

Size dependence of the orientational disorder and melting transitions of finite N₂ islands deposited on graphite

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The orientational order-disorder and melting transition temperatures for quasi two-dimensional islands of N₂ molecules deposited on graphite are calculated for sizes $1 < N < 256$ molecules, using a Monte Carlo procedure with free surface boundary conditions. These transition temperatures are strong functions of N , and the values for 256 molecules are close to those measured experimentally for fractional macroscopic monolayers. Calculated results show that the two sublattice herringbone orientational structure persists up to the orientational transition temperature, above which hindered planar rotation occurs. The registered $\sqrt{3} \times \sqrt{3}$ mass center structure exists until melting, where the islands disassociate. These features are consistent with experiment. Below melting, the root mean square fluctuations of the mass centers away from their $\sqrt{3} \times \sqrt{3}$ equilibrium values are substantially larger than for bulk N₂ or for small three-dimensional rare gas clusters. The fluctuations are also substantially larger for edge molecules than for those in the center.

I. INTRODUCTION

This work was motivated by experimental evidence that N₂ molecules deposited on graphite form $\sqrt{3} \times \sqrt{3}$ registered islands¹ when the coverage is less than that for a complete monolayer, where $\rho = 1$, in units of 0.0636 mol/Å². The monolayer undergoes a transition from an ordered herringbone structure into an orientationally disordered phase at $T_{OD} \approx 27$ K, where the molecules undergo planar rotation.^{2,3} Remarkably, T_{OD} remains nearly constant at all surface densities $\rho \leq 1$. Similarly, the melting temperature is nearly constant^{1,4-6} at $T_M \approx 47$ K for $0.2 \lesssim \rho < 0.9$, above which it rapidly rises to approximately 85 K. This constancy in T_{OD} and T_M at fractional monolayer coverages strongly supports the notion of island formation at these densities. It would be difficult to imagine different behavior unless the lateral interactions with the substrate dominate the admolecule-admolecule potential. This is strongly not the case for N₂ on graphite, nor is it for any physisorbed layer on graphite. Of the various simulations for N₂ on graphite, none directly compare with this work. However, the closest connection is probably with the molecular dynamics calculations of Joshi and Tildesley⁷ and of Talbot, Tildesley, and Steele,⁸ which will be elaborated upon in Sec. IV.

As a consequence of the above mentioned experimental information and a continuing interest in the behavior of finite systems,⁹ we have calculated properties of various sized island clusters containing $1 < N < 256$ nitrogen molecules. In particular, the size dependence of the orientational and melting transition temperatures is investigated. Also, structures, root mean square mass center fluctuations, binding energies, orientational probability distributions, and various order parameters are calculated.

II. METHOD AND POTENTIAL

Thermodynamic properties of clusters composed of N₂ molecules deposited on graphite, ranging in size $1 < N < 256$, have been examined using a Monte Carlo method with free surface boundary conditions. Lattice sums were taken out to 9 Å, and averages were typically taken over 10⁵ steps after 10⁴ were neglected to minimize initial transients. All $5N$ molecular degrees of freedom are randomly sampled in each step. Essential to the analysis is that thermal fluctuations and expansion may proceed in response to changing thermodynamic conditions, not only in the (x,y) plane of the substrate but also normal to it. Initial conditions were generally constructed so that all $\sqrt{3} \times \sqrt{3}$ lattice sites were occupied out to a boundary as nearly circular as possible, and the molecules were initially oriented normal to the substrate plane. Other starting configurations were occasionally used to insure that final averages are independent of the initial state.

Several order parameters are calculated to assist in interpreting the results. These are

$$O_1 = (3N)^{-1} \sum_{i=1}^N \left\langle \sum_{s=1}^3 \cos(\mathbf{g}_s \cdot \mathbf{r}_i) \right\rangle, \quad (1)$$

$$O_2 = \frac{2}{3N(N-1)} \sum_{i < j=1}^N \left\langle \sum_{s=1}^3 \cos(\bar{\mathbf{k}}_s \cdot \mathbf{r}_{ij}) \right\rangle, \quad (2)$$

$$C(T) = \frac{4}{N(N-1)} \sum_{i < j=1}^N \left| \langle (\hat{n}_i \cdot \hat{n}_j)^2 \rangle - \frac{1}{2} \right|, \quad (3)$$

where the \mathbf{g}_s are reciprocal lattice vectors of the graphite surface, \mathbf{r}_i locates the projection of the i th molecular center onto the surface, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The brackets indicate thermal averages. The unit vector specifying the orientation of the i th molecule is \hat{n}_i . All vectors are specified with respect to a Cartesian reference frame with (x,y) axes on the substrate plane and the origin is at the center of a graphite hexagon. The z axis is normal to the plane. The \mathbf{k}_s are

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