# Monte Carlo Study of the Nematic–to–Smectic-$A$ Transition

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A Monte Carlo simulation of a lattice model of the nematic–to–smectic-$A$ transition in three dimensions shows a continuous phase transition with the specific-heat exponent $\alpha \simeq 0$. The order-parameter correlation functions show anisotropic critical behavior in the nematic phase, whereas the behavior of the correlation functions in the superconducting gauge strongly indicates an isotropic critical point. Several features observed in experiments are qualitatively reproduced in the simulation.

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Despite a great deal of theoretical and experimental effort, the nature of the nematic–to–smectic-$A$ ($N$-$A$) transition in liquid crystals remains incompletely understood. Theoretical studies[1] of this phase transition have been based on a phenomenological model proposed by de Gennes,[2] or on a dislocation-loop model[3,4] that can be shown[5] to be equivalent to the de Gennes model. There is as yet no theoretical consensus about the critical behavior of the de Gennes model. The most recent analysis[3] indicates that this model should exhibit an inverted $XY$ transition,[6] with the order-parameter correlation functions exhibiting a crossover[1,7,8] from isotropic to anisotropic critical behavior as the transition is approached from the nematic side. Alternative theoretical predictions include a weakly first-order transition,[9] and anisotropic scaling[3] with the correlation-length exponents parallel and perpendicular to the direction of smectic ordering having the ratio 2:1. The predictions of none of these theories are in complete agreement with all the available experimental data.[10–13] The situation is made more confusing by the fact that the experimentally observed critical behavior differs from one system to another.[14,15]

For a complete understanding of the situation, it is necessary to determine (a) whether the de Gennes model provides an adequate description of the $N$-$A$ transition, and (b) which of the various theoretical predictions about the nature of the phase transition in the de Gennes model is correct. I have addressed these questions in a numerical simulation of the thermodynamics of a lattice version of the de Gennes model. The simulation qualitatively reproduces several features observed experimentally, and thus provides strong support to the validity of the de Gennes model. The results also provide strong evidence indicating that the phase transition in this model belongs in the inverted-$XY$ universality class. The observed behavior of the order-parameter correlation functions is in agreement with the gauge-transformation analysis of Lubensky and coworkers.[1,7,8]

The model studied here is a straightforward generalization[5] of the de Gennes model. It is defined by the Hamiltonian

$$H=\sum_i\Big\{B_0(1-\cos\Delta_z\theta_i)+D_0\sum_{\mu=x,y}[1-\cos(\Delta_\mu\theta_i-A_{i\mu})]+\tfrac{1}{2}K_1^0\Big(\sum_{\mu=x,y}\Delta'_\mu A_{i\mu}\Big)^2$$
$$+\tfrac{1}{2}K_2^0(\Delta_x A_{iy}-\Delta_y A_{ix})^2+\tfrac{1}{2}K_3^0\sum_{\mu=x,y}(\Delta_z A_{i\mu})^2\Big\}. \qquad (1)$$

Here $\theta_i$ is an angular (phase) variable ($-\pi\le\theta_i\le\pi$) at site $i$ of a three-dimensional simple cubic lattice, and $A_{i\mu}$, $\mu=x,y$, are real variables defined on the directed links between adjacent sites. $\Delta_\mu$ and $\Delta'_\mu$ represent right and left lattice derivatives, respectively. The smectic order is described by the phase variable $\theta$ and $A_x$,$A_y$ represent director fluctuations with $A_z=0$. The length scale is chosen such that the wave number associated with the smectic order is unity. $B_0$ and $D_0$ represent "bare" stiffness constants, and $K_1^0$, $K_2^0$, and $K_3^0$ are the "bare" Frank elastic constants. If the splay elastic constant, $K_1^0$, is 0, then this model reduces, via a gauge transformation, to an anisotropic version of the lattice superconductor model studied in Ref. 6. In the present work, I chose the values $B_0=D_0=5.0$, $K_2^0=K_3^0=1.0$ in order to remain close in parameter space to the simulation of Ref. 6. The role of the splay term was studied by simulation of the thermodynamics for two values (0.5 and 5.0) of $K_1^0$. I did not find any significant difference between the critical properties for the two different values of $K_1^0$.

The standard Metropolis method was used in the Monte Carlo simulation. Typically, 1000–2000 Monte

 

Carlo steps per variable were used for equilibration, and 5000–10 000 steps per variable were used for the calculation of averages. I did not find any indication of a first-order transition. All measured thermodynamic quantities (the internal energy, the specific heat, and the order-parameter susceptibility) showed behavior characteristic of a continuous phase transition. The results for the specific heat, $C$, for samples with linear dimension $L=6$, 8, and 10 with periodic boundary conditions are shown in Fig. 1. The data points shown were obtained from a numerical differentiation of the internal energy with respect to temperature. The specific heat exponent, $\alpha$, of the three-dimensional $XY$ model is known to be close to 0. For a system with $\alpha=0$, the specific heat in the critical region is expected[16] to have the form

$$C=-A\ln|t|-\tfrac{1}{2}DAt/|t|+B, \tag{2}$$

where $t=(T-T_c)/T_c$ and $D\simeq 4$ for the $XY$ model. A plot of $C$ vs $\ln(|T-T^*|/T^*)$, where $T^*$ ($=6.15$) is the temperature at the specific-heat peak for $L=10$ and $K_1^0=0.5$, is shown in the inset of Fig. 1. The data points are clearly consistent with Eq. (2). The size dependence of the height of the specific-heat peak is also consistent with $\alpha\simeq 0$. However, the asymmetry parameter $D$ appears to have a rather small value ($\simeq 0.25$) and its sign is the same as that expected for an $XY$ transition. Thus, the inversion of the temperature axis predicted in recent theories[4,6] does not show up in the simulation. The reason for this discrepancy is not clear. It may be related to correction-to-scaling effects arising from the $K_1^0$ term. It is interesting to note that a similar behavior of the specific heat near the $N$-$A$ transition has been observed in experiments[10,17] on systems for which $\alpha\simeq 0$.

The most intriguing feature of the $N$-$A$ transition is the anisotropic critical behavior of the order-parameter correlation lengths measured in x-ray scattering experiments.[10,15] In the simulation, I calculated the order-parameter correlation function, $g(\mathbf{r})$, defined by

$$g(\mathbf{r})=N^{-1}\textstyle\sum_i\langle\cos(\theta_{i+\mathbf{r}}-\theta_i)\rangle, \tag{3}$$

where $\langle\ldots\rangle$ represents a thermal average and $N=L^3$ is the total number of sites. In order to determine the correlation lengths for $T>T_c$, I followed a procedure similar to the one used in the analysis of x-ray scattering data. This procedure consists of fitting $g(\mathbf{k})$, the discrete Fourier transform of $g(\mathbf{r})$, by a Lorentzian of the form

$$g(\mathbf{k})=\frac{T\chi}{1+(\xi_{\parallel}^x)^2|\alpha_z(\mathbf{k})|^2+(\xi_{\perp}^x)^2(|\alpha_x(\mathbf{k})|^2+|\alpha_y(\mathbf{k})|^2)}, \tag{4}$$

where $\chi$ is the order-parameter susceptibility, $\xi_{\parallel}^x$ and $\xi_{\perp}^x$ are the so-called x-ray correlation lengths, and

$$\alpha_\mu(\mathbf{k})=1-\exp(ik_\mu),\quad \mu=x,y,z, \tag{5}$$

with $k_\mu=2\pi n_\mu/L$, $n_\mu=-L/2+1,\ldots,L/2$. For $\mathbf{k}$ in the $\parallel$ ($z$) direction, the form (4) provides a good fit to the data. However, for $\mathbf{k}$ in the $\perp$ ($x$-$y$) plane, plots of $[g(\mathbf{k})]^{-1}$ vs $|\alpha_x|^2+|\alpha_y|^2$ show considerable upward curvature, and it is necessary to include an additional term, $\delta(|\alpha_x|^2+|\alpha_y|^2)^2$, in the denominator of the right-hand side of Eq. (4) in order to obtain adequate fits. Typical results are shown in Fig. 2. The value of the parameter $\delta$ increases as $T$ approaches $T_c$. Very similar features have been observed in x-ray scattering experiments.[10,15] The inset of Fig. 2 shows the temperature dependence of the calculated value of the ratio $\xi_{\parallel}^x/\xi_{\perp}^x$ for $K_1^0=0.5$ and $L=10$. The results clearly exhibit an anisotropic growth of the two correlation lengths. Large numerical uncertainties in the values of $\chi$ made an accurate determination of the absolute values of $\xi_{\parallel}^x$ and $\xi_{\perp}^x$ impossible.[18] Because of this reason, and the smallness of sample size, I was not able to obtain any reliable estimate of the values of the

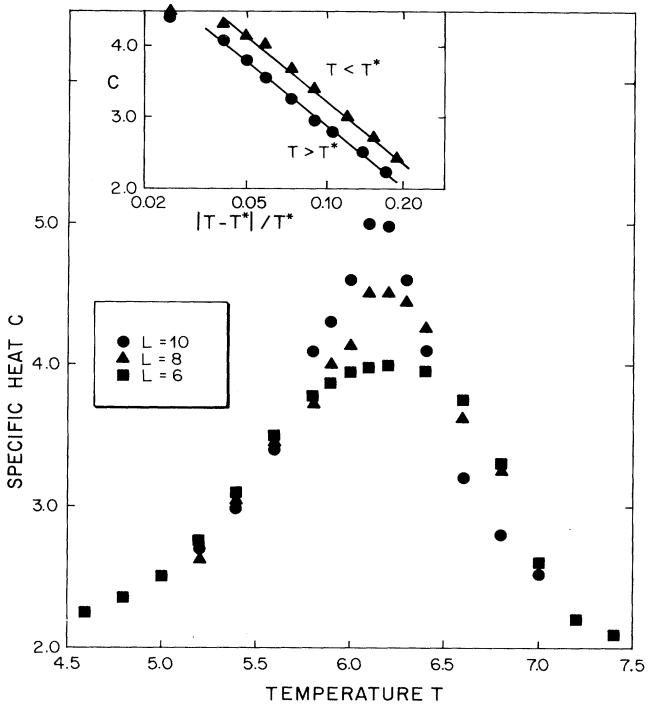


FIG. 1. Variation of the specific heat $C$ with temperature $T$ for $K_1^0=0.5$. The inset shows semilog plots of $C$ for the $L=10$ sample vs $|T-T^*|/T^*$, where $T^*$ ($=6.15$) is the temperature at the specific-heat peak.

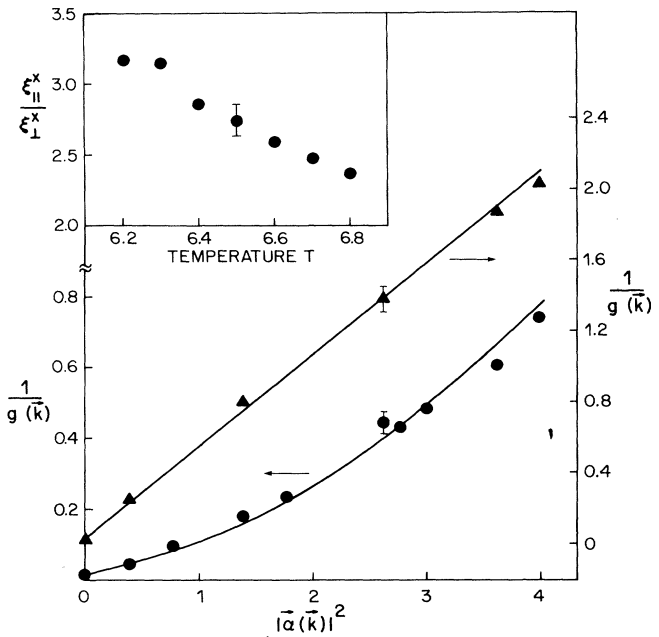


FIG. 2. Plots of the inverse of the Fourier transform of the order-parameter correlation function ($K_1^0=0.5$, $L=10$, $T=6.2$) vs $|\alpha(\mathbf{k})|^2$ (see text) for $\mathbf{k}$ in the $\|(z)$ direction (triangles, right-hand scale), and in the $\perp(x$-$y)$ plane (circles, left-hand scale). The solid lines are best fits with the form of Eq. (4), with an $\alpha^4$ term (see text) included in the fit for the perpendicular direction. The inset shows the temperature dependence of the ratio of the two x-ray correlation lengths for $K_1^0=0.5$ and $L=10$.

exponents associated with the growth of $\xi_{\parallel}^x$ and $\xi_{\perp}^x$. Thus, a quantitative comparison with experimental results is not possible at this stage.

Several authors[1,4,7,8] have pointed out the fact that the anisotropic behavior of the x-ray correlation lengths does not necessarily imply that the $N$-$A$ critical point is described by anisotropic scaling. The true nature of the critical point is expected to manifest itself in the behavior of gauge-invariant quantities (such as the stiffness constants $B$ and $D$, and the Frank elastic constants $K_2$ and $K_3$) and the correlation function in the "superconducting gauge," defined by the transformation[1,7]

$$\theta_i = \phi_i - L_i, \tag{6a}$$

$$A_{i\mu} = B_{i\mu} - \Delta_\mu L_i, \quad \mu = x,y,z, \tag{6b}$$

where the variables $L_i$ are determined from the condition

$$\sum_\mu \Delta_\mu B_{i\mu} = 0. \tag{7}$$

In the simulation, I calculated the correlation function $g_s(\mathbf{r})$, in this gauge, defined by

$$g_s(\mathbf{r}) = N^{-1}\sum_i \langle \cos(\phi_{i+\mathbf{r}} - \phi_i)\rangle. \tag{8}$$

Since all experiments are restricted to the physical gauge ($A_{iz}=0$), a numerical simulation is the only way of "experimentally" studying the properties of $g_s$. The large amount of computation involved in the determination of the values of $\phi_i$ and $\mathbf{B}_i$ corresponding to a particular configuration of the $\theta$ and $\mathbf{A}$ variables restricted the calculation of $g_s$ to samples with $L \leq 8$. In this calculation, I came across a problem arising from the smallness of the system size. It is evident from Eq. (6) that $B_z(k_z=0)=0$, whereas there is no such restriction on $B_x(\mathbf{k})$ and $B_y(\mathbf{k})$. This asymmetry between the parallel and perpendicular directions is unimportant in the thermodynamic limit; but in small samples, it makes $g_s$ anisotropic even when $K_1^0=0$.[19] In order to eliminate this spurious finite-size effect, I carried out a set of simulations in which the constraints $A_x(k_x=0)=0$ and $A_y(k_y=0)=0$ were imposed on the allowed values of the variables $A_{i\mu}$. These constraints remove the asymmetry mentioned above, and restore the isotropy of $g_s(\mathbf{r})$ in the $K_1^0=0$ limit. In the $L=8$ and $L=10$ samples studied, the imposition of these constraints produces a (10–15)% increase in the transition temperature, but does not affect the critical behavior in any significant way. I found that the Fourier transform, $g_s(\mathbf{k})$, of $g_s(\mathbf{r})$ calculated in this restricted ensemble can be fitted quite well by the Lorentzian form of Eq. (4). Results for $K_1^0=0.5$ and $T=7.4$ are shown in Fig. 3. Values of the correlation lengths, $\xi_{\parallel}^s$ and $\xi_{\perp}^s$, associated with $g_s(\mathbf{r})$ were extracted from such fits. The inset of Fig. 3 shows the observed temperature dependence of the ratio $\xi_{\parallel}^s/\xi_{\perp}^s$ as the transition is approached from the nematic side. Both $\xi_{\parallel}^s$ and $\xi_{\perp}^s$ change by factors of $\simeq 3$ over the temperature range shown, whereas their ratio remains constant to within 5%. From this observation, I conclude that this phase transition is described by an isotropic critical point. This conclusion in turn implies[1] that the phase transition in the de Gennes model belongs in the inverted-$XY$ universality class. I have also found that the gauge dependence of the correlation function [i.e., the relation between $g_s(\mathbf{r})$ and $g(\mathbf{r})$] is well described by the "decoupling approximation" proposed by Lubensky *et al.*[7,8] for temperatures close to $T_c$. These results imply that in the $N$-$A$ transition, all gauge-invariant quantities should exhibit inverted $XY$ behavior, and the x-ray correlation lengths should show a crossover from isotropic to anisotropic behavior as the transition is approached from the nematic side. The fact that some of the experimental results do not agree with these predictions remains somewhat puzzling. Crossover effects arising from the presence of a nearby tricritical point[14,15] may account for some of the discrepancies. A detailed calculation of these crossover effects would be very useful in clarifying the situation.

This study was initiated during a visit to the Physics

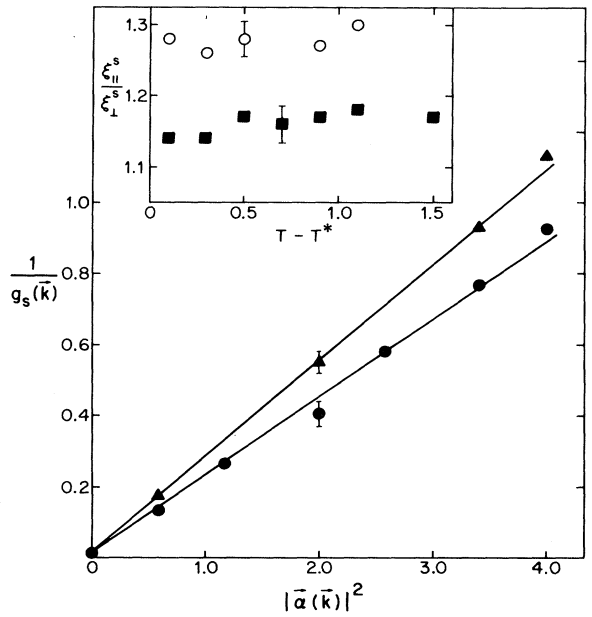


FIG. 3. The inverse of the Fourier transform of the correlation function in the superconducting gauge ($K_1^0 = 0.5$, $L = 8$, $T = 7.4$) vs $|\alpha(\mathbf{k})|^2$ for the parallel (triangles) and perpendicular (circles) directions. The inset shows the temperature dependence of the ratio of the two superconducting-gauge correlation lengths for $K_1^0 = 0.5$ (squares) and $K_1^0 = 5.0$ (open circles). $T^*$, the temperature at the specific-heat peak, is 7.1 and 7.9 for $K_1^0 = 0.5$ and 5.0, respectively.

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[18]The values of $(\xi_{\parallel}^{x})^2/\chi$ and $(\xi_{\perp}^{x})^2/\chi$, and, therefore, the value of the ratio $\xi_{\parallel}^{x}/\xi_{\perp}^{x}$, could be determined with reasonable accuracy from the fits described in the text.

[19]For $B_0 = D_0$, $K_2^0 = K_3^0$, and $K_1^0 = 0$, the transformation defined in Eq. (6) reduces the Hamiltonian (1) to an isotropic lattice version of the Ginzburg-Landau model of superconductivity. Thus, in the thermodynamic limit where the restriction $B_z(k_z = 0) = 0$ is irrelevant, the correlation function $g_s(\mathbf{r})$ should be isotropic if $K_1^0 = 0$.