Fluctuation-Induced First-Order Phase Transition in an Anisotropic Planar Model of N_2 on Graphite

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Monte Carlo simulations are used to show that the orientational ordering transition of planar quadrupoles on a triangular lattice is first order. The orientational ground state is a herringbone structure, and the transition lies in the universality class of a ($n=3$, $d=2$) Heisenberg model with face-oriented cubic anisotropy. The Monte Carlo results are related to recent low-energy electron-diffraction studies of N_2 on graphite. Domain-wall motion and the applicability of this model to herringbone phases of liquid crystals are also discussed.

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In this Letter we report the results of Monte Carlo studies of a model which is thought to describe the orientational order-disorder transition to the herringbone phase of monolayers of N_2 on the surface of graphite. The order parameter for the herringbone phase has three real components and is predicted to lie in the universality class of the ($n=3$)-component Heisenberg model with "face-type" cubic anisotropy.[1] Mean-field theory predicts a second-order transition for our model,[1] while renormalization-group (RG) arguments suggest that fluctuations drive the transition first order.[2,3] The results reported here show clear evidence of a first-order transition in the presence of large fluctuations. Monte Carlo studies are particularly useful for this problem because the RG arguments either are based on ϵ expansions[2] which are of doubtful validity in two dimensions or, in the case of the only two-dimensional (2D) calculation,[3] they refer to a model for which the transition is tricritical in mean-field theory.[4]

At temperatures below 47 K and coverages less than $\frac{1}{3}$ the number of hexagonal sites, N_2 molecules on the surface of graphite form a registered $(\sqrt{3}\times\sqrt{3})30°$ commensurate structure.[5] As the system is cooled below 30 K a further transition occurs which was first detected by specific-heat measurements.[6] Later neutron-scattering studies[7] showed that this transition involves the formation of a superlattice structure with a doubling of the lattice constant in at least one of the crystal directions. Quite recently, low-energy electron-diffraction (LEED) measurements[8] have led to the identification of the low-temperature phase as a 2×1 herringbone structure of oriented molecules as shown schematically in Fig. 1.

The structure of this orientationally ordered state is determined by the anisotropic interactions of the N_2 molecules with the substrate and with each other. The N_2-substrate interaction is expected to orient the internuclear axes in the plane of the graphite,[9] so that N_2 is effectively a planar rotor, rather like the spins in an *XY* model. However, the intermolecular interaction is not *XY* like. Instead it is known from studies of solid N_2 to be well described by the electric quadrupole-quadrupole (EQQ) interaction.[10] Thus we can model N_2 on graphite by classical planar quadrupoles on a triangular lattice. That the ground state for this model is the herringbone structure has been demonstrated by Monte Carlo calculations for classical planar quadrupoles[11]

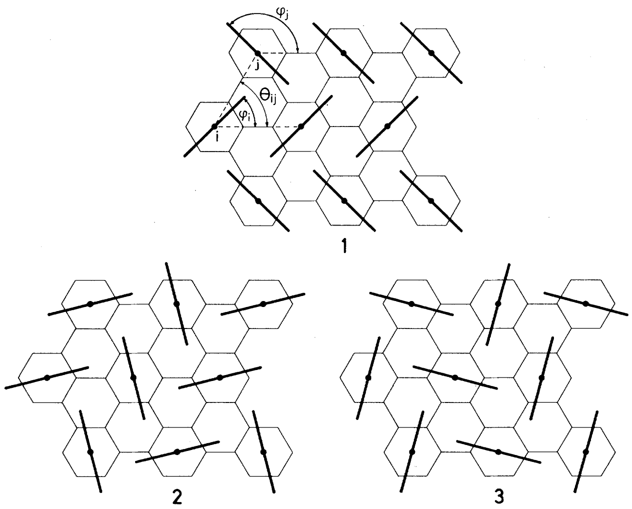

FIG. 1. Schematic representation of the three degenerate ground states of the anisotropic planar model on a triangular lattice. The heavy bars represent the long molecular axes of diatomic molecules adsorbed in a commensurate $(\sqrt{3}\times\sqrt{3})30°$ overlayer on a hexagonal substrate of graphite. The angles φ_i and θ_{ij} enter the Hamiltonian in Eq. (1).

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and by energy minimization calculations for N_2 on graphite, based on the EQQ interaction and atom-atom potentials.[12]

As shown in Fig. 1, there are three equivalent orientations for the herringbone structure, and each of these can sit on the lattice in two ways since the molecules can be translated along the direction of alternation. Thus there are six equivalent ground states, and the order parameter has three degenerate components

$$\Psi_\alpha = N^{-1}\left\langle \sum_{i=1}^{N} \sin(2\varphi_i - 2\theta_\alpha)\exp(i\vec{Q}\cdot\vec{r}_i)\right\rangle, \qquad \alpha = 1, 2, 3, \quad (1)$$

which can take on values between -1 and 1. According to Fig. 1, the wave vectors, $\vec{Q}_\alpha$, which describe the three states are $\vec{Q}_1 = (2\pi/a)(0, 2/\sqrt{3})$, $\vec{Q}_2 = (2\pi/a)(-1, 1/\sqrt{3})$, and $\vec{Q}_3 = (2\pi/a)(-1, -1/\sqrt{3})$, where a is the lattice constant, φ_i describes the orientation of molecule i, and $\theta_1 = 0$, $\theta_2 = \pi/3$, and $\theta_3 = 2\pi/3$.

The EQQ interaction for planar quadrupoles on a two-dimensional lattice may be written as

$$H = J\sum_{(i,j)} \cos(2\varphi_i - 2\varphi_j) + K\sum_{(i,j)} \cos(2\varphi_i + 2\varphi_j - 4\theta_{ij}), \quad (2)$$

where θ_{ij} is the direction of the line joining the centers of molecules i and j, and the sum is over $3N$ nearest-neighbor pairs (i, j). For pure EQQ interactions, the ratio $K/J = 35/3$, and the second term is completely dominant. It is this term which stabilizes the herringbone structure. The model Hamiltonian which we have studied is obtained by setting $J = 0$ in Eq. (2).

Our numerical study is based on a conventional Monte Carlo importance sampling technique designed to calculate the thermodynamic equilibrium properties of the model, Eq. (2) with $J = 0$, for a lattice with N sites and toroidal periodic boundary conditions. We calculate the internal energy per site, $E(T) = \langle H\rangle/N$, and the three components of the order parameter $\Psi_\alpha(T)$, together with coarse-grained averages and distribution functions.[13] These distribution functions, in simulation of other lattice models with many-component order parameters,[13,14] have proved extremely helpful in determining the equilibrium thermodynamic averages, especially near phase transitions where the order may shift between the various components. To investigate the effects of the finite size of the system, we have carried out the calculations for a series of N, $N = 400$, 1600, 6400, and 10 000. Our results are based on statistics ranging from 500 to 5000 Monte Carlo steps per site.

In Fig. 2 the results are given for the order parameter, $\Psi(T)$. For $k_BT/K \lesssim 0.775 \equiv k_BT_c/K$ the system is ordered in one of the components, Ψ_α, which we will call *the* order parameter Ψ. The two remaining components are equal, but finite because of finite-size effects. For $T \gtrsim T_c$, the finite-size order also resides in one component in the immediate vicinity of T_c, but not far above T_c it is equally distributed among the three components. When the system develops order during a temperature sweep through T_c, the dominant ordering component is equally likely to be any one of the three. The most important information contained in Fig. 2 concerns the finite-size effects of Ψ. For $T < T_c$, all four lattice sizes produce identical order parameters. By contrast, for $T > T_c$ a pronounced rounding occurs which decreases with increasing values of N. For $N = 400$ and 1600, Ψ varies continuously through T_c, but for $N = 6400$ there is a slight indication of a discontinuity at T_c, although the jump is somewhat smeared because of a rapid shifting of the order between the three components. However, for $N = 10\,000$ a clear discontinuity has developed.

In Fig. 3, which gives an enlargement of the region around T_c, this discontinuity is more clearly exposed, and the results for increasing

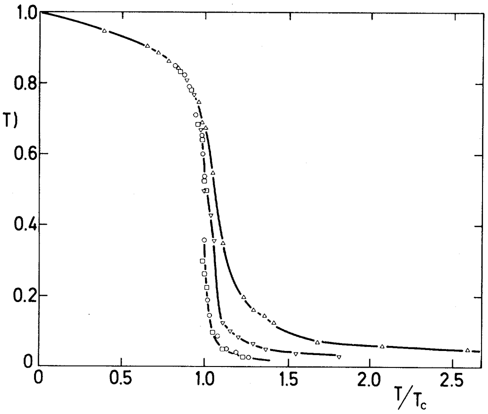

FIG. 2. Temperature dependence of the order parameter Ψ defined in Eq. (1) for the anisotropic planar model of Eq. (2) with $J = 0$. The results are obtained from Monte Carlo calculations on systems with N particles. Triangles, $N = 400$; inverse triangles, $N = 1600$; circles, $N = 6400$; and squares, $N = 10\,000$. The temperature is scaled with the "transition" temperature, $T_c = 0.775K/k_B$.

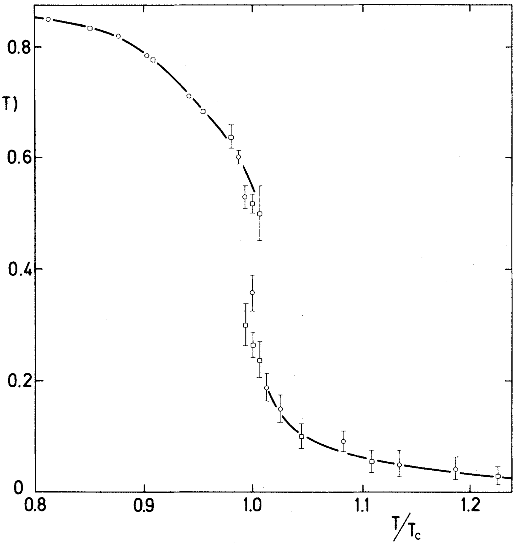

FIG. 3. Temperature dependence of the order parameter Ψ for the anisotropic planar model in the transition region. The temperature is scaled with the transition temperature, T_c. The results are derived from Monte Carlo calculations on systems with $N = 6400$ (circles) and $N = 10\,000$ (squares) particles.

and decreasing series of temperature exhibit a pronounced hysteresis of width $\Delta T/T_c = 1.5\%$. A small hysteresis loop is also observed in the internal energy of the $N = 10\,000$ system, corresponding to a discontinuity of about 1.3% in the energy at T_c. This effect is completely smeared out for the smaller lattices. Figure 3 also shows that the size of the jump in Ψ is larger for the larger system, as expected for a first-order transition. This should be contrasted with the results of Landau and Swendsen[15] for a system on the second-order side of a tricritical point where the gap in the distribution function was observed to decrease with increasing system size. We conclude that the transition for our model is first order in the presence of large fluctuations and that, in light of the mean-field-theory prediction of a continuous transition,[1] the first-order behavior is fluctuation induced.

Next we discuss the implications of our work for experimental systems which order in the herringbone structure. The most direct application is to the LEED data for N_2 on graphite.[8] A striking feature of these data is the persistence of the order parameter, i.e., the intensity of the 2×1 superlattice diffraction peaks, above the apparent T_c, which resembles the finite-size effects observed in our Monte Carlo (MC) data. It is useful to compare the relevant length scales in the two cases. The graphite surface may have regions which are coherent over thousands of angstroms.[16] On the other hand the resolution of the LEED experiment was such that domain sizes as small as 100 Å would not have significantly broadened the peaks. The linear dimensions of the systems studied by MC ranged up to about 400 Å. Thus it is possible, as suggested by Diehl, Toney, and Fain,[8] that scattering by small domains of N_2 molecules, which would naturally exhibit finite-size rounding, accounts for the apparent nonzero order parameter above T_c.

We wish to remark on certain nonequilibrium features of the anisotropic planar model, which are of interest in connection with recent theories of domain-wall formation and domain growth in systems with degenerate order parameters.[17] When changing the temperature in the vicinity of T_c, or by quenching the system through T_c, we often observe that transients develop in those components where the dominant order does not reside. The creation of these transients costs almost no internal energy. The transients are nonequilibrium properties which, however, turn out to have extremely long lifetimes. Similar transients (or glasslike metastable states) were observed in Monte Carlo simulations of the $n = 6$ model of Ref. 13 and the three-dimensional antiferromagnetic four-state Potts model.[18] We consider these transients as indications of formation of a time-dependent domain structure with the three types of ordering—a picture which is verified by inspection of snapshots of microscopic configurations. The dynamics of the domain walls are found to be extremely slow. This accords with the theoretical calculations by Safran,[17] which show that the domain sizes equilibrate as a logarithmic function of time for $n \geq d+1$. By performing only very small steps in temperature when T_c is approached, we expect to have minimized the effects of this slowly relaxing mechanism on the equilibrium properties of the model.

Finally we note that the Hamiltonian of Eq. (2) may also be used to describe herringbone ordering in some of the smectic phases of liquid crystals. A particularly interesting case is the "stacked-hexatic" phase recently reported by Pindak *et al.*[19] The generalization required is to treat the bond angles θ_{ij} as dynamical variables and to add a term to H of the form $\cos(6\theta_{ij} - 6\theta_{ji})$ which will induce long-range (although algebraically decaying) correlations in the bond angle variables.[20]

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