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Long-range orientational order in two-dimensional liquid crystals

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We have shown, using Monte Carlo stimulations, that long-range order exists in the nematic liquid-crystal phase in two dimensions when realistic interparticle potentials are used.

Virtually no two-dimensional system with continuous degrees of freedom has long-range order (LRO) at finite temperatures. This result follows from harmonic or continuum theories.[1,2] It has been demonstrated rigorously using Bogoliubov inequalities for superconductors, superfluids, magnets, translation order in crystals,[3] and certain classes of liquid crystals.[4] In this paper we present evidence for the existence of LRO in two-dimensional nematic liquid crystals when there is a "realistic" interaction between the molecules.

If the pair potential between liquid-crystal molecules can be written as

$$V(r,\theta)=\sum_{a} f_a(r)g_a(\theta)\ , \tag{1}$$

where r is the distance between the centers of mass of the molecules and θ is their relative orientation, then no LRO exists in two dimensions at a finite temperature.[4] However, realistic potentials do not have this form. An example of a realistic potential[5] for interacting ellipsoidal particles is

$$V(\hat{u}_1,\hat{u}_2,\hat{r})=4\epsilon(\hat{u}_1,\hat{u}_2)\left[\left(\frac{\sigma(\hat{u}_1,\hat{u}_2,\hat{r})}{r}\right)^{12}-\left(\frac{\sigma(\hat{u}_1,\hat{u}_2,\hat{r})}{r}\right)^{6}\right]\ , \tag{2}$$

where

$$\epsilon(\hat{u}_1,\hat{u}_2)=\epsilon_0[1-\chi^2(\hat{u}_1\cdot\hat{u}_2)^2]^{-1/2}$$

and

$$\sigma(\hat{u}_1,\hat{u}_2,\hat{r})=\sigma_0\left[1-\frac{\chi}{2}\left(\frac{(\hat{r}\cdot\hat{u}_1+\hat{r}\cdot\hat{u}_2)^2}{1+\chi(\hat{u}_1\cdot\hat{u}_2)}+\frac{(\hat{r}\cdot\hat{u}_1-\hat{r}\cdot\hat{u}_2)^2}{1-\chi(\hat{u}_1\cdot\hat{u}_2)}\right)\right]^{-1/2}\ .$$

Here $\chi=(a^2-1)/(a^2+1)$, where a is the anisotropy of the ellipse and $\hat{u}_i$ is a unit vector in the direction of the long axis of the ith molecule. We will call this potential nonseparable (NS) because it cannot be written in the form of Eq. (1). If $\hat{u}_1$, $\hat{u}_2$, and $\hat{r}$ are parallel then $\sigma=\sigma_0[(1+\chi)/(1-\chi)]^{1/2}$, but if $\hat{u}_1$ is parallel to $\hat{u}_2$ and both are perpendicular to $\hat{r}$ then $\sigma=\sigma_0$ and the repulsive interaction is much weaker.

We have simulated this model using Monte Carlo techniques. The potential was cut off at 3 in the y direction and $3a$ in the x direction. This means an imaginary rectangle of size ($6a\times 6$) surrounds the ith molecule and only molecules whose centers are within this rectangle interact with the ith molecule. Although this procedure introduces an anisotropic potential, its tendency is to disorder the angular degrees of freedom by leaving out interactions of molecules which would tend to orient the ith molecule. Thus, LRO in this system clearly implies LRO in the system where all interactions are included. This procedure was used because it reduces the computer time by an order of magnitude. The rectangular box enclosing the molecules was $\sqrt{3}/2L$ by aL in size, where $L\times L=N$ is the total number of molecules. Periodic boundary conditions were used and the starting configuration was usually one of perfect order.

For comparison we also simulated a system with a separable potential:

$$V(r)=4\epsilon\left[[1-\alpha\cos(\theta_i-\theta_j)]\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{3}$$

$$\epsilon>0,\ \alpha>0\ .$$

We call this model separable (S) since it is in the form of Eq. (1). This potential favors alignment of neighboring molecules. The cutoff here was 3σ and the box size was $\sqrt{3}/2L$ by L.

The Monte Carlo step consisted of a move in r space and a simultaneous move in θ. Both systems were run at a reduced temperature such that spatial order was absent. This is discussed in more detail below. The reduced temperature was $T^* = 1.6$ for the separable system and $T^* = 2.0$ for the nonseparable.

To determine whether LRO exists the following quantities were computed. (a) $\langle r^2 \rangle$ is the mean-square deviation of the particles from their original lattice sites (corrected so that the center of mass is fixed). (b) $\langle \theta^2 \rangle$ is the mean-square fluctuation of the angular orientation of the particles ($-\pi \leq \theta \leq \pi$ for the S model and $-\pi/2 \leq \theta \leq \pi/2$ for the NS model). The angle θ_i for the ith molecule was measured relative to the instantaneous net direction of the molecules, i.e., such that $\sum \theta_i = 0$. The quantity $\langle \theta^2 \rangle$ denotes the average $(1/N) \sum_i \langle \theta_i^2 \rangle$, where $\langle \theta_i^2 \rangle$ is the average of the square of θ_i over all configurations. (c) $g(x)$ and $g(y)$ are the pair distribution functions, where $g(x) \equiv g(x,y{:}y \leq 1)$ and x and y are the molecular separations in the x and y directions, respectively. (d) $c(x)$, $c(y)$, and $c(r)$ are the angular correlation functions. Here $c(r) = \langle \cos[\theta(0) - \theta(r)] \rangle$ for the S model and $c(r) = \langle \cos\{2[\theta(0) - \theta(r)]\} \rangle$ for the NS model. The factor of 2 does not appear in the S model because this model was originally meant to simulate a magnetic system. In fact potentials of this form are appropriate for classical magnetic systems and not for liquid crystals. In a liquid crystal we expect $\langle r^2 \rangle$ to increase during a Monte Carlo run, showing that the system has no translational order. In addition we expect the correlation function $g(x)$ to be liquidlike. If, however, there is no long-range angular order then harmonic theory predicts that $\langle \theta^2 \rangle \sim \ln N$ for large N and $c(r) \sim r^{-\eta}$ where η is a small exponent which depends on the temperature.[2] With LRO then $\langle \theta^2 \rangle \sim \text{const} + f(N)$, where $f(N) \to 0$ as $N \to \infty$ and $c(r) \to \text{const}$ as $r \to \infty$.

We simulated both systems in a region where $\langle r^2 \rangle$ increased steadily during the simulation. In Figs. 1 and 2 we show $g(x)$ for each model. The steady decay of the oscillations in g shows clearly that there is no translational order. We adjusted the reduced temperature for each model to obtain this result. To determine the presence or absence of angular order it is important that the system have no translational order. We confirmed these data by making plots of the Monte Carlo trajectories of the particles. These also showed translational disorder. Similar results were found for $g(y)$. The distances in Figs. 1 and 2 are in units of $L/100$.

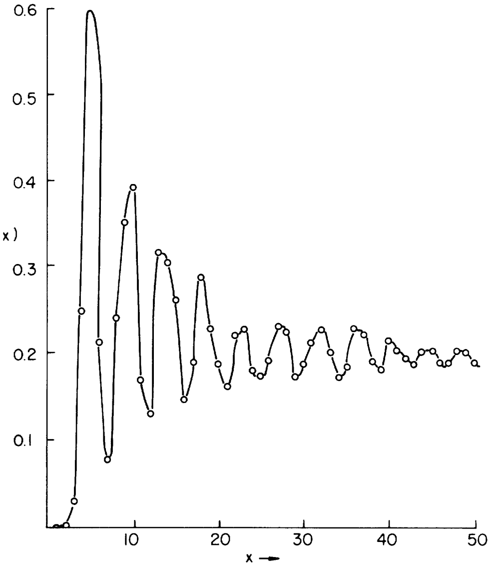

FIG. 1. $g(x)$ vs x. For the S model, $N = 256$, $T^* = k_B T/\epsilon = 1.6$, $\rho\sigma^2 = 0.856$, $\alpha = 0.8$, and x is the molecular separation in units of $L/100$. Number of passes is 16000.

Figure 3 shows a plot of $\langle \theta^2 \rangle$ vs $\ln N$ for the S model which clearly shows that this model has no long-range order. The slope of the line is consistent with the predictions of harmonic theory.[2] To make this prediction we used an elastic constant, for the angular displacements, of $4\epsilon\alpha$. Our confidence in these data is in part based on our experience[6] with the magnetic X-Y model where we were able to generate similar data for the magnetic order. We should also mention that Young and Alder[7] have shown that the positional disorder in the two-dimensional hard disc system increased without limit as $\ln N$. The $\langle \theta^2 \rangle$ data for the NS model after long Monte Carlo runs have error bars that are too large to allow us to determine the dependence on N. Because this model has a

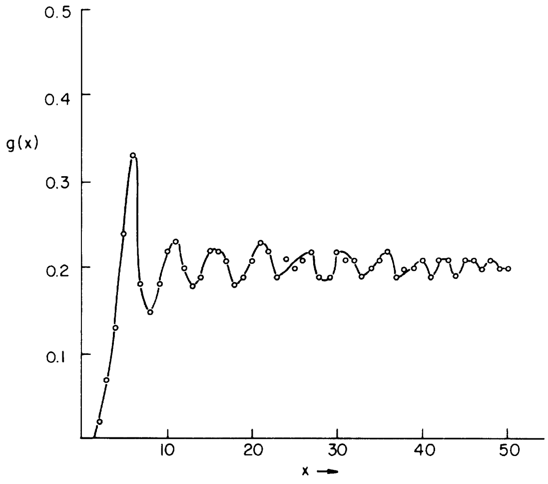

FIG. 2. $g(x)$ vs x. For the NS model, $T^* = 2.0$, $N = 256$, $a = 4$, $\rho\sigma_0^2 = 0.206$, and x is the molecular separation in units of $L/100$. Number of passes is 7200.

much more complicated potential the computation times were much longer than for the separable model. In addition the strong coupling of the angular and translational degrees of freedom appear to increase the Monte Carlo relaxation times. These differences prevented us from acquiring data of comparable accuracy.

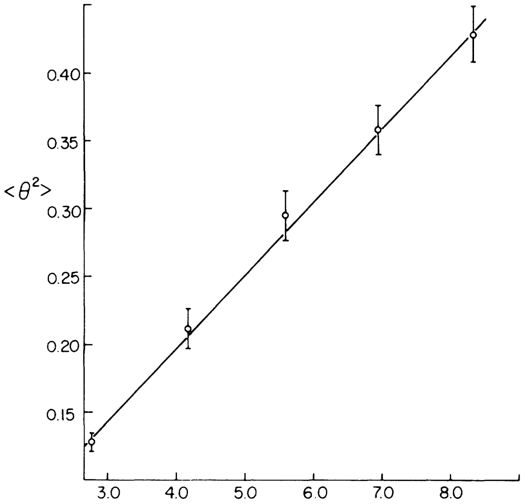

FIG. 3. $\langle\theta^2\rangle$ vs $\ln N$ for the S model. $T^* = k_BT/\epsilon = 1.6$, $\rho\sigma^2 = 0.856$, $\alpha = 0.80$. Number of passes averaged over as follows: $N = 16$, 153 600 passes; $N = 64$, 64 000 passes; $N = 256$, 16 000 passes; $N = 1024$, 4000 passes; $N = 4096$, 4800 passes. About 30% of the passes were used in each case for equilibration.

In Fig. 4 we show a plot of the angular correlation function for the S model. In this model there is a monotonic decrease in the correlation function $c(x)$ consistent with a power-law decay. Harmonic theory[2] based on small deviations from perfect angular order predicts that the correlation function will have a power-law decay $c(x) \sim x^{-\eta}$. This type of decay is of the same form as that predicted in other two-dimensional systems where strong fluctuations destroy "long-range order."[3] If the data are fitted to a power law then the exponent η is consistent with the harmonic predictions.[2] A virtually identical curve is found for $c(y)$. However, in the NS model, Fig. 5, $c(r)$ rapidly reaches a constant value. This is strong evidence that LRO exists in this model. Indeed, unless there is a very slow decay of the asymptotic value this result shows we have long-range order. We note that it is easier to show the asymptotic form of $c(x)$ than it is to show that $\langle\theta^2\rangle$ remains finite as N increases. To find the asymptotic form for $c(x)$ we only have to simulate one system with a large enough number of molecules. To determine the behavior of $\langle\theta^2\rangle$ we have to simulate several systems with different N values—including at least one with a value for N considerably larger than that used for $c(x)$. Moreover, $\langle\theta^2\rangle$ and $\langle r^2\rangle$ take a much longer time to reach equilibrium than do the correlation functions. This explains why we can find strong evidence for LRO in $c(x)$ but cannot detect it in $\langle\theta^2\rangle$. (Note that since the box is longer in the x than the y direction for most values of r, $r \approx x$.)

We now discuss the reasons why we have found LRO in the NS system and the phase transition from the ordered liquid-crystal phase to the disordered liquid. First the continuum elastic theory, which is nearly always qualitatively correct,[1,3,4] may not work in this two-dimensional (2D) system because it does not predict LRO.[2] In 3D the molecules can roll around each other using three degrees of freedom so that the orientational degrees of freedom are only loosely coupled to the translational degrees of freedom. This is not true in 2D, which necessitates a continuum theory where this coupling is strong. Such a theory has not been constructed. Nelson and Pelcovitz[8] have shown that, if the two Frank constants for splay and bend are not equal, nevertheless they are renormalized at very long wavelengths where they become equal. Thus, LRO may appear to exist over many interparticle spacings, but not on longer-length scales. This idea was extended by the work of

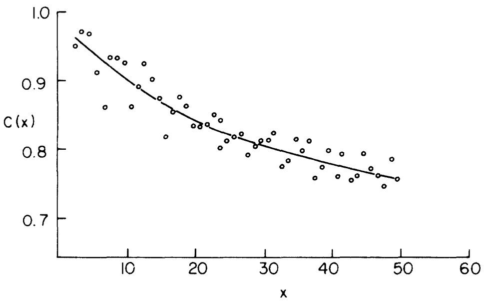

FIG. 4. $c(x)$ vs x for S model. The parameters are the same as in Fig. 1.

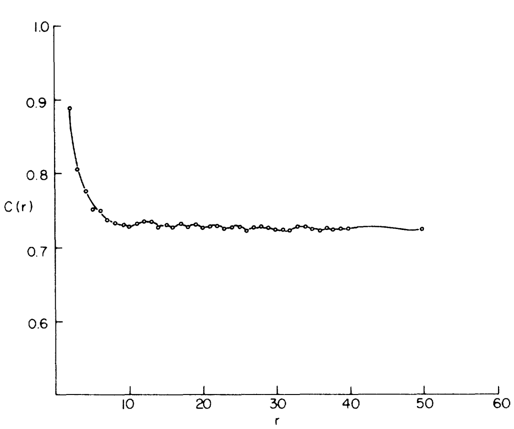

FIG. 5. $c(r)$ vs r for NS model. The parameters are the same as in Fig. 2.

Ostlund and Halperin[9] who suggested a crossover from the two behaviors as a function of temperature and system size.

If LRO exists, then the Kosterlitz-Thouless[10] theory of 2D phase transitions cannot be adequate for our NS model since that theory assumes that the Hamiltonian can be broken down into a nonsingular continuum part and a disclination part. The strong coupling of the translational and orientational degrees of freedom prevents such a simple decomposition. One might speculate that the transition to angular disorder will be first order.

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