2(b)] and the pair distribution functions as shown in Fig. 3(a) indicate that the system is composed of a highly ordered trilayer solid. But the addition of only 10% more argon atoms causes a dramatic change in both N_3 and N_4 . These *additional* atoms cause a *drop* in the population of the *third* layer and a corresponding rise in the fourth layer population. This results in a destabilization of the third layer solid. In fact, at a nominal coverage of 3.22, $G_3(r)$ in Fig. 3(b) shows clearly that the third layer

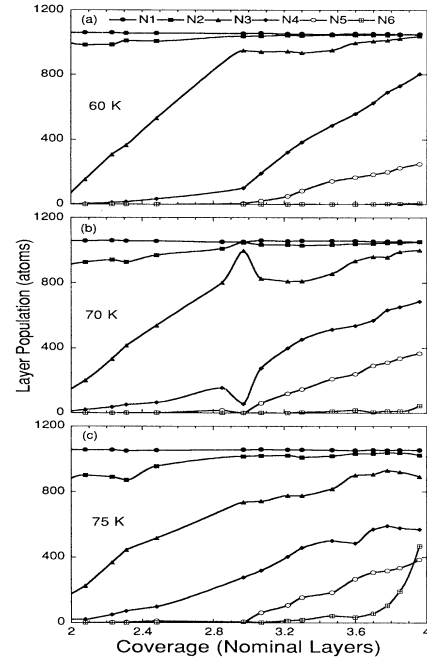


FIG. 2. Computer simulation results for i th layer population, N_i , of argon on graphite as a function of nominal coverage at (a) 60, (b) 70, and (c) 75 K. The solid lines have been inserted as guides to the reader's eyes and have no theoretical significance.

has become quite disordered. Earlier work involving the melting properties of multilayer argon films on graphite indicated that layer promotion initiates surface melting [11]. Indeed at a coverage of 3.22 the simulation shows that the system consists of two layers of solid and more than one full layer of liquid, consistent with the layer promotion melting mechanism (tests for atomic mobility within the simulation indicate that the atoms in both layers 3 and 4 are mobile). When the nominal coverage is increased to 3.6 a further change occurs. N_3 increases and $G_3(r)$ shows that long range order is reestablished in layer 3 [see Fig. 3(c)]. Thus the increase in coverage has induced a "re"solidification of the third layer. This occurs at a total coverage *less than* the amount necessary to produce a completed *fourth* layer.

But does this "re"solidification process produce any noticeable effect in an isotherm? The answer to this question can be found in the behavior of the in-plane virial $\langle \phi/NkT \rangle$, plotted as an inset to Fig. 3(c). The inset illustrates the behavior of the virial derived from the simulations in the coverage regime between 2.5 and 4.0 layers. Presumably the prominent peak near 3.0 and the small jump near 3.6 correspond to the nonvertical step and weak bump (i.e., small density change), respectively, in the experimental isotherms taken near 70 K. The similarity in behavior of the virial and the isotherms lends additional support to the idea that a coverage driven disordering and subsequent reordering of the *third* layer is re-

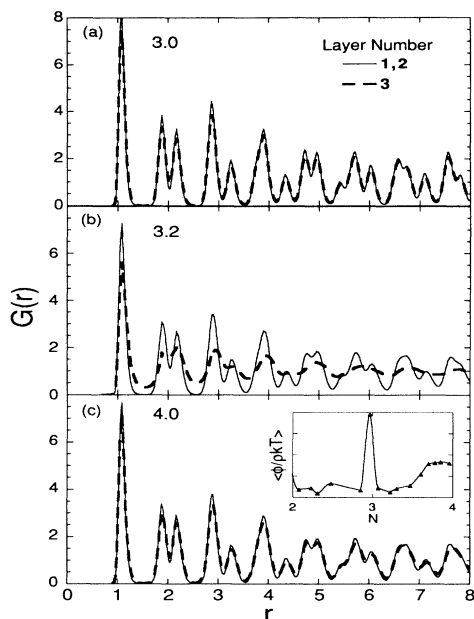


FIG. 3. (a) Individual layer pair distribution functions $G(r)$ as determined from computer simulations at 70 K for nominal argon coverages of (a) 3.0, (b) 3.2, and (c) 4.0. The inset to (c) displays the behavior of the virial at 70 K between 2 and 4 nominal layers (see text).

sponsible for the behavior reported in Ref. [2] and seen in our isotherm measurements in this temperature regime.

Now consider the isotherms at 75 K in the three layer region (as noted in Fig. 1). Here a different aspect of the layering process is at work. The vapor-pressure trace in Fig. 1 shows a very weak inflection point in the three layer regime followed by a well-defined, sharp step at higher coverages. Although there are not enough atoms in the system to complete a fourth layer, the layer populations plotted in Fig. 2(c) clearly show that the film interface has broadened. Unlike the isotherms at lower temperatures, the three layer solid does not form at a coverage of 3.0 nominal layers [see Fig. 4(a)]. Instead the population of the third layer grows almost linearly until the coverage reaches about 3.6 (nominal) layers at which point the pair distribution function $G_3(r)$ in Fig. 4(b) shows the first signs of long range order (i.e., solidlike properties). At a nominal coverage of 4.0 the film is composed of three layers of solid covered by a stratified liquid which extends upward over a range of three more potential layers [see Figs. 2(c) and 4(c)]. This behavior is well illustrated in the coverage dependence of $G_N(r)$ shown in Fig. 4. The virial in this region (not shown) exhibits a marked decrease in the peak located near $N=3.0$ while the weak bump near 3.6 becomes significantly more pronounced. Thus the "re"appearance of the step in the isotherm here (i.e., near $N=3.6$) presumably reflects the increase in density of the third layer as it converts from liquid to solid. This is consistent with an advance of the solid-liquid interface, in contrast to the advance of a solid-

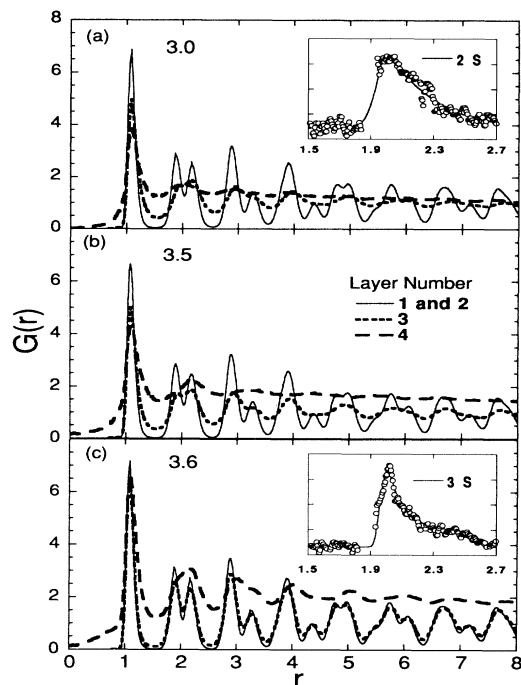


FIG. 4. (a) Individual layer pair distribution functions $G(r)$ as determined from computer simulations at 75 K for nominal argon coverages of (a) 3.0, (b) 3.2, and (c) 4.0. The inset to (a) shows an x-ray difference diffraction pattern recorded at 73 K at the base of the reentrant step, while the inset to (c) displays a difference pattern taken at the top of the same step. The solid lines in each case represent a fit to the data assuming a two layer solid (2S) and three layer solid (3S), respectively.

vapor interface at lower temperatures.

Such behavior is not difficult to understand. In the vapor-pressure isotherm experiments there is a sequential increase in the number of adsorbed atoms which produces a corresponding increase in both the 3D vapor pressure and 2D spreading pressure. Consider the following analogy. A fixed volume Dewar containing *liquid* argon (at SVP) is held at *constant* temperature a few degrees above the triple point. If the pressure of the vapor in equilibrium with the liquid is steadily increased, inevitably, at some point, solidification of the liquid argon occurs. This phase transformation is essentially the same process that occurs in the multilayer argon-on-graphite system. Presumably the liquid argon layers above the solid argon layer furthest from the substrate are responsible for applying the pressure necessary to condense the next solid layer.

Turning now from our macroscopic measurements to our microscopic measurements, the inset to Fig. 4(a) shows a representative x-ray diffraction profile recorded at the base of the sharp "reentrant" step at 75 K. A detailed description of the method used to determine the solid and liquid components of the film from such profiles can be found in Ref. [18]. Analysis of the profile of Fig. 4(a) indicates that at this point the film is composed of

two solid layers plus liquid. The inset to Fig. 4(c) shows how the diffraction pattern changes when the argon coverage is increased to the top of the 75 K step. Analysis of this diffraction pattern indicates that three layers of solid argon plus liquid are present at the higher coverage. Note that the argon coverage at the top of the step is not sufficient to form a complete fourth solid layer.

At even higher temperatures the isotherm measurements suggest that this process repeats itself in layer 2. An indication of this appears in the 79 K isotherm traces in Fig. 1 as well as in the computer simulations at 80 K. In fact, evidence for similar coverage driven processes was obtained in an earlier neutron investigation [16]. In that study, the evolution of the solid and liquid components of the argon film at several different film thicknesses was investigated as a function of temperature. Figure 2 in Ref. [16] shows that at 79 K "re"solidification of the *second layer* occurs as the coverage is increased from two to three nominal layers. Such behavior is consistent with a simple, layer-by-layer advance of the solid-fluid interface. We see no need to invoke *pre-roughening* [17,19,20] to explain the reappearance of the isotherm step feature, particularly since it is difficult to understand how the surface profile necessary for the model to be applicable can be generated in films so thin.

In summary, evidence has been presented which details the microscopic processes underlying the reappearance of vertical steps in isotherms at temperatures above that at which they first disappear. It has been demonstrated that in the argon-on-graphite system at temperatures in the neighborhood of 67 K a coverage driven process involving layer promotion destabilizes the outermost layer of the solid film causing a liquid to appear. Our computer simulations show that this process is driven by a shifting balance between the entropic and configurational components of the free energy which alternately favor layer disordering and layer solidification as the coverage is increased. Once layer destabilization takes place, long range order is then reestablished in the mobile *liquid layer closest to the substrate* by a further increase in coverage. Each layer in turn is solidified by the pressure of the liquid layers above it. We note that compression of *bulk* rare gas liquids not too far above the triple point induces the analogous 3D phase transition. Thus one can understand the reappearance of the isotherm steps by realizing that film growth at higher temperatures is a progressive movement of a spatially extended solid-fluid interface away from the solid surface. This behavior differs significantly from the discrete, step-by-step motion of the sharp, solid-vapor interface which accompanies film growth at lower temperatures. There seems to be no need to introduce the concept of *preroughening* to explain the reappearance of isotherm steps in either our data or that of YH. The mechanism described here should apply equally well to krypton and xenon films on graphite [20, 21] and to argon films on boron nitride [22]. Finally, we believe that coverage-driven disordering and reordering

could also influence the layering behavior of helium [23,24] and methane-on-graphite films and underlie the reentrant superfluidity recently observed in ^4He films adsorbed on graphite [25].

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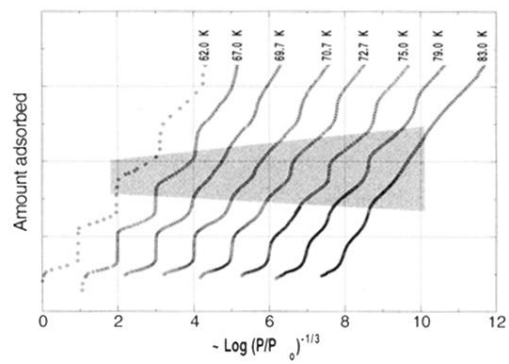


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