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Electric quadrupole-quadrupole interaction in two dimensions: Fluctuation effects with zero substrate potential

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Computer experiments are used to study the phase diagram of an array of interacting classical quadrupoles on a plane triangular lattice. Careful analysis of variously defined order parameters corroborates the mean-field prediction of multiple phase transitions, but defect formation prevents observation of the highly anisotropic intermediate phase on a macroscopic scale.

The electric quadrupole-quadrupole (EQQ) interaction as a model for the orientational ordering of molecular crystals has recently received considerable attention.[1-12] The experimentally accessible systems consist for the most part of two- and three-dimensional arrays of triangular planes [pt (plane triangular), hcp, and fcc lattices] and in some cases (pt and hcp) mean-field analysis[8,13] predicts complicated phase diagrams resulting from the interaction of multiple order parameters. The two-dimensional case has been particularly well studied,[5,8,11] and consideration of the limiting case of extreme anisotropy, or substrate potential, in this model suggests that fluctuation effects may be important in describing the ordering when the system consists effectively of planar rotators.[11]

We discuss here the opposite limit of zero substrate field in the case of the pt lattice, and show that for three-dimensional rotators the long-range order predicted by mean-field theory appears to be unstable against domain formation. In particular, the anisotropy expected in the intermediate phase regime is destroyed, if observation is carried out on a macroscopic scale. This fact may be relevant to recent experimental work[6] on the so-called "quadrupolar glass" in three dimensions, where the "glass" transition, if it occurs, fails to manifest itself as an observable change in symmetry from that of the paraorientational phase.

The definition of order parameter in the present system may be made in a number of ways. Most commonly, one uses the Fourier transform of the microscopically defined quadrupole moments evaluated at special symmetry points of the Brillouin zone. Given the present five-component order parameter and hexagonal lattice symmetry one is able to provide a description of the five distinct two- and four-sublattice states as points in a 20-parameter space. Because we are dealing with computer simulations, however, it is both more convenient and more informative to use an order parameter which is a suitably defined overlap with certain reference states and which gives a direct indication of the symmetry of the ordering. This "tangent-space" analysis permits significant reduction in the number of degrees of freedom which must be considered. The formal aspects of this analysis will be given in another paper. Here we simply describe our procedure. We have computed both Fourier transform and tangent-space order parameters, with their associated susceptibilities, for the present system, and we compare the information obtained using the two techniques.

We have used a standard single-site Monte Carlo (MC) rejection procedure using the EQQ Hamiltonian expressed in Cartesian coordinates

$$H=\frac{\dot{\gamma}}{2}\sum_{\substack{ij\\ \alpha\alpha'\\ \sigma\sigma'}}K^{\alpha\alpha'\sigma\sigma'}(\vec{r}_i-\vec{r}_j)D^{\alpha\alpha'}(\hat{\omega}_i)D^{\sigma\sigma'}(\hat{\omega}_j)\ . \qquad (1)$$

$D^{\alpha\alpha'}(\hat{\omega}_i)$ is the classical second-rank quadrupole tensor[14] computed from the molecular orientation $\hat{\omega}_i$ at site i. K is taken to be the usual fourth-rank tensor which produces an interaction invariant under simultaneous rotation of spatial and molecular axes.[14] Sample sizes varied between 64 and approximately

2000 lattice sites. All of the data displayed here are for samples of 552 sites and the data shown are averages evaluated between 4000 and 9000 MC steps per spin. Nonperiodic boundary conditions were used to avoid prejudicing the sublattice structure. For the particular runs shown, the samples were prepared in the known ground state at $T=0$ and warmed slowly. Other runs on samples of similar size following a slow cooling process from infinite temperature produced domains with the correct symmetry, but unlike earlier work on smaller samples,[11] always showed evidence of defects. Energy curves at these run times do not display hysteresis and do not distinguish between fully ordered and domain structures for temperatures greater than $\gamma/2$. The usual comparison of the temperature derivative of the energy and the fluctuation-determined specified heat indicated consistency with thermodynamic equilibrium.

The Fourier transform order parameters were calculated directly using the classical spherical harmonic definition

$$Q_m(\vec{k}) = \frac{1}{N}\left(\frac{4\pi}{5}\right)^{1/2} \sum_i \exp(i\vec{k}\cdot\vec{r}_i)\langle Y_{2m}(\hat{\omega}_i)\rangle \quad . \tag{2}$$

The tangent-space definition of order parameter is given in terms of a site-by-site scalar product defined between two arbitrary states α and ϕ:

$$(\alpha,\phi) = \frac{4\pi}{5}\sum_{im}[Y^*_{2m}(\hat{\omega}_i)]_\alpha [Y_{2m}(\hat{\omega}_i)]_\phi \ . \tag{3}$$

We first take reference configurations $[Y_{2m}(\hat{\omega}_i)]_\alpha$ in the state α to correspond to the three distinct "herringbone" structures and two distinct "pinwheels" of Ref. 8. Values of $\hat{\omega}_j$ are used which correspond to the lowest-energy state of given symmetry. These reference states are not, however, orthogonal under our inner product definition. We have therefore constructed five states σ as linear combinations of the α's. They have the following properties: (1) $(\sigma_i,\sigma_j)=\delta_{ij}$; (2) σ_4 and σ_5 are symmetric and antisymmetric combinations of the pinwheels, therefore σ_4 is orthogonal to all of the anisotropic herringbone states, while σ_5 is not. (3) Each of σ_1, σ_2, σ_3 has a large overlap with one of the anisotropic states, and small overlaps with all the other α states. The tangent-space order parameters are now defined

$$\Psi_s = \langle(\sigma_s,\phi)\rangle \ , \tag{4}$$

where the ϕ are arrays generated by the MC procedure. [Triangular brackets in Eqs. (2) and (4) indicate averages over MC configurations.] Thus nonzero values of Ψ_s for $s=1,2,3$ indicate anisotropy of the system. Ψ_4 indicates a state invariant under C_6 (pinwheel only) and Ψ_5 contains components of all five α states.

Specification of a certain set of $Q_m(\vec{k})$ specifies the projection of an orientational configuration on a portion of $\vec{k}$ space. In the cases of interest, $\vec{k}$ is restricted to $k=0$ and the three vectors specifying the centers of the Brillouin-zone (BZ) edges. The Ψ_s give the projection of the configuration on a *subspace* of the subspace specified by the $Q_m(\vec{k})$. (An explicit transformation is possible.) In Figs. 1 and 2 we display the nonzero order parameters defined through Eqs. (2)–(4) for a series of warming runs. The notation used is such that for $i=1,2,3$, nonzero values of Ψ_i correspond to nonzero values $Q_2(\vec{k}_i)$ evaluated at the single point $\vec{k}_i$ on the BZ edge. Finite values of Ψ_4 and Ψ_5 correspond to finite values at all three $\vec{k}_i$ vectors. In general a significant difference in the magnitude of the $Q_m(\vec{k}_i)$ computed for different $\vec{k}_i$ indicates a deviation from C_6 symmetry. All of the $Q_m(\vec{k})$ tend to zero in the paraorientational state.

The $Q_m(\vec{k})$ displayed in Fig. 1 show evidence of a low-temperature phase possessing long-range order and C_6 symmetry. Judging from the $Q_0(\vec{k})$ curves, a sharp transition occurs at about $T=2.0\gamma$. Above this temperature there occurs a region of noise, with a gradual decay to a rotationally invariant state at $T\simeq 2.4\gamma$. Finite values of $Q_0(\vec{0})$, indicating some form of ordering, persist to $T\simeq 3.0\gamma$. A similarly noisy curve of the $Q_2(\vec{k}_i)$ vs T suggests anomalies at $T\simeq 2.0\gamma$ and $T=2.8\gamma$.

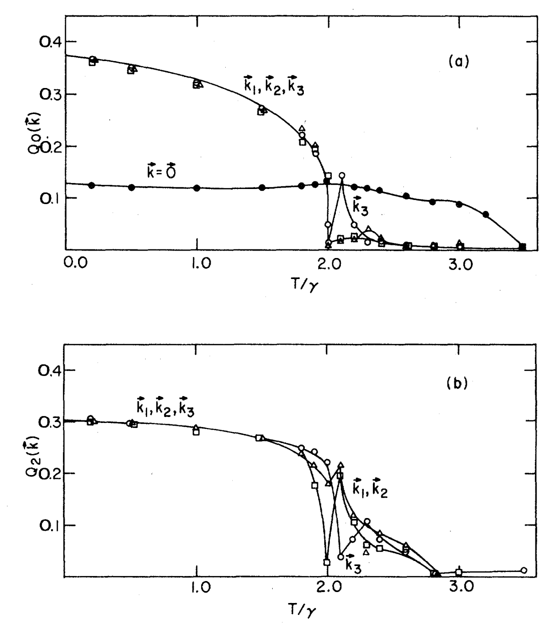

FIG. 1. Standard Fourier transform order parameters, as defined by Eq. (2) plotted as a function of temperature. $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$ are vectors to the center of the three Brillouin-zone edges and γ is the EQQ coupling constant. The curves indicate a rotationally symmetric (C_6) macroscopic state for temperatures below about 2.8γ. The lines are drawn merely as a guide to the eye.

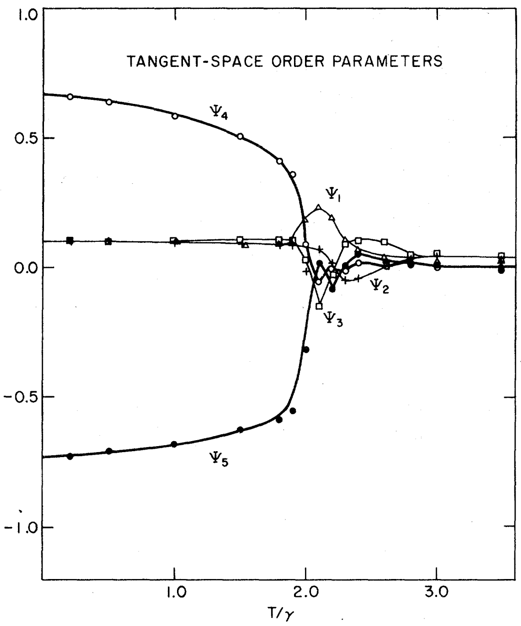

FIG. 2. Tangent-space order parameters, as defined by Eqs. (3) and (4). The curves indicate a sharp transition between the rotationally invariant low-temperature state and a coexistence regime of the three anisotropic (C_2') states at intermediate temperatures as evidenced by the oscillatory behavior of their order parameters. Transition to the paraorientational phase appears to be gradual.

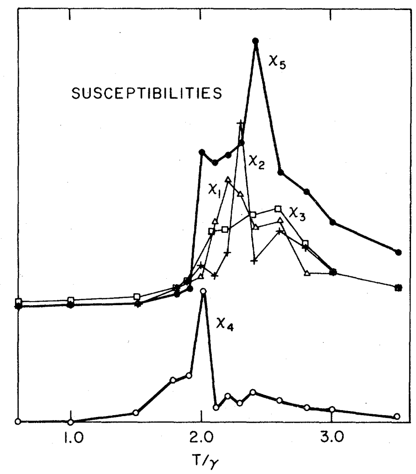

FIG. 3. Susceptibilities associated with the tangent-space order parameters, as determined from fluctuations. χ_4 describes only rotationally symmetric states; χ_1, χ_2, χ_3 describe only anisotropic states; χ_5 mixes the various symmetry components.

The tangent-space order parameters (Fig. 2) provide a somewhat less ambiguous picture of the symmetry change which occurs. Here both Ψ_4 and Ψ_5 (which contain C_6 symmetry) show a smooth but sharp transition at a temperature between 2.0γ and 2.1γ. (Energy curves show no clear sign of a first-order transition, although an inflection point occurs near this temperature.) Above the transition all three of the anisotropic modes show oscillatory behavior and approach the paraorientational limit at $T \simeq 3.0\gamma$. The roughly equal magnitudes would seem to indicate a persistence of C_6 symmetry on a macroscopic scale well above disappearance of the long-range ordered C_6-symmetric state.

For each of the $Q_m(\vec{k})$ and Ψ_s order parameters, a fluctuation-determined susceptibility may be defined, e.g., associated with Ψ_s:

$$\chi_s \equiv \frac{\langle |(\sigma_s, \phi)|^2 \rangle - |\Psi_s|^2}{T} , \tag{5}$$

Our statistically determined values are displayed in Fig. 3. Recall that Ψ_4 is orthogonal in the present formulation to all of the anisotropic states. Its susceptibility shows a sharp peak at $T \simeq 2.0\gamma$, where both Ψ_4 and Ψ_5 effectively vanish. Ψ_5, which contains all five rotational symmetric and anisotropic states has an associated susceptibility which rises sharply with χ_4 but attains a maximum at $T \simeq 2.4\gamma$. This double transition is in qualitative agreement with mean-field results,[15] but it apparently does not correspond to a change in the macroscopic symmetry of the system. It is not, furthermore, clearly observable in χ_1, χ_1, χ_3, which display only a broad noisy region. Nor is it manifested in the susceptibilities associated with the $Q_m(\vec{k})$ (not shown) whose behavior is noisy over the entire temperature range between 2.0γ and 3.0γ.

From all of the above we conclude that, while the mean-field prediction of multiple phase transitions is qualitatively correct the intermediate temperature regime consists of an admixture of the nonrotationally invariant phases rather than of a single long-range ordered phase. In addition, we conclude from visual examination of the MC-generated arrays, that isolated pinwheels are a common localized defect appearing in domains of the anisotropic phase. The creation of a single pinwheel plaquette is apparently a low-energy event, and the existence of such defects accounts for the appearance of well-defined anomalies in χ_5, despite their absence in the anisotropic susceptibilities χ_1, χ_1, χ_3.

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[14]See, e.g., Landau and Lifschitz, *The Classical Theory of Fields* (Addison-Wesley, Reading, Mass., 1962), p. 111ff.
[15]Our value of γ differs from the Γ of Ref. 8 by a factor of approximately 1.9. Thus conversion of temperature scale indicates a suppression of both transition temperatures by a factor of about 3 below their mean-field values.