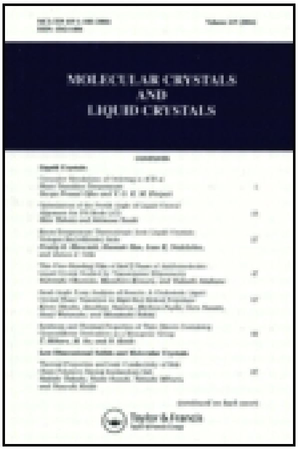

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Validity of the Landau Approximation in the Nematic Phase

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Validity of the Landau Approximation in the Nematic Phase

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The Landau approximation is known to give a good description of the pretransitional phenomena in the isotropic phase of nematic liquid crystals. We prove that, in the nematic phase too, just below the nematic–isotropic transition, the variations with temperature of the order parameter Q are well described by the theory based on the Landau expansion of the free energy F. The coefficients of the expansion of F are determined and the variations of F with Q are given for two nematic liquid crystals. The calculated values of $T_c - T^*$ and of the latent heats are in good agreement with the values obtained by independent way.

The present statistical theories of the nematic phase which predict the nematic-isotropic transition to be first-order, are nevertheless unable to provide a good description of the phenomena near the transition temperature T_c, i.e. the variations of the order parameter just below T_c and the pretransitional phenomena above T_c.

In the absence of a satisfactory statistical theory, the Landau approximation based on the expansion of the free energy in terms of the order parameter, yields a phenomenological approach of great interest. This approach also leads to the first-order character for the nematic ⇄ isotropic transition[1] and further shows how the latter can be considered an "almost second order" one.[2,3]

Using the Landau approximation, De Gennes[2] predicted the temperature behaviour laws for various pretransitional phenomena in the isotropic phase. These predictions have been verified with considerable success for the Kerr effect,[4,5] the Cotton–Mouton effect,[6,8] the light scattering and the relaxation time for fluctuations of the order parameter[6] which all exhibit a $(T - T^*)^{-1}$ variation law in a certain temperature range (T^* would be the transition temperature if the transition were second-order).

It seems natural to examine whether or not the Landau type treatment which successfully accounts for the pretransitional phenomena also applies to the nematic phase ($T < T_c$). De Gennes[2] indicates that the approximation only yields a qualitative description of the nematic phase. We show below that the description takes quantitative meaning provided that the temperature range below T_c is sufficiently restricted.[9]

For the free energy F we take the expression

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

where S stands for the amount of order and a, b, c are assumed to be temperature independent. Minimizing the free energy with respect to $S(\partial F/\partial S = 0)$ and expressing that at $T = T_c$ both isotropic ($S = 0$) and nematic ($S = S_c$) phases correspond to the same free energy, we obtain

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

with $S_c = 2b/3c = 3a(T_c - T^*)/b$. Thus with the Landau approximation (1) for the free energy, we can derive law (2) for the variations of the order parameter with temperature.

In order to examine whether this law applied, we need accurate experimental values of S versus T. These have been obtained by measuring the diamagnetic anisotropy $\Delta\chi$ using a translation balance.[10] Different experimental precautions[9] ensure that accurate measurements were made upon very pure samples, the properties of which did not vary during the course of the experiment. The temperature resolution was better than 0.03 K. The results for the two nematogens MBBA and HBN appear on Figure 1 in the form of $S = \Delta\chi/\Delta\chi_0$, $\Delta\chi_0$ being the diamagnetic anisotropy of the oriented vitreous phase obtained by quenching a nematic monocrystal in liquid nitrogen.

In order to compare the experimental data with law (2) and simultaneously to obtain T^* and S_c which are not directly given by experiment, we can apply a least-meansquare procedure either on the linear T distribution or on the quadratic S distribution. We choose the second way, which is more instructive, and minimized the expression

$$Z = \sum_{1}^{n}\left[a_2S^2 + a_1S + a_0 - \frac{1}{2}\frac{T - T^*}{T_c - T^*}\right]^2$$

with respect to the coefficients a_i ($i = 0, 1, 2$), which leads to their determination. The law (2) will be verified only if the two following conditions are fulfilled:

$$9a_2 + 4a_1^2 = 0, \qquad a_0 = 0$$

T_c being known, there is only one parameter, T^*, to be determined. We adjust the T^* value so as the first condition to be satisfied. It then appears that the second independent condition is also satisfied ($a_0/a_1 < 4\ 10^{-4}$, see Table I); this clearly shows that the order parameter varies as indicated by (2). We can further remark that the r.m.s. departure of the experimental points from the best approximation is low (Figure 1 and Table I) and that the present determination of T^* (see Table II) very well agrees with that obtained from the pretransitional phenomena.[5,8] Therefore it appears that the Landau expansion of free energy provides a description for both the nematic and isotropic phases in the vicinity of the transition point.

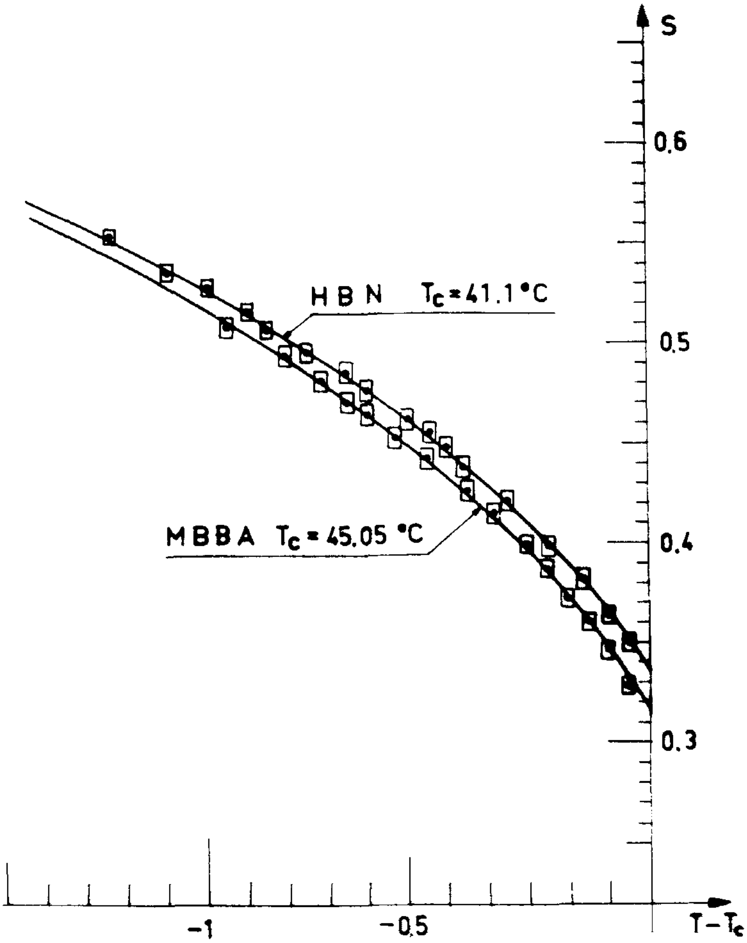

FIGURE 1 The variations, versus temperature, of the order parameter just below T_c.

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
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	$3.95\ 10^{-4}$	$1.48\ 10^{-4}$
Standard S deviation	$3.7\ 10^{-3}$	$2.3\ 10^{-3}$
S_c	0.312	0.335

TABLE II

Comparison of the present determination of $T_c - T^*$ and L with the values obtained by independent ways

	MBBA	HBN
$T_c - T^*$ from data in the nematic phase	0.73 ± 0.08	0.90 ± 0.08
$T_c - T^*$ from pretransitional phenomena	0.7 ± 0.1[a]	0.9 ± 0.1[a]
L obtained from the Landau approximation (J cm^{-3})	1.43	3.30
Direct measurement of the latent heat (J cm^{-3})	1.5[b]	3.50 ± 0.2[c]

[a] From Ref. 5.
[b] From Ref. 6.
[c] From Ref. 9.

This result is somewhat unexpected because there is a fundamental objection against the validity of applying an expansion like (1) to the nematic phase: as S takes finite values, the series is truncated at a level for which it presumably has not nearly converged. We may observe that a satisfactory agreement only occurs when retaining experimental points in a rather narrow temperature range of about 1.5 K below T_c.[9] Expression (1) fails to provide a description of the whole nematic range which would require a much less drastic truncation. Near T_c however, perhaps due to compensation for the first neglected terms, (1) leads to a satisfactory quantitative description.

We can have a further confirmation through comparison of the calculated and measured latent heats of transition. The calculation of $L = (1/2)aT_cS_c^2$ requires the knowledge of the value of a. The latter has been determined from the measurements of the Kerr B and Cotton–Mouton C coefficients in the isotropic phase, which obey the laws:[11]

$$\frac{1}{B\lambda} = \frac{3a(T - T^*)}{\Delta n_0 \Delta\varepsilon_0}, \qquad \frac{1}{C\lambda} = \frac{3a(T - T^*)}{\Delta n_0 \Delta\chi_0}$$

where λ stands for the light wave-length, Δn_0 and $\Delta\varepsilon_0$ for respectively the refractive and dielectic anisotropies for $S = 1$. A previous experimental verification of the above laws gives the following estimations of a:[11]

$$a \simeq 0.0925\ \mathrm{J\ cm^{-3}\ K^{-1}} \quad \text{for MBBA}$$

$$a \simeq 0.187\ \mathrm{J\ cm^{-3}\ K^{-1}} \quad \text{for HBN}$$

which leads to the calculated L values given in Table II. Comparison with the experimental determinations (Table II) of the latent heat does not show any significant difference. Consequently, it appears that terms of power

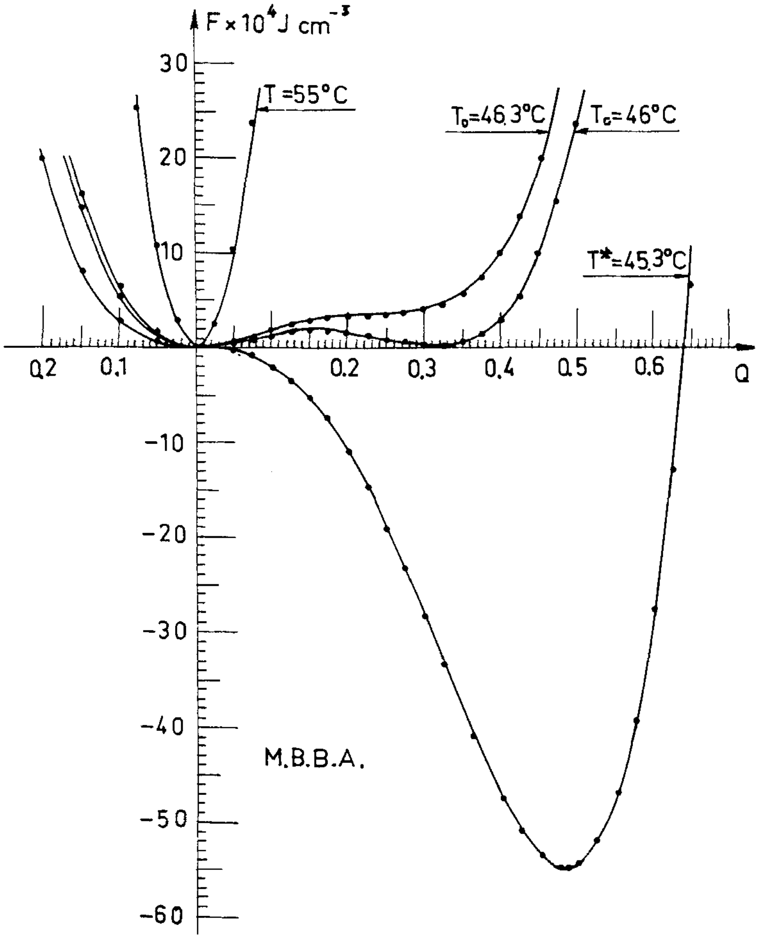

FIGURE 2 The free energy as a function of the order parameter for MBBA.

higher than the fourth in the expansion of F only introduce a negligible contribution, at least for $T = T_c$.

As every coefficient appearing in (1) has been determined,[11] we can represent the variations with S of the free energy F for different temperatures (Figures 2 and 3).

The consistency of the different accurate obtained results allows us to conclude that the theory based on the Landau approximation leads to a

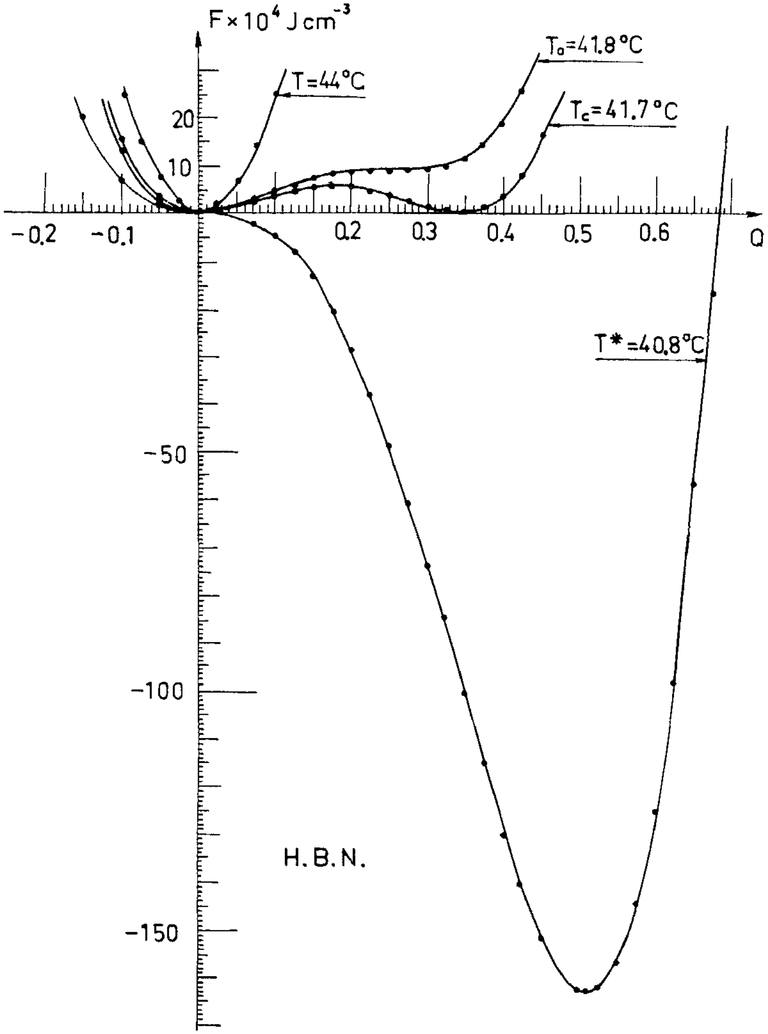

FIGURE 3 The free energy as a function of the order parameter for HBN.

good quantitative description of the phenomena in the vicinity of the transition temperature. In the isotropic phase, the predictions seem to be valid up to about 15 K above T_c[12] with the exception, of course, of a narrow transitional range just above T_c. In the nematic phase, the temperature interval where the order parameter variations are well described, is narrower (about 1.5 K for the studied nematics). Nevertheless, this can be understood because of the fact that the strongest variations of the order parameter with temperature take place in this interval.

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