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ON THE PRETRANSITIONAL EFFECTS IN NEMATOGENS

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Abstract We show in this note that the experimentally observed strong pretransitional effects in nematogens can be described in terms of a mean field theory if the free energy expansion is not truncated at the quadratic term. A simple uniform fluctuation model gives rise to light scattering intensity in good agreement with experiment.

Light scattering and magnetic birefringence measurements in the isotropic phase of nematogens indicate strong pretransitional effects. By using the Landau theory of phase transitions, de Gennes[1] found it possible to estimate the correlation length and its temperature dependence. His theory, however, led to the conclusion that the mean field analysis of Maier and Saupe,[2] while valid in the nematic phase, gives rise to certain inconsistencies in the isotropic phase. We wish to review de Gennes' arguments, and in light of our own "mean field" analysis point out that what is really at fault is the truncation of the free energy expansion at the quadratic term. A new estimate of the correlation length based on a renormalization-group argument leads to good agreement with experiment, and thereby removes the difficulty.

Let us begin with de Gennes' criticism of the Maier-Saupe analysis.

At a given density ρ, the Helmholtz free energy F can be expanded in powers of the order parameter S:

$$F = F_o + A'(T-T^*)S^2 - BS^3 + CS^4 + \cdot \cdot \cdot \cdot \cdot , \qquad (1)$$

where A', B, C, and T* are positive constants. The interpretation of T* is crucial to the following discussions. It represents the temperature at which F(S) displays zero curvature at S=0. Below this temperature, the isotropic phase becomes completely unstable with respect to nematic ordering. For this reason, T^* is sometimes referred to as the maximum supercooling temperature. It is our view, however, that the "spontaneous" setting-in of nematic order actually occurs at a much higher temperature. At fixed density ρ, the maximum supercooling temperature occurs at T_ρ, where the free energies in the isotropic and nematic phases coincide.[3]

That T^* was identified as the maximum supercooling temperature was a direct consequence of de Gennes' description of the pretransitional phenomenon. By truncating the free energy at the S^2 term and augmenting it by an elastic distortion contribution, de Gennes wrote the local free energy as:

$$F(\vec{r}) \approx F_o + A'(T-T^*)S^2(\vec{r}) + K[\nabla S(\vec{r})]^2. \qquad (2)$$

The total free energy $F = \int F(\vec{r})dV$ can then be expressed in terms of S_q, the Fourier transform of $S(\vec{r})$. Using this result in the Boltzmann factor, $\langle S_q^2\rangle$, or alternately $\langle S(0)S(r)\rangle$, can be evaluated. He found

$$\langle S(0)S(r)\rangle = \frac{kT}{8\pi\rho K}\,\frac{\exp(-r/\xi(T))}{r} \qquad (3)$$

and therefore

$$\int_\infty \langle S(0)S(r)\rangle dV = \frac{kT}{2\rho A'(T-T^*)}\;, \qquad (4)$$

where $\xi(T) = \left[\frac{K}{A'(T-T^*)}\right]^{\frac{1}{2}}$ denotes the correlation length. If this derivation is valid, T^* will also represent the temperature at which $\xi(T)$ diverges: a seemingly apt definition for the maximum supercooling temperature.

In the Maier-Saupe theory, the free energy takes the form

$$F = \frac{1}{2} A_o S^2 + kT\ln(C/4\pi) - aS, \qquad (5)$$

with

$$C = \{\int \exp[-aP_2(\cos\theta)/kT]d\Omega\}^{-1}, \qquad (6)$$

and

$$S = C\int P_2(\cos\theta)\exp[-aP_2(\cos\theta)/kT]d\Omega. \tag{7}$$

By combining Eqs. (5)-(7), F can be rewritten in the form (1). The parameters A', B, C, and T* are then identifiable. In particular, one finds[4]

$$A' = \frac{3}{2}\frac{A_o}{T}, \quad \text{and} \quad T^* = \frac{A_o}{5k}. \tag{8}$$

It turns out that such a calculation yields $(T_c-T^*)/T_c \approx 10^{-1}$, or $T_c-T^* \approx 30^\circ C$, in violent disagreement with the light-scattering determination of (T_c-T^*) at about $1^\circ C$, where $\xi(T)$ diverges by extrapolation. This is often thought to be a major inconsistency in the Maier-Saupe theory.

We wish to point out that the inconsistency exists only if one identifies the T* in Eq.(1) with the T* defined by a diverging correlation length. If Eq. (2) is <u>invalid</u>, as we contend, the identification becomes unjustifiable. For this reason, we shall denote the temperature at which $\xi(T)$ diverges by T_ξ. It is perfectly acceptable, then, to have $T_c-T^* \approx 30^\circ C$ and $T_c-T_\xi \approx 1^\circ C$. What remains to be shown is that in place of de Gennes' theory, another analysis can be carried out which yields $T_c-T_\xi \approx 1^\circ C$ without requiring the truncation of F(S) at S^2.

Incidentally, that T* and T_ξ are different can be seen from yet one more angle. Putting aside the Maier-Saupe theory altogether, one can still fit Eq. (1) to data. If one insists that $T_c-T^* \equiv T_c-T_\xi \approx 1^\circ C$, then an inevitable consequence is that $S(T_\xi)/S(T_c) = 1.5$. It occurs independently of the way (A',B,C) are chosen to fit data. Since the order parameter below T_c is known to change by only a few percent per degree, such a drastic change of S (from about 0.4 at T_c to about 0.6 at T_ξ — a mere $1^\circ C$ away) is unacceptable.

Let us now recalculate $\xi(T)$ using a very crude model. Consider the fluctuations and thus the order parameter S uniform within a correlation volume V_ξ. The fluctuation part of the free energy is then given by $\rho V_\xi F(S) \sim \frac{1}{2}kT$, or

$$V_\xi \sim \frac{1}{2}\frac{kT}{\rho F(S)}. \tag{9}$$

The light scattering intensity is then proportional to the relevant quantity

$$\int_{\infty} \langle S(0)S(r)\rangle dV \approx \int_{V_\xi} \langle S(0)S(r)\rangle dV \approx S^2 V_\xi \sim \frac{kT}{2\rho} \frac{S^2}{F(S)} \; . \qquad (10)$$

The first thing we note is that if S is uniformly small or if for any reason the S^3 and higher-power terms are negligible in Eq. (1), Equation (10) reduces to de Gennes' form Eq. (4). But since those terms are not negligible, and in fact F(S) goes through a minimum at $S \approx 0.43$ at temperature near T_ρ or T_c, approximating F(S) by a quadratic is certainly not valid.

The correct thing to do is to evaluate the correlation function $\langle S(0)S(r)\rangle$ by statistical mechanics. The ensemble contains all distributions of S(r) and thus presents us with a prohibitive task. To approach it properly, one must make use of the full renormalization apparatus.[6] For a crude estimate, we shall take $S \simeq 0.43$ in Eq. (10). The justification is as follows.

As in all simple scaling procedures,[6] we begin with a lattice model with unit interparticle spacing and represent the nearest-neighbor interaction strength by α_o. S_o denotes the order parameter at this stage. As blocks of progressively increasing sizes are placed under scrutiny, the interaction strengths between neighboring blocks become α_1, $\alpha_2, \cdots$. At temperature T_ξ, the correlation length diverges, hence $S_o(T_\xi) = S_1(T_\xi) = S_2(T_\xi) = \cdots$. In turn one finds $\alpha_o/kT_\xi \cong \alpha_1/kT_\xi \cong \alpha_2/kT_\xi \cong \cdots$. A plot of α_n/kT_ξ versus n displays a horizontal line. Now, at a slightly higher temperature T, $S_o(T) \geqslant S_1(T) \geqslant S_2(T) \geqslant \cdots$ for $n < \xi(T)$. $S_n(T) \approx 0$ for $n > \xi(T)$. Hence $\alpha_o/kT \geqslant \alpha_1/kT \geqslant \alpha_2/kT \geqslant \cdots$ within the correlation length. However, since $T \gtrsim T_\xi$, $\alpha_o/kT \leqslant \alpha_o/kT_\xi$. Thus for $n < \xi(T)$, i.e., within the correlation volume at temperature T, $\alpha_n/kT \leqslant \alpha_n/kT_\xi$, and $S_n(T) \leqslant S_n(T_\xi)$. As it is known from experiment that $T_\xi = T_c \approx T_\rho$, and $S(T_\rho) \simeq 0.43$ in the Maier-Saupe theory, we find $S_n(T) \leqslant 0.43$ for $n < \xi(T)$. Or $S \approx 0.43$ throughout the correlation volume under our uniform-order approximation. Using this result in Eq. (10), we obtain in the Maier-Saupe theory:

$$\int \langle S(0)S(r)\rangle dV$$

$$= \frac{kT}{2\rho} \frac{1}{\frac{-A_o}{2} + kT\{\frac{\ln[C(0.43)/4\pi]}{(0.43)^2} - a(0.43)0.43\}}$$

$$= \frac{kT}{2\rho A'(T-T_\xi)} , \qquad (11)$$

where

$$2\rho A' = 2\rho k\{\frac{\ln[C(0.43)/4\pi]}{(0.43)^2} - a(0.43)0.43\}$$

$$\simeq 4.4\rho k \simeq 1.2 \times 10^6 \text{erg cm}^{-3}\text{K}^{-1} \qquad (12)$$

with ρ taken at the typical value $\frac{1}{300} \times 6 \times 10^{23}$ cm^{-3}. Our earlier work[3] indicated that the incorporation of spatial short-range correlation in an orientational mean field theory results in a temperature dependent A_o and a factor of about 0.3 for PAA (or 0.25 for MBBA) in the denominator of Eq.(11), or on the right hand side of Eq. (12). Thus our estimate compares well with e.g. the known value of 3.1×10^5 erg cm^{-3}K^{-1} determined for MBBA.[6] An equally interesting quantity is T_ρ-T_ξ :

$$T_\rho-T_\xi = \frac{\rho F(0.43,T_\rho)}{A'} = \frac{F(0.43,T_\rho)}{2.2k} = 0. \qquad (13)$$

Since the choice of S=0.43 is not exact, let us look at T_ρ-T_ξ for S ranging from say 0.42 to 0.44 to obtain a feel of the uncertainty. We find that T_ρ serves as an upper limit to T_ξ, deviating from the latter never by more than 0.2°C. In Ref. 3, we determined T_c-T at (2.6-3.4)°C for PAA and (0.8-1.0)°C for MBBA. In comparison to the experimental values of 3.3°C and 0.8°C respectively for T_c-T_ξ, we find the agreement totally satisfactory.

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