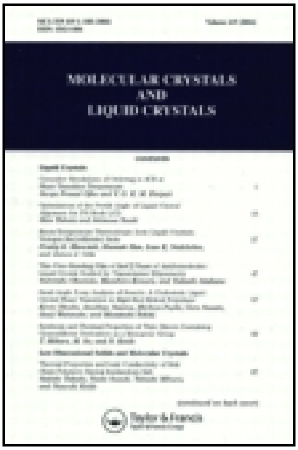

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Isotropic-Nematic Transition: Landau-de Gennes vs Molecular Theory

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Isotropic-Nematic Transition: Landau-de Gennes vs Molecular Theory

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Landau-de Gennes and molecular mean-field descriptions of the isotropic-nematic transition are compared. We use two methods to calculate the order parameter correlation function and show that corrections due to cubic and quartic terms in the Landau expansion are non-negligible. In the first method we apply lowest order diagrammatic perturbation theory using as perturbation both cubic and quartic terms. The second method essentially treats the cubic term to all orders and the quartic term to leading order. A comparison of the results with experiment indicates only qualitative agreement. It is also found that the supercooling temperature T^* is different from T_ξ, the temperature at which the correlation length diverges. The fact that the corrections are not small and that the results obtained by the two different methods are inconsistent cast grave doubt on the quantitative validity of the Landau-de Gennes approach in its present form.

We propose a numerical way to establish contact between the meanfield theory and the Landau-de Gennes theory. Our results indicate that the two approaches are irreconcilable.

I INTRODUCTION

The isotropic-nematic (I-N) phase transition in liquid crystals is generally accepted to be weakly first-order. The familiar Maier-Saupe[1] (MS) mean field theory is the first successful theory based on a molecular model. Since then there have been contributions by other authors[2] to the molecular theory, some of which take short-range spatial correlations into account.[3] The Maier-Saupe theory gives a reasonable value of the discontinuity in the orientational order parameter at the transition temperature T_c, and seems to give a reasonably good qualitative description of the essential features of the I-N transition.

A macroscopic model (Landau-de Gennes model) based on the Landau theory of phase transitions has been used by de Gennes[4] to study the I-N transition. It is commonly accepted in the phase transition community that while the simple Landau theory is quantitatively inaccurate, it does provide an adequate qualitative description. In particular it is believed that the order of a phase transition is correctly described by the simple Landau theory. When fluctuations are taken into account the nature of the transition is believed to still depend on the actual values of the bare parameters in the free energy expansion. For the I-N transition there are (at least) five parameters in the model which have to be determined empirically.

Light scattering and magnetic birefringence experiments in the isotropic phase of nematic liquid crystals indicate strong pretransitional behavior due to order parameter fluctuations. Stinson and Litster[5,6] measured the Cotton-Mouton coefficient and the correlation range of fluctuations of the orientational order parameter in the isotropic phase of the liquid crystal *p*-methoxy benzylidene *p*-*n*-butylaniline (MBBA). They found that their data can be consistently and quantitatively interpreted by using the Landau-de Gennes (L-deG) model in a Gaussian approximation (GA) (i.e. neglecting the cubic and quartic terms in the free energy expansion) except for a region very close to T_c. Their results indicate that T^*, the fictitious second order I-N transition temperature[4] is about 1 K below T_c. T^* is also referred to as the maximum supercooling temperature.

In order to make a comparison between the L-deG and MS models Stephen and Straley[7] used an expansion in powers of the order parameter to express the MS free energy in the L-deG form. They then identified the corresponding coefficients and obtained a T^* which turned out to be about 30 K below T_c. The fact that this T^* is so different from that obtained by fitting experiments to the GA of the L-deG model has led to a generally accepted conclusion that the molecular mean field theory, while valid in the nematic phase, gives rise to certain inconsistencies in the isotropic phase.

In this paper we deal with several questions. First of all we point out that the procedure used in Ref. 7 to make contact between MS and L-deG is not valid for all values of the order parameter. We describe a numerical way of determining the L-deG parameters using microscopic variables of the molecular theory. Second, we believe that if the L-deG model can be taken beyond the GA, i.e. when the cubic and quartic terms are included in the free energy expansion, it can be expected to give results which are quantitatively more reliable. To check if this is so we use two different methods to calculate the short-range correlation effects. If it does not turn out so, the validity of the GA will come under suspicion. Third, in the L-deG theory the experimental result that $T_c - T^* \sim 1$ K is known to be inconsistent with order parameter measurements. If T^* is 1 K below T_c, then according to the L-deG theory the ratio of the order parameter value at T^* to that at T_c should be 1.5 independently of the other parameters in the theory. But experimentally the order parameter at 1 K below T_c is known to differ from that at T_c by only a few percent rather than 50% as implied above. In this paper we investigate whether a significant correction to T^* could arise from the inclusion of the cubic and quartic terms. If so, again the validity of the GA will come under suspicion.

In Section II we give a brief review of the L-deG model. A new calculation of the amplitudes of fluctuations in order parameter and the correlation range of fluctuations appears in Section III. In Section IV we determine the parameters in the L-deG model by using a new analysis to interpret the experimental results on light scattering and magnetic birefringence. We describe in Section V a numerical way of making contacts between the molecular mean field theory and the L-deG theory. Finally, Section VI discusses some implications and conclusions of our results.

Our main conclusions are: (i) perturbation corrections due to the cubic and quartic terms are far from negligible; (ii) results obtained with the two perturbative methods are very different; (iii) thus the GA, in fact the L-deG model itself, cannot be quantitatively reliable; and (iv) the MS and L-deG theories are irreconcilable. While we have no positive contributions to offer, we hope that these negative conclusions would help to call attention to the limitations in present theoretical approaches toward describing the I-N transition.

II LANDAU-DE GENNES MODEL

The Landau-de Gennes model[4] containing a third order term of the order parameter in the free energy expansion was proposed and used to describe first order transition in liquid crystals. Retaining only terms which have rotational invariance, the free energy per unit volume, $\mathcal{F}$, is given by

$$\mathcal{F} = \mathcal{F}_I + \frac{3}{4} A S_{\alpha\beta} S_{\beta\alpha} + \frac{3}{2} B S_{\alpha\beta} S_{\beta\gamma} S_{\gamma\alpha} + \frac{9}{16} C [S_{\alpha\beta} S_{\beta\alpha}]^2 \qquad (2.1)$$

Here $\mathcal{F}_I$ is the free energy density of the isotropic phase, $S_{\alpha\beta}$ is the tensor order parameter which describes the degree of order in a nematic liquid crystal and a summation over repeated indices is implied. The coefficient A is assumed to have the form $A = a(T - T^*)$, while B and C are regarded as constants independent of the temperature. All coefficients are assumed independent of the volume.

For a liquid crystal of uniaxial symmetry the single preferred direction of the molecules is along the director $\mathbf{n}$, and $S_{\alpha\beta}$ takes the form

$$S_{\alpha\beta}(\mathbf{r}) = S(\mathbf{r}) \left[n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}) - \frac{1}{3} \delta_{\alpha\beta} \right] \qquad (2.2)$$

where n_α are the components of $\mathbf{n}$, and $S(\mathbf{r})$ denotes the fraction of molecules at $\mathbf{r}$ aligned parallel to $\mathbf{n}$.

For a uniform uniaxial crystal substituting Eq. (2.2) into Eq. (2.1) leads to the free energy expansion

$$\mathcal{F} = \mathcal{F}_I + \frac{1}{2}AS^2 + \frac{1}{3}BS^3 + \frac{1}{4}CS^4. \tag{2.3}$$

The equilibrium value of S is that which gives the minimum value for the free energy. Thus equating the derivative of Eq. (2.3) to zero S will be a root of the equation

$$AS + BS^2 + CS^3 = 0 \tag{2.4}$$

The solutions of this equation which correspond to relative minima of the free energy are:

$$S = 0, \text{ isotropic phase,} \tag{2.5}$$

and

$$S = -\frac{B}{2C} + \left[\left(\frac{B}{2C}\right)^2 - \frac{A}{C}\right]^{1/2}, \text{ nematic phase,}$$

where $B < 0$. At the transition temperature T_c the free energies of the isotropic and nematic phases are equal. From Eqs. (2.3) and (2.5) and the definition $A = a(T - T^*)$ we obtain

$$T_c = T^* + \frac{2}{9}\frac{B^2}{aC}. \tag{2.6}$$

The value of the order parameter at the I-N transition is

$$S_c = -\frac{2}{3}\frac{B}{C}. \tag{2.7}$$

Finally from the free energy expression (2.3) we obtain the latent heat per unit volume L as:

$$L = \frac{2}{9}\left(\frac{aB^2}{C^2}\right)T_c. \tag{2.8}$$

The parameters a, B, C and T^* in the L-deG model are material parameters. They are determined from experiment. A direct measurement gives the transition temperature T_c, the order parameter value S_c, and the latent heat per unit volume L. Then once T_c, S_c and L are known, Eqs. (2.6)–(2.8) represent three equations with four unknowns. From Eqs. (2.7) and (2.8) a and the ratio B/C can be uniquely determined. To determine the individual parameters B, C, and T^*, we will need one additional piece of information and the solution of Eq. (2.6). For this purpose short-range order effects were calculated using the model and used to interpret pretransitional phenomena in the isotropic phase of nematic liquid crystals. The quantities commonly measured are light scattering intensities and Cotton-Mouton coefficients, both of which are related to the correlation function of the order parameter. In order to interpret the experimental results,[5,6] the fluctuations in the order parameter were calculated using GA to the free energy. In other words, the cubic and quartic terms in Eq. (2.3) were neglected, which made the calculation quantitatively somewhat dubious. In the hope of getting a more reliable quantitative result we use a diagrammatic perturbation theory to calculate the contribution of the cubic and quartic terms to thermal fluctuations of the order parameter. Our hope is, of course, that these perturbative corrections will be small.

III ORDER PARAMETER FLUCTUATION

The free energy density associated with the long wavelength part of the order parameter fluctuation for a uniaxial liquid crystal is given by:

$$\mathcal{F}(\mathbf{r}) = \mathcal{F}_I + \frac{1}{2}AS^2(\mathbf{r}) + \frac{1}{3}BS^3(\mathbf{r}) + \frac{1}{4}CS^4(\mathbf{r}) + \frac{1}{2}D(\nabla S(\mathbf{r}))^2. \quad (3.1)$$

for systems in which director fluctuation can be neglected. Since $\mathcal{F}_I$ is independent of S, the free energy density giving the statistical weight of a given distribution $S(\mathbf{r})$ can be written in the form

$$\mathcal{H}(\mathbf{r}) = \frac{1}{2}AS^2(\mathbf{r}) + \frac{1}{3}BS^3(\mathbf{r}) + \frac{1}{4}CS^4(\mathbf{r}) + \frac{1}{2}D(\nabla S(\mathbf{r}))^2. \quad (3.2)$$

Then the partition function, averages, and correlation function are calculated with the weight

$$W\{S\} = \exp\left(-\beta\int\mathcal{H}(\mathbf{r})d\mathbf{r}\right) \quad (3.3)$$

where $\beta = 1/\mathrm{kT}$. For the sake of completeness we will briefly review the results of the Gaussian mode.[4]

Gaussian Model

In the Gaussian model we take $B = C = 0$ in Eq. (3.2). Then the total free energy of the system with volume V can be written as

$$F_0 = \int\mathcal{H}(\mathbf{r})d\mathbf{r} = \frac{1}{2}\sum_{\mathbf{q}}(A + Dq^2)|S_q|^2 \quad (3.4)$$

where S_q is the Fourier transform of $S(\mathbf{r})$ such that

$$S(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} S_q \exp(i\mathbf{q}\cdot\mathbf{r}). \tag{3.5}$$

Using Eq. (3.4) the correlation function of the order parameter $G(\mathbf{r})$ can be calculated from the functional integral

$$\langle S(\mathbf{r})S(0)\rangle_0 = G_0(\mathbf{r}) = \frac{1}{Z_0}\int \mathfrak{D}S(\mathbf{r})S(\mathbf{r})S(0)\exp(-\beta F_0) \tag{3.6}$$

where Z_0 is the partition function:

$$Z_0 = \int \mathfrak{D}S(\mathbf{r})\exp(-\beta F_0). \tag{3.7}$$

Then the Fourier transform of the correlation function is easily obtained from Eq. (3.6). We have

$$G_0(q) = \left(\frac{1}{\beta}\right)\frac{1}{A + Dq^2}. \tag{3.8}$$

This is the expression used to interpret the experimental results.[5,6] According to Eq. (3.8) the correlation length $\xi(T)$ is given by

$$\xi^2(T) = \left(\frac{D}{A}\right) = \frac{D}{a(T - T^*)}, \tag{3.9}$$

which implies that T^* is the temperature at which $\xi(T)$ diverges.

From the free energy expression Eq. (2.3) we also not that T^* represents the temperature at which $\mathcal{F}$displays zero curvature at $S = 0$. Below this temperature the isotropic phase becomes completely unstable with respect to nematic ordering and so T^* is sometimes referred to as the maximum supercooling temperature.

Contributions of the Cubic and Quartic Terms

The contributions of the cubic and quartic terms in the free energy to the order parameter fluctuations can be obtained by using perturbation theory with the Gaussian model taken as the zeroth order approximation. For this purpose we will use two approaches. If the effects of the cubic and quartic terms are small, these two approaches should yield comparable results.

A. *First Method:* We divide the total free energy into two parts; $F = F_0 + F_1$ where F_0 is the free energy in the Gaussian model and F_1 is given by

$$F_1 = \int d\mathbf{r}\left\{\frac{1}{3}BS^3(\mathbf{r}) + \frac{1}{4}CS^4(\mathbf{r})\right\}. \tag{3.10}$$

We will take F_1 to be the perturbation. Then the correlation function is obtained from the expression

$$\langle S(\mathbf{r})S(\mathbf{r}')\rangle = G(\mathbf{r}-\mathbf{r}') = \frac{\int \mathfrak{D}S(\mathbf{r})S(\mathbf{r})S(\mathbf{r}')\exp[-\beta(F_0+F_1)]}{\int \mathfrak{D}S(\mathbf{r})\exp[-\beta(F_0+F_1)]}$$

$$= \frac{\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\beta^m\langle S(\mathbf{r})S(\mathbf{r}')F_1^m\rangle_0}{\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\beta^m\langle F_1^m\rangle_0} \tag{3.11}$$

where $\langle\ \ \rangle_0$ denotes averaging in the GA. Using the method of Feynman graphs[16] the Fourier transform of $G(\mathbf{r})$ can be obtained by the sum of diagrams given in Figure 1(a). We obtain

$$G(\mathbf{q}) = G_0(\mathbf{q})[1 - G_0(\mathbf{q})\Sigma(\mathbf{q})]^{-1} \tag{3.12}$$

where $\Sigma(\mathbf{q})$ is the self energy part. To first order in C and to second order in B the self energy part is given by

$$\Sigma(\mathbf{q}) = \Pi(0, C) + \Pi(\mathbf{q}, B) \tag{3.13}$$

with $\Pi(0, C)$ and $\Pi(\mathbf{q}, B)$ corresponding to graphs given in Figure 1(b) and Figure 1(c), respectively. These diagrams are evaluated in the Appendix and we obtain

$$\Pi(0, C) = -\frac{3C}{2\pi^2\xi_0 D}[\xi_0 q_m - \tan^{-1}(\xi_0 q_m)], \tag{3.14}$$

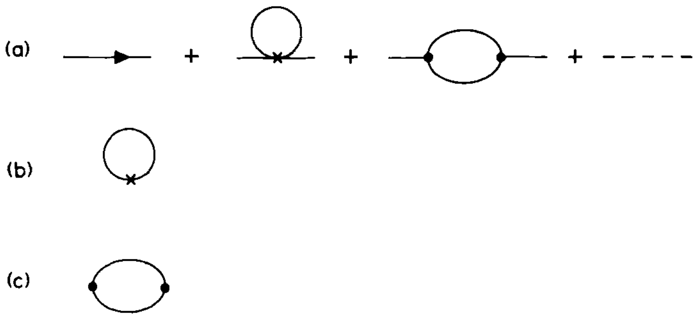

FIGURE 1 Graphs contributing (a) to the correlation function $G(q)$, (b) to the self energy part $\Pi(0, C)$ and (c) to the self energy part $\Pi(q, B)$. A dot represents a factor of $(\beta B/3)$ and a cross represents a factor $(\beta C/4)$.

and

$$\Pi(\mathbf{q}, B) = \frac{1}{8\pi^2}\left(\frac{B}{D}\right)^2 \int_0^{(\xi_0 q_m)} \frac{dy}{q} \frac{y}{1+y^2} \ln\left[\frac{1+(y+\xi_0 q)^2}{1+(y-\xi_0 q)^2}\right] \tag{3.15}$$

where $\xi_0^2 = D/A \equiv D/a(T - T^*)$ and q_m is a cut-off wavenumber approximately related to the reciprocal of the interparticle separation. In the long wavelength limit, i.e. for small enough q, the integral in Eq. (3.15) can be performed to obtain

$$\Pi(\mathbf{q}, B) \simeq \left(\frac{B}{2\pi D}\right)^2 \xi_0 \left\{\tan^{-1}(\xi_0 q_m) - \frac{\xi_0 q_m}{1+\xi_0^2 q_m^2} - \frac{q^2 \xi_0^2}{4}\left[\tan^{-1}(\xi_0 q_m) + \frac{\xi_0 q_m(\xi_0^2 q_m^2 - 1)}{(1+\xi_0^2 q_m^2)^2}\right]\right\}. \tag{3.16}$$

Finally, using the above results the correlation function in the small q limit and to first order in C and second order in B can be written in the form

$$G(\mathbf{q}) = \frac{kT}{A + q^2\left[D + kT\left(\frac{B}{D}\right)^2 \xi_0^3 f_3\right] + kT\left(\frac{C}{D}\right)\frac{f_1}{\xi_0} - kT\left(\frac{B}{D}\right)^2 \xi_0 f_2} \tag{3.17}$$

where

$$f_1 \equiv \frac{3}{2\pi^2}\left[\xi_0 q_m - \tan^{-1}(\xi_0 q_m)\right] \tag{3.18}$$

$$f_2 \equiv \frac{1}{4\pi^2}\left[\tan^{-1}(\xi_0 q_m) - \frac{\xi_0 q_m}{1+\xi_0^2 q_m^2}\right] \tag{3.19}$$

and

$$f_3 \equiv \frac{1}{16\pi^2}\left[\tan^{-1}(\xi_0 q_m) + \frac{\xi_0 q_m(\xi_0^2 q_m^2 - 1)}{(1+\xi_0^2 q_m^2)^2}\right] \tag{3.20}$$

A similar result as the above is given for the x-y component of the tensor order parameter $S_{\alpha\beta}$ in Ref. 8. The correlation length $\xi(T)$ can easily be deduced from Eq. (3.17). We have

$$\xi^2(T) = \frac{D + kT\left(\frac{B}{D}\right)^2 \xi_0^3 f_3}{A + kT\left(\frac{C}{D}\right)\frac{f_1}{\xi_0} - kT\left(\frac{B}{D}\right)^2 \xi_0 f_2} \tag{3.21}$$

B. *Second Method:* In this method we start with the assumption that the cubic term is the more influential of the two small perturbation terms and that Eq. (3.2) for the free energy expansion has already converged. Then in calculating average values we can use a translation in the order parameter space to eliminate the cubic term since the average value is unchanged by the transformation. This procedure has been used in Ref. 17 in a different context. Such a translation corresponds to summing the cubic perturbation to all orders.

Let us define σ by

$$S(\mathbf{r}) = \sigma(\mathbf{r}) - \frac{B}{3C} \tag{3.22}$$

Substituting (3.22) in Eq. (3.2), the part of the free energy giving the statistical weight of a given distribution $\sigma(\mathbf{r})$ can be written in the form $F_\sigma = F_{0\sigma} + F_{1\sigma}$, where

$$F_{0\sigma} = \frac{1}{2}\int d\mathbf{r}\left[\left(A - \frac{B^2}{3C}\right)\sigma^2(\mathbf{r}) + D(\nabla\sigma(\mathbf{r}))^2 + \left(\frac{4B^3}{27C^2} - \frac{2AB}{3C}\right)\sigma(\mathbf{r})\right] \tag{3.23}$$

and

$$F_{1\sigma} = \frac{C}{4}\int d\mathbf{r}\,\sigma^4(\mathbf{r}). \tag{3.24}$$

We now take $F_{1\sigma}$ to be the perturbation. Furthermore, the coefficient of the linear term in Eq. (3.23), to be denoted as H, can be estimated using the results obtained by the first method (see Table I). (This is legitimate if the two methods were to give consistent results.) Then close to T_c we obtain $H \simeq 10^{-3}$. Since the lowest order contribution of the linear term is of order H^2, it can be neglected. So $F_{0\sigma}$ essentially becomes a renormalized Gaussian model free energy.

TABLE I

Values of the free energy expansion as obtained from light scattering and magnetic birefringence experiments and the Maier-Saupe theory.

	Light Scattering (T_c = 314 K sample)		Magnetic Birefringence (T_c = 317.8 sample)		Maier-Saupe	
Parameter	First Method	Second Method	First Method	Second Method	Stephen & Straley	Our Result
$T_c - T^*$, K	1	5	2.2	11.8	29	29
a, J cm^{-3} K^{-1}	0.0537	0.0537	0.0530	0.0530	0.145	0.160
B, J cm^{-3}	−0.413	−2.581	−1.121	−6.014	−27.15	−32.56
C, J cm^{-3}	0.883	5.516	2.395	12.851	24.65	50.59

The calculation for the correlation function $G_\sigma(q) = \langle |\sigma_q|^2 \rangle_{0\sigma}$ will be similar to that in the first method. We obtain to first order in C:

$$G_\sigma(q) = \frac{kT}{A_\sigma + Dq^2 + kT\left(\frac{C}{D}\right)\frac{f_\sigma}{\xi_\sigma}}, \tag{3.25}$$

where

$$A_\sigma = A - \frac{B^2}{3C} = a(T - T^*) - \frac{B^2}{3C}, \tag{3.26}$$

$$\xi_\sigma = \frac{D}{A_\sigma}, \tag{3.27}$$

and

$$f_\sigma = \frac{3}{2\pi^2}\left[\xi_\sigma q_m - \tan^{-1}(\xi_\sigma q_m)\right]. \tag{3.28}$$

The correlation length in the above approximation becomes:

$$\xi^2(T) = \frac{D}{A_\sigma + kT\left(\frac{C}{D}\right)\frac{f_\sigma}{\xi_\sigma}}. \tag{3.29}$$

IV COMPARISON WITH EXPERIMENT

Experiments on light scattering and magnetic birefringence in the isotropic phase of nematogens indicate strong pretransitional effects as a result of fluctuation inhomogeneities. In this section we will use the results of the previous sections to interpret the magnetic birefringence[5] and light scattering[6] experiments on MBBA. As input to our theory we take the measured values of the transition temperature $T_c (T_c = 317.8\ \mathrm{K})$,[9] the latent heat $L (L = 0.82\ \mathrm{J\text{-}cm^{-3}})$,[9] and the discontinuity in the order parameter S_c at $T_c (S_c = 0.312)$.[10] These values can be used to determine some of the parameters in the L-deG free energy expansion:

(i) According to Eq. (2.7) we have $S_c = -2B/3C$. The experimental value $S_c = 0.312$ gives

$$\frac{B}{C} = -0.468 \tag{4.1}$$

(ii) From Eq. (2.8) we have $L = (2/9)(aB^2/C^2)T_c$. Using the measured values of T_c, L, and Eq. (4.1) we obtain

$$a = 0.053 \text{ J cm}^{-3} \text{ K}^{-1}. \tag{4.2}$$

(iii) Finally from Eqs. (2.6), (4.1), and (4.2) we derive expressions for the parameters B and C in terms of T^*:

$$B = \left(\frac{T^* - 317.8}{1.962}\right) \text{ J cm}^{-3}, \tag{4.3}$$

$$C = \left(\frac{317.8 - T^*}{0.918}\right) \text{ J cm}^{-3}. \tag{4.4}$$

As mentioned earlier we need additional experimental data in order to determine T^*. For this purpose, we make use of the measured[6] correlation range for fluctuations of the orientational order parameter.

Note that in this reference the intercept of $\xi^{-2}(T)$ on the temperature axis reads 40°C, or 313 K. If, as pointed out by the authors, that $T_c - T^* \sim 1$ K in the GA, T_c for this sample must be about 314 K instead of 317.8 K. We must correspondingly redetermine the L-deG parameters before fitting our theory to the data. With T_c taken as 314 K we find $a = 0.0537 \text{ J cm}^{-3}\text{K}^{-1}$, $B = ((T^* - 314)/1.937) \text{ J cm}^{-3}$, and $C = ((314 - T^*)/(0.468 \times 1.937)) \text{ J cm}^{-3}$. With these assumed inputs to the theory, the correlation length $\xi(T)$ calculated by perturbation theory now depends on only three parameters: T^*, D, and the cutoff q_m. We take for q_m values which are around the reciprocal of the molecular length, i.e., $q_m^{-1} \simeq 25$ Å.

To determine T^* and D, we calculate $\xi(T)$ for a series of their values and choose that which gives the best fit to experimental data. Actually, as long as we assume D independent of the temperature (in the spirit of the Landau theory), the best value for D will be the same as that given by the GA. This is because at $T \gg T^*$ our results for $\xi(T)$ reduce to the expression obtained in the GA. In particular, the slope of $1/\xi^2(T)$ with respect to T is equal to a/D at $T \gg T^*$ in our two methods, just as it would be in the GA. Thus[6] $D = 7.68 \times 10^{-14}$ J/cm.

A Correlation Length

The result of a fit using the first method of Section III and $T_c = 314$ K is shown in Figure 2 for $q_m^{-1} = 25$ Å. We obtain $T^* = 313.2$ K. Note that at temperatures above about 315 K, we have a straight line. Below 315 K, the calculated $1/\xi^2(T)$ begins to bend downward, just as in the experiment. (This was alluded to by Fan and Stephen in a qualitative discussion in Ref. 8.) It intercepts the temperature axis at $T_\xi = 313.2$ K.

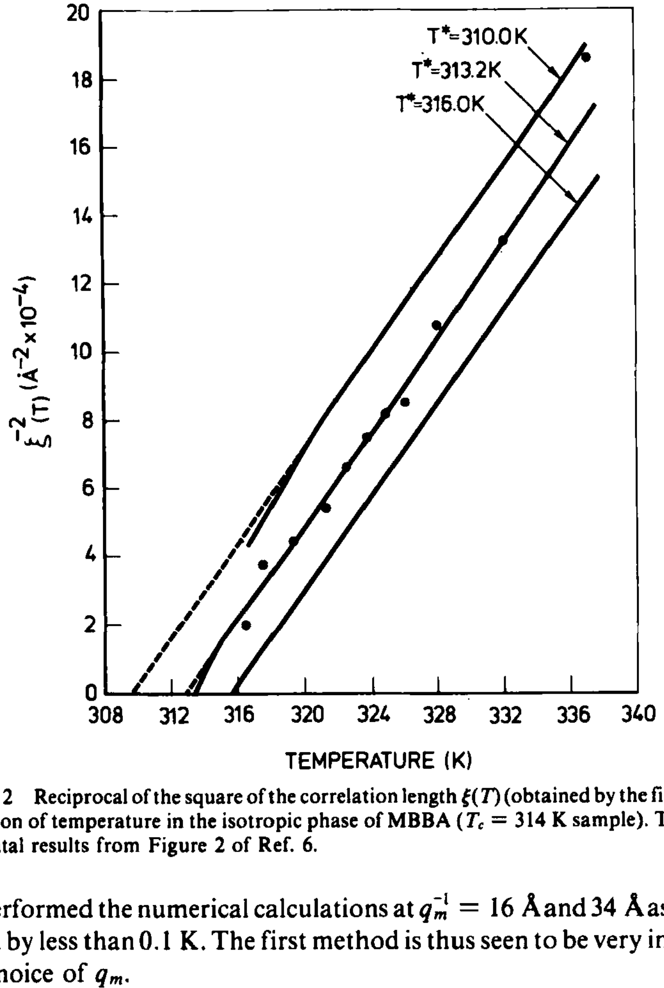

FIGURE 2 Reciprocal of the square of the correlation length $\xi(T)$ (obtained by the first method) as a function of temperature in the isotropic phase of MBBA ($T_c = 314$ K sample). The dots are experimental results from Figure 2 of Ref. 6.

We performed the numerical calculations at $q_m^{-1} = 16$ Å and 34 Å as well. T^* changed by less than 0.1 K. The first method is thus seen to be very insensitive to the choice of q_m.

For $T^* = 313.2$ K, $B = -0.413$ J/cm^3, and $C = 0.883$ J/cm^3.

According to the second method of Section III, the correlation length is given by Eq. (3.29). At $T \to T^*_\sigma \equiv T^* + B^2/3aC \equiv (3/2)T_c - (1/2)T^*$, Eqs. (3.26) and (3.27) give $A_\sigma \to 0$ and $\xi_\sigma \to \infty$. Below T^*_σ, we must have $\xi_\sigma = \infty$ independent of temperature. This permits us to reduce Eqs. (3.28) and (3.29) to

$$f_\sigma \to \frac{3}{2\pi^2}\,\xi_\sigma q_m, \tag{4.5}$$

and

$$\xi^2(T) \to \frac{D}{A_\sigma + \dfrac{3kTC}{2\pi^2 D}\,q_m}. \tag{4.6}$$

The reduced expression is good as long as ξ_a is sufficiently large.

With $q_m^{-1} = 25$ A, the best fit to data (again assuming $T_c = 314$ K for this sample) gives $T^* = 309$ K. This is shown in Figure 3. The intercept of $1/\xi^2(T)$ on the temperature axis is still 313 K. This means that we must now distinguish the maximum supercooling temperature T^* (the temperature at which the curvature of the free energy at $S = 0$ vanishes) from the temperature T_ξ at which the correlation length diverges. T^* and T_ξ differ by 4 K.

In this calculation, we find T^* lying 5 K below the clearing temperature T_c, instead of 1 K as in the GA. The perturbation correction is far from negligible.

For $T^* = 309$ K, $B = -2.581$ J/cm^3, and $C = 5.516$ J/cm^3.

The second method is, however, quite sensitive to the choice of q_m. For $q_m^{-1} = 34$ Å, T^* drops to 288 K: 26 K below T_c. For $q_m^{-1} = 16$ Å, T^* rises to 312 K: 2 K below T_c. In this entire range of q_m, however, $(T_c - T^*)$ differs quite significantly from the 1 K given by the GA.

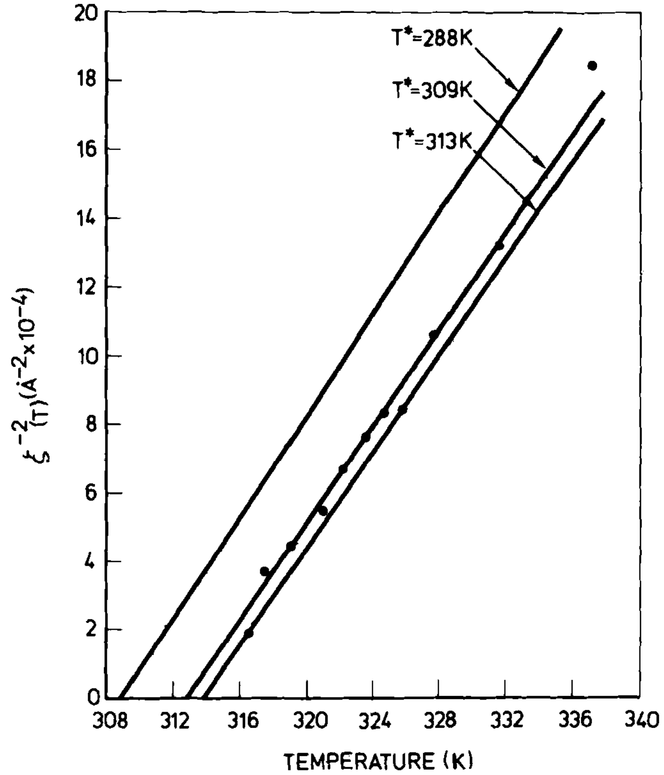

FIGURE 3 Reciprocal of the square of the correlation length $\xi(T)$ (obtained by the second method) as a function of temperature in the isotropic phase of MBBA ($T_c = 314$ K sample). The dots are experimental results from Figure 2 of Ref. 6.

The meaning of q_m is not exactly clear. It is related to the size of the molecules, i.e., the range of intermolecular repulsion, and can be regarded as an attempt to introduce steric effects into a volume-free theory. In our future work relating the Landau-de Gennes theory to molecular theory, we intend to examine q_m more closely from the point of view of a molecular model.

At this point we wish to call attention to the fact that $(T_c - T^*) = 5$ K would help to solve one of the puzzles in the L-deG theory. We mentioned earlier that the L-deG model requires that

$$S(T^*) = \frac{3}{2} S(T_c). \tag{4.7}$$

While the GA yields $(T_c - T^*) = 1$ K and consequently from experimental data $S(T^*) \lesssim 1.1\, S(T_c)$, our present value of $(T_c - T^*)$ will yield from the same data a relation very close to Eq. (4.7). This seems to lend some support for our second method. (We do not mean for the reader to take this seriously. The main point that we wish to point out is that something must be drastically wrong with the GA.)

B Cotton-Mouton Coefficient

In this section, for the sake of completeness, we first present a brief derivation of the Cotton-Mouton coefficient given in Ref. 11. In the presence of an external magnetic field **H** the free-energy density is given by

$$\mathcal{F}_H = \mathcal{F} - \frac{(\Delta\chi)_{\max}}{3} S(\mathbf{r}) H^2 \tag{4.8}$$

where $\mathcal{F}$ is the expression in Eq. (2.3) and $(\Delta\chi)_{\max}$ is the maximum possible value of the magnetic susceptibility anisotropy. The average value of the order parameter in the presence of magnetic field can be calculated using (4.8). Denoting this order by $\bar{S}(H)$ we have

$$\bar{S}(H) = \left\langle \frac{1}{V}\int d\mathbf{r}\, S(\mathbf{r}) \right\rangle_H = \frac{1}{V^{1/2}} \langle S(q=0)\rangle_H$$

$$= \frac{\displaystyle\int \mathfrak{D}S(\mathbf{r}) \left[\frac{1}{V}\int d\mathbf{r}\, S(\mathbf{r})\right] \exp\left[-\beta \int d\mathbf{r} \left(\mathcal{F} - \frac{(\Delta\chi)_{\max}}{3} S(\mathbf{r}) H^2\right)\right]}{\displaystyle\int \mathfrak{D}S(\mathbf{r}) \exp\left[-\beta \int d\mathbf{r} \left(\mathcal{F} - \frac{(\Delta\chi)_{\max}}{3} S(\mathbf{r}) H^2\right)\right]} \tag{4.9}$$

where $\langle\ \rangle_H$ denotes the thermal average in the presence of **H**. Above T_c we have $\bar{S}(H = 0) = 0$. Thus for a small enough magnetic field we can carry out an expansion in H^2 to obtain

$$\bar{S}(H) = \eta H^2 + \cdots$$

where

$$\eta = \left.\frac{\partial \bar{S}(H)}{\partial (H^2)}\right|_{H^2=0} \tag{4.10}$$

is the paranematic susceptibility which can be evaluated in the limit $H^2 \to 0$ from Eq. (4.9). We find

$$\eta = \frac{\beta(\Delta\chi)_{\max}}{3}\left[\langle|S(q=0)|^2\rangle_{H^2=0} - \langle S(q=0)\rangle^2_{H^2=0}\right]$$

$$= \frac{\beta(\Delta\chi)_{\max}}{3}\langle|S(q=0)|^2\rangle. \tag{4.11}$$

We can now substitute the results for $\langle|S(q=0)|^2\rangle$ from Section III into Eq. (4.11) to obtain η for our two approximations.

In the first method we obtain from Eqs. (3.17) and (3.21)

$$\eta = \frac{(\Delta\chi)_{\max}\xi^2(T)}{3\left[D + kT\left(\frac{B}{D}\right)^2 \xi_0^3 f_3\right]}. \tag{4.12}$$

In the second method, Eqs. (3.25) and (3.29) give the result:

$$\eta = \frac{(\Delta\chi)_{\max}\xi^2(T)}{3D}. \tag{4.13}$$

To obtain the Cotton-Mouton coefficient we use the fact that any anisotropic physical quantity is proportional to the induced order.[12] Specifically we can write

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \simeq (\Delta\epsilon)_{\max}\bar{S}(H) \tag{4.14}$$

where $(\Delta\epsilon)_{\max}$ is the maximum value of $(\epsilon_{\parallel} - \epsilon_{\perp})$ and $\epsilon_{\parallel}(\epsilon_{\perp})$ is the long wavelength $(q = 0)$ dielectric constant parallel (perpendicular) to **H**. Furthermore, $\Delta\epsilon \simeq 2n(\Delta n)$ where n is the average refractive index given by $n = (2n_{\perp} + n_{\parallel})/3$ and $\Delta n = n_{\parallel} - n_{\perp}$. We also have the relation $n = \bar{\epsilon}^{1/2}$ where $\bar{\epsilon} = (2\epsilon_{\perp} + \epsilon_{\parallel})/3$. Thus substituting Eqs. (4.10)–(4.13) for $\bar{S}(H)$ in Eq. (4.14) and rearranging the resulting equations we obtain:

$$\frac{\Delta n}{H^2} = \frac{(\Delta\epsilon)_{\max}}{6\bar{\epsilon}^{1/2}}\,\frac{(\Delta\chi)_{\max}\xi^2(T)}{D + kT\left(\frac{B}{D}\right)^2 \xi_0^3 f_3}\ \text{(first method)}, \tag{4.15}$$

and

$$\frac{\Delta n}{H^2} = \frac{(\Delta\epsilon)_{\max}}{6\bar{\epsilon}^{1/2}}\,\frac{(\Delta\chi)_{\max}\xi^2(T)}{D} \text{ (second method).} \qquad (4.16)$$

Finally, in order to fit our results to the magnetic birefringence measurements on MBBA we need to know the values of the constants that appear in the expressions for the Cotton-Mouton coefficient ($\Delta n/H^2$). We take from Ref. 5, $(\Delta\bar{\epsilon})_{\max} = 1.09$, $\epsilon = 2.605$, $(\Delta\chi)_{\max} = 1.25 \times 10^{-7}$ erg G^{-2} cm^{-3}.

Figure 4 shows our theory fitted to the experimental data.[5] The data used came from a sample with $T_c \simeq 317.8$ K (actually one with the intercept at about 316.5 K). The value of T^* turns out to be 315.6 K in the first method and 306 K in the second method. Or, $(T_c - T^*)$ turns out to be 2.2 K and 11.8 K in the two methods, respectively. In both cases, then, the value of $(T_c - T^*)$ determined by fitting magnetic birefringence data turns out to be about twice as big as that determined by fitting light scattering data. This discrepancy may

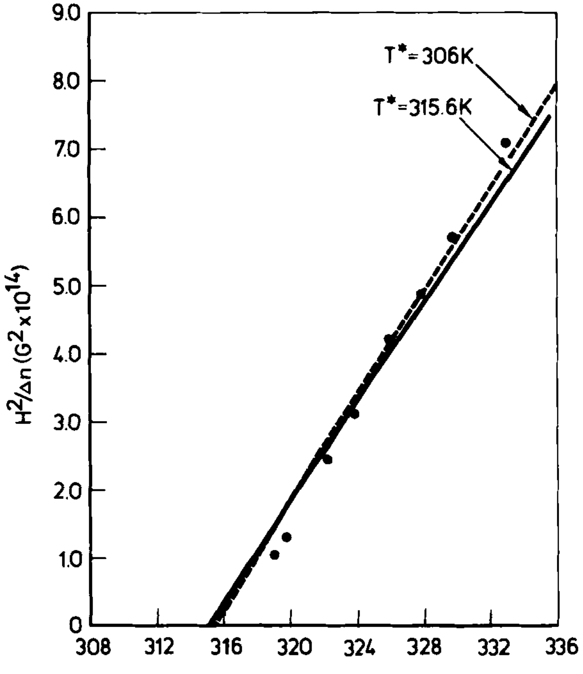

FIGURE 4 Inverse of the Cotton-Mouton coefficient vs temperature for MBBA with $T_c = 317.8$ K. Results from the first method and second method are shown by solid and dashed lines respectively. The dots represent experimental results from Ref. 5.

have been there in the Gaussian approximation as well but masked by the inaccuracy in the determination of T_c and T^*.

At this point, more distress signals appeared. $(T_c - T^*)$ differs significantly from that obtained with the GA, and the values obtained with two perturbative methods differ significantly from each other. These facts cast serious doubts on the negligibility of the cubic and quartic terms, and thus the quantitative usefulness of the GA. Moreover, the discrepancy between $(T_c - T^*)$ values obtained from fitting magnetic birefringence and light scattering data suggests fundamental difficulties in the L-deG expansion itself. The determination of $(T_c - T^*)$ from data is strongly model-dependent. The uncertainty in the model now prevents us from meaningfully interpreting the data.

We are also puzzled by our inability to fit the slope of $H^2/\Delta n$ better than what appears in Figure 4. As we delved into this matter, we were appalled by the even larger inconsistencies in the experimental data themselves. The data of Stinson and Litster in Ref. 5 and those of Keyes and Shane in Ref. 13 may both have appeared as straight lines extrapolatable to the same intercept on the temperature axis, but the magnitudes differ by as much as a factor of 3!

V CONTACT BETWEEN MOLECULAR THEORY AND LANDAU-DE GENNES THEORY

Most molecular-theoretic calculations of nematic liquid crystals start with a model interaction between a pair of molecules at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, with respective orientations $\hat{\Omega}_1$ and $\hat{\Omega}_2$ in the form[14]

$$v(1, 2) = v_0(r_{12}) + v_2(r_{12})P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2) \tag{5.1}$$

In the mean field approximation the Helmholtz free-energy functional for a system at given density $\rho = N/V$ and temperature T is then given by

$$\mathcal{F}[f(\theta)] = \mathcal{F}_0 + NkT\int f(\theta)\ln f(\theta)\,d\hat{\Omega} + \frac{1}{2}\rho^2\iint f(\theta_1)f(\theta_2)v(1, 2)\,d\tau_1 d\tau_2, \tag{5.2}$$

where $f(\theta)$ provides a measure of the long-range orientational order and $\tau \equiv (\mathbf{r}, \hat{\Omega})$ is a five-dimensional vector. The orientational order parameter is defined as

$$S = \int f(\theta)P_2(\cos\theta)\,d\hat{\Omega}. \tag{5.3}$$

Thus from Eqs. (5.2) and (5.3) we observe that $\mathcal{F}$ is an implicit function of S.

Our aim in this section is to describe a numerical way to obtain an expression of the Landau-de Gennes form Eq. (2.3) from Eq. (5.2). In the following we will determine the parameters a, B, C and T^* using molecular mean-field theory and compare them with the results of Section IV.

One method of deriving a L-deG type expansion from Eq. (5.2) is that given by Stephen and Straley.[7] In their approach one takes

$$f(\theta) = \frac{1}{Z} \exp\left[\frac{A_0}{kT} S P_2(\cos\theta)\right] \tag{5.4}$$

where

$$\begin{aligned} A_0 &= \rho\gamma_2, \\ \gamma_2 &= \int v_2(r)\, d\mathbf{r} \end{aligned} \tag{5.5}$$

and

$$Z = \int \exp\left[\frac{A_0}{kT} S P_2(\cos\theta)\right] d\Omega. \tag{5.6}$$

The free-energy can then be written in the Maier-Saupe form

$$\mathcal{F}[f(\theta)] = \mathcal{F}_I - NkT \ln Z - \frac{1}{2} N\rho\gamma_2 S^2. \tag{5.7}$$

This free-energy expression is valid *only at the extrema of Eq.* (5.2) where the self consistency Eq. (5.3) and (5.4) are satisfied. In Ref. 7 the expression for ln Z is expanded in powers of S and substituted in Eq. (5.7) to give:

$$\mathcal{F} = \mathcal{F}_I + N\left[\frac{1}{3} AS^2 - \frac{2}{27} BS^3 + \frac{1}{9} CS^4\right], \tag{5.8}$$

with the results

$$\begin{aligned} A &= \frac{3A_0}{2T}\left(T - \frac{A_0}{5k}\right), \\ B &= \frac{9A_0^3}{70(kT)^2}, \end{aligned} \tag{5.9}$$

and

$$C = \frac{9A_0^4}{700(kT)^3}.$$

Clearly the expansion first of the exponential in Eq. (5.6) and then of ln Z itself would not be valid for large values of S. It is easy for the reader to demonstrate numerically that in the range of S of interest to liquid crystals the expansions fail rapidly. Adding higher power terms to the expansion would remedy the situation (if the free energy is an analytic function), but it would not get around the fact that the expression (5.7) is invalid except at the extrema of Eq. (5.2).

In this paper we start with Eq. (5.2) but regard $f(\theta)$ in the form of Eq. (5.4) as a variational function. We define

$$f(\theta)=\frac{1}{Z(\alpha)}\exp\left[\frac{A_0}{kT}\,\alpha P_2(\cos\theta)\right] \tag{5.10}$$

where α represents a variational parameter. It can be identified to S only where the self-consistency Eq. (5.3) and (5.4) are solved. Everywhere else we use Eq. (5.3) as a definition of the order parameter and calculate S with the equation:

$$S(\alpha)=\frac{1}{Z(\alpha)}\int P_2(\cos\theta)\exp\left[\frac{A_0}{kT}\,\alpha P_2(\cos\theta)\right]d\Omega. \tag{5.11}$$

For every choice of the temperature and α we now calculate $\mathcal{F}(\alpha)$ and the corresponding $S(\alpha)$. In this way we can plot the free-energy as a function of $S(\alpha)$ for a series of temperatures and obtain the curves shown in Figure 5 for MBBA, with $T_c = 317.8$ K.

Now, in order to present the free energy in the form of a Landau-de Gennes expansion, which is a quartic polynomial in S, we fit the curves at the minima to a quartic polynomial. (One can do this whether the free energy is an analytic function or not.) The dots in Figure 5 represent a polynomial of the form

$$\frac{\mathcal{F}-\mathcal{F}_I}{N}=\frac{1}{2}a(T-T^*)S^2+\frac{1}{3}BS^3+\frac{1}{4}CS^4 \tag{5.12}$$

where

$$\begin{aligned} T^* &= 288.6\ \text{K},\\ a &= 5.0\ \text{k/N},\\ B &= -10193.13\ \text{kK/N} \end{aligned} \tag{5.13}$$

and

$$C = 1583.74\ \text{kK/N},$$

B and C having been fixed by using their values at $T = T_c$. To compare the present result with previous results we need the free energy per unit volume

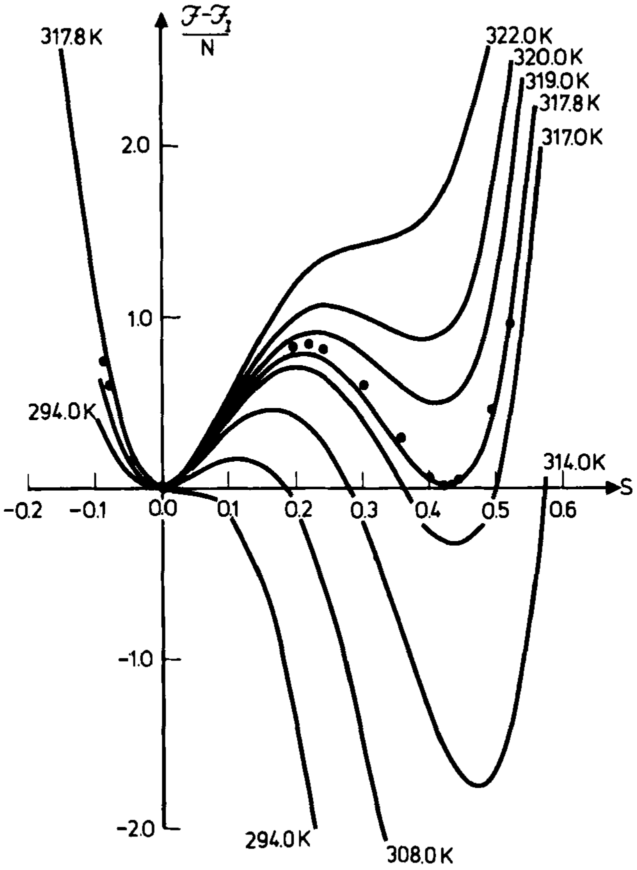

FIGURE 5 The free energy per particle vs order parameter for several values of the temperature.

instead of the free energy per particle as given in Eq. (5.12). For MBBA, we note that the specific volume is 432 Å^3 ($\rho = 0.002315$ Å^{-3}). Thus,

$$a = 0.160 \text{ J cm}^{-3}\text{ K}^{-1},$$

$$B = -32.56 \text{ J cm}^{-3}, \qquad (5.14)$$

and

$$C = 50.59 \text{ J cm}^{-3}.$$

As can be seen from Figure 5, a very good fit can be made even though only a small portion of the curves has been used.

For easy comparison, the values of the parameters a, B, C and T^* obtained by the first method and the second method and from the MS theory are given in Table I.

Equation (5.14), with the help of Eqs. (2.7) and (2.8), gives

$$S_c = -\frac{2B}{3C} = 0.429,$$

and

$$L = \frac{2}{9}\left(\frac{aB^2}{C^2}\right) T_c = 4.68 \text{ J/cm}^3,$$

values which are well known to be too large compared to experiment.

Note that the parameters from the MS theory as interpreted by Stephen and Straley[7] are very different from those obtained by us. If one uses a free energy with parameters given by the former, the order parameter at transition would be close to unity rather than the MS value of 0.429. This says that Eqs. (5.8)–(5.9) do not faithfully represent the Maier-Saupe theory.

The conclusion arrived at by Stephen and Straley, however, remains true: we see no way to reconcile the L-deG theory and the MS theory. Both are too crude in their present forms.

VI CONCLUSION

Using perturbation theory we have calculated the contributions to the order parameter fluctuations of the cubic and quartic terms in the Landau-de Gennes model by two methods. In the literature, it is generally felt that the fit of experimental results by the Gaussian approximation validated the predictions of the Landau-de Gennes theory. If one accepts this, one is led to the conclusion that B and C are very small, and therefore if we include the cubic and quartic terms the corrections to the Gaussian model should be negligible. In particular the use of a perturbation theory should be valid, and calculations carried out with the two different methods outlined in the text would give essentially identical results. But this is not the case; the values of the parameters obtained with the two methods turn out to be very different (see Table I). Moreover the values of B and C obtained from the experimental fit are not so small. This suggests the Landau-type series expansion of the free energy may be a poor approximation, especially close to the transition.

We feel very uncomfortable about the way in which the Landau-de Gennes theory has been applied by theoreticians and experimenters alike. The samples have been difficult to control, resulting in clearing temperatures which can be several degrees apart—several times larger than the heretofore accepted value of $(T_c - T^*)$. The parameters depend too sensitively upon the data to tolerate that kind of uncertainty. In addition, there are uncertainties in most other measured macroscopic quantities as well. For example, even for the most popular MBBA, the latent heat can vary from 0.82 J/cm^3 (Ref. 9) to 1.5 J/cm^3

(Ref. 15), which can affect the parameter *a* by a factor of 2. The order parameter at transition can vary from 0.31 to 0.35 depending on how one chooses to extrapolate the data. The magnetic birefringence can vary by a factor of 3 (see Section IV). And the fit of $[S(T^*) - S_c]/S_c$ can be off by an order of magnitude. Despite these difficulties, the Landau-de Gennes theory continues to be used in a casual manner for studying quantitative details of experiments far beyond the capability of the theory.

Both the Landau-de Gennes theory and the Maier-Saupe theory provide us with but the lowest of approximations. In the former, the temperature dependence is much too simple. It can be readily demonstrated from molecular-theoretic considerations that the short range order effects in B and C depend rather sensitively on temperature. Also, despite the weakness of the first order transition, volume dependence is far from negligible. The transition temperature at constant pressure differs from the transition temperature at constant volume by an amount comparable to the value of $(T_c - T^*)$. In the MS theory, only the strength of the intermolecular potential has been allowed a role. The range, and with the consideration of the range the appearance of short range spatial correlations, need be accounted for. We believe that it is the crudeness of both approximations which makes the phenomenological and the molecular theories so irreconcilable at this time.

The advantage of a Landau-type theory is its simplicity. We have found it necessary to go beyond the Gaussian approximation, but that does not increase the number of parameters. For quantitative applications (for that matter even for reliable qualitative applications), it now appears that one must introduce new temperature and volume dependences, and thus new parameters which would destroy its usefulness. Rather than introducing such repairs, we feel that it is time to abandon the phenomenological approach and delve more deeply into molecular theories. Just as the ideal gas law and hard sphere models had to give way to classical liquid theories, simple theories such as L-deG and MS must eventually yield to deeper levels of theoretical investigation and understanding. They have served their purposes, and offered us directions. Now let them rest while we seek new advances.

Acknowledgments

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APPENDIX

In this appendix we present details on the calculation of the self energy parts Σ, i.e. $\Pi(0, C)$ and $\Pi(q, B)$. From the diagram representing $\Pi(0, C)$, (*b*) in Figure 1, we have

$$\Pi(0, C) = -\frac{C}{4}\frac{(4!)}{2}\frac{1}{(2\pi)^3}\int d\mathbf{k}\, G_0(\mathbf{k}), \qquad \text{(A.1)}$$

where $G_0(\mathbf{k}) \equiv (A + Dk^2)^{-1}$ is the bare propagator, and $(4!)/2$ represents the internal symmetry factor giving the number of equivalent diagrams. Assuming a value of q_m for the cut-off, Eq. (A.1) becomes

$$\begin{aligned}\Pi(0, C) &= \frac{-3C}{2\pi^2}\int_0^{q_m} dk\, \frac{k^2}{A + Dk^2} \\ &= \frac{-3C}{2\pi^2 D}\left[q_m - \sqrt{\frac{A}{D}}\tan^{-1}\left(q_m\sqrt{\frac{D}{A}}\right)\right]. \qquad \text{(A.2)}\end{aligned}$$

We next define $\xi_0^2 \equiv D/A$. Then Eq. (A.2) can be written in the form

$$\Pi(0, C) = \frac{-3C}{2\pi^2 D\xi_0}\left[\xi_0 q_m - \tan^{-1}(\xi_0 q_m)\right]. \qquad \text{(A.3)}$$

Next, consider the diagram corresponding to $\Pi(q, B)$, (*c*) in Figure 1. We have

$$\Pi(q, B) = \frac{1}{2}\left(\frac{B}{3}\right)^2 (18)\frac{1}{(2\pi)^3}\int d\mathbf{k}\, G_0(k)\, G_0(\mathbf{k} - \mathbf{q})$$

$$= \frac{B^2}{(2\pi)^2}\int_0^{q_m} k^2 dk \int_{-1}^{1} dx \frac{1}{(A + Dk^2)[A + D(k^2 + q^2 - 2kqx)]}. \quad (A.4)$$

Let us define a new variable $y \equiv \xi_0 k$, where ξ_0 is defined as above. Then performing the x integration in Eq. (A.4) we find

$$\Pi(q, B) = \frac{1}{2}\left(\frac{B}{2\pi D}\right)^2 \frac{1}{q}\int_0^{\xi_0 q_m} dy \frac{y}{(1 + y^2)} \ln\left(\frac{1 + (y + \xi_0 q)^2}{1 + (y - \xi_0 q)^2}\right). \quad (A.5)$$

To obtain an approximate expression for Eq. (A.5) in the long wavelength limit we assume $q \ll 1$. Then we have

$$\ln\left(\frac{1 + (y + \xi_0 q)^2}{1 + (y - \xi_0 q)^2}\right) = \frac{4q\xi_0 y}{1 + y^2}\left(1 - \frac{(\xi_0 q)^2}{1 + y^2}\right) + O(q^4). \quad (A.6)$$

Substituting the result of Eq. (A.6) into Eq. (A.5) the integration becomes straightforward. We thus obtain the long wavelength limit

$$\Pi(q, B) = \left(\frac{B}{2\pi D}\right)^2 \xi_0\left\{\tan^{-1}(\xi_0 q_m) - \frac{\xi_0 q_m}{1 + \xi_0^2 q_m^2} - \frac{\xi_0^2 q^2}{4}\left[\tan^{-1}(\xi_0 q_m) + \frac{\xi_0 q_m(\xi_0^2 q_m^2 - 1)}{(1 + \xi_0^2 q_m^2)^2}\right]\right\}. \quad (A.7)$$