Ferroelastic Phase Transition in Two-Dimensional Molecular Solids

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Using constant-pressure molecular-dynamics simulation we have studied the nature of ferroelastic phase transition in two-dimensional molecular monolayers. For Lennard-Jones interaction parameters appropriate for O_2 molecules, we find, in contrast to the prediction of the renormalization-group calculation of the associated Ginzburg-Landau-Wilson Hamiltonian, a first-order phase transition to the paraelastic phase precipitated by the formation of large density of localized defects of herringbonelike structure.

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The transition from an orientationally disordered (OD) plastic phase to an ordered ferroelastic phase in the three-dimensional (3D) molecular solids occurs in many physical systems and is a well-studied phenomenon.[1] However, the investigation of similar phenomena in 2D systems has been initiated only recently in adsorbed molecular monolayers on graphite substrates. Typical systems are molecular oxygen[2] and nitrogen[3] on a graphite substrate. In fact, the whole area of phase transition in molecular overlayers is of great current interest.[4,5]

One of the interesting characteristics of molecular solids is the competition between direct and indirect intermolecular interactions which lead to different types of orientational ordering. Because of enhanced fluctuations in 2D systems, the effect of this competition is pronounced and one may see multiple, and in certain situations, fluctuation-driven, first-order phase transitions.[6]

In this Letter we report the results of the first constant-pressure molecular-dynamics (MD) study of a 2D ferroelastic phase transition. The system consists of diatomic Lennard-Jones molecules whose mass centers and orientations are confined to a 2D plane. Oxygen molecules adsorbed on graphite resemble our system closely[2] since the molecular axis of O_2 is primarily confined to the graphite plane (XY plane). The corrugation of the substrate potential is known to be small and the oxygen overlayer is incommensurate with the graphite substrate.

In addition to the nature (continuous or discontinuous; one or two transitions) of the 2D ferroelastic-paraelastic phase transition, the present study also attempts to understand the nature of the topological excitations that drive such a transition. Since the system can be represented approximately by a 2D anisotropic XY Hamiltonian,[7] one expects, in addition to librons and phonons, the presence of vortex-antivortex pairs, domain walls, and vacancylike excitations to mediate the phase transition depending on their relative thermodynamic importance.

In the δ phase of the O_2/graphite system at low T, the molecules orient themselves parallel to each other and their centers of mass form a centered rectangular lattice (see Fig. 1) with $b/a=2.411$ which is equivalent to a distorted triangular lattice.[8] With an increase in T one expects the molecular orientations to disorder and the system to undergo a ferroelastic-paraelastic phase transition. In the paraelastic phase, which is an orientationally disordered (OD) 2D plastic crystal phase, the centers of mass form a triangular lattice. There are three possible ferroelastic structures which are related to each other by rotation of $2\pi/3$ and the ground state is threefold degenerate. If we describe this transition as being induced by a strain (the orientational degrees of freedom being integrated over) then the strains $(\psi_1,\psi_2)=(\epsilon_{xy},\frac{1}{2}(\epsilon_{xx}-\epsilon_{yy}))$ can be identified as the two components of the order parameter $\boldsymbol{\psi}$ and the Ginzburg-Landau-Wilson (GLW) Hamiltonian has the form

$$H_{\mathrm{GLW}}=\frac{1}{2}\sum_{i=1,2}|\nabla\psi_i|^2+\frac{1}{2}r_2\sum_i\psi_i^2+\bar{\omega}(\psi_2^3-3\psi_1^2\psi_2)+\bar{u}(\sum_i\psi_i^2)^2+\dots. \tag{1}$$

Although the mean-field theory gives a first-order transition due to the presence of the third-order term, the renormalization-group (RG) calculation predicts a continuous transition belonging to the same universality class as the three-state ferromagnetic Potts model.[9] Since the above Hamiltonian describes the actual system only approximately and since configurations with antiferroelastic ordering [herringbone (HB) structure] have relatively low free

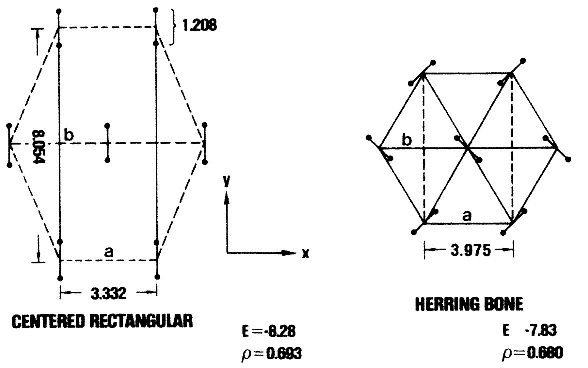

FIG. 1. Ferroelastic (centered rectangular or disordered triangular) and herringbone (triangular) structure of O_2 molecules on graphite substrate. All lengths are in angstroms.

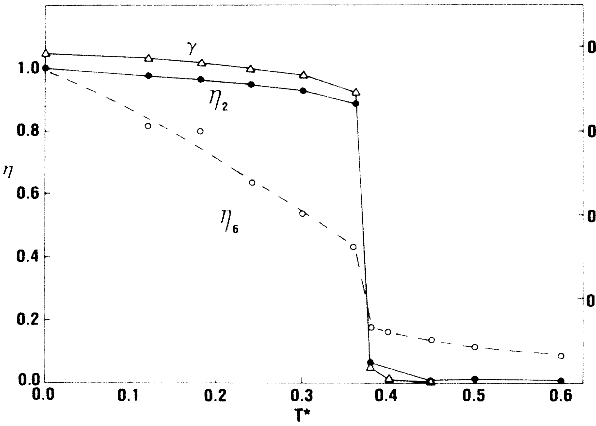

FIG. 2. Temperature (T^*) variation of orientational order parameters η_2, η_6, and strain order parameter γ (see text for definition); $T^* = 1$ corresponds to 54.21 K.

energy, one expects to find departures from the behavior predicted by the RG calculations. One of the aims of the present study is to investigate this issue.

Our system consists of 400 oxygen molecules which interact through an atom-atom Lennard-Jones potential. The parameters used are[10] intermolecular distance $2d = 1.208$ Å, $\sigma = 3.05$ Å, and $\epsilon = 54.34k_B$. MD calculations were performed for a constant-pressure (force/length) ensemble[11] and periodic boundary conditions were used. All our results are expressed in terms of reduced temperature $T^* = k_BT/\epsilon$, reduced length $L^* = L/\sigma$, and reduced energy $E^* = E/\epsilon$. The ground state[8] has a distorted triangular lattice structure with molecular axes parallel to each other in the ferroelastic phase. The HB structure in which the centers of mass form a triangular lattice has energy only slightly higher than the ground state. At finite but low T, the system has orientational long-range order (LRO) although translational LRO is absent. This is easily seen by study of the gap in the rotational excitation (libration) spectrum in the presence of a fluctuating lattice. Using spin-wave analysis we find[12] that the libration gap is reduced but it can only be zero for specific coupling constants. Thus if there is orientational LRO for a fixed lattice, it remains nonzero after the centers of mass are released to allow for the excitation of phonons.

To generate the configurations of the constant-pressure (P) ensemble in our MD calculations, we essentially follow the procedure of Parinello and Rahman[11] but generalize[12] their Lagrangean to the case of diatomic molecules. In this procedure, the change in the shape and the size of the MD cell is driven by the imbalance between the internal stress tensor $P_{\mu\nu}$ and the external pressure P, which is zero in our calculation. Furthermore, the antisymmetric component (ω) of $P_{\mu\nu}$ should be zero for a system with zero total angular momentum. In our calculation, ω and the total linear momentum **M** are monitored to test the accuracy of numerical algorithms used. We find that in 10^5 time steps (2000 ps), the standard deviations in ω and M are $O(10^{-14})$.

MD calculations show that the ferroelastic-paraelastic transition takes place in one stage at $T_1^* = 0.38$ (20.6 K), where the orientational LRO goes to zero and the lattice becomes triangular.[13] At a higher temperature $T_2^* = 0.70$ (38.0 K) there is a second transition where the OD triangular structure melts into a 2D liquid. For the first transition, we take $\eta_2 = \sum_i \cos[2(\theta_i - \bar{\theta})]$, where $N\bar{\theta} = \sum \theta_i$, as the primary and $\eta_6 = \sum_i \cos[6(\theta_i - \bar{\theta})]$ as an auxiliary order parameter. We find that the center-of-mass radial distribution function of the disordered phase shows only the triangular lattice structure. Both η_2 and η_6 have large drops at $T_1^* = 0.38$ (see Fig. 2). The lattice constants of the centered rectangular unit cell (a,b) change from (3.462, 8.055) to (4.006, 7.066) in angstrom units, the latter corresponding to a triangular lattice. An interesting outcome of it is that these values are very close to those for the HB structure. In Fig. 2 we also plot temperature variation of $\gamma = b/a\sqrt{3} - 1$ which shows a discontinuous jump.

The sharpness of the drop in the order parameters at T_1^* indicates that the transition is first order contrary to a continuous phase transition predicted from the analogy with a three-state ferromagnetic Potts model. The shape of the curve of E^*, which is the same as enthalpy for $P = 0$, vs T^* (Fig. 3) suggests a latent heat of amount $0.88k_B$. The coefficient of rotational self-diffusion D_R jumps from 4.2×10^9 to 1.4×10^{11} rad^2/sec.

Since the system is 2D, a sharp drop in the order parameter within a narrow temperature interval is not a sufficient condition for a discontinuous transition. To test whether the transition is first order, we have cooled the system slowly from the high-temperature

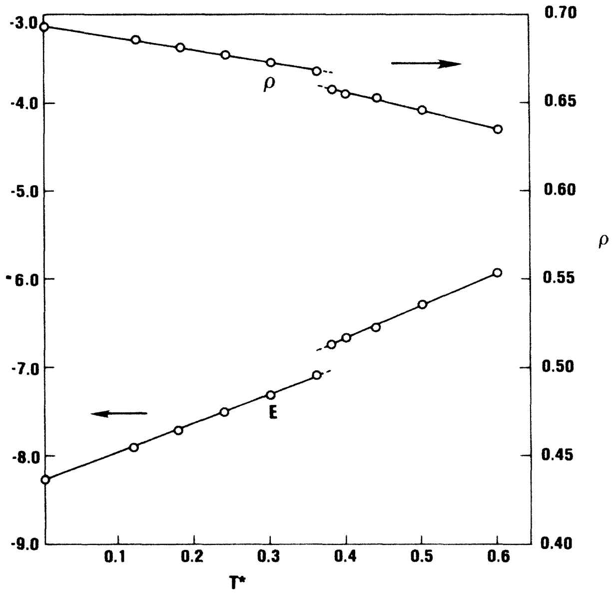

FIG. 3. Temperature (T^*) variation of energy $E^* \equiv E$ and ρ in units of ϵ and σ^{-2}, respectively.

paraelastic phase and this phase persists at $T^* = 0.36$, 0.34 for MD runs of $\sim 12\,000$ time steps indicating hysteresis effects. Furthermore, to detect the presence of a metastable state we quenched the disordered state at $T^* = 0.38$ to $T^* = 0.32 < T_c$ and monitored how the system warmed up as a function of time. In systems where a metastable state is known to exist,[14] the system temperature following the quench increases to a plateau, stays there for a long time, then rapidly increases to the value appropriate for the low-T equilibrium phase. Our quenched state preserves its disorder structure up to $\sim 15\,000$ time steps and shows no sign of approaching the equilibrium ferroelastic phase. This suggests the existence of metastable state and extremely long relaxation times.

To investigate the physical reason for the observed first-order transition, we have estimated temperature dependence of the vortex-antivortex (VA) density in the effective XY representation ($\theta_i = \frac{1}{2}\phi_i$, where θ_i and ϕ_i are molecular and effective spin angles measured from a given axis, respectively) on triangular plaquettes. Before the transition at $T^* = 0.36$, there is only one VA pair but after the transition at $T^* = 0.38$ the number jumps to 92. This phenomenon can be understood as follows.

In the low-T^* ferroelastic configuration on a triangular plaquette, if one molecule is fixed then the other two have to rotate at least $2\pi/6$ to form a vortex. However, in a herringbone configuration on the same plaquette where two of the three molecules are parallel, if the orientation of the odd one is fixed then the other two only need to rotate by a small angle in opposite directions to form a vortex. We have calculated the potential wells associated with the rotation of a single molecule for the above two situations with the assumption that all the neighboring molecules remain fixed. The potential well for the ferroelastic ordering on the centered rectangular lattice is much narrower and deeper when the lattice spacings are close to the values appropriate for the ground state but it is much shallower and wider for the HB structure on a triangular lattice. In fact, near $T^* = 0.36$, the potential has a shape close to that for the HB structure. This suggests that VA pairs are strongly suppressed at low T^* and as T^* is raised the potential well broadens and becomes shallower not only as a result of orientational fluctuations but also as a result of an increase in the lattice spacing caused by anharmonic phonons. At a critical temperature T_1^* the core energy of VA pairs becomes sufficiently small so that these pairs appear in a large number causing a first-order transition.[15]

The configuration of a VA pair on the triangular lattice resembles the HB configuration. To reduce the excitation energy in the region where the local density of VA pairs is high, it is favorable to change the lattice spacings to those characteristic of a triangular lattice. The net result is that a continuous three-state Potts transition is preempted by an orientational order-disorder transition to a triangular lattice structure caused by a sudden increase in the density of VA pairs which are localized defects with HB-like structure.

The above physical mechanism for the first-order transition is somewhat similar to that proposed by Van Himbergen[16] for an isotropic XY model with an interaction of the form

$$V(\theta_i - \theta_j) = V(\theta) = 2J[1 - (\cos^2\theta/2)^q], \quad J > 0. \qquad (2)$$

For $q^2 > 10$, the Kosterlitz-Thouless transition is found to be first order and for $q^2 < 10$ the potential is rather soft and the transition has the usual continuous form.

In summary, the transition from an orientationally ordered distorted triangular to an ordered triangular structure for O_2 on graphite is found to be first order. This is caused by the creation of a large number of local defects of HB structure. Since our simulations were performed for a 400 particle system, we would like to see if the nature of the transition and the proposed mechanism persists for larger systems. If the transition is indeed first order, we do not expect to see drastic changes in going to the larger system since the finite-size effects are expected to be small. We are planning to extend the present study to a 900-particle system. Although the detailed nature of this transition has not been carefully explored experimentally, our results should encourage further experimental work in this direction.

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