Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 13 Dec 2006.

To cite this article: B. J. Frisken , B. Bergersen & P. Palffy-Muhoray (1987): Phase Behaviour of Nematics in the Presence of Electric and Magnetic Fields, Molecular Crystals and Liquid Crystals, 148:1, 45-59

To link to this article: http://dx.doi.org/10.1080/00268948708071778

Mol. Cryst. Liq. Cryst., 1987, Vol. 148, pp. 45–59
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Printed in the United States of America

Phase Behaviour of Nematics in the Presence of Electric and Magnetic Fields†

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(Received June 30, 1986)

We employ mean field theory to study the phase behaviour of nematics in the presence of arbitrary electric and magnetic fields. A rotationally invariant pseudopotential is used. If the molecules have cylindrical symmetry, the most general situation is equivalent to perpendicular electric and magnetic fields. The numerical calculations are carried out within the Maier-Saupe model, but it is demonstrated how the formalism can be extended to a generalized van der Waals theory in which pressure dependence can also be studied. We consider the cases where the electric and magnetic susceptibility anisotropies are both positive, negative and of opposite sign. Relationships between the responses in these situations are found and predictions are made regarding the field dependence of the order parameters and the transition temperatures.

1. INTRODUCTION

In this paper we employ mean field theory to analyse the phase behaviour of nematics in the presence of both electric and magnetic fields. We will assume throughout that the intermolecular interaction as well as the electric and magnetic properties of the molecules have cylindrical symmetry about the same axis. As we shall see, the general situation in which the fields are oriented in arbitrary directions is then equivalent to one in which one has a magnetic and an electric field oriented along two perpendicular axes. In the presence of two fields the ordering will in general be biaxial, and two order parameters

Research Supported by the Natural Sciences and Engineering Research Council of Canada

†Paper presented at the 11th International Liquid Crystal Conference, Berkeley, CA, 30 June–4 July, 1986.

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which couple simultaneously to both fields are required to describe the nematic ordering.

Previous theoretical work on the biaxial phase behaviour in the presence of external fields has almost exclusively employed a Landau-de Gennes expansion.[1–5] The expansion parameters are in general field dependent[5] and the coefficients will take on different values in different regions of the phase diagram. We wish to concentrate on the global features of the phase diagram, and present numerical results using the Maier-Saupe theory[6] where the field dependence is taken into account self-consistently. We also show how corresponding results can be obtained in a van der Waals theory[7] which incorporates both the attractive and steric parts of the intermolecular interaction.

2. THEORY

a. Maier-Saupe theory

Consider a nematic in the presence of an electric field E and a magnetic field H. The molecules are assumed to be nonpolar and to have cylindrical symmetry. We let n_α be a cartesian component of a unit vector along the symmetry axis of a molecule. We write for the free energy per molecule

$$f = -kT \ln z \tag{1}$$

In the Maier-Saupe theory the partition function, z, can be expressed in terms of a single particle pseudopotential α

$$z = \int d^2\hat{n}\, e^{-\beta\alpha(\hat{n})} \tag{2}$$

where $\beta = 1/kT$ and

$$\alpha(\hat{n}) = -\frac{2}{3}\rho U\, S_{\alpha\beta}(\sigma_{\beta\alpha} - 1/2S_{\beta\alpha}) - D_{\alpha\beta}\sigma_{\beta\alpha} \tag{3}$$

Summation over repeated Greek indices is assumed and the generalized tensor field conjugate to the order parameter tensor is

$$D_{\alpha\beta} = \frac{1}{3}[\Delta x\, H_\alpha H_\beta + \Delta\varepsilon\, E_\alpha E_\beta] \tag{4}$$

where E_α and H_α are cartesian components of the electric and magnetic fields, respectively. The anisotropies of the magnetic and electric molecular polarisability are given by

$$\Delta x = x_{||} - x_\perp \qquad \Delta\varepsilon = \varepsilon_{||} - \varepsilon_\perp \tag{5}$$

The tensor order parameter

$$S_{\alpha\beta} = \langle\sigma_{\alpha\beta}\rangle \equiv \langle 1/2(3n_\alpha n_\beta - \delta_{\alpha\beta})\rangle \tag{6}$$

is traceless and symmetric. In a principal axis frame $S_{\alpha\beta}$ can be written

$$S_{\alpha\beta} = \begin{vmatrix} -1/2(Q-P) & 0 & 0 \\ 0 & -1/2(Q+P) & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{7}$$

The field tensor $D_{\alpha\beta}$ is also symmetric. For arbitrary fields there must exist a principal axis frame in which $D_{\alpha\beta}$ is diagonal. Since $D_{\alpha\beta}$ only enters our formalism in a product with $\sigma_{\beta\alpha}$, which is traceless, we find that the trace of $D_{\alpha\beta}$ is immaterial. An arbitrary configuration of constant electric and magnetic fields is therefore equivalent to a situation in which an electric and a magnetic field are oriented along two perpendicular axes. We note that the free energy, f, is a functional of the two rotational invariants

$$D_{\alpha\beta}D_{\beta\alpha} \text{ and } D_{\alpha\beta}D_{\beta\gamma}D_{\gamma\alpha}$$

which can be formed from the field tensor. Since

$$S_{\alpha\beta} = -\partial f/\partial D_{\alpha\beta}$$

a principal axis frame for $D_{\alpha\beta}$ will also be a principal axis frame for $S_{\alpha\beta}$. For special values of the fields degenerate situations may occur in which the order parameter is free to rotate about some axis at no energy cost.

In the principal axis frame the pseudopotential becomes, with the magnetic field chosen to be along the z axis and the electric field along x

$$\alpha = -\rho U[Qq - 1/2Q^2 + (Pp - 1/2P^2)/3\text{-}hq + 1/2e(q - p)] \tag{8}$$

where $Q = \langle q \rangle = \langle \sigma_{zz} \rangle$ and $P = \langle p \rangle = \langle \sigma_{xx} - \sigma_{yy} \rangle$ and

$$h = \frac{\Delta x H^2}{3\rho U} \qquad e = \frac{\Delta \varepsilon E^2}{3\rho U} \tag{9}$$

We are interested in determining the phase behaviour as a function of the three thermodynamic variables T, e and h. Negative values of e or h correspond to a negative susceptibility anisotropy.

The different regions in the e, h phase plane are symmetry related and it is only necessary to compute the order parameters and the free energy for $0 \leq e \leq h$. Since the two fields in (3) couple to the order parameters in the same way, the case $e > h$ can be handled by relabelling the electric and magnetic fields. In the case of a field with negative anisotropy parameters, we can use the fact that $\sigma_{\alpha\beta}$ is traceless to add a null term $b\delta_{\alpha\beta}\sigma_{\beta\alpha}$, where $\delta_{\alpha\beta}$ is the Kronecker symbol, to the pseudopotential (3). If we choose b to be the largest of $-e$ or $-h$ we see that a field with negative anisotropy is equivalent to fields with positive anisotropy along the two perpendicular axes. Also, since the molecules are assumed to be nonpolar, positive and negative directions of the field are equivalent. We also note that there are equivalence relations between the order parameters corresponding to relabelling of coordinate axes. These transformations are used in §2*e*.

b. Two-dimensional limit

It is interesting to examine the case $e = 0$, $h \to -\infty$. In this case only two-dimensional order is allowed, since the director will be forced to lie in the plane perpendicular to the magnetic field, corresponding to $Q = -\frac{1}{2}$ when H is along z. At high temperatures the molecular symmetry axes will be distributed uniformly in this plane and the system is uniaxial. At a certain temperature T_∞there will be a symmetry breaking transition to a biaxial phase with $P \neq 0$. Since states with positive and negative values of P will have the same free energy, the Landau expansion in powers of the biaxial order parameter will contain only even terms and a second order transition is allowed. Indeed we find that the transition is second order in our Maier-Saupe model. Expanding the free energy in the neighbourhood of the second order biaxial to uniaxial transition allows the calculation of T_∞. We find

$$f = \rho U \left(\frac{1}{6} - \frac{\rho U}{16kT} \right) P^2 + a_4 P^4 \tag{10}$$

with $a_4 > 0$. This gives

$$\frac{T_\infty}{T_{NI}} = \frac{3\rho U}{8kT_{NI}} = 1.703 \tag{11}$$

where $T_{NI} = \rho U/4.541k$ is the nematic to isotropic transition temperature for zero field. Note that although the ordering is two-dimensional, we are still dealing with a bulk three-dimensional system. Thus, the high field limit is analogous to the three dimensional xy-model.

c. Computational method

The pseudopotential, α, has the property that the average value of the order parameters

$$Q = \frac{1}{z}\int q\, e^{-\beta\alpha(\hat{n})} d^2\hat{n} \qquad P = \frac{1}{z}\int p\, e^{-\beta\alpha(\hat{n})} d^2\hat{n} \tag{12}$$

will minimise the free energy. These equations can be expressed in terms of integrals involving complex error functions and can be solved numerically by iterative methods for given values of the fields and the temperature. Once the order parameters are known the corresponding free energy can be computed from (1–3).

d. Van der Waals theory

The formalism used in this work can be generalised to mean field theories which take into account the dependence of system properties on density and pressure. An example of such an approach is a recent version of the van der Waals theory for anisotropic liquids.[7]

The van der Waals configurational free energy for an isotropic system can be written

$$A = N\varepsilon - NkT \ln [(V - Nv_m)/N] \tag{14}$$

where the internal energy per particle, ε, is proportional to the particle density ρ and v_m is the effective excluded volume per particle. We obtain a generalisation to anisotropic systems by adding an orientational entropy term to the free energy and letting

$$\varepsilon = -1/2\rho\gamma\left(1 + U\frac{2}{3}S_{\alpha\beta}S_{\beta\alpha}\right)$$

$$v_m = 1/2\, v_0\left(1 - W\frac{2}{3}S_{\alpha\beta}S_{\beta\alpha}\right) \tag{15}$$

where γ, v_0, U, W are constants. The pseudopotential is, as before, chosen so that the solutions to the self-consistent equations for the order parameter minimise the free energy and in the generalised van der Waals theory the pseudopotential responsible for orientational order takes the form[7]

$$\alpha = -\left[\frac{2}{3}\left(\rho U + \frac{WkT\rho V_0}{1 - \rho V_m}\right) S_{\alpha\beta} + D_{\alpha\beta}\right] \sigma_{\beta\alpha} + \text{const.} \quad (16)$$

By going to the principal axis frame one can now compute the order parameters P and Q in a way similar to that outlined in §d. One difference is that if one wishes to compute the phase diagram at constant pressure rather than constant density

$$P = -1/2\rho^2\left(1 + U\frac{2}{3}S_{\alpha\beta}S_{\beta\alpha}\right) + \frac{\rho kT}{1 - 1/2v_0\,\rho\left(1 - W\frac{2}{3}S_{\alpha\beta}S_{\beta\alpha}\right)} \quad (17)$$

e. Clausius-Clapeyron equation

It is useful to analyse the change in transition temperature with field[8] in terms of the Clausius-Clapeyron equation. We utilise the fact that the field tensor is conjugate to the order parameter to derive such an equation for the general case considered here. In the Maier-Saupe formulation the orientational entropy per particle is given by

$$S_{or} = k \ln \int d^2\hat{n} \exp\left(\beta\left[\frac{2}{3}\rho U S_{\alpha\beta} + D_{\alpha\beta}\right]\left[\sigma_{\beta\alpha} - S_{\beta\alpha}\right]\right) \quad (19)$$

If the field is changed by a small amount $dD_{\alpha\beta}$ the nematic to paranematic transition temperature T_{NpN} will change by

$$dT_{NpN} = -\frac{dD_{\alpha\beta}(S_{pN\beta\alpha} - S_{N\beta\alpha})}{S_{orpN} - S_{orN}} \quad (20)$$

The discontinuity in the orientational entropy at the transition is L/T_{NpN}, where L is the latent heat. In the limit of weak fields the

latent heat in the Maier-Saupe model is given by

$$L = 1/2\ \rho U\ Q_c^2 \tag{21}$$

where $Q_c = 0.429$, and we find for the change in transition temperature caused by small fields

$$\frac{dT_{NpN}}{T_{NpN}} = \frac{2}{Q_c}\left[\frac{hQ}{Q_c} - \frac{e(Q - P)}{2Q_c}\right] \tag{22}$$

We must now distinguish between the three cases:
i) $h > 0$, $e < h$
The director is oriented along z and[9] $Q \approx Q_c$, $P \approx 0$ and

$$\frac{dT_{NpN}}{T_c} = -2.331\ (2h - e)$$

ii) $e > 0$, $h < e$
The director is oriented along x and $Q \approx -1/2Q_c$, $P \approx 3Q_c/2$ and

$$\frac{dT_{NpN}}{T_c} = 2.331\ (-h + 2e)$$

iii) $h < 0$, $e < 0$
The director is oriented along y and $Q \approx -\ 1/2Q_c$ and $P \approx -3Q_c/2$

$$\frac{dT_c}{T_c} = 2.331\ (-h - e)$$

3. RESULTS

We have computed numerically the principal axis frame order parameters P and Q, the phase transition temperatures and the spinodal points (where the curvature of the free energy as a function of the order parameter changes sign).

It is well established[10] that in the case of a single field and positive susceptibility the transition temperature increases with field and the first order isotropic-uniaxial transition ends at a critical point. We show in Figure 1 the order parameters and the free energy for various

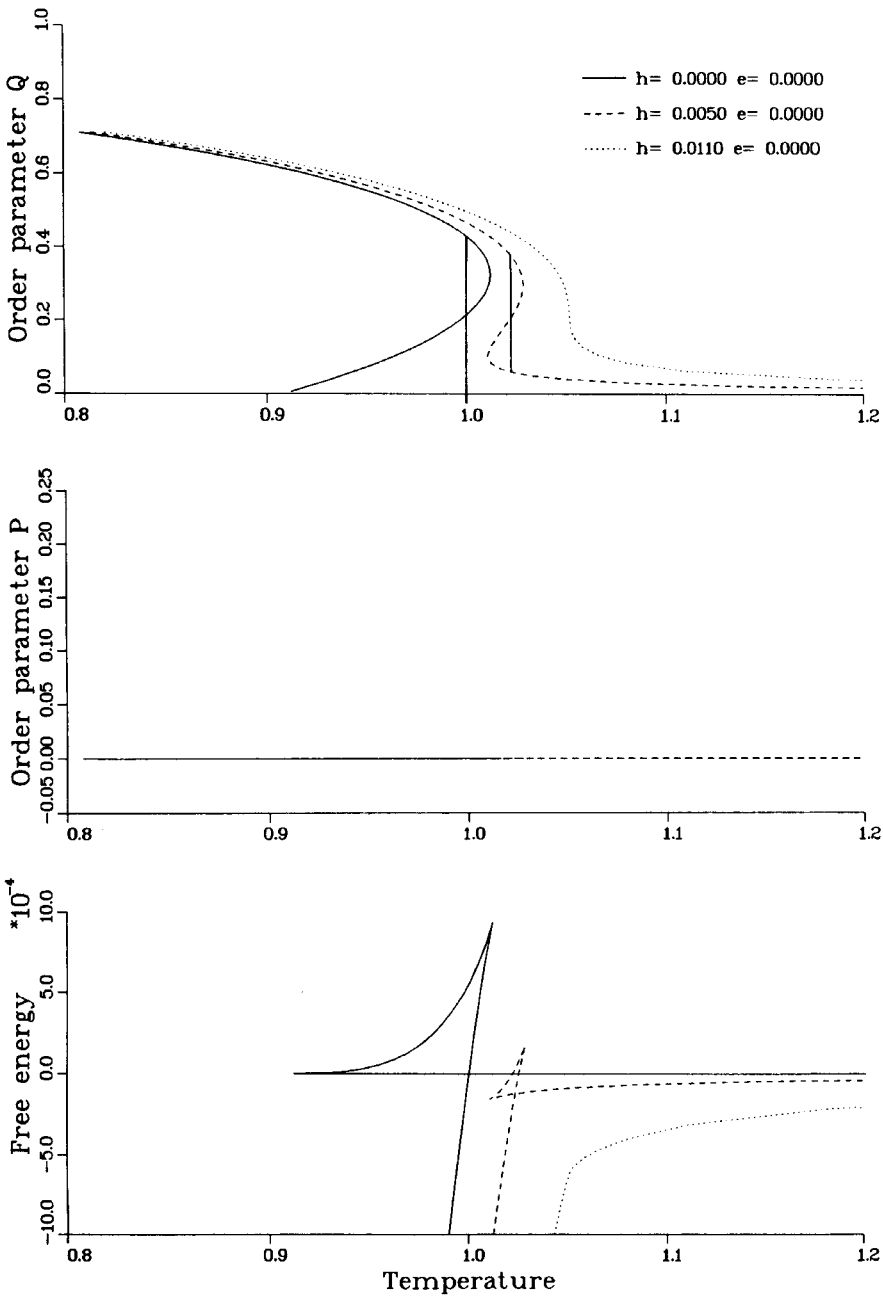

FIGURE 1 Order parameters Q and P and free energy f for $e = 0$ and different values of h.

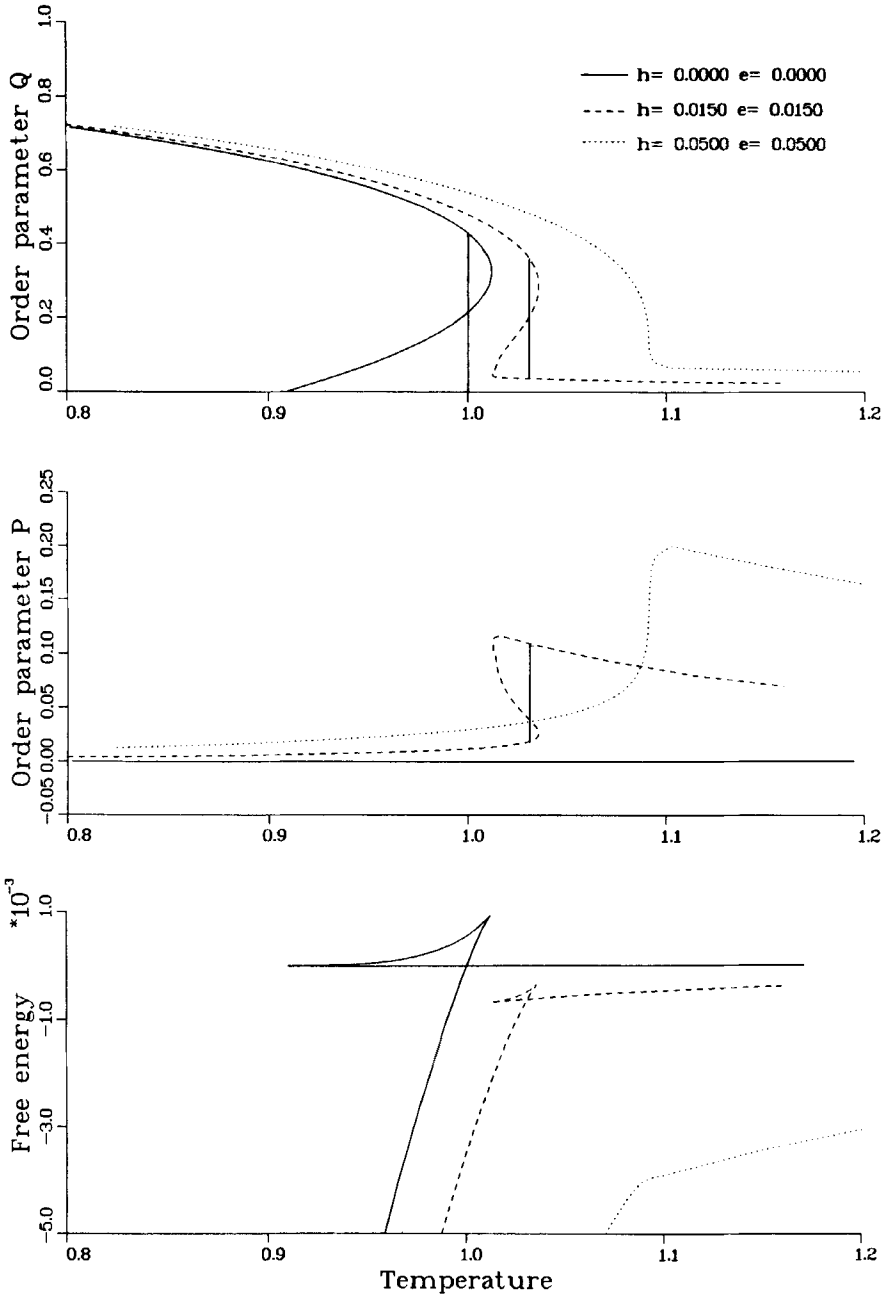

FIGURE 2 Order parameters Q and P and free energy f for different values of $h = e$.

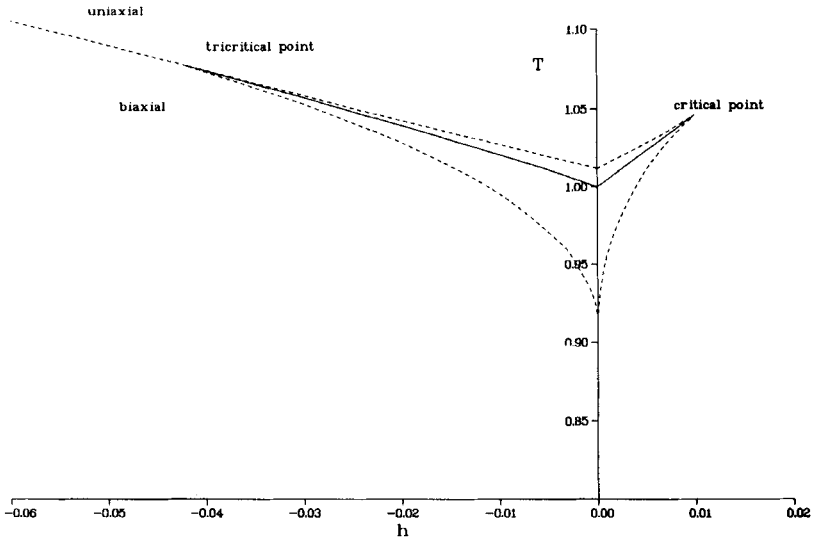

FIGURE 3 Phase diagram along line $e = 0$. Solid lines represent first order transitions, dashed lines correspond to second order transitions, while dotted lines are spinodals.

values of h with $e = 0$, reproducing results of ref. [10]. Temperatures are given in units of the the zero field nematic to isotropic transition temperature T_{NI}, while the free energy is given in units of kT_{NI}. The transition can be located by following the lowest free energy branch. Metastable states are expected between the transition and the spinodal points.

Figure 2 shows the order parameter and the free energy for some values of $h = e$. By symmetry this situation is equivalent to the case $h < 0$, $e = 0$ and field along y.

Along the line $e = 0$ and for negative susceptibilities the first order line ends at a tri-critical point[1-5] and becomes a second order line as shown in Figure 3. As $h \to -\infty$ the ordering becomes two-dimensional and the transition temperature approaches 1.703 monotonically from below (see section 2b). This result is different from that of the usual Landau approach,[5] where the transition temperature has a maximum for a finite field. The spinodals are shown as dotted lines.

In Figure 4 we show a projection of the phase diagram onto the $e-h$ plane, with a three-dimensional plot of the phase diagram shown in Figure 5. The surface of first order transitions looks somewhat like an umbrella that has been turned inside out by the wind and with

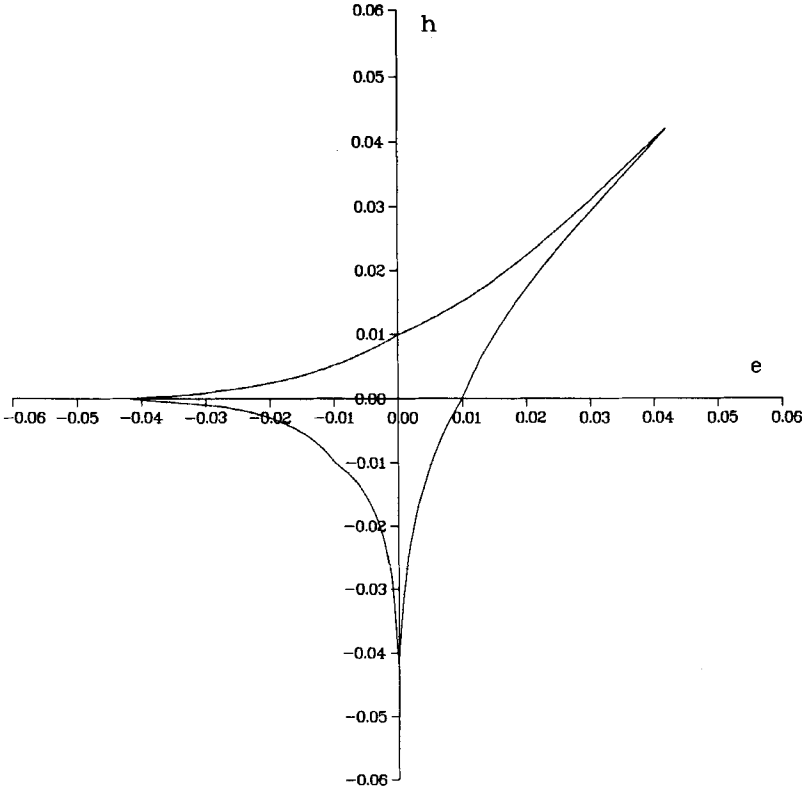

FIGURE 4 Projection of the phase diagram on the $e-h$ plane. A surface of first order transitions is suspended between three symmetry related tri-critical points and bounded by lines of ordinary critical points.

spokes in the $-e$, T and $-h$, T and $e = h$, T planes. In addition to the surface of first order transitions also shown in Fig. 4 there are three vertical sheets of transitions between two phases in which the biaxial order parameter P changes sign. There is neither latent heat nor spinodals for this transition, which can take place continuously through a rotation in the $x - y$ plane.

We show in Figure 6 order parameters at the transition along two directions in the $e-h$ plane.

The transition temperature T_{NpN} has an absolute minimum T_{NI} for $e = h = 0$, and for small fields this temperature increases as discussed in §2e by an amount which is proportional to e or h (i.e. proportional to the field squared).

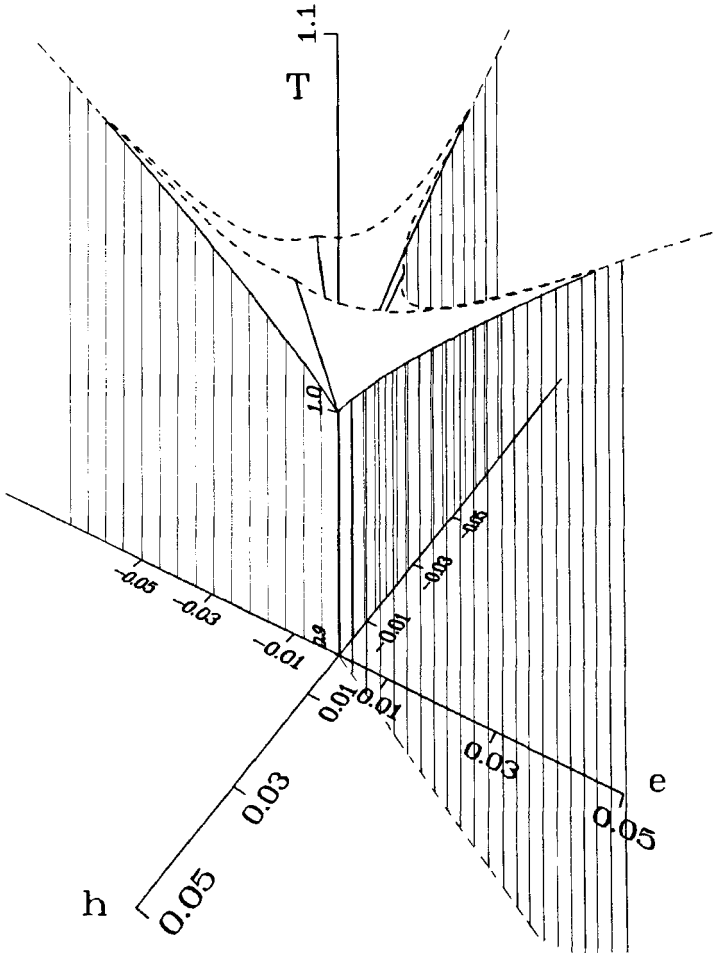

FIGURE 5 Three dimensional plot of phase diagram.

4. DISCUSSION

The theory presented in this paper describes the effects of two external fields with arbitrary directions on the orientational order in nematics within the framework of a generalised Maier-Saupe theory. We have shown that the principal axis frame of the order parameter tensor coincides with the frame in which the generalised field tensor (4) is diagonal.

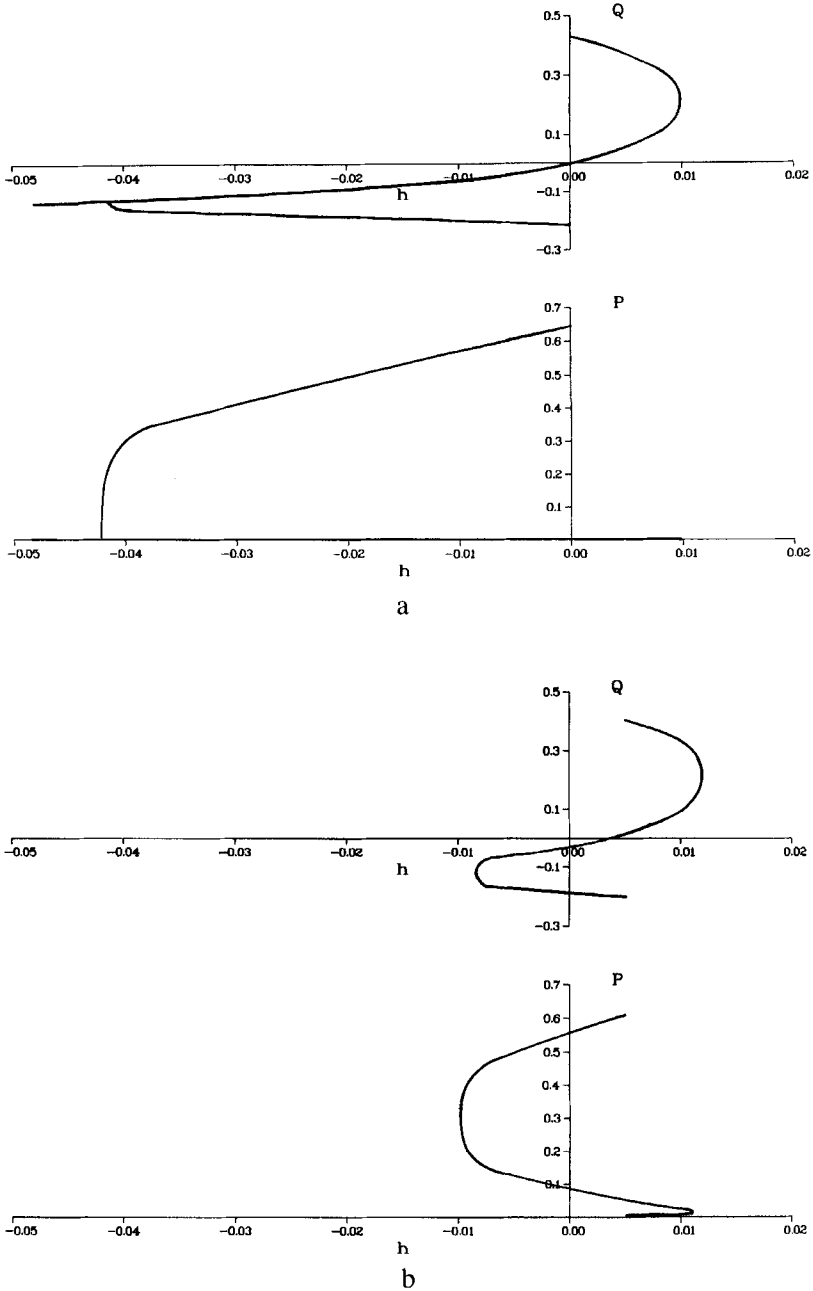

FIGURE 6 Order parameters at the transition along two directions in the phase plane (a) $e = 0$, (b) $e = 0.005$.

The numerical calculations were carried out assuming cylindrically symmetric molecules, constant density and neglecting steric effects and the effect of fluctuations. While we expect the effects which we have neglected to be important for a quantitative understanding of experiments, we feel that it is useful to present the detailed predictions of a simple theory.

It is well known that for a pure material the fields needed to reach the critical or tricritical points, or even to cause a significant change in the transition temperature, will be very large. As an example we mention that in the case of 5CB, with a transition temperature $T_{NI}(0) = 308$K, we find the ordinary critical point at $1.045\ T_{NI}(0) = 322$K. With known[11,12] anisotropies $\Delta\chi$ and $\Delta\varepsilon$ of 5CB, the critical field $h = 0.0097$ would correspond to a magnetic field of 847T or an electric field of $7.8\ 10^7$ V/m. In the case of the tricritical point $h = e = 0.042$, $T = 1.078\ T_{NI} = 332$K and the situation is even more extreme. The tricritical fields are then 1765T for the magnetic field and $1.62\ 10^8$ V/m for the electric field. It has been pointed out by Hornreich[13] that the discrepancy between the predictions of Maier-Saupe theory and observed values for the difference in temperature between the *NI* transition point T_{NI} and spinodal point T^* suggests that the critical fields may be smaller than predicted by the Maier-Saupe theory.[14] A similar conclusion is suggested by the estimate given by Nicastio and Keyes[15] for the critical electric field. Their estimate is roughly a factor five smaller than predicted by the present theory. It would therefore be of interest to carry out calculations similar to the ones discussed here in van der Waals theory[7] where we have found this discrepancy to be smaller.

The change in transition temperature with field is more accessible. Rosenblatt[8] has measured the change in the transition temperature with field and obtained a value consistent with the Clausius-Clapeyron equation and thermodynamic data. Our theory would predict a value which is which is too small by a factor of 1.78 if the same susceptibility data is used, due to the overestimate of the latent heat in Maier-Saupe theory.

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