Renormalization-group calculation of T_c-T^* of the nematic-isotropic phase transition

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The low value of $(T_c-T^*)/T_c \approx 0.1\%$, 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 for the nematic-isotropic transition is a long-standing puzzle. We show in this paper that by extending the renormalization-group calculation to second order of ε and, alternatively, by considering that the nematic-isotropic transition is close to the tricritical point, considerable improvement over previous results is possible.

INTRODUCTION

The low value of $(T_c-T^*)/T_c \approx 0.1\%$ for the nematic-isotropic (NI) transition has been a long-standing puzzle. de Gennes[1] has pointed out how Maier-Saupe (MS) theory implies $(T_c-T^*)/T_c \approx 8.0\%$. In order to gain insight into this, several workers showed how the inclusion of fluctuations can give considerable improvement. This was done by including spatial inhomogeneity in the order parameter in Landau–de Gennes theory. T^* is interpreted as the temperature at which the light-scattering intensity will diverge in the supercooled isotropic phase. T^* and T_c are expressed in terms of several phenomenological Landau expansion parameters. It is usually shown that $T_c-T^*=1$ K [i.e., $(T_c-T^*)/T_c=0.3\%$ in the case of *p*-azoxyanisole (PAA)] is consistent with the jump in entropy and jump in the order parameter at T_c. These calculation include Gaussian fluctuations only and, as mentioned above, depend on several parameters to be fixed. For including higher-order fluctuations Priest[2] did a renormalization-group calculation to show that $T_c-T^*=12.8$ K. The only experimental datum needed in the analysis is the jump of 0.4 in the order parameter at T_c, and his method was an ε expansion about a critical point. In a very recent paper, Tao, Sheng, and Lin[3] argued that fluctuation effects, being higher-order effects, a remedy for the mean-field calculation, e.g., MS theory should be considered first. They have included a density-dependent term in the pseudopotential and have shown how only one adjustable parameter can give consistent results in $(T_c-T^*)/T_c$ and also in the drop in specific volume at T_c. Their further argument against fluctuation methods is that the measured critical indices do not corroborate with the model critical indices.

The present work is an analysis with fluctuations as the basis. The primary reason for doing this is that in the work of Tao, Sheng, and Lin the divergence of the light-scattering intensity at T^* is bypassed. Moreover, the discrepancy involving the model critical indices is not serious if we consider that the nematic-isotropic transition may occur near a tricritical point.

THEORY

We have followed the method adopted by Priest in our analysis. Initially, we have tried to improve this result by doing a renormalization-group calculation up to second order in ε. The model free energy of the Landau–de Gennes form can be written as

$$F=\int d^d x\,[\tfrac{1}{4}(rQ_{ij}^2+\nabla_k Q_{ij}\nabla_k Q_{ij}) - bQ_{ij}Q_{jk}Q_{kl}+u(Q_{ij}Q_{ij})^2-H_{ij}Q_{ij}]\,. \tag{1}$$

Here $d^d x$ indicates a functional integration in d dimensions over the 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 absent, T^* would be the mean-field second-order transition temperature. Since in our model $b>0$, T^* is 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_{ij} and H_{ij} can be expressed as

$$Q_{ij}=S\begin{pmatrix}1 & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & -\frac{1}{2}\end{pmatrix}, \tag{2a}$$

$$H_{ij}=H\begin{pmatrix}1 & 0 & 0\\ 0 & -\frac{1}{2} & 0\\ 0 & 0 & -\frac{1}{2}\end{pmatrix}. \tag{2b}$$

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 have followed the same ε and Feynman-graph expansion technique[4–7] to calculate the equation of state for the uniaxial state. The equation of state in scaling form can be written as

$$\frac{H}{S^\delta}+\frac{b}{S^\omega}=1+X+\frac{\varepsilon}{26}[3(X+3)\ln(X+3)+4(X+1)\ln(X+1)+6X\ln(2)-9(X+1)\ln(3)]$$
$$+\frac{\varepsilon^2}{576}\{[4+6\ln(2)-9\ln(3)+4\ln(X+1)][3(X+3)\ln(X+3)+4(X+1)\ln(X+1)$$
$$+6X\ln(2)-9(X+1)\ln(3)]$$
$$+\tfrac{5}{2}(X+1)[\ln^2(X+3)-\ln^2(3)]+36[\ln^2(X+3)-(X+1)\ln^2(3)+X\ln^2(2)]$$
$$-54\ln(2)[\ln(X+3)+X\ln(2)-(X+1)\ln(3)]+12\ln(\tfrac{27}{4})(X+1)\ln(X+1)$$
$$+\tfrac{197}{13}[(X+3)\ln(X+3)+2X\ln(2)-3(X+1)\ln(3)]+4(X+1)\ln(X+1)\ln(X+3)$$
$$-10(X+1)\ln^2(X+1)+\tfrac{748}{13}(X+1)\ln(X+1)-8[(X+6)I_1(\rho)-6(X+1)I_1(\tfrac{3}{4})]$$
$$-24[I_2(\rho)-(X+1)I_2(\tfrac{3}{4})]+16[I_3(\rho)-(X+1)I_3(\tfrac{3}{4})]\}\ , \tag{3}$$

where

$$\rho=(X+3)/4(X+1),\quad X=t/S^{1/\beta}\ ,$$
$$I_1(\rho)=\int_0^\rho du[\ln(u)/u(1-u)][(1-u/\rho)^{1/2}-1]-\int_\rho^\infty du[\ln(u)/u(1-u)]\ , \tag{4a}$$
$$I_2(\rho)=\rho\frac{\partial(I_1(\rho))}{\partial\rho},\quad I_3(\rho)=I_1(\rho)+2I_2(\rho)\ , \tag{4b}$$

and

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

From thermodynamic arguments we know that $H=-\partial F/\partial S$. The free energy may therefore be found by integrating the equation of state with respect to S. The conditions 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 can be expressed as

$$\int_0^S H(S')dS'=0\ , \tag{5a}$$
$$H(S)=0\ . \tag{5b}$$

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 $t_c=(T_c-T^*)/T^*$. This requires a numerical solution of Eq. (5) as a function of b by putting the experimental value $S_c=0.4$. Comparisons of results are given in Table I.

In order to avoid some of the obvious drawbacks and also to conform with experimental value of β and γ, we have done an analysis near a tricritical point. In general, when two coefficients of the same symmetry in the Landau free energy vanish simultaneously, such a point is called tricritical.[7,8] Therefore the experimental situation has led to the question of whether or not the NI transition is close to the tricritical point $r=u=0$. This leads to an alternative formulation of the NI phase transition by taking $u=0$. In that case a positive stabilizing w term must be added to the free energy:

$$F=\int d^dx[\tfrac{1}{4}(rQ_{ij}^2+\nabla_k Q_{ij}\nabla_k Q_{ij})$$
$$-bQ_{ij}Q_{jk}Q_{kl}+w(Q_{ij}Q_{ij})^3-H_{ij}Q_{ij}]\ . \tag{6}$$

When the dimensionality of the system is above its upper critical dimensionality, Landau's theory becomes exact and renormalization-group theory reduces to the Landau theory. Since the marginal dimensionality in this case is 3, we avoided the ε expansion altogether. The scaling form of the equation of state can be written as

$$\frac{H}{S^\delta}+\frac{b}{S^\omega}=1+X\ , \tag{7}$$

where

$$\delta=5,\quad \omega=3,\quad \beta=0.25,\quad X=\frac{t}{S^{1/\beta}}\ .$$

Applying the same procedure adopted above, we get the results of b, S_c, t_c, and dS/dt. The results are given in Table I.

TABLE I. Calculated values of different parameters.

	$\varepsilon=1$ $O(\varepsilon^2)$	$\varepsilon=1$ $O(\varepsilon)$[a]	$\varepsilon=0$ (mean field)[a]	Tricritical case (mean field)
S_c	0.4	0.4	0.4	0.4
t_c	0.024 899	0.042 83	0.08	0.0256
b	0.210	0.3819	0.60	0.128
$\frac{dS}{dt}$	−9.485 496	−6.08	−5.0	−7.812
T_c-T^*	7.469 99 K	12.48 K	24 K	7.68 K

[a]Data are taken from Ref. 2.

DISCUSSION

As can be seen from the table, the renormalization-group result for the second order of ε is approximately

one-half as small as the previous result while still being too large in comparison with experiment. In our calculation the value of the cubic coupling is smaller than Priest's value. The objection against taking the b term as a perturbation is therefore not serious in the present case. In our renormalization-group calculation, we have applied the Maxwell construction. The validity of this is still an open question in renormalization-group theory. But in our second calculation, this has been bypassed. It is not necessary to take a term $\sim Q^5$ into account, as it can be shown that in the presence of the cubic term it leads to only minor corrections. So all the drawbacks of Priest's work have been bypassed in our work. Although this result is still far from the experimental result, the improvement is encouraging. The justification for doing such an analysis instead of the standard Landau–de Gennes analysis considering the Gaussian fluctuations is that this method needs only one experimental data input, namely, the jump in the order parameter at T_c.

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