Studies of the Orientational Ordering Transition in Nitrogen Adsorbed on Graphite

A. D. Migone, H. K. Kim, and M. H. W. Chan
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

and

J. Talbot and D. J. Tildesley
Department of Chemistry, The University, Southampton S09 5NH, United Kingdom

and

W. A. Steele
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

(Received 24 January 1983)

High-precision heat-capacity and molecular-dynamics-simulation studies on the orientational transition of nitrogen molecules adsorbed on graphite are reported here. The peak in the heat-capacity data is rather narrow and shows no observable finite-size effects. The simulation studies show that, in addition to the loss of orientational order in the plane of the surface, significant reorientation in the direction perpendicular to the surface is also found as temperature is increased.

PACS numbers: 68.40.+e, 64.70.Kb, 67.70.+n

Diffraction studies indicate that at submonolayer coverages, N_2 molecules form a commensurate ($\sqrt{3} \times \sqrt{3}$) structure on the graphite basal plane at $T < 49$ K,[1] and that molecules in the commensurate phase become orientationally ordered at $T < 30$ K,[2,3] with a structure that agrees with minimum-energy calculations.[4,5] Previous heat-capacity measurements showed a small, rather broad anomaly at this temperature.[6] The low-energy electron-diffraction (LEED) intensity measurements[3] also indicated that some residual orientational ordering for the low-temperature "herringbone" lattice persists at $T > 30$ K. The diffraction results were interpreted as due to a first-order orientational phase transition at $T < 30$ K (affected by the finite size of the system) and residual short-range order at higher temperature. Support for this view is given by the Monte Carlo simulations of Mouritsen and Berlinsky,[7] who studied two-dimensional systems of variable numbers of quadrupolar molecules.

In this Letter, high-precision heat-capacity measurements and a molecular-dynamics simulation are reported for the N_2-graphite system in the vicinity of the orientational transition. Satisfactory agreement is found between these studies. Whereas our experimental results confirm earlier work in some respects, there are important differences: We found the width of the heat-capacity anomaly to be an order of magnitude narrower than the transition region seen in the LEED and the earlier heat-capacity studies. Our experimental results also suggest that finite-size effects of the graphite crystallites are not important for the heat capacity of this transition. Finally, the computer simulation indicates that reorientation in the direction perpendicular to the surface is significant and may play a role in determining the energy and temperature of the transition.

An ac calorimetric technique[8,9] was used in the heat-capacity study. The substrate was a piece of Graphite Foam[10] with dimensions of 10×10×4 mm^3, mass of 0.073 gm, and surface area of 1.14 m^2. Our study includes twelve N_2 coverages below 0.064 molecule Å^{-2}, the $\sqrt{3} \times \sqrt{3}$ commensurate coverage (which we define to be $n = 1$), and several more between this coverage and $n = 1.2$. One panel of Fig. 1 shows the heat-capacity trace of one submonolayer coverage between 23 and 30 K. The background for the peak, representing the heat-capacity contribution from the calorimeter, the solid substrate, and the N_2 heat capacity not related to the orientational ordering, is shown as the dashed line. Also shown in Fig. 1 are orientational-ordering heat capacities (with the background subtracted) for two coverages below and one above the $\sqrt{3} \times \sqrt{3}$ coverage. These plots plus those for other coverages show that (1) the temperature of the maximum-heat-capacity peaks remains constant at 27.00 ± 0.03 K for $n \leqslant 1$, and then shifts upward with coverage above $n = 1$ reaching a value of 27.3 K for a coverage of $n = 1.2$; (2) the shape of the heat-capacity peaks, as defined by the peak height and half-width, also remains constant for all submonolay-

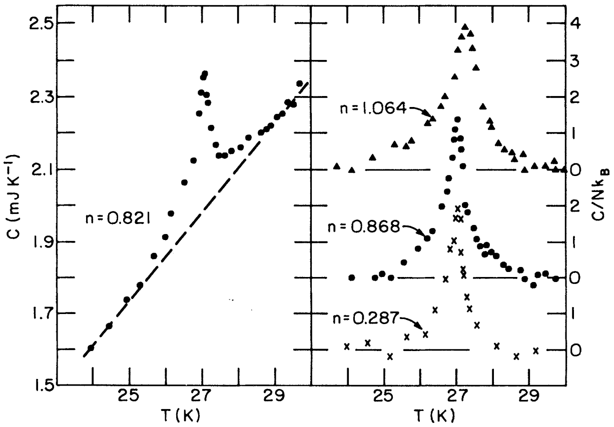

FIG. 1. Total heat capacity near 27 K for one coverage, and heat capacity related only to orientational ordering expressed in units of C/Nk_B for coverages below and above $n=1$.

er coverages. The peak height in units of C/Nk_B is 4.3 ± 0.3, where N is the total number of adsorbed molecules and k_B Boltzmann's constant. The half-width is 0.50 ± 0.08 K. When heats of transition are calculated from the areas under the heat-capacity peaks, they are found to be constant and equal to 36 ± 5 J/mole, for $n<1$ coverages. As the coverage is increased beyond $n=1$ the half-width of the peak broadens to 0.8 K and the peak height shows a slight decrease to 3.5 ± 0.4. Since our temperature excursion during a heating cycle is on the order of 0.05 K, the sharpness of our heat-capacity peak is particularly striking in view of the broad transition observed in the LEED measurement. The heat-capacity results show no evidence of finite-size effect: As the N_2 coverage is increased from $n=0.290$ toward the commensurate value, the size of the $\sqrt{3}\times\sqrt{3}$ patches coexisting with the fluid region should increase up to a maximum of 10^6 Å^2 (the single-crystallite size on the Graphite Foam basal plane[11]). If finite-size effects are significant, one expects a shift in the transition temperature and a sharpening of the heat-capacity peak as the coverage is increased.[12,13] These predictions are expected to be valid for higher-order-like[12] as well as first-order-like[13] phase transitions. We observe no such phenomena.

We made an attempt to apply critical-point analysis to our heat-capacity results. In Fig. 2, the excess heat capacity for one representative coverage is plotted versus the reduced temperature $t=|T-T_t|T_t^{-1}$ on a log-log scale with T_t being the temperature of the maximum. If the transition is second order we expect a straight line with a slope equal to $-\alpha$, with α the specific-heat exponent. Data show scatter in C/Nk_B on the order of 0.2 and inside $|t|=6\times10^{-3}$, rounding is evident. This rounding can be attributed to oscillation in the temperature of the calorimeter produced by the ac heating current and substrate inhomogeneity. For $t>10^{-2}$ the slope is found by a linear least-squares fit to be equal to -1.3 ± 0.2, indicating that in this region critical-point analysis is probably inappropriate since a value of $\alpha \geq 1$ implies a divergent entropy change in the transition. This result suggests either that the true critical region is very small or that it is *never* reached because a first-order transition intervenes. Renormalization-group calculations predicted this transition to be weakly first order.[14]

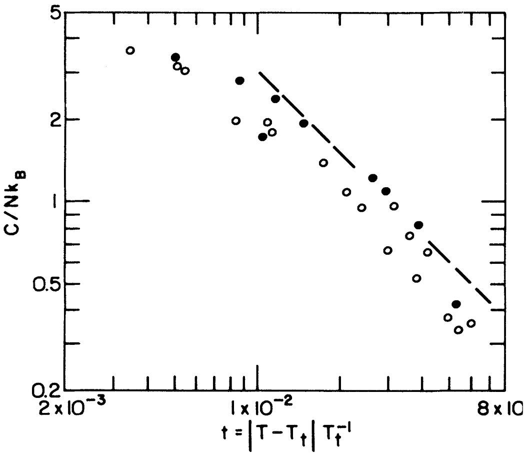

FIG. 2. Orientational heat capacity plotted as a function of reduced temperature $t=|T-T_t|T_t^{-1}$ for $n=0.868$. Open circles are for $T>T_t$ and filled circles are for $T<T_t$. The dashed line is drawn with a slope of -1. This plot shows that critical-point analysis is not appropriate for this transition.

The molecular-dynamics simulations were performed on 96 nitrogen molecules in a rectangular cell, 44.28 Å × 34.09 Å, at a coverage of $n=1$. The simulation is three-dimensional and periodic boundary conditions are used parallel to the surface. An N_2-N_2 potential was constructed from four site-site Lennard-Jones potentials and an additional quadrupole-quadrupole interaction.[15] This pairwise-additive potential gives an adequate representation of the bulk solid and liquid.[16] The N_2-graphite potential is obtained from a similar site-site representation summed over substrate atoms. Complete details of this model are given by Steele.[4] Figure 3 shows the simulated internal energies, at $n=1$, as a function of T. There is a

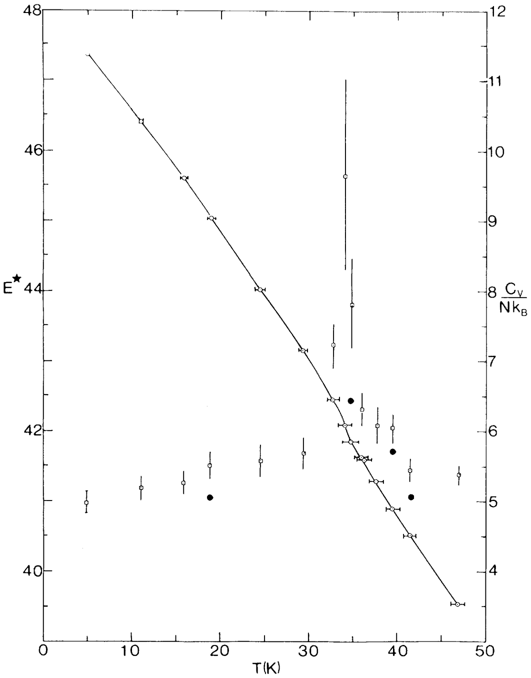

FIG. 3. Simulated internal energy and heat capacity for $\sqrt{3} \times \sqrt{3}$ coverage. $E^* = E/N$, where N is the number of adsorbate molecules. $\epsilon/k_B = 31$ K. Open circles with error bars stand for E^*; squares with error bars, C_v/Nk_B by differentiation; and filled circles, C_v/Nk_B from the fluctuation theorem.

rapid change of slope around 33 K and a maximum in the specific heat at 34 K. The specific heats obtained by numerical differentiation are in reasonable agreement with the heat capacities obtained from the fluctuation theorem,[17] which can only be accurately applied to runs in excess of 10^4 time steps of $\sim 0.5 \times 10^{-14}$ sec. The narrow heat-capacity peak found here is in excellent agreement with our experimental result.

To characterize this transition we calculate three orientational order parameters:

$$O_3 = \frac{1}{N}\left\langle \sum_i^N \left(\frac{3}{2}\cos^2\beta_i - \frac{1}{2}\right)\right\rangle,$$

where β_i is the angle between the axial vector of the N_2 molecule and the normal to the surface; $O_3 = -0.5$ at $T = 0$ K.

$$O_4 = \frac{1}{N'}\left\langle \sum_{i=1}^{N'} \cos 2\varphi_i' \right\rangle$$

and

$$O_5 = \frac{1}{N''}\left\langle \sum_{i=1}^{N''} \cos 2\varphi_i'' \right\rangle,$$

where the sums over N' and N'' are over molecules in the two sublattices of the herringbone structure, and φ is the angle between the projection of the axial vector onto the surface and the space-fixed x axis of the simulation cell. At 0 K $\varphi' = 15°$, $\varphi'' = 105°$, $N' = N'' = N/2$, and $O_4 = O_5 = \frac{\sqrt{3}}{2}$. (The glide line[3] makes an angle of 150° with the x axis.) The temperature dependence of these order parameters is shown in Fig. 4. O_3 falls slowly showing no dramatic change in out-of-plane ordering, while O_4 and O_5 fall to zero. This behavior is in agreement with an earlier mean-field calculation on hydrogen.[18] We also find "ordering" with a sixfold symmetry induced by the crystal field of the adsorbate. We note no sharp change in translational order parameters on passing through the transition, and conclude that the heat-capacity peak is due to a loss of in-plane ordering. A simulation of the distribution of $\cos\beta$ shows that the fluctuation in this quantity becomes large as temperature rises, with nearly perpendicular orientations becoming significantly probable at the higher temperatures. This point is illustrated qualitatively in the snapshots of Fig. 5. The effective vacancies created by these out-of-plane molecules may facilitate in-plane disordering. Despite a substantial spread of out-of-plane orientations above the transition, the most probable orientation is still parallel to the surface. The simulated heat of transition (given by the shift in straight-line portions of the energy plot in Fig. 3) is 67 ± 15 J mole^{-1}. Since both the temperature and the energy of the simulated transition are slightly high, it appears that the well depth of the N_2-N_2 interaction should be somewhat reduced for molecules on the surface, as one might expect for substrate-

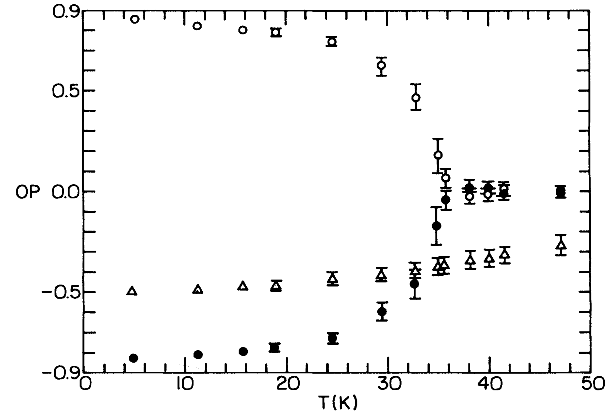

FIG. 4. The order parameters (OP) as a function of temperature; O_3 (triangles), O_4 (open circles), and O_5 (filled circles).

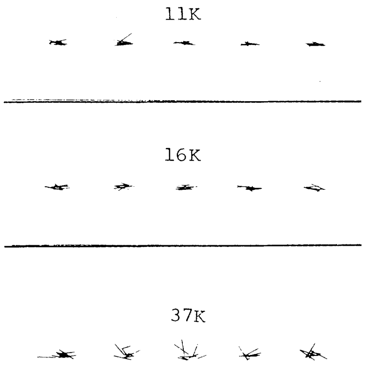

FIG. 5. Snapshots of the system of N_2 molecules at three temperatures. The lines represent the projection of the symmetry axes of the molecules on a plane perpendicular to the graphite surface. Side views are shown for five groups of eight superimposed molecules. These molecules never move far from a site center, but show significant changes in orientation as the temperature increases.

mediated interactions. (In fact, the largest omitted term is probably due to the image-charge interactions produced when a molecule with quadrupolar charge distribution is placed near a polarizable solid.) These simulations are not sufficiently sensitive to discriminate between a second and a weakly first-order transition, but are certainly not in disagreement with the experimental findings.

The model used in the computer work was designed to be as faithful a reproduction of the actual three-dimensional gas-solid system as possible. In that respect, it differs significantly from other computer studies of orientational behavior in monolayers. The combination of molecular and macroscopic information obtained from simulation and experiment on this system is emerging as a powerful tool for the study of these transitions.

We have benefited from conversation with J. G. Dash, R. D. Diehl, S. C. Fain, Jr. M. Giri, and A. J. Berlinsky. We thank them. One of us (M.H.W.C.) would like to thank O. E. Vilches for suggesting this experiment. We are grateful to M. B. Dowell of Union Carbide for supplying us the graphite substrate. Financial support for this work is provided by a NATO grant, the National Science Foundation through Grants No. DMR 8113262 and No. DMR 8206109, and the Research Corporation.

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