

# ACCOUNTS OF CHEMICAL RESEARCH®

JULY 1993

Registered in U.S. Patent and Trademark Office; Copyright 1993 by the American Chemical Society

## Multilayer Argon Films on Graphite: Structural and Melting Properties

J. Z. LARESE

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

Received December 21, 1992

### Introduction

Neutron scattering techniques are widely employed in the field of condensed matter science, because the energies and wavelengths of thermal neutrons span the length and energy scales associated with the interatomic distances and dynamical response of most substances. They have made *fundamental* contributions to many fields: crystal structure, phase transitions and critical phenomena, magnetism, superconductivity, liquids, glasses, etc. However, neutrons have found only limited application in the field of surface science, in part because they interact so weakly with matter (thus necessitating the use of high surface-to-volume substrate materials) and in part because the fluxes available at even the most advanced sources are much lower than the X-ray fluxes produced at synchrotrons. Nonetheless, there exist surface overlayer systems where neutrons can be employed to advantage, and in these systems they provide a remarkably complete and detailed picture of both overlayer structure and dynamical response.<sup>1-4</sup> Here we will describe investigations of the growth and melting of multilayer argon films adsorbed on graphite surfaces using both elastic and inelastic neutron scattering techniques. As will soon be evident, the most direct way to obtain information relating to collective and diffusive motions in such systems is via inelastic and quasi-elastic neutron spectroscopy.<sup>5,6</sup> Furthermore, unlike traditional surface adsorption studies, which

often require the use of complex ultrahigh vacuum equipment and additional sample restrictions, these neutron surface studies can be performed at high ambient gas pressures and under thermodynamic equilibrium conditions. A comprehensive understanding of surface behavior, however, requires the use of many different probes; hence, complementary X-ray diffraction, thermodynamic, and computer simulation studies will also be discussed.

The melting of ordinary matter is an abrupt, first-order phase transition, typically exhibiting two-phase coexistence and a latent heat. But what does this mean on an atomic scale? Is melting the result of a sudden collapse of the solid structure throughout the material, or is there a premonitory process at the surface followed by a subsequent breakdown of the bulk structure? Over the past few years the latter point of view, the so-called "surface premelting" concept, has stimulated new efforts, both experimental and theoretical, to define the microscopic process involved.<sup>7-9</sup> As the name "premelting" suggests, the melting of three-dimensional

(1) Sinha, S. K., Ed. *Ordering in Two Dimensions*; North-Holland: Amsterdam, 1980.

(2) Taub, H. In *The Time Domain in Surface and Structural Dynamics*; Long, G. J., Grandjean, F., Eds.; NATO ASI Series C, 228; Kluwer: Dordrecht, 1988; p 467.

(3) See, for example: Larese, J. Z.; et al. *Phys. Rev. Lett.* **1988**, *61*, 432 and references therein.

(4) McTague, J. P.; Nielsen, M.; Passell, L. *Crit. Rev. Solid State Mater. Sci.* **1979**, *8*, 135.

(5) White, J. W. In *Dynamics of Solids and Liquids by Neutron Scattering*; Lovesey, S. W., Springer, T., Eds.; Springer-Verlag: Berlin, 1977; pp 197.

(6) Bienfait, M.; Gay, J. M. In *Phase Transitions in Surface Films*; Taub, H., Torzo, G., Lauter, H. J., Fain, S. C., Eds.; Plenum Press: New York, 1991; p 307. Lauter, H. J. *Ibid.* p 135.

(7) Dash, J. G. *Contemp. Phys.* **1989**, *30*, 89 and reference therein.

(8) Van der Veen, J. F.; Frenken, J. W. F. M. *Surf. Sci.* **1986**, *178*, 382.

(9) Trayanov, A.; Tosatti, E. *Phys. Rev.* **1988**, *B39*, 6916.

John Z. Larese received his Ph.D. degree in physics from Wesleyan University in 1982, where he studied adsorbed hydrocarbon films on graphite using pulse NMR techniques with R. J. Rollefson. He spent 1982-1985 as a postdoctoral fellow at Penn State University working with D. R. Frankl using helium atom scattering techniques. It was during this period that he first became interested in surface diffraction. In 1985, Larese joined Brookhaven National Laboratory, where he currently continues to pursue his interests in surface adsorption and the properties of materials employing neutron scattering methods.

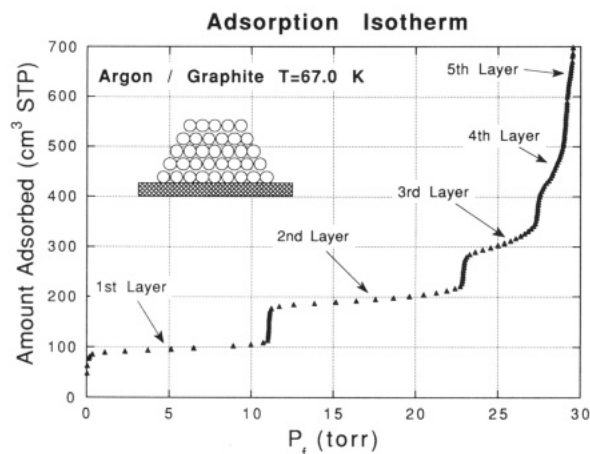
(3D) solids is, in this view, initiated by surface atoms (or molecules). A disordered, mobile film forms at the solid-vapor interface at temperatures close to, but below, the bulk melting point,  $T_m$ ; the thickness of this film is then thought to diverge as  $T_m$  is approached. Limited experimental evidence in support of surface premelting has recently been obtained from studies of several fcc metal solids.<sup>10-12</sup> (Computer simulations suggest that certain crystal faces may be much better candidates than others for observing the premelting film.)

There have been a number of theoretical investigations of the melting of *two-dimensional* (2D) solids,<sup>13</sup> i.e., solids in which melting is, by definition, a surface process. One that attracted particular attention was published about 15 years ago by a small group of authors collectively referred to as KTHNY.<sup>14,15</sup> They suggested that a 2D system passes from the solid to liquid phase via a continuous, *two-step* process, in which an intermediate phase exhibiting bond directional order intervenes between the 2D solid and isotropic 2D liquid phases (the bond directional phase which appears between 2D solids that are 6-fold symmetric and the isotropic 2D liquid is generally referred to as a *hexatic phase*). 2D melting was thus predicted to be dramatically different from bulk melting on a microscopic scale. Numerous experimental studies have been aimed at testing the predictions of KTHNY theory employing both monolayer atomic and molecular films adsorbed on solid surfaces and free-standing liquid crystal films as prototype 2D systems. Results to date have not been definitive, however.

The ideas mentioned above led us, and others, to wonder if it would be possible to employ surface overlayer systems that can be investigated with neutrons, specifically multilayer films adsorbed on graphite surfaces, to learn more about what happens near the melting point. The reader should recognize that the results of these studies, although suggestive, should not be viewed as directly applicable to the bulk surface melting problem because inevitably, in films, there is the interaction of the film atoms (e.g., argon atoms) with the substrate (e.g., graphite atoms) in addition to the usual atom-atom (e.g., argon-argon) interactions.

## Motivation

We chose to study argon multilayer growth on graphite for several reasons. First, the <sup>36</sup>Ar isotope is an excellent neutron scatterer, possessing one of the largest coherent neutron scattering cross sections of any element.<sup>16</sup> Second, the argon-argon and the argon-graphite potentials are well-known, thus making the system an ideal candidate for both first principles theoretical and computer modeling. Third, graphite is, in some sense, an ideal substrate material: it presents (almost exclusively) a single adsorption surface, the basal plane; it is easily cleaned and prepared; and it is



**Figure 1.** Vapor pressure isotherm at  $T = 67.0$  K for argon adsorbed on graphite foam. Data were recorded using a computer-automated gas-dosing apparatus.<sup>17</sup> Layer formation is easily identified by noting the stepwise increase in the amount of adsorbed as a function of the vapor pressure  $P_t$ . The terms layer 1, layer 2, etc. have been used to identify the mean layer thickness.

readily available in an exfoliated form with a high surface-to-volume ratio (necessary because of the small scattering cross sections of neutrons). Finally, whereas many of the physical properties of monolayer argon films on graphite have been thoroughly investigated, the melting properties are still not fully understood.<sup>17</sup>

Multilayer molecular films on graphite and MgO substrates have also been extensively investigated with neutrons. In addition to the layering and melting properties that we will describe in this paper, molecular films exhibit additional physical properties which can be related to the structures of the molecules.

## Film Deposition: Vapor Pressure Isotherms

In order to investigate layer-by-layer film growth on uniform substrates experimentally, a method of determining the film thickness is needed. Vapor pressure isotherms have been employed to define film growth for more than a century and are a simple and reproducible way to follow the thermodynamics of the process. An excellent review of this technique and its application in determining the thermodynamic properties of adsorbed films can be found in a review paper by Thomy, Duval, and Regnier.<sup>18</sup> Figure 1 shows a typical isotherm for the growth of argon films on graphite basal plane surfaces. Each step represents the condensation of a single layer. Such films can be deposited and removed easily because no chemical bonds are formed between the adsorbed argon atoms and the graphite substrate. It is not our intention to provide a detailed description of isotherm features as a function of either thickness or temperature here because a complete discussion requires more space than is available and excellent treatments can be found elsewhere.<sup>19-21</sup> It is important to note that although vapor pressure isotherm techniques have been in use

(10) Pluis, B.; et al. *Phys. Rev. Lett.* **1987**, *59*, 2678.

(11) Stock, K. D. *Surf. Sci.* **1980**, *91*, 655.

(12) Denier van der Gon, A. W.; et al. *Surf. Sci.* **1990**, *227*, 143.

(13) Strandburg, K. *Rev. Mod. Phys.* **1988**, *60*, 161 and references therein. See also: Phillips, J. M.; Bruch, L. W. *Phys. Rev. Lett.* **1988**, *60*, 1681.

(14) Kosterlitz, J. M.; Thouless, D. J. *J. Phys.* **1973**, *C6*, 1181.

(15) Nelson, D. R.; Halperin, B. I. *Phys. Rev.* **1979**, *B19*, 2457. Young, A. P. *Phys. Rev.* **1979**, *B19*, 1855.

(16) See, for example: Sears, V. F. *Neutron News* **1992**, *3*, 26.

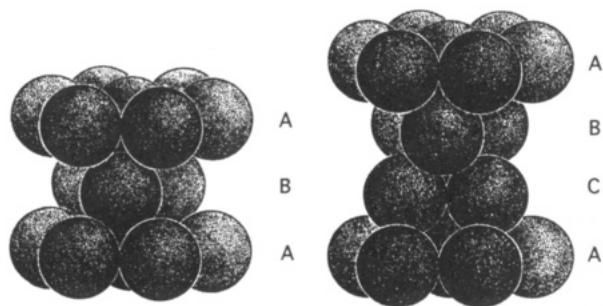
(17) Zhang, Q. M.; Larese, J. Z. *Phys. Rev.* **1991**, *B43*, 938.

(18) Thomy, A.; Duval, X.; Regnier, J. *Surf. Sci. Rep.* **1981**, *1*, 1.

(19) Dash, J. G. *Films on Solid Surfaces*; Academic Press: New York, 1975.

(20) Steele, W. A. *The Interaction of Gases with Solid Surfaces*; Pergamon: New York, 1974.

(21) Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley: New York, 1990.

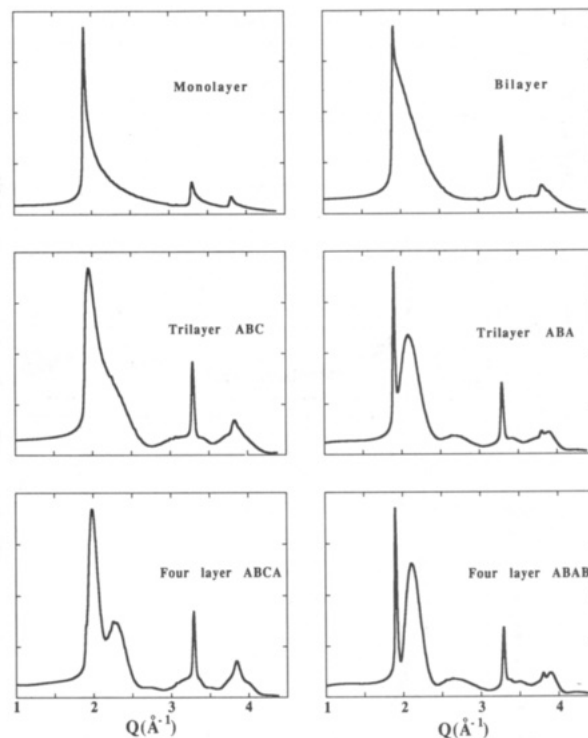


**Figure 2.** Schematic illustration of the closest packing of spheres in the hexagonal close-packed (ABA) and the cubic close-packed (ABC) arrangements.

for many years, they are still one of the best methods of obtaining an overall view of surface film behavior. In the present case, isotherms were used to gauge the quantity of gas necessary to condense successive layers of argon on the graphite substrate. They were also employed to map out, in detail, a large portion of the multilayer argon/graphite phase diagram in order to identify those regions where phase transitions are likely to occur. This reduces the thermodynamic region over which detailed diffraction investigations need to be made. A phase diagram for argon on graphite based on both vapor pressure isotherm and diffraction measurements will be presented later in this discussion.

### Diffraction Profiles: Layer-by-Layer Growth

Having briefly reviewed the use of vapor pressure isotherms as a means of determining the number of layers deposited on the graphite surface, we turn now to the question of how changes in the microscopic structure of an adsorbed film are reflected in changes in the neutron diffraction profiles. Figure 2 displays the two simplest stackings of close-packed spheres. These two sequences serve as the starting point for model structure-factor calculations. The value of considering such simple geometric assemblies is underscored by the fact that a vast number of common materials are close-packed structures. For example, bulk argon at low temperatures has a face-centered cubic lattice,<sup>22</sup> the structure type resulting from ABC stacking of close-packed planes. Figure 3 shows how the powder diffraction profiles evolve as the solid is built up layer by layer. A more detailed discussion of these calculations can be found elsewhere, but several qualitative observations are appropriate here.<sup>23,24</sup> First, the asymmetric, sawtooth-like shape which characterizes the diffraction profile of a monolayer solid is readily apparent. This profile, which is often referred to as "the Warren line shape",<sup>25</sup> is the direct result of orientational averaging of a 2D reciprocal lattice of rods rather than points (for 2D systems, only two Bragg conditions, not the usual three, need to be satisfied). This line shape can be understood rather easily. Significant scattering occurs at angles well beyond the nominal Bragg angle because only the projection of the scattering vector  $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$  ( $\mathbf{k}_i$  and  $\mathbf{k}_f$  are the incident and scattered wave vectors, respectively) onto the



**Figure 3.** Model line shape calculations of powder-averaged diffraction profiles for an ideal system of close-packed isotropic scatterers. A comparison is made of the two stacking sequences shown in Figure 2 (i.e., ABA and ABC) as a function of layer thickness. All the in-plane structures are triangular with a near-neighbor spacing of 3.76 Å and a fixed interplanar separation of 3.07 Å. The curves presented include the effects of folding a Gaussian instrument resolution function (with a full width at half-maximum of  $\approx 0.03 \text{ \AA}^{-1}$ ) in order to illustrate what would be recorded in an idealized experiment.

scattering plane must satisfy the Bragg condition. As additional layers of atoms are introduced, the powder diffraction profile changes. A modulation of the uniform rods of the ideal 2D lattice occurs as ordering in the third dimension commences. As is evident in Figure 3, characteristic changes take place in the diffraction profiles as the thickness increases. The differences depend on the spacing between the individual layers as well as on how they are stacked (e.g., whether the stacking is ABAB... or ABCABC...). In the many-layer limit ( $>20$  layers) these patterns evolve into the usual powder diffraction profiles (with symmetric, Gaussian-shaped peaks) characteristic of a face-centered cubic (fcc, ABC stacking) or hexagonal close packed (hcp, ABA stacking) solid (i.e., the 2D reciprocal lattice of rods transforms into the traditional 3D lattice of points). In the present discussion, no attempt has been made to consider all the possible stacking sequences that can be associated with simple close-packed models. We simply note that stacking faults do occur and their effects are considered in the analysis of the observed diffraction profiles.<sup>23,26</sup> Figure 4 illustrates how the experimental profiles change with film thickness. The results show clearly that the growth of argon on graphite at low temperature occurs layer by layer and that an ABC stacking of the atoms predominates. When the nominal argon film thickness exceeds about four layers, however, small crystallites of bulk solid argon begin to form as a result of capillary effects within

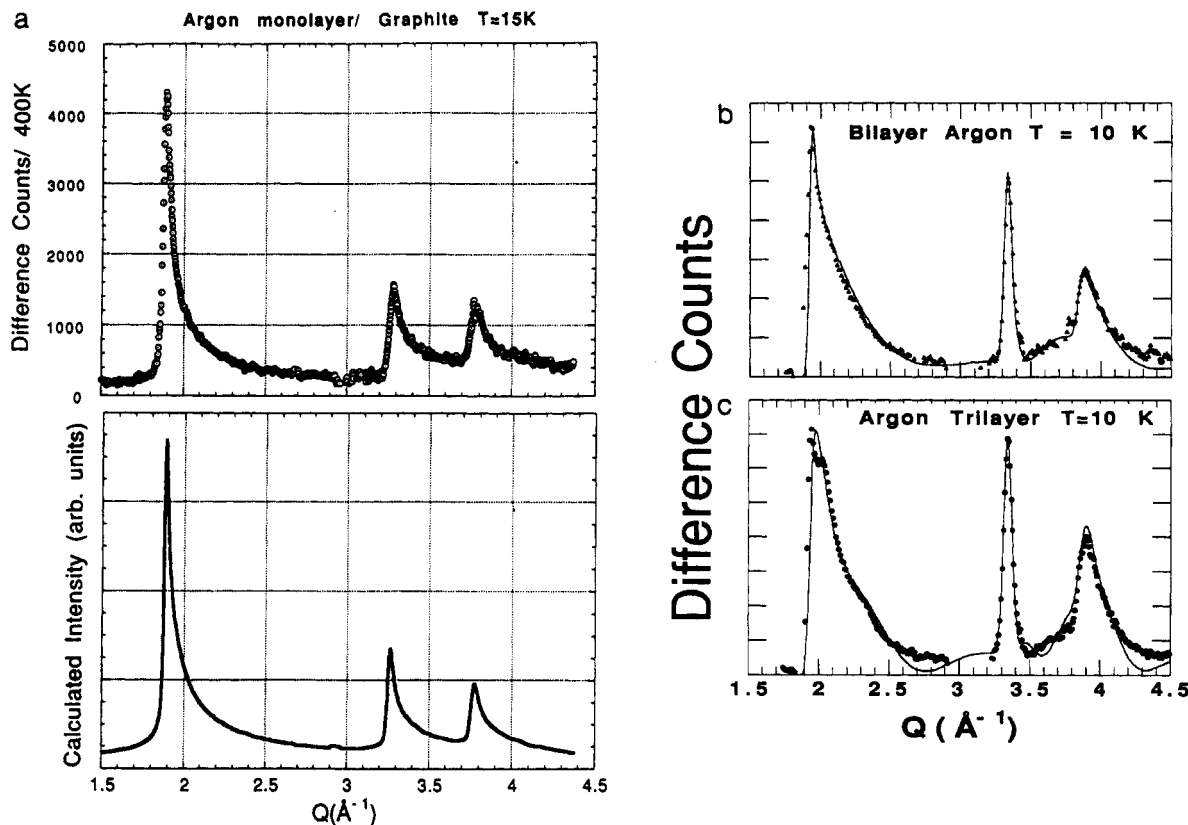
(22) Henshaw, D. G. *Phys. Rev.* 1958, 6, 1470. Dobbs, E. R.; et al. *Nature* 1956, 178, 483.

(23) Larese, J. Z.; et al. *Phys. Rev.* 1989, B40, 4271.

(24) Larese, J. Z.; et al. *Phys. Rev.* 1988, B37, 4735.

(25) Warren, B. E. *Phys. Rev.* 1941, 59, 693.

(26) Gay, J. M.; et al. *J. Phys. I* 1991, 1, 1279.



**Figure 4.** (a) Typical monolayer difference profile (upper panel) from a monolayer film of  $^{36}\text{Ar}$  adsorbed on graphite substrate at  $T = 15\text{ K}$ . The lower panel illustrates a powder-averaged fit to the data based on the assumption that a triangular solid, incommensurate with the graphite substrate, forms. The lattice constant of the solid is found to be  $3.80\text{ \AA}$ , and a Debye-Waller factor of  $0.03\text{ \AA}^2$  was used. Superposition of the two panels makes it difficult to distinguish the fit from the individual data points. This data was recorded using a new, 15-detector powder diffraction spectrometer. (b) Diffraction profile recorded for a nominal bilayer solid of  $^{36}\text{Ar}$  adsorbed on graphite substrate at  $10\text{ K}$ . The solid line represents a fit to the data using a triangular AB bilayer structure which employs the same near-neighbor distance of  $3.775\text{ \AA}$  in each layer and an interlayer spacing of  $3.17\text{ \AA}$ . A  $0.045\text{-\AA}^2$  Debye-Waller factor was used. (c) Diffraction profile recorded for a nominal trilayer solid of  $^{36}\text{Ar}$  adsorbed on graphite substrate at  $10\text{ K}$ . The solid line represents a fit to the data using a composite line shape constructed by combining both ABC and ABA stacking sequences in the amount of 85% and 15%, respectively. A near-neighbor distance of  $3.760\text{ \AA}$ , an interlayer spacing of  $3.17\text{ \AA}$ , and a  $0.045\text{-\AA}^2$  Debye-Waller factor were used in producing the fit. For a more detailed account, see refs 23 and 24.

the graphite substrate.<sup>24,26-28</sup> The details of this process appear to be related to the morphology of the particular graphite substrate used in the experiment. Our interest here centers on the few-atomic-layer films that form below four atomic layers, not the capillary-condensed bulk solid crystallites that form at higher coverages. Because *capillary condensation* is not an intrinsic part of the physical adsorption process, we will therefore only comment in passing that detailed discussions of it and related effects can be found elsewhere.<sup>21,26-28</sup>

### Computer Simulations of Film Growth

Computer simulation methods are a necessary complement to state-of-the-art surface film investigations. An excellent introduction to the application of computer simulation techniques in the study of solids and liquids can be found in the text of Allen and Tildesley<sup>29</sup> and in the monograph edited by Ciccotti, Frenkel, and McDonald.<sup>30</sup> Computer models, in combination with thermodynamic and spectroscopic data, provide a much more complete understanding of a given overlayer

system than could be obtained from any one discipline alone. Simulations of the growth properties of argon films on graphite have been performed by Phillips and co-workers.<sup>31,32</sup> In these studies they found that low-temperature argon film growth is a layer-by-layer process with the individual layers in registry with one another (i.e., the lattice constant is nominally uniform throughout the system) but not in registry with the substrate. Furthermore, they found that although ABC stacking predominates, small regions of ABA stacking were also present. Their findings are in close agreement with the neutron diffraction measurements. At higher temperatures and intermediate coverages<sup>32</sup> and with other adsorbed gases,<sup>33</sup> they have found that solid layers sometimes go out of registry with one another in response to strains which develop within the system, primarily because of competition between the atom-atom and the atom-substrate interactions. This effect has also been confirmed experimentally.<sup>24</sup>

### Multilayer Melting: Thermodynamics

Several years ago, Zhu and Dash<sup>34,35</sup> (ZD) reported a detailed thermodynamic study of the melting prop-

(27) Ser, F.; Larher, Y.; Gilquin, B. *Mol. Phys.* 1989, 67, 1077.

(28) Day, et al. *Phys. Rev.* 1993, B47, 10716.

(29) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Clarendon Press: Oxford, 1987.

(30) *Simulations of Liquids and Solids*; Ciccotti, G., Frenkel, D., McDonald, I. R., Eds.; North-Holland: Amsterdam, 1987.

(31) Phillips, J. M. *Langmuir* 1989, 5, 571.

(32) Phillips, J. M.; Story, T. R. *Phys. Rev.* 1990, B42, 6944.

(33) Hruska, C. D.; Phillips, J. M. *Phys. Rev.* 1988, B37, 3801.

(34) Zhu, D. M.; Dash, J. G. *Phys. Rev. Lett.* 1988, 60, 432.

erties of multilayer argon films on graphite. A representative set of ZD's heat capacity traces at different film thickness are shown in Figure 5. ZD associated the anomalies in the heat capacity traces with the roughening and melting of individual argon layers. Originally, they proposed that their results could be interpreted as evidence for the existence of surface melting in bulk solid argon and suggested that their higher coverage data indicated uniform layer thicknesses up to about 20 layers. Subsequently, however, studies have shown that the presence of capillary-condensed argon solid may complicate the initial interpretation of the data beyond three or four layers.<sup>26</sup> More recent high-resolution heat capacity results by Day et al.<sup>36</sup> both confirm the existence of the earlier observed heat capacity anomalies and extend the ZD measurements to higher temperatures. Day et al. found that the melting of the argon layer closest to the substrate occurred about 15 deg above 83.8 K, the melting temperature of the bulk solid. The higher melting temperature of the first-layer solid is due in part to the strong interaction of the argon with the graphite substrate and in part to the additional stabilization introduced by the liquid argon layers above the monolayer solid film.

### Neutron Diffraction

Having characterized the diffraction profiles associated with the formation of multilayers of solid argon on graphite, we turn next to the melting properties of argon films of fewer than four layers. We will restrict the discussion here to the melting of an argon film initially three layers thick. Although the detailed temperature dependence of the disordering of bilayer and four-layer films is somewhat different, the melting process we will present here for an argon trilayer changes only slightly in thinner and thicker films.<sup>37,38</sup> Figure 6 illustrates the evolution of the trilayer neutron diffraction pattern with temperature. Comparison of the profiles of Figure 6 with those in Figure 3 shows that they are quite sensitive to the amount of solid film present. Because the amount of solid signal decreases as the temperature of the system increases, it is relevant to ask where the signal from the rest of the film appears. The answer can be found by concentrating on the diffraction data at  $Q$ 's below  $1.7 \text{ \AA}^{-1}$ . As the temperature of the system is increased, it is evident that a monotonic rise in the intensity at low  $Q$  occurs. The reader is reminded that as the long-range order in a solid disappears, the diffraction profile increasingly broadens. In 2D systems the thermal evolution of the film can therefore be followed by monitoring the temperature dependence of the intensity at the leading edge of the diffraction peaks. A plot of the integrated intensity

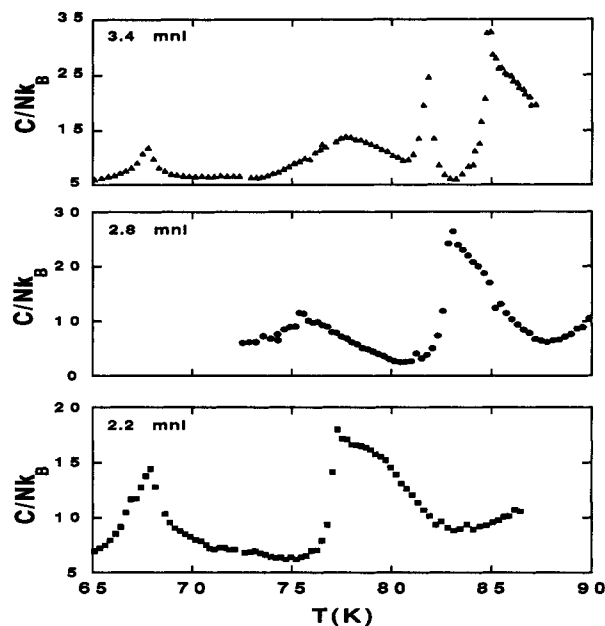


Figure 5. Heat capacity traces recorded at several different film thicknesses for argon films adsorbed on graphite by Zhu and Dash. The bold numerals located at the left-hand side of each trace indicated the nominal film thickness in monolayers. The authors have identified the heat capacity anomalies with the melting of individual layers.

from a  $1.3 < Q < 1.7 \text{ \AA}^{-1}$  window as a function of temperature is shown in Figure 7 (earlier neutron measurements of the 2D liquid structure factor for argon-on-graphite films indicate that this is the best  $Q$ -range to study). The staircase-like shape of this window scan intensity is reminiscent of an adsorption isotherm. In this case, the window scan signal is associated with the disordering (i.e., melting) of the individual layers. The stepwise decrease of the solid-phase signal and the corresponding stepwise increase in the disordered-phase signal strongly suggest a layer-by-layer process. Presumably, the promotion of some argon atoms upward to the fourth layer initiates translational diffusion in the third layer. Diffraction patterns recorded at temperatures intermediate to those in Figure 6 indicate that the fluid which first forms in the outermost layer is most likely a modulated or lattice fluid.<sup>31,46,47</sup> This means that although the atoms exhibit finite translational mobility, the atomic positions are highly correlated with the atoms which reside in the solid layer immediately below. The temperature dependence of the low- $Q$  window scan in Figure 7 strongly suggests that a fluid phase is present, but elastic diffraction measurements alone are insufficient to establish that translational diffusion has actually begun. With that reservation in mind, we believe that the diffraction data support a process where melting of the outermost (third) layer occurs near 67 K, the second layer near 85 K, and the layer closest to the substrate near 95 K! The remarkable stabilization of the near-substrate solid layer dramatically underscores the importance of the substrate in the melting of the films.

To identify the temperature at which translational diffusion begins, we recently performed inelastic and quasi-elastic neutron scattering measurements on the IN5 time-of-flight spectrometer at the Institut Laue-

(35) Zhu, D. M.; Dash, J. G. *Phys. Rev.* 1988, *B38*, 11673.

(36) Day et al., preprint, to be published in *Phys. Rev. B*.

(37) Larese, J. Z.; Zhang, Q. M. *Phys. Rev. Lett.* 1990, *64*, 922.

(38) Larese, J. Z.; Zhang, Q. M. To be published.

(39) Bée, M. *Quasielastic Neutron Scattering*; Adam Hilger: Bristol, 1988.

(40) See, for example: Coulomb, J. P.; Bienfait, M. *J. Phys. (Paris)* 1986, *47*, 89.

(41) Larese, J. Z.; Passell, L. To be published.

(42) Taub, H.; et al. *Phys. Rev.* 1977, *B6*, 4551.

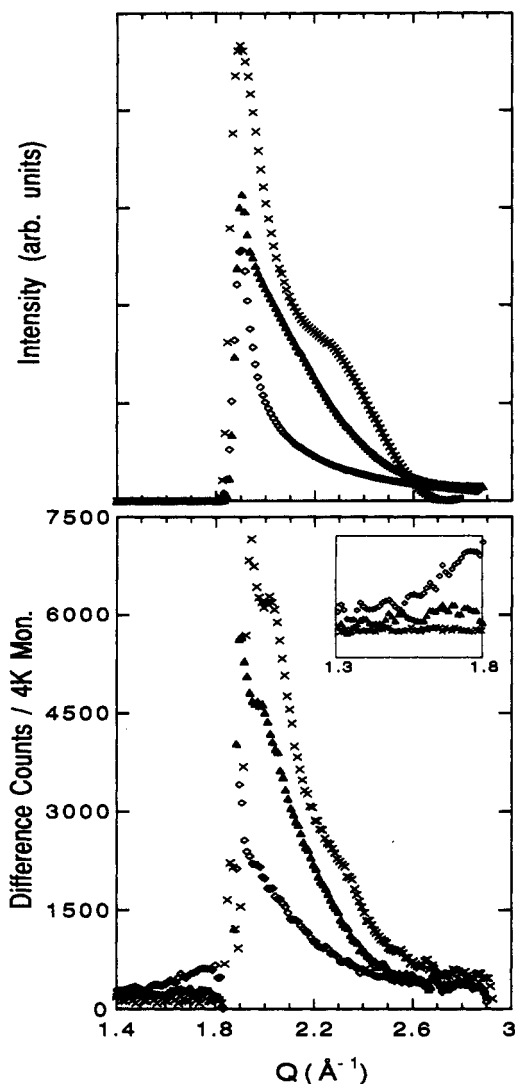
(43) Tiby, C.; Lauter, H. *J. Surf. Sci.* 1982, *117*, 277.

(44) Broughton, J. Q.; Gilmer, G. H. *J. Chem. Phys.* 1983, *79*, 5105, 5119.

(45) Broughton, J. Q.; Gilmer, G. H. *J. Chem. Phys.* 1986, *84*, 5741.

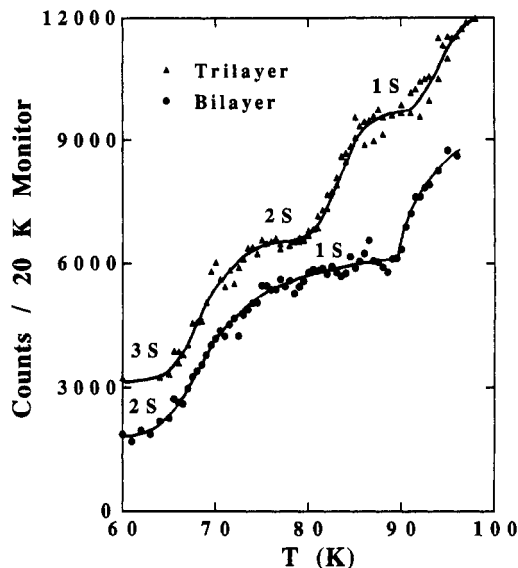
(46) Cheng, A. L.; Steele, W. A. *Langmuir* 1989, *5*, 800.

(47) Phillips, J. M. *Phys. Lett.* 1990, *A147*, 54.

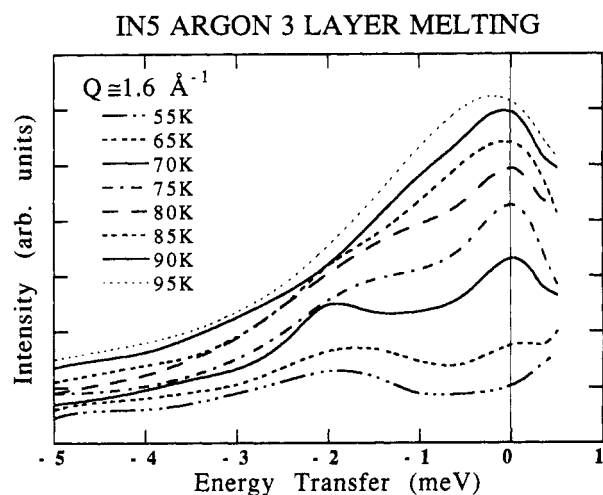


**Figure 6.** Calculated diffraction profiles (upper panel) for idealized ABC stacked trilayer (x), AB bilayer (BL) (Δ) close-packed solids, and triangular monolayer (ML) (◇) solid. A near-neighbor distance ( $a_{nn}$ ) of 3.76 Å and a Debye-Waller factor (DWF) of 0.02 Å<sup>2</sup> were used for the trilayer, an  $a_{nn}$  of 3.81 Å was used for both BL and ML solids, and a DWF of 0.15 Å<sup>2</sup> for the BL and 0.20 Å<sup>2</sup> for the ML were used. The lower panel displays the experimental neutron diffraction profiles for a trilayer film recorded at 10 K (x), 77 K (Δ), and 92 K (◇) for respectively a three-layer solid, a BL solid plus liquid, and a ML solid plus liquid. Notice the incremental increase in the scattered intensity at low Q (1.3–1.8 Å<sup>-1</sup>) shown in the inset. See ref 37 for a more extensive discussion.

Langevin.<sup>39</sup> Figure 8 shows the inelastic data recorded for several different temperatures. It is important to bear in mind that the spectra presented in this figure were obtained by subtracting off the scattering from the graphite-filled aluminum sample cell. Only when translational diffusion begins in the argon film will significant broadening of the elastic line be evident.<sup>40</sup> What follows is a brief synopsis of the salient features. A detailed analysis of the Figure 8 spectra will be presented at a later date.<sup>41</sup> At temperatures below 65 K no broadening of the elastic line is apparent. There is a broad peak near 2.0 meV, probably associated with phonons propagating within the trilayer solid film. This peak is most likely due to zone boundary phonon modes. Similar spectra were reported many years ago for solid monolayer argon films on graphite.<sup>42,43</sup> Above about 65 K, the first indication of broadening in the elastic

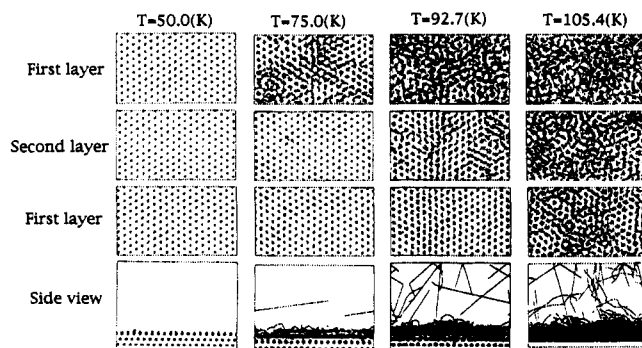


**Figure 7.** Fixed Q-window scan illustrating the layer-by-layer melting of argon films initially three layers (Δ) and two layers (●) thick. The bold labels 1S, 2S, and 3S indicate the number of solid layers present at that temperature. The solid line has been introduced for clarity and serves only as a guide to the reader's eye. From ref 37.



**Figure 8.** Inelastic neutron difference data recorded at the Institut Laue-Langevin IN5 time-of-flight spectrometer. Data presented were recorded at the various temperatures indicated for an argon film which was initially three layers thick. The feature near 2 meV has been associated with a zone boundary phonon mode while the increase in scattering near 0 is taken to indicate the onset of translational diffusion (melting) at  $T > 65$  K.

line appears. This suggests that the rise in the window-scan intensity in the elastic diffraction measurements discussed above (shown in Figure 7) was correctly identified with the onset of melting of the solid layer farthest from the substrate. In addition, the phonon portion of the signal decreases in intensity and shifts to a slightly lower energy. This behavior is consistent with a softening of the elastic constants of the multilayer argon film and the disordering of the solid third layer. Further increases in temperature result in a steady growth in the intensity and breadth of the quasi-elastic signal and a concomitant decrease in the signal we have nominally attributed to the "phonon". The integrated "phonon" intensity decreases in a manner consistent with a layer-by-layer melting process and thus with the elastic measurements we described earlier. The in-



**Figure 9.** Computer-generated argon atom trajectories created using molecular dynamics simulations by Cheng and Steele for a trilayer argon film on graphite. Top views of the atoms in each layer and a side view of all the atoms in the film are shown. The onset of individual layer melting as the temperature increases is readily apparent.

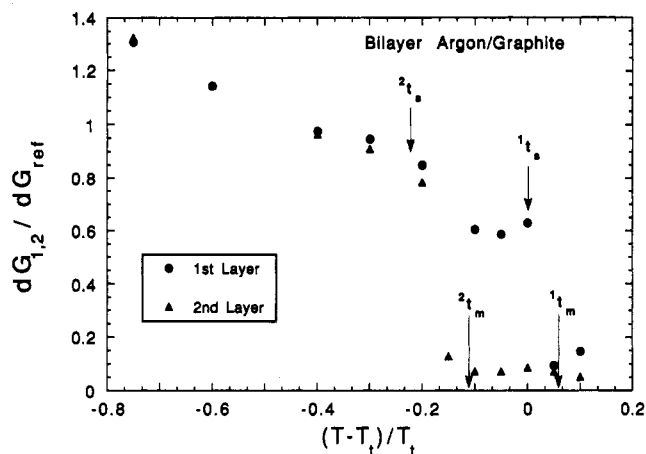
elastic spectrum recorded at 95 K no longer contains any signal which can be associated with phonons (the curve is symmetric in energy transfer about the origin), suggesting that the entire film is liquid. Therefore, it is fair to say that our inelastic measurements confirm our layer-by-layer interpretation of the adsorbed melting process.

### Computer Simulations

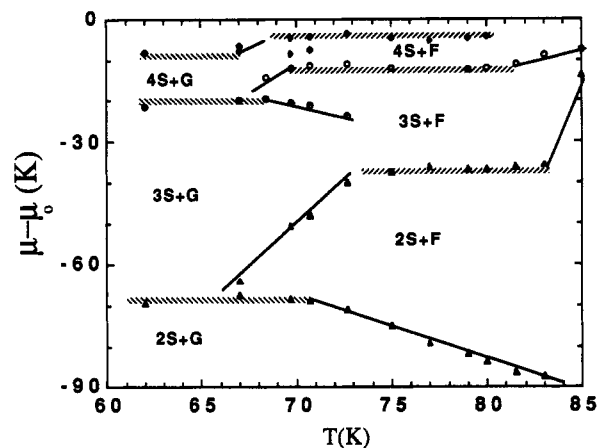
Computer methods can also be employed to provide insight into the microscopic processes associated with multilayer film melting. An excellent example of how molecular dynamics (MD) simulations were used to investigate bulk surface melting can be found in the work of Broughton and Gilmer.<sup>44,45</sup> Among other systems investigated, they explored the behavior of the (111) surface of a Lennard-Jones solid and found that the first few layers of the solid disordered successively with increasing temperature. Computer studies of the melting properties of argon multilayers on graphite have also been performed. Using a MD approach, Cheng and Steele<sup>46</sup> followed the disordering of a three-layer solid argon film, constrained initially to be an ideally-stacked fcc solid. Figure 9 summarizes their results. Phillips has also extensively studied the argon-on-graphite system, using Monte Carlo techniques.<sup>31,47</sup> In addition to observing a layer-by-layer melting process, his simulations suggest that the disordering process is initiated by layer promotion of argon atoms in the outermost solid portion of the film. This action creates vacancies within the remaining solid and thereby creates the space necessary for translational diffusion to begin. At first, the diffusion process is lattice-like, the atoms forming what is sometimes referred to as a modulated fluid phase since they tend to spend less time in regions occupied by atoms in the layer immediately below. Figure 9 illustrates this property (the MD tracks leave open spaces which are 6-fold symmetric). Figure 10 illustrates how in-plane correlations decay with increasing temperature. These are in excellent agreement with the neutron diffraction measurements. This reinforces the idea that computer simulations clearly yield accurate microscopic descriptions of film systems when reliable interatomic potentials are available.

### Phase Diagram and Reentrant Layering

Figure 11 is a phase diagram of the argon-on-graphite



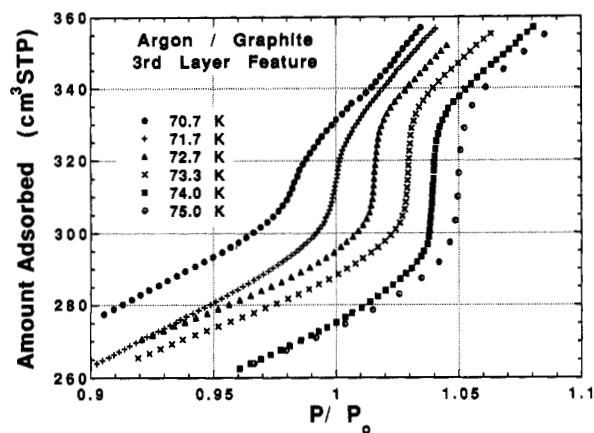
**Figure 10.** Results from Monte Carlo computer simulations by Phillips (see ref 12) which follow the decay of in-plane correlations by plotting the ratio of the difference between the maximum and minimum for the 2D pair distribution function,  $G_{1,2}(R)$ , at the distance of the 12th shell of neighbors to a reference difference. The arrows mark the temperatures which signal the beginning and end of the vertical sections shown in the experimental neutron window scan trace of Figure 7.



**Figure 11.** Phase diagram for argon multilayers on graphite. The thick cross-hatched lines indicate first-order phase transition regions (vertical isotherm steps) while the thin lines denote possible continuous transition lines (kinks in the isotherms). The symbols S, G, and F, represent solid, gas, and fluid phase, respectively. The fluid or disordered phase most likely exists in a region where the vertical extent of the liquid phase is not well defined. Layer critical temperatures are located at  $T_c(2) = 70.0 \pm 0.3$  K,  $T_c(3) = 68.3 \pm 0.5$  K, and  $T_c(4) = 67.2 \pm 0.2$  K and the layer triple points at  $T_t(2) = 66.5 \pm 0.5$  K and  $T_t(3) = 67.2 \pm 0.5$  K.

system based primarily on our neutron diffraction and vapor pressure isotherm measurements. Where appropriate, we have also incorporated results from the heat capacity studies of Zhu and Dash and from Day et al. which provide definitive identifications of the phase boundaries. The similarities of the first-, second-, third-, and fourth-layer regions of the phase diagram suggest that the lower layers act, in effect, as modified substrates for the upper layers. We would also like to call attention to the portion of the phase diagram where the reentrant first-order behavior reported by Youn and Hess<sup>48</sup> occurs. Figure 12 illustrates vapor pressure isotherm data recorded at Brookhaven National Laboratory (BNL). These isotherms were measured at a series of closely spaced steps in temperature in the

(48) Youn, H. S.; Hess, G. B. *Phys. Rev. Lett.* 1990, 64, 918.



**Figure 12.** Vapor pressure isotherm measurements for argon on graphite at various temperatures. These data show the evolution of the reentrant behavior associated with the third argon layer (as indicated by the cross-hatched lines near  $\mu-\mu_0 = -40$  K and within the temperature range 73–80 K in Figure 11). Data were recorded using a computer-automated gas-dosing system whose general operating characteristics are described in ref 17.

neighborhood of the reentrant region associated with the third layer. We remind the reader that these temperatures are above the layer critical temperature<sup>48–50</sup> (i.e., the point beyond which discrete layer-by-layer growth occurs) and that a three-layer film has two solid layers and one (outermost) fluid layer at the base of the step.<sup>37,38</sup> On the basis of X-ray diffraction data obtained at the National Synchrotron Light Source X7-B facility<sup>38</sup> and an extensive computer modeling study,<sup>51</sup> we suggest that the reentrant feature in the isotherms is the result of a resolidification of the previously mobile third layer of the film, i.e., the system goes from two layers of solid + fluid to three layers of solid + fluid. Other isotherm and X-ray diffraction studies we have completed of this reentrant phenomena employing xenon multilayer films on graphite (a much more attractive candidate for X-ray studies) suggest that the same mechanism occurs. Analysis shows that during the reentrant process a reduction of the near-neighbor distance occurs, indicating that some compression (densification) of the argon film takes place. Presumably the compression is the result of reincorporation of atoms from the upper portions of the film into the previously fluid layers below. This is somewhat reminiscent of the (re)solidification that can occur in a 3D fluid at constant temperature when the pressure is increased. More extensive microscopic investigations (using both diffraction and computer simulation) of this phenomenon are currently underway, and a more

(49) Gilquin, B. D.Sc. Thesis, Nancy; CEA Note 2091 (1979).

(50) A nice survey can be found in the following: Hess, G. B. In *Phase Transitions in Surface Films*; Taub, H., Torzo, G., Lauter, H. J., Fain, S. C., Eds.; Plenum Press: New York, 1991; p 357.

(51) Phillips, J. M.; Larese, J. Z. *Bull. Am. Phys. Soc.* 1993, 38, 748.

detailed description of the physical processes involved will be forthcoming.<sup>52</sup>

## Summary

The layer-by-layer growth and melting processes of argon films adsorbed on a graphite surface have been described. It has been shown that a remarkably complete picture of such behavior can be obtained by combining thermodynamic, diffraction, and computer methods. Similar behavior is expected in other multilayer rare-gas/graphite systems. Although it is tempting to suggest that these multilayer film studies provide direct insight into the 3D melting process, it must be kept in mind that the role played by the substrate in the melting of adsorbed films raises questions about the validity of such extrapolations. This is best underscored by pointing to the substrate-induced stabilization of the solid argon layer closest to the graphite surface at temperatures about 15 deg above the 3D triple point.

Apart from detailing the film-melting process, a preliminary explanation of reentrant layering has been put forward and a phase diagram for films up to three layers thick has been presented. More detailed investigation of the individual-layer phase transitions and of the behavior of the elastic properties of these multilayer films is planned and should prove to be illuminating. Investigation of reentrant layering phenomena using single-crystal graphite substrates is contemplated as well.

Space does not permit us to describe other work involving multilayer molecular films of simple molecules like methane and ethylene on graphite<sup>60</sup> and MgO surfaces.<sup>53</sup> These studies show that incommensurate interlayer and intralayer structures appear and that the structures of the molecules themselves often introduce severe constraints on the nature of the adsorbed film. They also indicate that growth modes other than layer-by-layer-like can occur. Future work will most likely focus on molecular films of increased complexity.

*It has been my great fortune to have collaborated with a number of colleagues and students on these adsorption studies. In particular I would like to express my gratitude to Laurence Passell, who is solely responsible for stimulating my interest in neutrons as surface probes. Much of this work would not have been performed without the tireless efforts of Qiming Zhang and Julius Hastings. I have also greatly benefited from discussions with Jim Phillips, Moses Chan, Ailan Cheng, Greg Dash, George Hess, Bill Steele, and Haskell Taub. This research was performed under the auspices of the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.*

(52) Phillips, J. M.; Larese, J. Z. To be published in *Phys. Rev.*

(53) See, for example: Coulomb, J. P. In *Phase Transitions in Surface Films*; Taub, H., Torzo, G., Lauter, H. J., Fain, S. C., Eds.; Plenum Press: New York, 1991; p 113 and references therein.