Critical behavior of the nematic-isotropic phase transition

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(Received 28 December 1994)

In this paper we establish the equation of state near the coexistence curve (the region of small external field, below the critical temperature) of the nematic-isotropic phase transition. The temperature difference of $T_c - T^*$, where T_c is the nematic-isotropic phase transition temperature and T^* is the temperature at which the light scattering intensity diverges in the supercooled isotropic phase of nematic-isotropic transition, is obtained. The present results show considerable improvement over an earlier work utilizing the equation of state near a critical and a tricritical point.

PACS number(s): 64.70.Md, 64.60.Ak

INTRODUCTION

The nematic-isotropic (*N-I*) phase transition has been a topic of active theoretical and experimental studies over the past few decades [1]. Early theories include the phenomenological model of Landau–de Gennes [2] and the Hamiltonian approach of Maier-Saupe [3]. There still remains a series of fascinating problems associated with the *N-I* transition that are not completely settled. The most conspicuous shortcoming concerns the ratio $(T_c - T^*)/T_c$ [4]. The temperature T_c is the *N-I* transition temperature and temperature T^* is the temperature at which the light scattering intensity diverges in the supercooled isotropic phase. The experimental value of $T_c - T^* = 1$ K. In order to gain insight into this, several workers showed how the inclusion of fluctuations can give considerable improvement. The Maier-Saupe theory gives this result as $T_c - T^* = 30$ K and the Landau mean field theory gives $T_c - T^* = 24$ K. These calculations include Gaussian fluctuation only. To include higher order effects Priest [5] did a renormalization group calculation to show that $T_c - T^* = 12.8$ K. In our earlier work [6] we pointed out how the higher order epsilon (ε) expansion in the renormalization group calculation gives an improved result of $T_c - T^* = 7.46$ K. The works of Refs. [5] and [6] utilized only one experimental datum, namely, the jump of 0.4 in the order parameter at T_c. The present work is also an analysis with fluctuation as the basis. In this paper we have considered the property of uniaxial system with continuous symmetry. We obtain the equation of the uniaxial state near the coexistence curve of the *N-I* phase transition. This equation of state is then utilized in evaluating $T_c - T^*$, which shows a definite improvement over earlier results. Considering the uniaxial system with a continuous symmetry, there exists massless modes, Goldstone bosons at all temperature $T < T_c$ (critical temperature) when the external field H is taken to be zero, leaving a spontaneously broken symmetry. Because of these Goldstone modes, the limit $H \to 0$ can be thought of as a critical point, for all $T < T_c$. In other words the transverse susceptibility becomes infinite when $H \to 0$.

THEORY

We have followed the same method as adopted in our previous work [6] and also the method of [5] throughout this paper. The model free energy of the Landau–de Gennes form can be written as

$$F = \int d^d x \left[\tfrac{1}{4}(r Q_{ij}^2 + \nabla_k Q_{ij} \nabla_k Q_{ij}) - b Q_{ij} Q_{jk} Q_{ki} + u (Q_{ij} Q_{ij})^2 - H_{ij} Q_{ij} \right] . \quad (1)$$

Here $d^d x$ indicates a functional integration in d dimension over tensor field $Q = Q(x)$. The tensor Q is 3×3, symmetric, and traceless. The quadratic coefficient r is written as $r = r_0[(T - T^*)/T_c]$ and b, u, and H are temperature independent. Here r_0 is a positive constant. If b were zero T^* would be the mean-field second order transition temperature. We have $b > 0$, T^* is therefore the (mean-field) absolute stability limit of the isotropic phase. In the isotropic state $\langle Q \rangle = 0$. If H_{ij} is uniaxial, then $Q_{11} = S$, $Q_{22} = Q_{33} = -\frac{1}{2}S$, $H_{11} = H$, and $H_{22} = H_{33} = -\frac{1}{2}H$. Here $S = \langle P_2(\cos\theta) \rangle$ is the usual order parameter, where θ is the angle between the molecular long axis and the director. We consider the case for which F does not change the symmetry of the spontaneous breaking state. We have followed the same ε and Feynman graph expansion technique [7–10] to calculate the equation of state for the uniaxial state. It has been shown in the ε expansion approach that the equation of state is well defined in the vicinity of the coexistence curve [10]. More specifically, in terms of the scaling variables defined by $X = t/S^{1/\beta}$ in Eq. (3) of Ref. [6], one has the structure

$$H/S^{\delta} \sim (X+1)[1 + A\varepsilon \ln(X+1) + B\varepsilon^2 \ln^2(X+1) + C\varepsilon^2 \ln(X+1)], \quad X \to -1 . \quad (2)$$

We start with the scaling equation of state of Ref. [6] and observe that in the region X close to -1, it has the expression

$$\frac{H}{S^{\delta}} + \frac{b}{S^{\omega}} = f(X) , \quad (3)$$

where

$$f(X)=(X+1)\{1+\varepsilon[A\ln(X+1)+B]+\varepsilon^2[C\ln^2(X+1)+D\ln(X+1)+E]\}\ , \tag{4}$$

where we have neglected the term like $(X+1)$ near $X=-1$. The coefficients A, B, C, D, and E can be written as

$$A=\tfrac{4}{26}\ , \tag{5a}$$

$$B=\tfrac{1}{26}[3+9\ln(2)-9\ln(3)]\ , \tag{5b}$$

$$C=-\tfrac{10}{676}\ , \tag{5c}$$

$$D=\tfrac{1}{676}[72\ln(2)-36\ln(3)+\tfrac{1424}{13}]\ , \tag{5d}$$

$$E=\tfrac{1}{676}[\tfrac{335}{6}\ln^2(3)-\tfrac{27}{2}\ln^2(2)-\tfrac{56}{3}\ln(2)]\ , \tag{5e}$$

and $\delta=3+\varepsilon+O(\varepsilon^2)$, $\beta=\frac{1}{2}-\frac{3}{26}\varepsilon+O(\varepsilon^2)$, $\omega=1+\frac{7}{13}\varepsilon+O(\varepsilon^2)$, $t=(T-T^*)/T^*$, and $X=t/S^{1/\beta}$.

To define Eq. (3) uniquely, we choose the scales of H, T, and S so that $f(0)=1$ and $f(-1)=0$, i.e., $X=-1$ corresponds to the coexistence curve [11]. In particular, the longitudinal mass operator, i.e., exact self-energy $r_L=\partial H/\partial S$, behaves like $r_L\sim(1/\beta)S^{\delta-1}f'(X)$ as $X\to-1$, i.e.,

$$\frac{\beta r_L}{S^{\delta-1}}=1+\varepsilon[A\ln(X+1)+A+B]+\varepsilon^2[C\ln^2(X+1)+(D+2C)\ln(X+1)+E+D]\ ,\quad X\to-1\ . \tag{6}$$

Following Wallace and Zia [11], we considered

$$(\beta r_L/S^{\delta-1})^{-1}\sim C_1+C_2(H/S^{\delta})^{-\varepsilon/2}\ , \tag{7}$$

where C_1 and C_2, the critical amplitudes, depend on ε. Now inverting Eq. (6) and reexpressing the right-hand side in terms of H/S^{δ} from Eq. (4), Eq. (7) can be rewritten as

$$(\beta r_L/S^{\delta-1})^{-1}=1-\varepsilon(A\ln y+A+B)-\varepsilon^2[\ln^2(y)(C-A^2)+\ln(y)(D+2C-3A^2-2AB)]+\text{const}\ , \tag{8}$$

where $y=H/S^{\delta}$.

The coefficients of $\varepsilon\ln y$ and $\varepsilon^2\ln^2 y$ in (8) are hence consistent with the expansion of $\varepsilon y^{-\varepsilon/2}$. Comparing Eqs. (7) and (8) we obtain the coefficients C_1 and C_2 upto the order of ε,

$$C_1=\frac{1}{13}\left[9-\frac{\varepsilon}{26}\left[117\ln(2)-81\ln(3)+\frac{1411}{13}\right]\right]+O(\varepsilon^2)\ , \tag{9}$$

$$C_2=\frac{4}{13}\left[1+\frac{\varepsilon}{338}[117\ln(3)+57]\right]+O(\varepsilon^2)\ . \tag{10}$$

With these values of C_1 and C_2 we find that the diverging term in Eq. (7) will take over from the constant term when

$$(H/S^{\delta})^{\varepsilon/2}\lesssim C_2/C_1=\frac{4}{9}\left[1+\frac{\varepsilon}{18}\left[\frac{148}{13}+9\ln(2)\right]\right]+O(\varepsilon^2)\ . \tag{11}$$

We see that the divergent term should be noticeable for $H/S^{\delta}<77\%$. The coefficient E in Eq. (4) is not required to obtain C_1 and C_2. Hence the scaling equation of state near the coexistence curve can be written as [by dropping E from $f(x)$ of Eq. (4)]

$$\frac{H}{S^{\delta}}+\frac{b}{S^{\omega}}=X+1+\frac{\varepsilon}{26}[4\ln(X+1)+3+9\ln(2)-9\ln(3)](X+1)+\frac{\varepsilon^2}{676}\left[-10\ln^2(X+1)+\left[72\ln(2)-36\ln(3)+\frac{1424}{13}\right]\ln(X+1)\right](X+1)\ . \tag{12}$$

From thermodynamic arguments we know that $H=-\partial F/\partial S$. Now we apply the same conditions as in Ref. [6], namely, that the free energies of the isotropic and nematic states be equal and that the free energy be a local minimum with respect to S, which can be expressed as

$$\int_0^S H(S')dS'=0\ , \tag{13a}$$

$$H(S)=0\ . \tag{13b}$$

For fixed b these equations are to be solved for $S=S_c$ and $t=t_c$. The resulting value of t_c is then expressed as

TABLE I. Calculated values of different parameters.

	Previous results[a]		Present results
Parameter	$\varepsilon=0$ (mean field)	$\varepsilon=1$	$\varepsilon=1$
S_c	0.4	0.4	0.4
t_c	0.08	0.024 899	0.01
b	0.60	0.210	0.2208
$\frac{dS}{dt}$	−5.0	−9.485 496	−5.5966
T_c-T^*	24 K	7.4699 K	3 K

[a]Data are taken from Ref. [6].

$t_c=(T_c-T^*)/T^*$. Here b and S_c are two unknown parameters. This requires a numerical solution of Eq. (13) as a function of b by setting the experimental value $S_c=0.4$. The variation of order parameter with temperature are also examined. Table I shows the results of this work and a comparison with our earlier result of Ref. [6]. The values are for the case $T^*=300$ K.

DISCUSSION

As can be seen from Table I, the present calculation gives a value of T_c-T^* much closer to observation. The improvement is due to the fact that we utilized the equation of state near a coexistence curve on which the *N-I* transition point falls, instead of using the equation of state near a critical or a tricritical point, as was done in Ref. [6]. The closeness of the present result with the observed T_c-T^* supports the idea that a renormalization group calculation can lead to the resolution of the T_c-T^* puzzle. This is contrary to the assertion of Tao *et al.* [12] that a density dependent mean field and not a fluctuation incorporating theory is needed for a stationary resolution.

ACKNOWLEDGMENTS

One of us (P.K.M.) wishes to thank the Council of Scientific and Industrial Research, India for financial support. The computation facilities provided by the Departmental Special Assistance Programme of the Department of Physics are thankfully acknowledged.

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