

Structure of axially compressed monolayers of N_2 physisorbed on graphite

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Monte Carlo calculations have been used to study the effect of compressing monolayers of N_2 physisorbed on graphite. Axial compression of a commensurate (ordered herringbone) monolayer initially generates striped domain walls about 35 Å wide rather than a uniform incommensurate structure. The onset of rotational diffusion for molecules in the domain-wall regions occurs at higher temperatures than in the commensurate domains.

Computer simulations^{1,2} have played an important role in elucidating the behavior of rare-gas overlayers physisorbed on graphite. For example, when the surface density of Kr adsorbed on graphite is raised to just beyond that of a commensurate ($\sqrt{3} \times \sqrt{3}$) monolayer (hereafter defined as $n=1$) the system organizes itself into commensurate patches separated by a hexagonal array of domain walls.¹ On a hexagonal substrate, such as provided by the graphite basal plane, domain walls can form in either hexagonal or striped structures.^{3,4} Indeed, striped domain walls have been reported for CF_4 adsorbed on graphite⁵ and for Br_2 intercalated graphite.⁶

The adsorption of N_2 on graphite has been afforded a great deal of attention lately.⁷⁻²³ The low-temperature solid structure, for $n > 1$ is a planar ($\sqrt{3} \times \sqrt{3}$) commensurate herringbone.⁷ A uniaxial incommensurate (UI) phase has been reported⁸ for coverages $1.02 \leq n \leq 1.05$. Further compression eventually yields a triangular incommensurate (TI) structure in which the molecules are no longer lying flat on the surface.⁹⁻¹¹ The orientational order-disorder transitions that occur upon heating these different overlayer structures have been studied by a variety of experimental techniques.⁷⁻¹⁴

This wealth of experimental information has spawned a number of theoretical investigations.¹⁵⁻¹⁹ If sufficiently realistic molecule-surface^{20,21} and molecule-molecule potentials²² are used, the rotator transition in commensurate films^{15,16} and the melting or sublimation of submonolayer patches¹⁹ are both well reproduced. However, to date such simulations have employed relatively few molecules; hence it was not possible to comment on the nature of domain walls or indeed even to discuss their possible existence.

The present article goes part way to rectifying this situation. Through extensive Monte Carlo calculations, carried out on periodically replicated systems containing up to 2704 N_2 molecules, we have established that axial compression of a commensurate ($\sqrt{3} \times \sqrt{3}$) herringbone structure initially generates striped UI domain walls (with a width of about 35 Å) rather than a uniform UI phase.⁸ Moreover, orientational order in the domain walls persists to higher temperatures than in the commensurate regions. These results may offer a possible explanation for some of the multiple peaks that are observed in the heat capacity of compressed films of N_2 on graphite.¹⁴ They also suggest the need for a more thorough experimental study of the initial stages of compression.^{8,9}

The model employed in the Monte Carlo calculations was essentially the same as that which gave an excellent account of the rotator transition of the commensurate phase.¹⁶ The N_2 - N_2 potential consisted of atom-atom ($\exp -6$) contributions plus the interactions between four charges suitably arranged on the molecular axis.²² Evaluation of the substrate screened intermolecular potential was rather time consuming.¹⁶ This fact considerably reduced the possible system size that can be adopted compared with comparable studies of atomic systems.^{1,2} The N_2 -graphite potential was somewhat different than we used previously.¹⁶ In particular, we adopted an anisotropic (12-6) atom-atom potential whose anisotropy parameters ($\gamma_R = -0.54$, $\gamma_A = 0.4$) were fitted to the bound-state resonances of 4He scattering from graphite.²¹ While the (12-6) parameter, $\sigma = 3.36$ Å was similar to those used by other authors²⁰ the value of $\epsilon = 34.5$ K was scaled to fit the isosteric enthalpy of adsorption for N_2 on graphite.²³ (In actual calculations a Fourier decomposition was used to sum over the graphite carbon atoms.²⁰) The anisotropy parameters γ_R and γ_A increase the surface corrugation by about 60% but have little effect on the binding energy. The enhanced surface corrugation was found to be important in describing the melting or sublimation of N_2 on graphite at submonolayer coverages.¹⁹

The potential model was first tested using a four-molecule Monte Carlo (MC) procedure.¹⁶ In this method the system consists of a periodically replicated four-molecule unit cell. The molecular orientations and center-of-mass heights are sampled along with the position of the cell origin and its two-dimensional lattice vectors; the latter can be done under the constraint of constant surface area. The potential described above yields a commensurate ($\sqrt{3} \times \sqrt{3}$) herringbone structure at $T = 5$ K when the unit cell area is unconstrained and a UI herringbone with the constraint, $n = 1.025$. These findings are in excellent accord with experimental observations.^{7,8} Unfortunately, further compression did not yield the observed canted TI (2-out) herringbone phase¹⁰ but instead a pinwheel structure, similar to that observed in dense physisorbed films of CO on graphite.²⁴

Notwithstanding this apparent failure of the model under very high compression more detailed MC studies were carried out on systems constrained to have $n = 1.026$ via the use of periodic boundary conditions. The systems were always initially uniaxially compressed in the x direction (see Fig. 1), via *uniform scaling* of the center-of-mass positions in accordance with the observed low-energy electron-

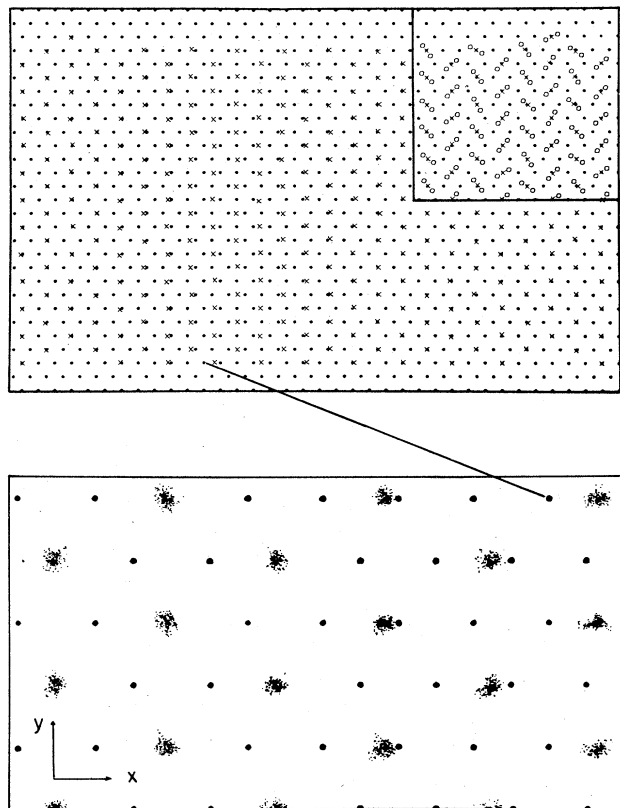


FIG. 1. Striped domain wall observed in Monte Carlo calculations at $T=10$ K for a monolayer of N_2 on graphite uniaxially compressed in the x direction by 1.026 with respect to a $(\sqrt{3} \times \sqrt{3})$ commensurate structure; dots denote centers of basal plane hexagons and crosses the mean positions of the N_2 centers of mass. Inset at the top is the herringbone order in the commensurate region. The center-of-mass distributions in the region of the domain wall are shown at the bottom. The simulation system was a periodically replicated array of (52×12) molecules. Analogous results were obtained for larger systems (see text).

diffraction structure⁸ and the results of the four-molecule minimization calculations (y compression is energetically less favorable^{16,17}). First, a system of (52×52) molecules was arranged on a rectangular patch of graphite hexagons. The calculation commenced from ordered herringbone orientations and at $T=10$ K rapidly evolved to a structure with two striped UI domain walls separating commensurate regions. In order to check on the influence of the periodic boundaries the MC calculation was repeated using a system of (104×26) molecules. This time, four stripes were produced. The calculation was then repeated on systems of (52×12) and (26×12) molecules which yielded, respectively, two and one striped domain walls. The results are thus strictly proportional to the system size and nicely illustrate the Frank-Van der Merwe principle.²⁵ The centers of the graphite hexagons from the (52×12) calculation are shown as dots in Fig. 1 and the mean positions of the N_2 centers of mass as crosses. The striped domain wall is seen to have a half width of about five columns of N_2 molecules; the total width of the stripe is thus about 35 Å. Inset in Fig. 1 is a

portion of the commensurate herringbone region showing the characteristic molecular orientations. Also shown in Fig. 1 are the phase-space trajectories (Debye-Waller cloud) of the N_2 centers of mass in the region of the domain wall, which confirm that the latter is quite stable.

The above-mentioned MC runs were carried out at $T=10$ K. Two of the systems (52×12) and (26×12) were then heated to investigate the onset of rotational diffusion. The former system was studied at temperatures of $T=20, 25, 29, 33, 36,$ and 40 K and the latter at $T=27, 31,$ and 34.5 K. Figure 2 shows the temperature variation of the mean potential energy $\langle E \rangle$ and the orientational-order parameter $\langle \cos(2\theta) \rangle$, where θ is the difference between the instantaneous value of the azimuthal angle of a molecule and its value in a $T=10$ K reference configuration; the brackets indicate an ensemble average, which at the higher temperatures involved sampling each molecule 36 000 times. As with our previous study of the commensurate N_2 -graphite system, rotational diffusion appears to set in $T < 30$ K.¹⁶ However, a detailed investigation of the system reveals a more complex behavior. Thus, while the orientational order in the commensurate regions was little affected at $T=20$ K, the domain walls moved closer together by about 15 Å and some molecules stand up thereby generating isolated pinwheel defects in the domain walls, whose central regions are laterally compressed by about 9%. Such defects were also observed in our previous simulations of compressed N_2 monolayers.¹⁶ Heating caused more pinwheel defects to appear in the wall regions and the stripes to move closer together. At $T=29$ K the two domain walls have almost coalesced; molecules in the large commensurate region now exhibit rotational diffusion but the domain walls continue to retain a degree of orientational order. This behavior is illustrated in Fig. 3, where $\langle \cos(2\theta) \rangle$ is plotted at $T=20, 25,$ and 29 K for each of the 52 columns of N_2 molecules comprising the total system. In the latter case the orientational order decays away slowly from the center of the

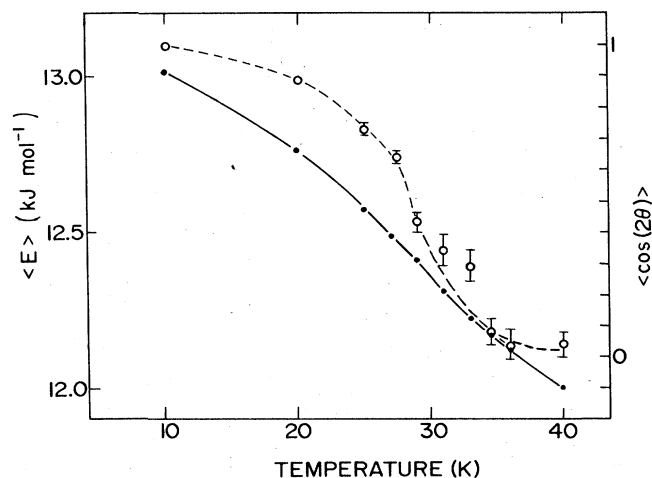


FIG. 2. Temperature dependence of $\langle E \rangle$, the mean potential energy (dots) for N_2 on graphite, uniaxially compressed by 1.026 with respect to a commensurate monolayer. The circles denote $\langle \cos(2\theta) \rangle$, the mean orientational-order parameter. The point at 33 K differs from the dashed curve because of persistent orientational order in the domain walls (see text).

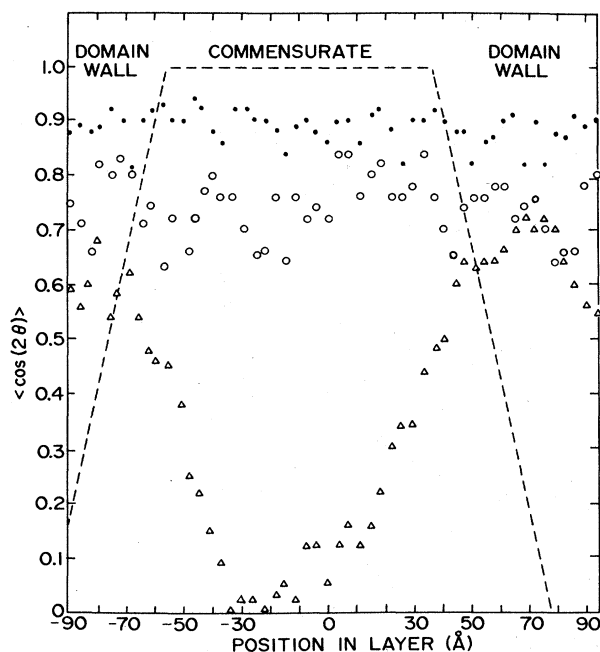


FIG. 3. Temperature dependence of the orientational-order parameter $\langle \cos(2\theta) \rangle$ as a function of column position for N_2 on graphite, uniaxially compressed in the x direction by 1.026 with respect to a commensurate monolayer. The rotator transition in the commensurate region has clearly occurred at $T = 29$ K (triangles) but not at $T = 25$ K (circles) or $T = 20$ K (dots). The dashed line indicates the degree of discommensuration; values 0 and 1 denoting registered columns and 0.5 the center of the domain wall.

domain walls. Upon further heating, the molecules in the wall regions continue to disorder. It proved more difficult to obtain good statistics for the runs performed at $T = 31$ and 33 K (recall Fig. 2) because the herringbone order in the wall region appeared to recrystallize along an axis rotated by 90° from the $T = 10$ K reference orientation. However, at $T = 34.5$ K the herringbone order readily disappeared but the domain walls remained and even began to separate again.

As a further check on the nature of the domain walls additional MC runs were carried out on systems with an x -compression factor of 1.013. Here one-half the number of stripes were produced but the character of the walls remained the same. Finally, a (26×12) system was also studied with an x compression of 1.05. This exhibited a UI structure with two broad striped density modulations and no commensurate regions. At a compression of 1.08 an essentially uniform UI phase results.

In summary, we find that uniaxial compression of a $(\sqrt{3} \times \sqrt{3})$ commensurate monolayer of N_2 on graphite first generates striped domain walls rather than a uniformly compressed system.²⁵ Moreover, the walls persist even beyond the temperature at which rotational diffusion sets in.⁹ The observation of persistent orientational order in the domain walls may offer an explanation of the multiple peaks in the heat capacity of compressed films of N_2 on graphite.¹⁴

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