

Molecular-dynamics study of interlayer incommensurability in adsorbed multilayers

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Molecular-dynamics simulations on large multilayer systems with power-law edge potentials have independently shown commensurate-incommensurate transitions between layers. The large-scale mosaic of the incommensurate structure reconciles the simulations with neutron-diffraction experiments on the CH₄/graphite bilayer. The elastic character of the solid films suggests that many previous attempts to use “rigid” models to describe multilayers are insufficient to explain some of the thermodynamic and structural properties.

INTRODUCTION

Solid adsorbed multilayers have an anisotropic elastic character. Adsorbate atoms are often subject to reasonably strong interactions with the substrate. The substrate-adsorption potential vertically stresses the film. This perpendicular force varies so sharply with height above the substrate that in some systems a commensurate-incommensurate (C-IC) transition occurs between the first two layers nearest the substrate. These commensurability transitions are the structural responses of a film to the sizable differences in shearing stress between the layers. The source of these shearing stresses is the vertical variation of the substrate potential. These forces laterally compress the first layer of the film, resulting in a smaller lattice constant than for the rest of the film. This mismatch of differing length scales causes the first and the second layers of some films to be incommensurate at certain coverages and temperatures.

The system is anisotropic because it is a crystal lattice and not an isotropic continuum. It is inhomogeneous because of the variation of the density and the net intermolecular interactions across the adsorbate-substrate interfacial region.

This study was initiated to investigate the large-scale mosaic structure resulting from two elastic incommensurate layers. The results extend our understanding of interlayer C-IC transitions.^{1,2} Insofar as possible, the mosaic structure we found reconciles the points of disagreement between simulation^{1,2} and experiment.³

In a previous paper² we made an attempt to create an analogy between the detailed intermolecular-interaction system and continuum anisotropic-elasticity theory. Such a phenomenological comparison has been helpful to some⁴⁻⁷ in visualizing the interplanar interactions without the notational complexities of calculating ensemble averages of the collective interparticle effects. These recent studies on two-dimensional phenomena have improved our appreciation of the role continuum models have in bringing some understanding to our study of intermolecular interaction systems.

The role of the pressure tensor in continuum fluid films has been extensively discussed by Steele⁴ and by Rowlinson and Widom.⁵ Bruch and co-workers⁶ have given layer-to-layer coexistence criteria in terms of increasing spreading pressure in thin solid multilayers. In an important clarification of an ambiguity found in previous definitions of the shear components of the stress tensor in films, Baus and Lovett⁷ have used the force-balance equation and Saint-Venant’s strain-compatibility conditions to obtain a well-defined stress tensor for nonuniform equilibrium fluids and solids. The theoretical framework now exists to visualize the structural response of a thin film to substrate-induced elastic stresses. Again, we point out the use of these macroscopic models is a comparison.

As shown,² the equations of equilibrium are given by the Euler-Cauchy stress principle. With the substrate-generated body force $F_j(x_3)$ per unit mass,

$$\frac{\partial \tau_{ij}}{\partial x_i} + F_j = 0, \quad i, j = 1, 2, 3, \quad (1)$$

where τ_{ij} is the stress tensor. The variable body force $F_j(x_3)$ is given by the gradient of the substrate potential $v(x_3)$ and scaled with the number density to provide a continuum body force.

In a recent effort to move the statistical mechanics of an adsorbed multilayer closer to current diffraction experiments, interlayer-commensurability transitions were observed.^{1,2} In low-temperature simulations, Phillips and Hruska¹ found the top layer of a CH₄/graphite bilayer to be incommensurate with the lower layer. Again, Phillips and Story² found that an argon/graphite multilayer experienced a similar transition as the film thickness exceeded four layers. The only direct experimental comparison currently available is a neutron-diffraction study of the CH₄/graphite bilayer by Laresse *et al.*³ They found the line shape to be inconsistent with a pure AB-stacked bilayer or two incommensurate unmodulated “monolayers.” This important experiment agrees with the simulation in that elastic stress in the film has produced a structural change in the bilayer. However, the oblique

unit cell found in the simulation would be clearly visible in the experiment. It was not. Were spurious simulation results producing the oblique cell or at least magnifying the effect? The earlier simulations were with rather small systems. Although they gave quite detailed information on the microscopic structure, they merely implied the nature of a large-scale mosaic. Also, the constraints on the system due to the action of periodic boundary conditions could possibly influence the film structure.

A different computer program was used to provide as much independence as possible. Molecular dynamics replaced the Monte Carlo method. Much larger simulation cells were used, usually twenty times as many particles. The simulation cell is now a circular patch with an empirical-edge potential. The substrate potential is fundamentally the same but computed from an entirely new algorithm.

The net result leads to the realization that the earlier simulations gave a detailed picture of the microscopic structure within a domain wall, whereas the new simulation gives the configuration mosaic of the domain-wall system. This system of domain walls separates regions of *AB* stacking from *AC* stacking. Such a structure would fall within the limits of the diffraction study by Larese *et al.*³

METHODS

Molecular-dynamics simulations are performed for thin films on a finite surface substrate. The molecular-dynamics step algorithm is that of Swope *et al.*⁸ This "velocity-Verlet" scheme updates particle information according to

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \delta t \mathbf{v}(t) + \frac{1}{2}(\delta t)^2 \mathbf{a}(t) \quad (2)$$

and

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{1}{2} \delta t [\mathbf{a}(t) + \mathbf{a}(t + \delta t)]. \quad (3)$$

This ensures that positions and velocities are known with accuracy at the same time. Such a step scheme maintains a constant Hamiltonian to $(\delta t)^3$.

For this work, however, we desired to maintain a fixed temperature rather than a fixed total energy. To achieve a fixed temperature, the Hamiltonian is modified to include a velocity-rescaling parameter. As shown by Nosé,⁹ such a modified Hamiltonian with a constant temperature constraint will provide an ensemble which is canonical in potential energy and constant in kinetic energy.

The substrate interaction is obtained from the standard Steele potential for graphite. This potential involves a summation of individual Lennard-Jones adatom-carbon interactions. For the infinite-extent graphite slab this reduces to the form

$$V(\mathbf{r}, z) = V_0(z) + \sum V_g(z) e^{i\mathbf{g} \cdot \mathbf{r}}, \quad (4)$$

where the summation runs over all reciprocal-lattice vectors \mathbf{g} of the substrate, z is the height of the adatom above the substrate, and \mathbf{r} is the location of the adatom along the substrate. Calculations show that the summa-

tion can be truncated after the first shell of six \mathbf{g} 's. By symmetry, $V_g(z)$ does not vary with the orientation of \mathbf{g} and can be factored from the summation. The resulting factor $V_g(z)$ is known as the corrugation of the substrate. The lateral variation of Eq. (3) is too small, however, and we adopt the modified form

$$V(\mathbf{r}, z) = V_0(z) + s \sum V_g(z) e^{i\mathbf{g} \cdot \mathbf{r}}, \quad (5)$$

with $s = 1.5$ which provides a better match to experimental evidence on the rotation of adsorbed monolayers.

In order to model a finite-extent substrate we modify the holding term $V_0(z)$. This term is obtained as an averaged integral of the adatom-carbon interactions summed over each substrate layer. There are two parts to this term. An attraction, which varies as z^{-4} and a repulsion which varies as z^{-10} . To model the confinement of a thin to a circular substrate disk, we modify the attractive term. Rather than integrating the r^{-6} Lennard-Jones attraction term to infinity to obtain the z^{-4} dependence, we integrate this out only to a finite radius. This provides an attractive term that varies both with height z and lateral position \mathbf{r} . This method of producing an edge on the graphite layer has worked well in describing stepped surfaces.¹⁰

We include calculations of the two-dimensional structure factors $S(\mathbf{k})_n$ of individual layers. For N_n atoms in the n th layer the ensemble average is computed for

$$S_n(\mathbf{k}) = \left\langle \left| \sum_{\mathbf{r}_i, \mathbf{r}_j} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right|^2 \right\rangle / N_n. \quad (6)$$

The vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the position vector of atom pairs in the n th layer and \mathbf{k} is taken over an array centered on the reciprocal-lattice vector \mathbf{G}_n .

The Lennard-Jones interaction parameters used in the systems studied are as follows: for the argon-argon interactions $\sigma = 3.40 \text{ \AA}$ and $\epsilon/k = 120 \text{ K}$, the argon-carbon $\sigma = 3.402 \text{ \AA}$ and $\epsilon/k = 57.9 \text{ K}$, the methane-methane $\sigma = 3.6814 \text{ \AA}$ and $\epsilon/k = 137 \text{ K}$, the methane-carbon $\sigma = 3.2970 \text{ \AA}$ and $\epsilon/k = 85.419 \text{ K}$. These parameters scale the systems to be similar to our previous papers.^{1,2}

We report on just a few of the many simulations carried out under a variety of thermodynamic conditions. The temperature was $T = 25 \text{ K}$ in all runs reported. The number of particles in the system varied from 5000 to 20 000. The number of layers varied from two to five.

RESULTS

One of the several series of simulations we studied was an argon/graphite four-layer system with nearly 10 000 atoms on a smooth substrate at $T = 25 \text{ K}$. Duplicate simulations with substrate corrugation included indicated that the substrate periodicity appeared to make little difference in the interlayer-commensurability effects. The adsorbate-substrate interaction parameter ϵ is multiplied by a factor which varied from 1 to 2. Figure 1 is a schematic of the stacking structure of only the first two layers for three examples with progressively stronger substrate attractions in the series. The top diagram, Fig. 1(a), is a perfect *AB*-stacked commensurate unit, while

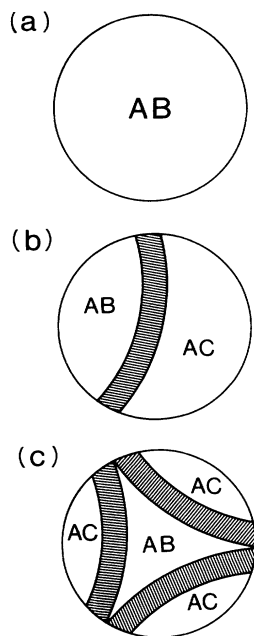


FIG. 1. A schematic diagram showing the introduction of domain walls observed in the incommensurate layer one of a four-layer film of argon on a flat graphite model. (a) is the normal holding potential, (b) is 1.5 times the normal holding potential, and (c) is 2.0 times the normal holding potential. This series demonstrates the onset of wall formation with increased compression of the film.

the second picture, Fig. 1(b), has developed two sections, one AB and the other AC stacked. Separating these sections is a domain wall (misfit dislocation). Figure 2 is a schematic of the internal structure of the domain wall as the system accommodates the change from AB to AC stacking over a few lattice constants. Figure 2 shows a

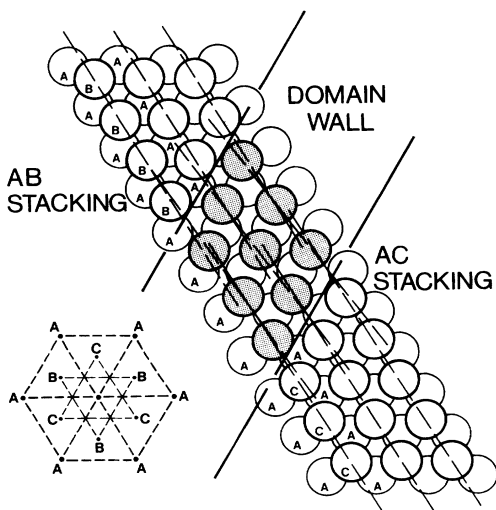


FIG. 2. A schematic diagram illustrating the structural details of the change from a region of AB stacking to AC stacking. The oblique nature of the unit cell in the domain wall is typical of all the incommensurate structures we observed. The inset shows the A , B , and C sites of the (111) plane for a fcc lattice.

second-layer row of atoms lying on B sites in the trough between first-layer A sites. This row distorts into a row of C sites again between first-layer rows of A sites. Figure 1(c) shows the larger mosaic of domain wall as the substrate ϵ has been doubled. Three domain walls appear in the three possible directions forming a rough equilateral triangle. Larger systems with many walls suggest these walls also fluctuate.¹¹ Figure 3 is the actual snapshot of the final configuration of the system [Fig. 1(c)] with double the substrate interaction.

Using Eq. (6), we have computed the two-dimensional structure $S_n(\mathbf{k})$ for the individual layers in the system ending in the configuration shown in Figs. 1(c) and 3. It is clear in Fig. 4, to a high degree of precision, that the top three layers of the film are commensurate and layer one (closest to the substrate) is compressed. The first layer contains 26% of the total number of atoms, 25% of the atoms are in layers two and three, 23% are in layer four, and less than 1% are observed in the vapor. The values of the $k_{\max} = 2.0 \text{ \AA}^{-1}$ for layer one and $k_{\max} = 1.96 \text{ \AA}^{-1}$ for layers two through four quantify the extent of the overcompression (2% for the first layer). This first layer is incommensurate relative to the three upper layers. It has domain walls (misfit dislocations) in the three allowed directions.¹² It should be pointed out that in stacking a (111) plane of one lattice constant on the (111) plane of another, only two sites are available, B and C . In the quite familiar monolayers on graphite systems near the $\sqrt{3} \times \sqrt{3}$ registry, there are three sites available, A , B , and C (see inset of Fig. 2). Topologically, instead of the hexagonal-wall structure found for such systems as krypton on graphite, we will see only patterns of two alternating domains and a basically triangular mosaic.

From Fig. 3, one can see that most of the atoms are in register positions, either AC or AB stacked. In the domain wall, the two-dimensional unit cell is slightly oblique^{1,2} and the half-width at half maximum of $S_n(\mathbf{k})$

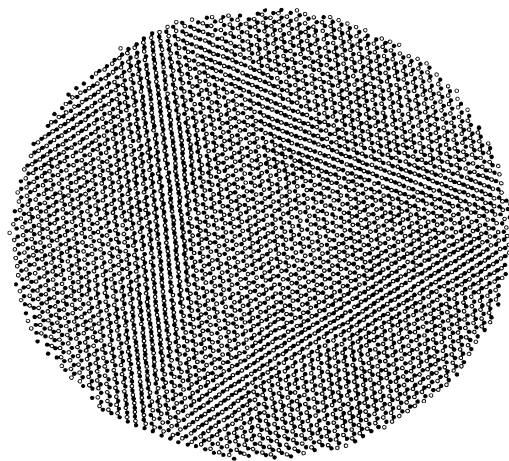


FIG. 3. This figure is a "snapshot" of layer one (open circles) and layer two (filled circles) taken from the final configuration of the system represented schematically in Fig. 1(c). The system was a four-layer stack of argon/graphite at 25 K after 20 000 time steps. The top three layers are commensurate (see Fig. 4).

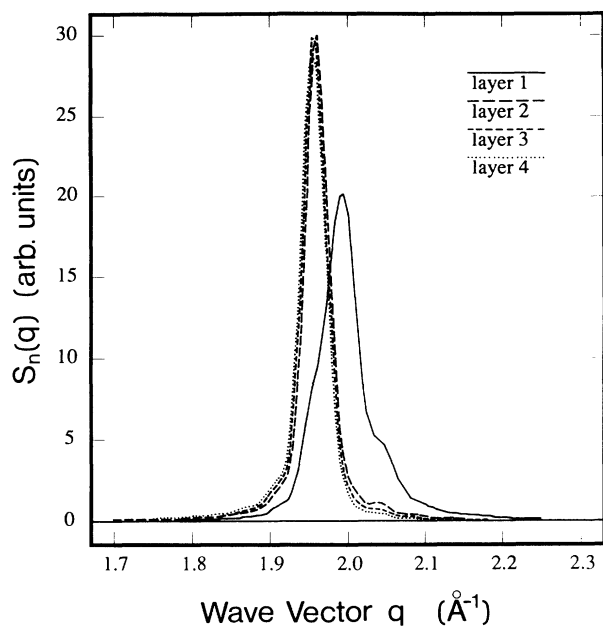


FIG. 4. A plot of the two-dimensional structure factors for each individual layer for the argon/graphite (25 K) four layer shown in Figs. 1(c) and 3.

differs from 0.019 \AA^{-1} in layer two to 0.027 \AA^{-1} in layer one. The correlation length in the solid three-layer slab of layers two, three, and four are noticeably longer than in the more modulated structure of layer one.

The shoulder on $S_1(k)$ is likely due to this obliquity. In our earlier work,² the structure factor had a distinct double peak. The small size of the system in that calculation may have enhanced the effect since nearly all of the atoms in the system are in the wall itself. The semblance of oscillations in the foot of $S(k)$ may be due to the finite-size effects. The new result is more compatible with the experiments of Larese *et al.*³

Methane-on-graphite bilayer simulations were run with and without substrate corrugation. With the first layer being compressed well below the $\sqrt{3} \times \sqrt{3}$ commensurate lattice constant, the substrate corrugation appears to have little effect on the first- and second-layer commensurability.

Generally, the structural results from the methane films were quite similar to those using argon adsorbates. Since the relative strength of the adsorption potential for methane is higher, the compressive stress on the first layer critical to initiating a C-IC transition is achieved with only a bilayer of coverage (at 25 K). This low-temperature bilayer result for methane is in contrast to the argon result. For argon, the critical coverage was greater than four layers.

The IC structure for the methane, again, is a pattern of domain walls separating regions of *AB*- and *AC*-stacked commensurate structure. An interesting observation occurs in the methane bilayer. Vacancies appearing in the second layer act as structural-accommodation centers disrupting long domain walls like those depicted in Fig. 1(c). Equilateral triangles of *AC*-stacked domains with vacancies at the vertices are islands (*AC*) completely sur-

rounded by (*AB*) commensurate bilayer. The domain walls are "sharp." At higher coverages (> 2.0 monolayers) and higher temperatures, the vacancies in the second layer are filled in and the structure is, once more, much like the argon-film results.

DISCUSSION AND CONCLUSIONS

Commensurate-incommensurate transitions between the first two layers in a multilayer occur in our molecular-dynamics simulation at approximately the same conditions of temperature and coverage as the earlier simulations for both the $\text{CH}_4/\text{graphite}$ and the $\text{Ar}/\text{graphite}$ systems. The larger size of the system allows a much more complete observation of the IC structures. The detailed structure within a domain wall is the same as in the earlier simulations. The experiment³ and our simulations complement each other. The simulation could not have the size necessary to mimic the laboratory sample. On the other hand, the experiments cannot, at present, be done with sufficient resolution to distinguish the microscopic details of the wall structure observed in the simulation.

The consistency between the two studies gives reasonable support to the hope that the structural details observed in the simulations approximate reality.

From very different simulations, we now have shown that there again appears to be a C-IC transition between the first two layers closest to the substrate. The large size of our systems and the circular boundary has freed the film from several constraints thus allowing the structure to form domain walls spontaneously. Our simulations have clarified the results of earlier Monte Carlo studies for a few hundred atoms and periodic boundary conditions. Where the small-system results implied a rotation between the layers over the entire sample and an oblique unit cell, such features would be quite pronounced in a diffraction experiment. Although the experiment³ did not find either feature, it was possible to determine that the bilayer was not a strictly commensurate *AB*-stacked system. Nor was it two incommensurate perfectly triangular monolayers one upon the other. This study sought successfully to reconcile the structure observed in our simulations with diffraction experiments.³ We suggest the alternating domains of *AB* and *AC* stacking separated by a wall structure (see Figs. 1–3) could be the microscopic picture of the system in the experiments. Since the incommensurate structure we observe is a direct result of the elastic response of the film, it seems clear to us that attempts to model solid multilayers should include the elastic properties.

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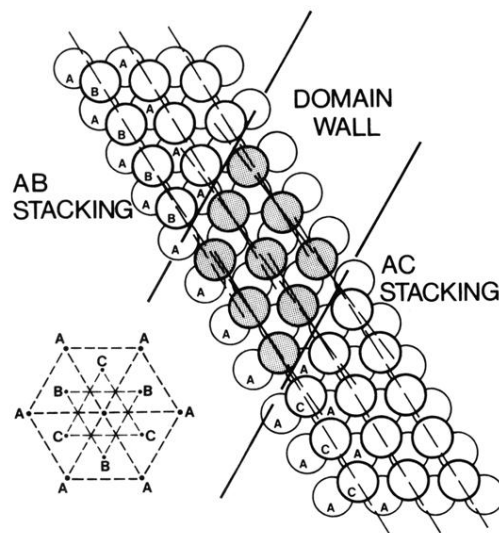


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