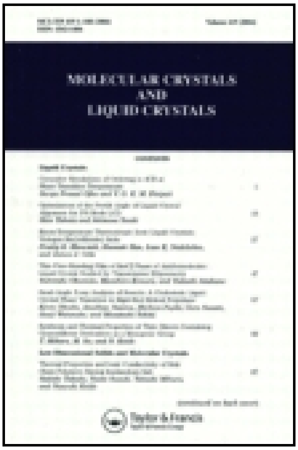

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Field-Induced Order in Nematic Liquid Crystals

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Field-Induced Order in Nematic Liquid Crystals

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The effect of an external magnetic field on the orientational order of a nematic liquid crystal has been examined using both Landau-de Gennes and Maier-Saupe theories. In the Maier-Saupe approach a rotationally invariant form of the pseudo-potential is introduced, which in the absence of an external field leads to three degenerate isomorphic solutions for the order parameter, corresponding to alignment along three principal axes; a similar result is obtainable from the Landau-de Gennes theory. Application of a magnetic field lifts the degeneracy of these solutions, and for materials having a positive diamagnetic susceptibility anisotropy, the uniaxial solution with alignment along the field direction is always energetically favorable. For materials with a negative susceptibility anisotropy, a biaxial solution minimizes the free energy at low temperatures, but on increasing the temperature there is a transition from a biaxial phase to an uniaxial phase. The field dependence of the transition temperatures is evaluated, and for positive materials there is a critical field, corresponding to a second order transition above which the nematic and isotropic phases are indistinguishable. A contrasting behavior is predicted for negative materials, and above a certain critical field the biaxial/uniaxial transition changes from first order to second order. For weakly ordered systems it is shown that the Landau-de Gennes expression for the free energy is identical to that obtained from the Maier-Saupe theory. However, for more ordered systems, the results of the two approaches differ, and in particular the Maier-Saupe theory predicts a susceptibility divergence temperature T^* which increases with applied field, in agreement with recent experiments.

INTRODUCTION

Liquid crystals exhibit a divergence of a number of physical properties as the nematic-isotropic transition temperature is approached. The intensity of scattered light, the electric field induced birefringence and the magnetic field induced birefringence all show such pretransitional divergences. Experimental measurements of these properties are usually analyzed in terms of the Landau-de Gennes (LdG) mean field theory of the nematic-isotropic transition. Recent light-scattering,[1,2] Kerr effect[3] and Cotton-Mouton effect[4] measurements indicate that experimental results differ from the predictions of this theory at temperatures close to the transition and at high temperatures. The discrepancy between experiment and theory may be due to the inappropriateness of the mean field approximation near the weakly first order nematic-isotropic transition,[5] or it may, at least in part, be due to unwarranted assumptions implicit in the LdG theory in the presence of fields.

In the usual formulation of the LdG theory, in the absence of externally applied fields the Landau free energy is expanded as a power series in a tensor order parameter. The effects of electric or magnetic fields are taken into account by including an additional energy term in the free energy; the expansion coefficients are assumed to be field independent.[6] Direct arguments regarding the field dependence of the expansion coefficients are difficult, since the LdG formulation is primarily phenomenological and the physical significance of the coefficients is not well established. It is possible, however, to obtain a free energy expansion in the mean field approximation from a single particle pseudopotential,[7,8,9] and thus obtain information about the field and temperature dependence of the expansion coefficients.

Although most nematic materials exhibit uniaxial symmetry, materials with biaxial symmetry have been found,[10] and uniaxial materials with a negative dielectric anisotropy are expected to show biaxiality in the presence of an applied electric field.[11] In this paper we obtain two expressions for the free energy of nematics in the presence of an applied magnetic field from a single particle pseudopotential, and compare the expansion coefficients with those of the LdG theory. In order to allow for the possibility of field-induced biaxiality, a rotationally invariant form of the Maier-Saupe (MS) pseudopotential is introduced; the resulting solutions for field induced order suggest that the LdG theory does not adequately describe the effects of external fields.

THEORY

1. The Landau-de Gennes free energy

The LdG expansion of the free energy density in terms of the traceless order parameter $Q_{\alpha\beta}$ is

$$\mathcal{F}_1 = \mathcal{F}_1^\circ + \frac{1}{3}a_1 Q_{\alpha\beta}Q_{\beta\alpha} - \frac{4}{9}b_1 Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{1}{9}c_1 Q^2_{\alpha\beta}Q^2_{\gamma\delta} \tag{1}$$

where $Q_{\alpha\beta}$ may be defined in terms of any second rank tensor property $A_{\alpha\beta}$ as

$$Q_{\alpha\beta} = \frac{1}{2}(3A_{\alpha\beta} - A_{\gamma\gamma}\delta_{\alpha\beta})/\Delta A^{(0)}$$

where $\Delta A^{(0)}$ is the anisotropy of the tensor property for a perfectly aligned uniaxial sample, and $A_{\gamma\gamma}$ is three times the value of $A_{\alpha\beta}$ in the isotropic phase. The effects of an external magnetic field **H** are taken into account by the inclusion of the additional term $-(1/3)\ \Delta\chi^{(0)}Q_{\alpha\beta}H_\alpha H_\beta$ in Eq. 1, where$\Delta\chi^{(0)}$ is the anisotropy of the magnetic susceptibility. It is usually assumed[6] that $a_1 = a_{0_1}(T - T^*)$ where T is the temperature, and that a_{0_1}, T^*, b_1 and c_1 are constants. Since $Q_{\alpha\beta}$ is real symmetric, it is possible to find a coordinate system where $Q_{\alpha\beta}$ is diagonal. In this principal axis system, if the order parameters P and Q are defined by $Q_{xx} = -(1/2)(Q - P)$, $Q_{yy} = -(1/2)(Q + P)$ and $Q_{zz} = Q$, the free energy becomes

$$\begin{aligned}\mathcal{F}_1 = \mathcal{F}_1^0 &+ \frac{a_1}{2}\left(Q^2 + \frac{P^2}{3}\right) - \frac{b_1}{3}(Q^3 - QP^2) + \frac{c_1}{4}\left(Q^4 + \frac{2}{3}Q^2P^2 + \frac{P^4}{9}\right)\\ &+ \frac{\Delta\chi^{(0)}}{3}H^2\left[\frac{1}{2}(Q - P)\sin^2\theta_H\cos^2\phi_H\right.\\ &\left.+ \frac{1}{2}(Q + P)\sin^2\theta_H\sin^2\phi_H - Q\cos^2\theta_H\right]\end{aligned} \tag{2}$$

where θ_H and ϕ_H are the polar and aximuthal angles of **H**. To determine the direction of **H** in the principal axis system, it is necessary to minimize Eq. 2 with respect to θ_H and ϕ_H. This gives $\theta_H = 0$ or $\theta_H = \pi/2$ and $\phi_H = 0$ or $\pi/2$, that is, **H** is along one of the principal axes. It is worth noting that this result does not hold in general if an electric and a magnetic field are both present, or in the presence of a surface anchoring term. Finally, the free energy becomes

$$\begin{aligned}\mathcal{F}_1 = \mathcal{F}_1^0 &+ \frac{a_{0_1}}{2}(T - T^*)\left(Q^2 + \frac{P^2}{3}\right) - \frac{b_1}{3}(Q^3 - QP^2)\\ &+ \frac{c_1}{4}\left(Q^4 + \frac{2}{3}Q^2P^2 + \frac{P^4}{9}\right)\\ &+ \frac{\Delta\chi^{(0)}}{3}H^2\left\{\begin{matrix}\frac{1}{2}(Q - P) & \text{if} \quad H = H_x, & \text{or}\\ -Q & \text{if} \quad H = H_z & \end{matrix}\right\}\end{aligned} \tag{3}$$

If the field is along the y-axis instead of x, that is if $H = H_y$, only the sign of P changes in Eq. 3, hence this case will not be considered separately. The equilibrium values of Q and P are those which minimize the free energy.

2. The Maier-Saupe free energy

In a fluid of axially symmetric rigid molecules with pair-wise additive interaction and number density ρ, the relation between the single $\mathbf{r}_{12}$ particle pseudopotential $\varepsilon(\hat{n})$ and the intermolecular potential $W(\mathbf{r}_{12}, \hat{n}_i, \hat{n}_j)$ is exactly[12]

$$\frac{\partial}{\partial n_{1_\alpha}} \varepsilon(\hat{n}_1) = \rho \int \frac{\partial}{\partial n_{1_\alpha}} W(\mathbf{r}_{12}, \hat{n}_1, \hat{n}_2) g(\mathbf{r}_{12}, \hat{n}_1, \hat{n}_2) f(\hat{n}_2)\, d^3\mathbf{r}_{12}\, d^2\hat{n}_2 \tag{4}$$

where $\hat{n}_i$ is a unit vector with components n_{i_α} along the symmetry axis of the i^{th} molecule, $g(\mathbf{r}_{12}, \hat{n}_1, \hat{n}_2)$ is the pair correlation function and $f(\hat{n})$ is the single particle orientational distribution function. The mean field approximation consists of ignoring the dependence of the pair correlation on molecular orientation, which enables the integration of Eq. 4. This gives

$$\varepsilon(\hat{n}_1) = \text{const.} + \rho \int W(\mathbf{r}_{12}, \hat{n}_1, \hat{n}_2) g(\mathbf{r}_{12})\, d^3\mathbf{r}_{12} f(\hat{n}_2)\, d^2\hat{n}_2 \tag{5}$$

The MS pseudopotential is obtained by truncating the expansion

$$\rho \int W(\mathbf{r}_{12}, \hat{n}_1, \hat{n}_2) g(\mathbf{r}_{12})\, d^3\mathbf{r}_{12} = U_0 - U P_2(\hat{n}_1 \cdot \hat{n}_2) + \ldots$$

in Legendre polynomials after the second term. It is useful to define $\sigma_{i_{\alpha\beta}} = (1/2)(3n_{i_\alpha} n_{i_\beta} - \delta_{\alpha\beta})$ and $Q_{\alpha\beta} = \langle \sigma_{\alpha\beta} \rangle$ where $\langle\ \rangle$ denotes the ensemble averaged value; then $P_2(\hat{n}_1 \cdot \hat{n}_2) = (2/3)\sigma_{1_{\alpha\beta}} \sigma_{2_{\beta\alpha}}$ and expansion of $f(\hat{n})$ in spherical harmonics and keeping terms to second order yields

$$f(\hat{n}) = 1 + \frac{10}{3} Q_{\alpha\beta} \sigma_{\beta\alpha} \tag{6}$$

Substitution into Eq. 5 and integration gives

$$\varepsilon(\hat{n}) = \varepsilon_0 - \frac{2}{3} U Q_{\alpha\beta} \sigma_{\beta\alpha} + \frac{1}{3} U Q_{\alpha\beta} Q_{\beta\alpha} \tag{7}$$

The constant of integration in Eq. 5 has been determined from the requirement that the average orientational energy per molecule equal one half of the orientational energy per pair. Eq. 7 is the rotationally invariant form of the MS pseudopotential, and in a principal axis system, in the presence of an applied field, becomes

$$\varepsilon(\theta, \phi) = \varepsilon_0 - UQ\frac{1}{2}(3\cos^2\theta - 1) - \frac{UP}{3}\frac{3}{2}\sin^2\theta\cos 2\phi + \frac{U}{2}\left(Q^2 + \frac{P^2}{3}\right) - \frac{\Delta\kappa}{3}\sigma_{\alpha\beta}H_\beta H_\alpha \qquad (8)$$

where $Q = \langle(1/2)(3\cos^2\theta - 1)\rangle$ and $P = \langle(3/2)\sin^2\theta\cos 2\phi\rangle$, θ and ϕ are the polar and azimuthal angles of $\hat{n}$ and the last term on the right-hand side of Eq. 8 is the interaction energy of the molecule with the externally applied magnetic field **H**; $\Delta\kappa = \Delta\chi^{(0)}/\rho$ is the anisotropy of the molecular diamagnetic susceptibility. If the free energy density of the system is the number density times the free energy per molecule, then

$$\mathfrak{F}_2 = -\rho kT \ln \frac{1}{4\pi}\int e^{\frac{-\varepsilon(\theta,\phi)}{kT}}\, d\Omega \qquad (9)$$

where $d\Omega$ is the element of solid angle. In the absence of a field, the free energy density $\mathfrak{F}_2$ is minimized if either $P = 0$ and $Q = Q_{\mathrm{MS}}$, the usual MS result, or if $P = \pm 3Q$. These three uniaxial solutions are isomorphic under transposition of the principal axes and are degenerate in the free energy; they correspond to alignment of the nematic director along the three principal axes. An externally applied field **H** perturbs these solutions and lifts the degeneracy; the equilibrium configuration of the system corresponds to that solution which is the global minimum of the free energy density $\mathfrak{F}_2$. The direction of **H** in the principal axis system is determined by minimizing Eq. 9 with respect to the direction of **H**; as before, this gives the result that **H** is along one of the principal axes. The free energy density $\mathfrak{F}_2$ of Eq. 9 can be expanded as a power series in the order parameters P and Q to give

$$\begin{aligned}\mathfrak{F}_2 = \mathfrak{F}_2^0 + \frac{T^*}{T}\Bigg\{&\frac{a_{0_2}}{2}\left[\left(T - T^*\left(1 + \frac{2\eta}{7}\right)\right)Q^2 + \left(T - T^*\left(1 - \frac{2\eta}{7}\right)\right)\frac{P^2}{3}\right] \\ &- \frac{b_2}{3}\left[\left(1 - \frac{3\eta}{5}\right)Q^3 - \left(1 + \frac{\eta}{5}\right)QP^2\right] \\ &+ \frac{c_2}{4}\left[\left(1 + \frac{20}{11}\eta\right)Q^4 + (1 - 3\eta)\frac{2}{3}Q^2P^2 + \left(1 + \frac{103}{54}\eta\right)\frac{P^4}{9}\right] \\ &+ \frac{\Delta\chi^{(0)}}{3}H^2\begin{Bmatrix}\frac{1}{2}(Q - P) & \text{if} \quad H = H_x, & \text{or} \\ -Q & \text{if} \quad H = H_z & \end{Bmatrix}\Bigg\}\end{aligned} \qquad (10)$$

where $T^* = U/5k$, $a_{0_2} = 5k\rho$, $b_2 = U^2\rho/7kT$, $c_2 = U^3\rho/35(kT)^2$ and $\eta = \Delta\kappa H^2/3kT$; the equilibrium values of P and Q are those which minimize $\mathfrak{F}_2$.

3. Free energy of a weakly ordered system

An alternate expansion of the free energy is obtained if the orientational entropy is expanded in terms of the order parameters. The orientational entropy per molecule is

$$S = -\frac{k}{4\pi}\int f(\hat{n}) \ln f(\hat{n})\, d^2\hat{n} = -k\langle \ln f(\hat{n})\rangle \tag{11}$$

For a weakly ordered system, the expansion of the orientational distribution function in spherical harmonics may be truncated after second order terms to give $f(\hat{n}) = 1 + 10/3\, Q_{\alpha\beta}\sigma_{\beta\alpha}$. In a principal axis system, on expanding the logarithm in Eq. 11 the expression for the entropy becomes

$$S = -k\left\{\frac{5}{2}\left(Q^2 + \frac{P^2}{3}\right) - \frac{25}{21}(Q^3 - QP^2) + \frac{125}{28}\left(Q^4 + \frac{2}{3}Q^2P^2 + \frac{P^4}{9}\right)\right\} \tag{12}$$

The average orientational energy in the presence of a field **H** is

$$\langle\varepsilon\rangle = \varepsilon_0 - \frac{U}{2}\left(Q^2 + \frac{P^2}{3}\right) + \frac{\Delta\kappa}{3}\left\{\frac{1}{2}(Q - P)H_x^2 + \frac{1}{2}(Q + P)H_y^2 - QH_z^2\right\} \tag{13}$$

Since $\mathfrak{F}_3 = \rho(\langle\varepsilon\rangle - TS)$ and again $\mathfrak{F}_3$ is minimized if **H** is along one of the principal axes,

$$\mathfrak{F}_3 = \mathfrak{F}_3^0 + \frac{a_{0_3}}{2}(T - T^*)\left(Q^2 + \frac{P^2}{3}\right) - \frac{b_3}{3}(Q^3 - QP^2) + \frac{c_3}{4}\left(Q^4 + \frac{2}{3}Q^2P^2 + \frac{P^4}{9}\right) + \frac{\Delta\chi^{(0)}}{3}H^2\begin{cases}\frac{1}{2}(Q - P) & \text{if } H = H_x, \quad \text{or} \\ -Q & \text{if } H = H_z\end{cases} \tag{14}$$

where $a_{0_3} = 5k\rho$, $T^* = U/5k$, $b_3 = (25/7)\, kT\rho$ and $c_3 = (125/7)\, kT\rho$.

RESULTS AND DISCUSSION

The free energy expansions of Eqs. 3, 10 and 14 are formally identical in the field free case; the factor T^*/T in Eq. 10 can be eliminated by scaling $\mathfrak{F}_2$. In the presence of a field, the MS free energy density of Eq. 10 is distinguished by the explicit field dependence of the expansion coefficients. Ignoring this field dependence, the equilibrium behavior of the system in all three cases is obtained by minimizing

$$\mathcal{F} = \mathcal{F}^0 + \frac{a}{2}\left(Q^2 + \frac{P^2}{3}\right) - \frac{b}{3}(Q^3 - QP^2) + \frac{c}{4}\left(Q^4 + \frac{2}{3}Q^2P^2 + \frac{P^4}{9}\right) + \frac{\Delta\chi^{(0)}}{3}H^2\left\{\begin{matrix} \frac{1}{2}(Q - P) & \text{if} \quad H = H_x, & \text{or} \\ -Q & \text{if} \quad H = H_z & \end{matrix}\right\} \qquad (15)$$

with respect to Q and P. It is useful to write Eq. 15 in dimensionless form by letting $F = (\mathfrak{F} - \mathfrak{F}_0)4c^3/9b^4$, $\beta = 2ca/3b^2$, $q = Qc/3b$, $p = Pc/3b$ and $\gamma = \Delta\chi^{(0)}H^2c^2/27b^3$, then

$$F = 3\beta\left(q^2 + \frac{p^2}{3}\right) - 4(q^3 - qp^2) + 9\left(q^4 + \frac{2}{3}q^2p^2 + \frac{p^4}{9}\right) + 12\gamma\left\{\begin{matrix} \frac{1}{2}(q - p) & \text{if} \quad H = H_x, & \text{or} \\ -q & \text{if} \quad H = H_z & \end{matrix}\right\} \qquad (16)$$

Setting $\partial F/\partial q = \partial F/\partial p = 0$ results in the uniaxial solution $3q^3 - q^2 + \beta q/2$ *or* $(1/2)\beta q - \gamma = 0$ and $p = 0$ if $H = H_z$, and the biaxial solution $q = (1/2)(-u + v)$ and $p = (1/2)(3u + v)$ where $u = -(1/12)(1 \pm \sqrt{1 - 6\beta - 36\gamma})$ and $v = -3u\sqrt{1 + \gamma/3u^2}$ if $H = H_x$. The biaxial solution appears different than in Ref. 11 since the polar (z) axis has been chosen so as to be always parallel to the nematic director in the absence of a field; the two solutions are isomorphic under transposition of axes. The order parameters q and p as well as the equilibrium free energy F are shown as functions of the scaled reduced temperature β on Figure 1 for positive ($\gamma > 0$) materials, and on Figure 2 for negative ($\gamma < 0$) materials. In the limit as $H \to 0$ ($\gamma \to 0$) the solutions for $H = H_z$ and $H = H_x$ are identical. Application of a field **H** perturbs these solutions as shown on Figures 1 and 2. For positive materials, the uniaxial solution with the

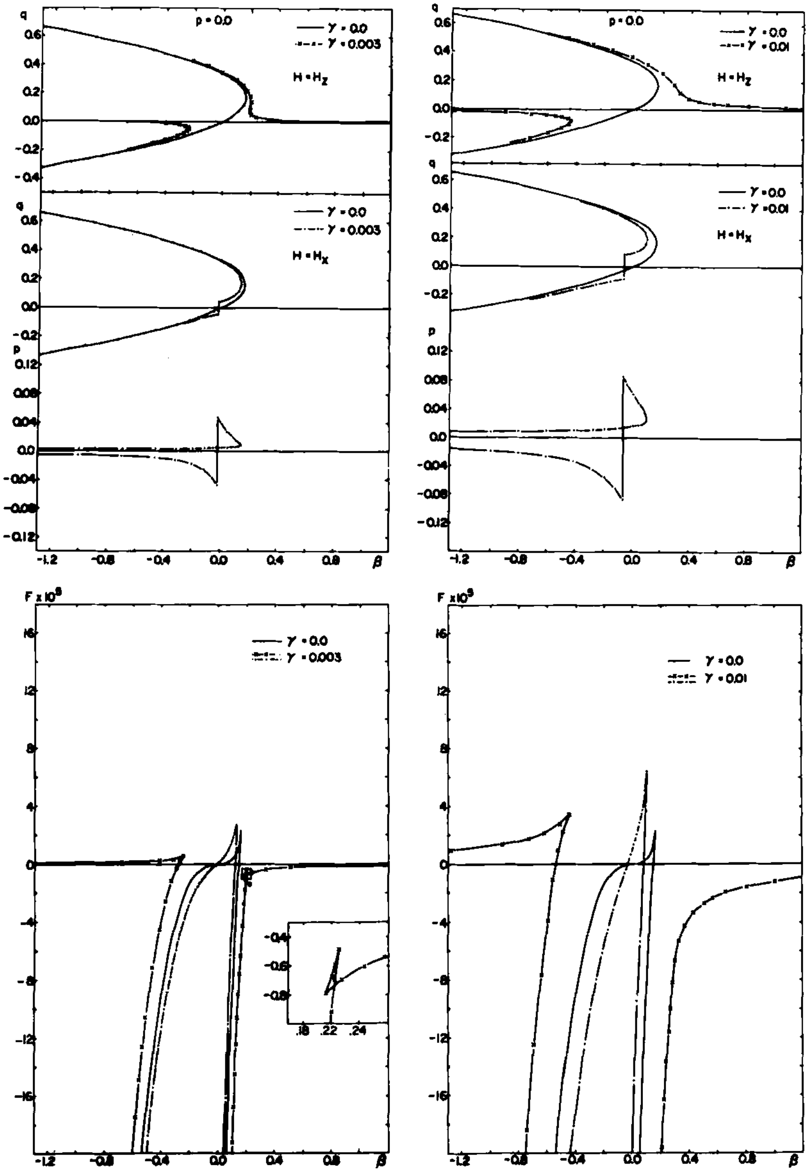

FIGURE 1 Order parameters q and p and free energy F vs $\beta = (2ca_0/3b^2)(T - T^*)$ for positive materials. $H = H_z$ indicates field parallel to the director; $H = H_x$ indicates field perpendicular to director. The point where the transition changes from first to second order is denoted by the sumbol ●, $\gamma = \Delta\chi^{(0)}H^2c^2/27b^3$.

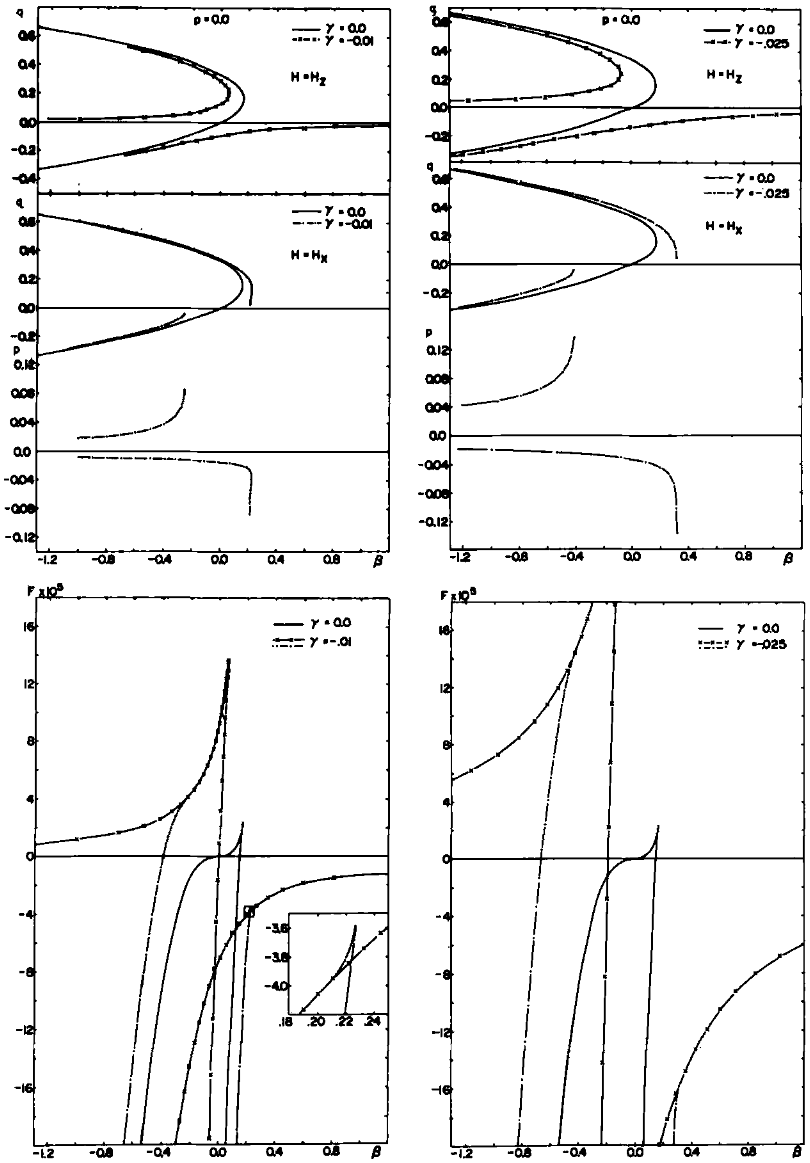

FIGURE 2 Order parameters q and p and free energy F vs $\beta = (2ca_0/3b^2)(T - T^*)$ for negative materials. $H = H_z$ indicates field parallel to the director; $H = H_x$ indicates field perpendicular to director. The point where the transition changes from first to second order is denoted by the symbol •, $\gamma = \Delta\chi^{(0)}H^2c^2/27b^3$.

director parallel to the field is always energetically favorable. The first-order transition temperature is $\beta = 4/27$ in the absence of a field, and it increases with the field until at $\gamma = 1/243$ (corresponding to a magnetic flux density of $B \simeq 3 \times 10^7$ Gauss for 5CB) $\beta = 2/9$ and the transition becomes continuous. For fields in excess of this critical field there is no transition. For negative materials at low temperature the biaxial solution with $q > 0$ corresponding to perpendicular alignment of the director with the field is energetically favorable. At higher temperatures, the free energy is minimized by the uniaxial solution with $q < 0$ and director parallel to the field. The transition becomes second order if $\gamma \leqslant -1/48$; the complete phase diagram is shown in Figure 3.

Since for both positive and negative materials the high-temperature phase is uniaxial, the field induced order at high temperatures is obtained by setting $H = H_z$, $P = 0$ and minimizing $\mathfrak{F}$ with respect to Q. If higher than second order terms are neglected, then this results in

$$Q = \frac{\Delta\chi^{(0)}H^2}{3a_{0_1}(T - T^*)}$$

from the LdG expansion of Eq. 3 while the MS free energy expansion of Eq. 10 which takes into account the field dependence of the expansion coefficients gives rise to

$$Q = \frac{\Delta\chi^{(0)}H^2}{3a_{0_1}(T - T^*_{\mathrm{MS}})}$$

where

$$T^*_{\mathrm{MS}} = T^*\left(1 + \frac{2\Delta\kappa H^2}{21kT}\right)$$

Recent light scattering and Kerr effect measurements[2] indicate that the susceptibility divergence temperature T^* increases with applied electric field; similar behavior is expected in the case of a magnetic field as predicted by the MS theory. The LdG theory predicts that Q^{-1} is approximately a linear function of T, but deviations of both the inverse Cotton-Mouton and Kerr constants from this temperature dependence have been observed near the nematic-isotropic transitions.[4,3] This behavior is at least qualitatively predicted by the MS theory where T^*_{MS} increases with decreasing T, and agreement with experiment is further improved if higher order terms are taken into account. In a recent paper[13] Keyes and Shane measured the Cotton-Mouton constant of MBBA, and showed the temperature dependence of the dimensionless quantity

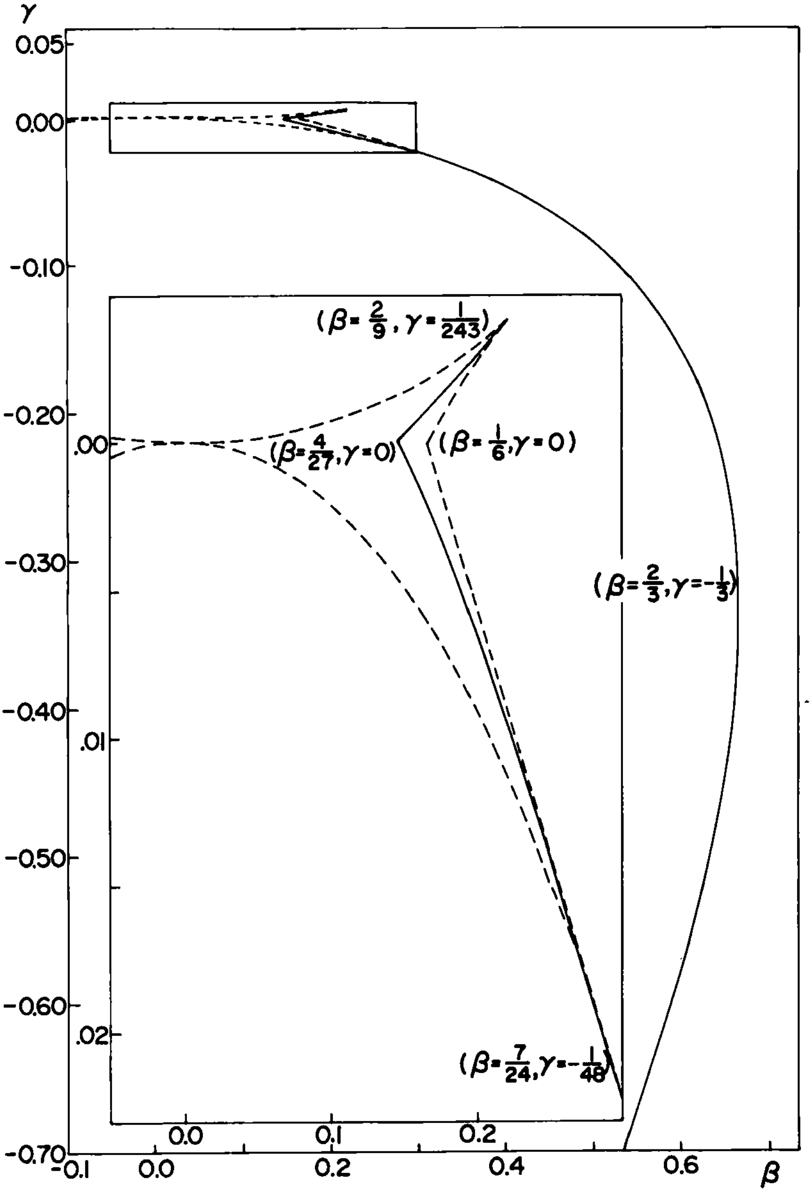

FIGURE 3 Phase diagram. The dashed lines indicate boundaries of the region where metastable states are allowed. $\gamma = \Delta\chi^{(0)}H^2c^2/27b^3$, $\beta = (2ca_0/3b^2)(T - T^*)$.

$$f = \frac{1}{2}h\left(\frac{\partial^2 Q}{\partial h^2}\right)_{h=0} \Big/ \left(\frac{\partial Q}{\partial h}\right)_{h=0}$$

to be $(T - T^*)^{-1.26\pm0.10}$ where $h = \Delta\chi^{(0)}H^2/3$. The LdG theory gives, from Eq. 3,

$$f = \frac{hb}{a_{0_1}^2(T - T^*)^2}$$

whereas the MS free energy expansion gives

$$f = h\left(\frac{b}{a_{0_1}^2(T - T^*)^2} + \frac{2T^*}{7\rho kT(T - T^*)}\right)$$

Although both the LdG and MS theories predict a value of f which is too small by an order of magnitude, the temperature dependence of the MS result, for small b, is in better agreement with experiment.

The significant difference in the predictions of the MS theory and the LdG theory is that the MS model predicts a T^*_{MS} which depends both on applied field and temperature, whereas the LdG T^* does not. Similarity between the LdG free energy and the free energy for a weakly ordered system in Eq. 14 suggests that the difference is caused by the assumption implicit in the LdG theory that the effects of an external field on the orientational entropy can be adequately described by changes in the order parameters alone; this assumption is not warranted in general. Since the MS pseudopotential does not accurately describe the nematic-isotropic transition in the absence of fields, a detailed comparison of theory with experiment has not been attempted. On the basis of the results presented, however, it is anticipated that the free energy expansion approach outlined in this paper based on a more realistic pseudopotential will further provide a better description of experimental measurements of field induced order than the usual LdG formalism.

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