Fluctuations near the nematic–smectic-C phase transition*

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We study the properties of a Ginzburg-Landau-Wilson Hamiltonian in which an order parameter is associated with each wave vector which points from the origin to one of two rings in reciprocal space. The existence of the order parameter breaks the two-dimensional rotational symmetry about the axis of the rings. The Hamiltonian may be interpreted as a simple model of the nematic–smectic-C phase transition of a liquid crystal, if we identify the order parameter with the density of the liquid crystal and the axis with the average direction of the director field. There are no cubic terms present in the Hamiltonian, and the phase transition predicted by mean-field theory is second order. Fluctuations are taken into account by means of a method due to Brasovsky, and the phase transition is found to be of first order.

I. MODEL AND SUMMARY

In this paper we apply the method of Brasovsky[1] to a simple model of the nematic–smectic-C transition of a liquid crystal. Brasovsky's original model was concerned with weakly anisotropic antiferromagnets and certain liquid crystals. An essential feature of Brasovsky's model was that an infinite number of degenerate order parameters, each associated with a finite nonzero wave vector, occurred in it. Brasovsky used perturbation theory to argue that a *first-order* transition would occur in his model, as a result of fluctuations, even though *no* cubic term was present in his model.

In this paper we introduce a simple ring model of the nematic-smectic-C phase transition. This model reflects the two-dimensional rotational invariance of the nematic state and favors the existence of a density wave in the smectic-C phase. As in Brasovsky's model there are an infinite number of order parameters, each associated with a finite wave vector. We briefly indicate below how Brasovsky's method may be applied to our model and show how the same result is obtained.

A. The model

Our model is based on the discussion of de Gennes[2,3] and is defined by a Ginzburg-Landau-Wilson[4-6] Hamiltonian given by

$$\frac{H}{kT}=\int\frac{d^3q}{(2\pi)^3}\tfrac{1}{2}[\tau+(q_\perp-q_{\perp 0})^2+(|q_z|-q_{z0})^2]\times|\tilde\psi(\vec{\mathbf{q}})|^2+\frac{\lambda}{4!}\int[d^3q_1\,d^3q_2\,d^3q_3/(2\pi)^9]\tilde\psi(\vec{\mathbf{q}}_1)\times\tilde\psi(\vec{\mathbf{q}}_2)\tilde\psi(\vec{\mathbf{q}}_3)\tilde\psi(-\vec{\mathbf{q}}_1-\vec{\mathbf{q}}_2-\vec{\mathbf{q}}_3)\,. \tag{1}$$

In Eq. (1), $\tilde\psi$ is the Fourier transform of a real scalar field $\psi(r)$, $q_\perp=(q_x^2+q_y^2)^{1/2}$, τ is proportional to the temperature minus the mean-field critical temperature, $q_{\perp 0}$ and q_{z0} are constants, and λ is a small parameter which describes the nonlinear coupling among fluctuations in the order parameter ψ.

The Hamiltonian of (1) favors the existence of order parameters associated with the two rings defined by

$$q_\perp=q_{\perp 0},\quad q_z=\pm q_{z0} \tag{2}$$

in reciprocal space.

The order parameter $\psi(\vec{\mathbf{r}})$ is to be identified with the density minus the average density of the liquid crystal. The preferred axis is defined by the average direction of the director field $\hat n$, which we take to be the z axis. Thus, our model favors the existence of a periodic density wave in the smectic-C state which makes an angle α ($\tan\alpha=q_{\perp 0}/q_{z0}$) with the director.

As noted by de Gennes,[3] no cubic terms in ψ should occur in the Hamiltonian. Also, note that our model does not allow for fluctuations in the director field.[3] Halperin, Lubensky, and Ma[7] have included the director field $\hat n$ as well as a scalar order parameter field ψ in their treatment of the smectic-A liquid crystal. They found that inclusion of the director field and the Frank free-energy terms had quite a drastic effect, changing the order of the phase transition from second to first. It is interesting to note that for the above model of a nematic–smectic-C phase transition, we already find a first-order phase transition without inclusion of the director field.

Note that our model respects the two-dimensional rotational symmetry of the high-temperature nematic state, as it is invariant with respect to rotations about the z axis. Thus, there are an infinite number of degenerate order parameters in

our problem, namely, those $\tilde{\psi}(\vec{q})$ for which $\vec{q}$ points to one of the rings defined by (2).

B. Summary of results

In Sec. II we discuss the essential similarities and differences between the phase space of our model and that of Brasovsky's. It turns out that Brasovsky's method may be applied step by step to our model. In two Appendices we give the formulae important to the argument, each of which corresponds to a formula or diagram in Brasovsky's paper. We briefly summarize and discuss the results of the calculation outlined there.

We introduced a Ginzburg-Landau-Wilson Hamiltonian which was invariant under rotations about the z axis in real space. The existence of a scalar order parameter which varies as $\cos\vec{q}_1 \cdot \vec{r}$, where $\vec{q}_1$ has a definite component perpendicular to the z axis, then spontaneously breaks the two-dimensional rotational symmetry displayed by our model.

There is no term in our Hamiltonian cubic in the order parameter so that mean-field theory predicts a second-order phase transition.[8] We find that terms not included in mean-field theory cause the transition to be of first order, at least when λ, the measure of the strength of the nonlinear coupling of fluctuations, is small.

We find that the discontinuity in the entropy at the transition is a number of order unity independent of the coupling constant.

The critical temperature is shifted downward from its value as given by mean-field theory by an amount proportional to $\lambda \ln(\Lambda^2/\lambda)$ as given in Eq. (A9).

We also find pretransitional fluctuations in our model. All Fourier components of the density whose wave vectors point to one of the rings discussed earlier exhibit fluctuations above the transition temperature.

Qualitatively, our results are not in disagreement with experiments on HBA,[9] in which the entropy of transition is given and pretransition phenomena found.

II. CONNECTION WITH BRASOVSKY'S WORK

We discussed above a model which contains, as an essential feature, degenerate order parameters associated with an infinite number of continuously distributed finite nonzero wave vectors.

As we mentioned in Sec. I, Brasovsky[1] has solved for the thermodynamic properties of a model in which the same essential feature occurs. Although our model differs in detail and interpretation from that of Brasovsky, we may use the same arguments and arrive at the same result, a first-order transition, for our present model of the nematic–smectic-C phase transition.

In a number of the phase transitions which have been discussed[4] to date, the phase space for important fluctuations in the order parameter is described, in reciprocal space, by a sphere centered about the origin.

In Brasovsky's original model there are an infinite number of order parameters $\tilde{\psi}(\vec{q})$; each $\tilde{\psi}(\vec{q})$ being associated with a wave vector $\vec{q}$ such that $|\vec{q}| = q_0$. This condition defines the surface of a sphere of radius q_0 in reciprocal space. The important phase space for fluctuations in Brasovsky's model is, then, a spherical shell, of inner radius $q_0 - \Lambda$ and, outer radius $q_0 + \Lambda$, and centered at the origin.

In lowest order of perturbation theory this phase space is effectively one dimensional. This is so because order parameters having wave vectors with the same magnitude are degenerate in energy; thus only the component of the vector normal to the surface of the sphere changes the energy. This leads to large fluctuations. (A one-dimensional phase space is well known to give rise to large fluctuations.[10])

Brasovsky showed that, due to this peculiar phase space of his model, in low-order perturbation theory the continuous phase transition predicted by mean-field theory was removed by fluctuations not included in the mean-field theory. In the temperature range in which perturbation theory was valid, Brasovsky found, by comparing the free energies of the two states, that there was a discontinuous first-order phase transition from the disordered to the ordered state. This first-order transition was found to take place at a temperature slightly lower than the mean-field transition temperature.

In the model of the present paper, degenerate order parameters $\tilde{\psi}(\vec{q})$ are associated with wave vectors which extend from the origin of reciprocal space to one of the two rings defined by (2). The important volume for fluctuations is then the two toroids of major radius $q_{\perp 0}$ and minor radius Λ, where Λ is a cutoff, whose major axes coincide with the axes of the two rings given by (2).

In the case of the present paper, the phase space is effectively two dimensional in low-order perturbation theory. The energy changes only when the wave vector moves off the minor axis of one of the toroids; either in the z direction or in the direction of the vector $q_x\hat{e}_x + q_y\hat{e}_y$. Again, a two-dimensional phase space is known to give large fluctuations.[10]

A calculation exactly analogous to that of Brasovsky may be carried out in the context of the model of this paper. Although the detailed functional forms of the terms occurring in perturbation theory differ from those in Brasovsky's

case, the argument in the present case can be carried through, step by step, in precisely the same manner. The conclusion that fluctuations give rise to a first-order phase transition is also true in this case.

Since the method and steps in the calculation have been discussed by Brasovsky (and also by Hohenberg and the author[11] in a different context), we do not repeat the details here, but in two appendices just give the most important formulas which correspond to those of Brasovsky.

In Appendix A we give those formulas which are needed in the calculation of the difference in free energy between the ordered and disordered states. Each formula corresponds to a formula of Brasovsky or Ref. 11.

In Appendix B we discuss higher-order diagrams and justify neglecting them. Again each term and restrictive condition finds a correspondence in Brasovsky or Ref. 11. Following Brasovsky, we also estimate here the size of the finite volume[12,13] to which our material must be restricted in order that the calculation be valid.

Note added in proof. M. Gabay and T. Garel, private communication, have recently used the same model and method to obtain similar results.

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APPENDIX A

The Hartree contribution to the self-energy [diagram (1b) of Ref. 11] is

$$\Sigma_H(r_H) \equiv -\lambda \int \frac{d^3q}{(2\pi)^3} G_H(r_H, \vec{q}) , \tag{A1}$$

where

$$G_H(r_H, \vec{q}) = [r_H + (|q_z| - q_{z0})^2 + (q_\perp - q_{\perp 0})^2]^{-1} . \tag{A2}$$

As explained in Sec. II, the integration is over two toroids of major radius $q_{\perp 0}$ and minor radius Λ. We find that the singular contribution to Σ_H is

$$\Sigma_H(r_H) \approx -\alpha\lambda \ln(\Lambda^2/r_H) , \tag{A3}$$

where $\alpha = q_{\perp 0}/2\pi$.

Here Λ plays the role of an upper momentum cutoff, measured from the minor axis of the toroid. A lower momentum cutoff, measured from the minor axis of the toroid and inversely proportional to the size of the system, is not needed for the above integration as long as the maximum correlation length encountered is small compared to the size of the system. This condition and certain diagrams in the low-temperature state, where a lower momentum cutoff is required, are discussed in Appendix B. The inverse susceptibility in the Hartree approximation in the disordered phase r_+, then satisfies

$$r_+ \equiv \tau - \Sigma_H(r_+) = \tau + \alpha\lambda \ln(\Lambda^2/r_+) . \tag{A4}$$

Consider an ordered phase in which the order parameter has the value

$$\langle \psi(\vec{r}) \rangle = 2a \cos \vec{q}_1 \cdot \vec{r} , \tag{A5}$$

where $|q_{1z}| = q_{z0}$ and $|\vec{q}_{1\perp}| = q_{\perp 0}$. In this ordered phase the Hartree theory gives an inverse susceptibility r_- which is

$$r_- = \tau + \alpha\lambda \ln(\Lambda^2/r_-) + \lambda a^2 . \tag{A6}$$

We show in Appendix B that higher-order terms in the perturbation series and "anamolous" contributions to the Hartree diagram in the ordered phase may be neglected.

We may then calculate $\Delta\Phi$, the difference in free energy between the ordered and disordered phases in the manner described by Brasovsky. This is

$$\Delta\Phi = (1/2\lambda)[2\alpha\lambda(r_- - r_+) - r_-^2 - r_+^2] , \tag{A7}$$

where r_- and r_+ are given by (A6) and (A4), respectively. We also use Eq. (10) of Brasovsky, $\lambda a^2 = 2r_-$, valid when the external field coupling to the order parameter is zero. One may verify that $\Delta\Phi$ passes through zero when $r_+ \approx r_c$, where

$$r_c \approx 0.23\alpha\lambda , \tag{A8}$$

or when $\tau \approx \tau_c$ where

$$\tau_c = -1.7\alpha\lambda - \alpha\lambda \ln(\Lambda^2/1.7\alpha\lambda) . \tag{A9}$$

This means that a first-order transition to the ordered state occurs when $\tau \approx \tau_c$ given in (A9).

By differentiating $\Delta\Phi$ with respect to τ and then evaluating the resulting derivative at τ_c, we find that the discontinuity in the entropy per particle ΔS at the first-order phase transition is

$$\Delta S = Ck , \tag{A10}$$

where k is Boltzmann's constant and C is a number order unity which depends on the details of the model but is independent of λ.

APPENDIX B

The second-order contribution to the self energy [diagram (1d) of Ref. 11] is

$$\Sigma^{(2)}(r_H) \equiv \lambda^2 \int \frac{d^3q_1}{(2\pi)^3} \frac{d^3q_2}{(2\pi)^3} G_H(r_H, \vec{q}_1) G_H(r_H, \vec{q}_2) \times G_H(r_H, \vec{q} - \vec{q}_1 - \vec{q}_2) , \tag{B1}$$

where $\vec{q}$ is a vector such that $|q_z| = q_{z0}$ and $q_\perp = q_{\perp 0}$.

We estimate by power counting methods[11] that $\Sigma^{(2)}$ is

$$\Sigma^{(2)}(r_H) \approx C_2 \lambda^2/(r_H)^{1/2}\ , \tag{B2}$$

where C_2 is a constant, independent of λ and r_H.

We may neglect $\Sigma^{(2)}$ compared to the terms we have retained, given in (A4), if

$$C_2\lambda^2/(r_H)^{1/2} \ll r_H\ , \tag{B3}$$

or if

$$r_H \gg \lambda^{4/3} C_2^{2/3}\ . \tag{B4}$$

Since the phase transition takes place when $r_H \approx r_c$ given in A8 and since for λ small $\lambda \gg \lambda^{4/3}$, we are justified in neglecting the second-order term (B2) in calculating the value of τ for which the first-order transition will occur.

Consider now the anomalous contribution to the Hartree diagram in the ordered state. This corresponds to a contribution

$$\delta\Sigma_H = \lambda \int_0^{\Lambda} dK_y \int_{L^{-1}}^{\Lambda} dK_x \int_{L^{-1}}^{\Lambda} dK_z \frac{1}{K_z^2 + K_x^2 + K_y^4/(q_{\perp 0})^2}\ . \tag{B5}$$

In (B5) we have chosen a coordinate system in which the wave vector associated with the order parameter lies in the x-z plane. Also, L is a measure of the size of the spatial region in which our system is supposed to be confined. We estimate that the dependence of (B5) on λ and L is

$$\delta\Sigma_H \approx \lambda \ln(\Lambda L)/L^{1/2}\ . \tag{B6}$$

We require that $L \gg \xi \equiv [(r_H)^{1/2}]^{-1}$, where ξ is the correlation length. Since the first-order phase transition takes place at a value of r_H given by (A8), the maximum value of the correlation length we have to work with is $\xi_{\max} \approx (\alpha\lambda)^{-1/2}$. Therefore, we require that

$$L \gg (\alpha\lambda)^{-1/2}\ . \tag{B7}$$

If L satisfies (B7) then (B6) is negligible compared to a term we kept, namely, (A3).

Consider the anomalous contribution to Σ corresponding to diagram (1c) of Ref. 7. By means of power counting we estimate this diagram to be

$$\delta\Sigma_c \approx \lambda^2 a^2 L^{3/2} q_{\perp 0}^{1/2}\ . \tag{B8}$$

Contribution (B8) is small compared to the λa^2 term we have retained in (A6) if

$$L \ll \lambda^{-2/3} q_{\perp 0}^{-1/3}\ . \tag{B9}$$

There are further correction terms, each of which is individually small if (B9) is satisfied. We can say nothing, though, about the sum of the infinite number of such terms.

We conclude that our theory may be correct if L satisfies

$$(\alpha\lambda)^{-1/2} \ll L \ll \lambda^{-2/3} q_{\perp 0}^{-1/3}\ , \tag{B10}$$

although our arguments are not rigorous.

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