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Melting transition and properties of the plastic crystal and fluid phases of N_2 deposited on graphite

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A Monte Carlo method using both constant-pressure and constant-surface-density ensembles, with free surface and deformable periodic boundary conditions is employed to examine the melting and orientational behavior of partial and complete monolayers of N_2 on graphite. A simple argument concerning the ability of these systems, or lack of it, to fluctuate and expand in the plane of the substrate is sufficient to explain the drastic change in melting temperature T_M , as the adlayer surface density is increased toward monolayer completion. The calculated average orientation of the N_2 molecules is parallel to the substrate plane at all temperatures investigated, $30 \leq T \leq 95$ K, although out-of-plane orientational fluctuations increase substantially with increasing T . The nature of the melting transition of partial and complete monolayers is discussed, and it is shown that a small 256-molecule patch with free-surface boundary conditions exhibits nearly asymptotic behavior. Various order parameters and distributions are calculated to interpret system behavior.

I. INTRODUCTION

Various experiments, including low-energy electron diffraction (LEED),¹⁻⁵ neutron diffraction,^{6,7} heat capacity,⁸⁻¹⁰ vapor-pressure measurements,⁹ and calorimetric studies,^{9,11,12} have provided a fairly detailed description of N_2 adsorbed on graphite at densities $\rho \leq 1$, where the upper limit refers to a complete monolayer, in units of 0.0636 molecules/ \AA^2 . At these densities and low temperatures the N_2 molecules form a two-sublattice herringbone arrangement, and the mass centers conform to the substrate symmetry by registering into the $\sqrt{3} \times \sqrt{3}$ structure. At $T_{OD} \approx 28$ K, an orientational order-disorder transition^{2,13} occurs, above which the molecules act as weakly hindered, planar rotors with short-ranged orientation correlations that diminish with increasing temperature. The $\sqrt{3} \times \sqrt{3}$ center-of-mass structure, however, persists until melting.⁶ It has also been observed^{6,7} that registered islands are formed for fractional monolayer coverages, and interpretation of the data suggests that these clusters may contain as few as $10^2 \lesssim N \lesssim 10^3$ molecules.

The melting temperature has been observed^{1,6,8,9} to be virtually constant at $T_M \approx 47$ K, for all surface densities below and within a few percent of monolayer completion. However, T_M dramatically rises⁸ to about 85 K as the density is further increased toward monolayer coverage, with $\rho = 1$. Interpretation of neutron diffraction⁶ and

heat-capacity data^{8,9} has led to the claim that the low-temperature melting transition is first order with an entropy change of $\Delta S/Nk_B = 2.3 \pm 0.1$, where k_B is Boltzmann's constant, and the high-temperature transition at monolayer coverage is second order. It has been further argued⁹ that the low value of T_M for partial monolayers is due to the large fraction of edge to interior molecules, where the former are expected to be more weakly bound because their bonds are not saturated.

Theoretical studies of two-dimensional melting have provided considerable insight into this transition. Kostertitz, Thouless, Halperin, Nelson, and Young¹⁴ (KTHNY) have constructed a general theory which is dislocation mediated and involves two second-order transitions. The first is from the solid into a hexatic phase in which the vectors connecting molecular mass centers to their nearest neighbors exhibit sixfold azimuthal symmetry. The second is from the hexatic phase into an isotropic liquid. It has been noted, however, that substrate interactions and ever-present departures of a physical layer from perfect translational symmetry could result in first-order transitions. Another complexity is that physical layers are only "quasi" two dimensional (2D), which diminishes the predictive qualities of strictly 2D models. Frenkel and McTague¹⁵ examined a strictly 2D layer of atoms interacting via a Lennard-Jones 6-12 potential in a molecular dynamics (MD) simulation using an (N, ρ, T) ensemble, where N is the number of particles, ρ is the sur-