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Application of the Landau approximation to the nematic phase of liquid crystals

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New accurate diamagnetic measurements of the order parameter, just below the nematic-isotropic transition temperature T_c, are given for two nematic liquid crystals. The variations with temperature of the order parameter are described well by theory based on the Landau expansion of the free energy. The subsequent determinations of $T_c - T^*$ and the latent heat are in good agreement with values obtained by an independent way.

The nematic-isotropic transition is of first order, but weak.[1] This first-order character has been indicated by different statistical theories[2,3] which give only a qualitative description of the nematic phase. The mean-field theory of Maïer and Saupe[4] also predicts a first-order transition, and leads to a better evaluation of the amount of order S; but the universal function $S(T/T_c)$, T_c being the transition temperature, departs from the experimental results, especially in the vicinity of T_c. These approaches are all unable to predict the important pretransitional phenomena observed in the isotropic phase. This is not surprising, because these statistical theories are very simple, with essentially only one kind of force being retained: steric repulsions in Onsager's theory,[2] and Van der Waals forces in Maïer and Saupe's approach.[4] A more realistic treatment should take into account both energetic attractions and steric repulsions which appear to have comparable importance.[5]

In the absence of such a theory, the Landau approximation (expansion of the free energy in terms of an order parameter[6]) yields a phenomenological approach of great interest. Thus, de Gennes[1] has shown through symmetry considerations that the nematic-isotropic transition is of first order. Moreover, he predicted various pretransitional phenomena in the isotropic phase. The latter theory has been verified with considerable success: The Cotton-Mouton constant,[7-9] the Kerr constant,[10-13] the light scattering intensity, and the relaxation time for fluctuations of the order parameter[7] all vary like $(T - T^*)^{-1}$ in a certain temperature range above T_c. If the transition were of second order (no third-order term in the free-energy expansion), the transition temperature would be T^*. As T^* is very near T_c ($T_c - T^* \simeq 1\,^\circ\mathrm{C}$) and as the latent heat of transition has low values ($L \sim 1\ \mathrm{J\,cm^{-3}}$), the transition is said to be weakly first order or sometimes "almost second order."[14] The agreement between experiment and theory in the isotropic phase suggests the application of the Landau theory to the nematic phase ($T < T_c$). Before examining this attempt, it is convenient to discuss the somewhat unexpected success of the Landau theory in the isotropic phase. It is well known that, for most critical phenomena, such a mean-field theory fails, because the effects of large fluctuations are not taken into account. Indeed, Stinson and Litster[7] have estimated for the nematic-isotropic transition a temperature range $T_1 - T_c < 1\,^\circ\mathrm{C}$ for which departures from the $(T - T^*)^{-1}$ law occur. We may then conclude that the Landau theory applies when

$$\epsilon = (T - T^*)/T^* \gtrsim 5 \times 10^{-3}.$$

Quantitative application of the Landau approximation to the nematic phase has, to our knowledge, never been successfully attempted, although one condition required for the validity of a mean-field theory is fulfilled: In the nematic phase, the fluctuations of the magnitude of S are weak, the main effect being related to orientational fluctuations of the optic axis.[1] However, fundamental objection to the validity of applying the Landau theory arises because the power-series expansion is generally truncated at a level for which the series has not nearly converged. Keeping this fact in mind, we nevertheless attempted to extend the quantitative analysis to the nematic phase, taking for the free energy F the expression retained by de Gennes[1]:

$$F - F_0 = \tfrac{1}{2}a(T)S^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}cS^4, \tag{1}$$

where S stands for the amount of order; here $a(T) = \alpha(T - T^*)$ and the coefficients α, b, and c are assumed to be temperature independent. Minimizing the free energy with respect to S, we derive the following law in the nematic phase:

$$\frac{3}{2}\frac{S}{S_c} - \left(\frac{S}{S_c}\right)^2 = \frac{1}{2}\frac{T - T^*}{T_c - T^*} \qquad (2)$$

with $S_c = 2b/3c = 3\alpha(T_c - T^*)/b$, S_c being the value at T_c. We focus our interest on two topics: (i) the variation of the order parameter with temperature and (ii) the determination of T^*.

The way for this study to obtain accurate experimental values of the order parameter was through careful measurements of the diamagnetic anisotropy[15,16] $\Delta\chi$ using a translation balance.[17] This was achieved by first evacuating the samples and the containers. During the experiment, the sample and the balance device were placed under a stainless-steel bell, and the measurements were made under a controlled atmosphere of helium, the pressure of which was 2 Torr. Such experimental precautions allow us to have no convection current, and most importantly to have no variations of T_c during the course of the experiment. The temperature was controlled to better than 0.03 °C, which permitted a very accurate determination of the variations, with temperature, of the diamagnetic anisotropy in the nematic phase. Two very pure compounds, the purity of which was controlled by chromatography in gaseous phase, were tested: methoxybenzylidene butylaniline (MBBA) and heptyl biphenyl nitrile (HBN).

The results are plotted (Fig. 1) as variations with temperature of the amount of order $S = \Delta\chi/\Delta\chi_0$, $\Delta\chi_0$ being the diamagnetic anisotropy of the oriented vitreous phase, obtained by quenching in liquid nitrogen a nematic monocrystal.[16]

In order to test whether the experimental results satisfactorily follow the law expressed by (2), we seek the quadratic form in S:

$$Y = a_2S^2 + a_1S + a_0 \qquad (3)$$

which approaches the n experimental dots. This is performed by minimizing the expression

$$Z = \sum_1^n \left(a_2S^2 + a_1S + a_0 - \frac{1}{2}\frac{T - T^*}{T_c - T^*}\right)^2 \qquad (4)$$

with respect to the coefficients a_i ($i = 0$, 1, and 2). In order to identify Y with the left-hand side of (2), we must have

$$a_0 = 0, \quad S_{c_1} = +\tfrac{3}{2}(a_1)^{-1}, \quad S_{c_1} = (-a_2)^{-1/2}$$

which give two independent conditions, with only one parameter T^* to adjust. The requirement $S_{c_1} = S_{c_2}$ leads to an accurate determination of T^* $[d(S_{c_1} - S_{c_2})/dT^* \simeq 0.15$ per °C in the vicinity of the solution $T^*]$. With this T^* value, the other condition $a_0 = 0$ is satisfactorily fulfilled as $a_0/a_1 < 4 \times 10^{-4}$ (see Table I). This means that the law (2) accounts very well for the experimental results. Further indications are given by the low rms departure from the best approximation (see Table I) and by an examination of Fig. 1. Also, the present determination of T^* (see Table I) agrees very well with previous independent results obtained from the pretransitional study of Cotton-Mouton and Kerr effects which gave $T_c - T^* = 0.7 \pm 0.1$ °C and 0.9 ± 0.1 °C, respectively, for MBBA and HBN.[9,11-13]

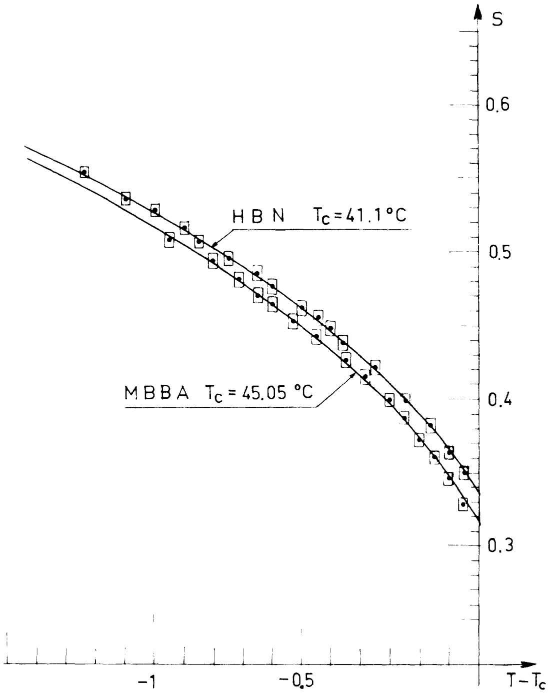

FIG. 1. Variations with temperature of the amount of order $S = \Delta\chi/\Delta\chi_0$ for HBN and MBBA. Solid line represents the best approximation; ⊡, experimental dots with their uncertainties.

The main point to be discussed concerns the

TABLE I. Results obtained from the curve fitting of the experimental measurements.

	MBBA	HBN
T_c (°C)	45.05 ± 0.03	41.10 ± 0.03
T^* (°C)	44.32 ± 0.11	40.20 ± 0.11
$T_c - T^*$	0.73 ± 0.08	0.90 ± 0.08
S_c	0.312	0.335
Standard S deviation	3.7×10^{-3}	2.3×10^{-3}
a_0	1.9×10^{-3}	6.6×10^{-4}
a_1	4.81	4.48
a_2	−10.28	−8.91
a_0/a_1	3.95×10^{-4}	1.48×10^{-4}
$L = \frac{1}{2}\alpha S_c^2 T_c$ (J cm^{-3})	1.43	3.30

truncation of terms of powers higher than 4. It is certain that such terms might be taken into account in any attempt to apply a truncated expansion of F to the whole nematic range. Indeed, we obtain the above satisfactory results only when the retained experimental dots correspond to temperatures ranging between approximately $T_c - 1.5$ °C and T_c. Enlarging this interval leads to results more and more inaccurate and also unrealistic (for instance S_c increases up to a value $\simeq 0.5$). However, when the fitting is applied to the rather narrow temperature range of about 1.5 °C, the consistency of the different accurate results appears not to be fortuitous. This is reenforced by the estimation of the latent heat of transition $L = (\frac{1}{2}\alpha)T_cS_c^2$. The results obtained (see Table I) using for α the mean of the values deduced from Kerr- and Cotton-Mouton-constant measurements in the isotropic phase[18] do not significantly differ from the experimental determinations $L = 1.5$ J cm^{-3} for MBBA[7] and $L = 3.5 \pm 0.2$ J cm^{-3} for HBN.[19]

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