Solution of a molecular statistical model for chiral nematic liquid crystals

B. C. H. Krutzen[a]; G. Vertogen[a]

[a] Institute for Theoretical Physics, Catholic University of Nijmegen, Nijmegen, The Netherlands

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by B. C. H. KRUTZEN and G. VERTOGEN

Institute for Theoretical Physics, Catholic University of Nijmegen, Toernooiveld,
6525 ED Nijmegen, The Netherlands

A molecular statistical model for the chiral nematic phase of liquid crystals is investigated. The model is treated in the molecular field approximation. The resulting set of coupled integral equations for the order parameters and the pitch determining equation are solved numerically. The model hamiltonian consists of a nematic and a twist producing term. If only the nematic term is present, the model is known to have a first order phase transition. The model containing only the twist producing term is shown to exhibit a second order phase transition. The order parameters and wave length are presented for three ratios of the coupling constants in the case that both interactions are present.

1. Introduction

The first molecular statistical model for the chiral nematic phase of liquid crystal-line materials was introduced by Goossens [1]. His model is a straight forward extension of the Maier–Saupe model for the nematic phase [2]. The origin of the chiral nematic phase is ascribed to the induced dipole–quadruple term of the dispersion interaction. This term is zero for the non-chiral molecules of the Maier–Saupe model.

Although the fundamental assumption of this theory for the chiral nematic phase, i.e. the higher order terms in the multipole expansion can be neglected, does not hold, the model is of interest from a phenomenological point of view. It gives a clear picture of the type of molecular interactions that are needed to produce a chiral nematic phase.

In order to discuss the appearance of this phase it suffices to consider molecules that are cylindrically symmetric around their long molecular axis and equipped with the property handedness representing their chirality. Then the model consists of only two competing interactions, namely the Maier–Saupe interaction and a twist producing interaction as proposed by v.d. Meer et al. [3]. Uptill now, the solutions of this model are known only for a relatively small twist interaction [4, 5]. The purpose of this paper is to present numerical solutions for the full range of the parameters using the molecular field approximation. Furthermore, the limit case, where the Maier–Saupe term is absent, is discussed partly in analytical terms.

This paper is organized in the following way. In §2, the model hamiltonian is introduced. The order parameters characterizing the chiral nematic phase are specified in §3. The expression for the Helmholtz free energy in the molecular field approximation and the attendant parameter equations can be found in §4. One of these equations determines the pitch and is dealt with in §5. The numerical solution of the other two equations, the selfconsistent equations for the order parameters, is presented in §6. The limit case, including only the twist producing term, is studied numerically as well as analytically in §7. Finally the conclusions are presented in §8.

2. The model hamiltonian

First we would like to explain the choice of the model hamiltonian for the chiral nematic phase with the help of symmetry arguments and tensor calculus [6]. Starting point of our consideration is a cylindrically symmetric chiral molecule with its symmetry axis denoted by the unit vector **a**. Since the chiral nematic phase does not show any polarity of the molecules, these should be represented by tensors of even rank composed of the components of the vector **a**. A traceless second rank tensor is

$$\Lambda_{\alpha\beta} \;=\; a_\alpha a_\beta \;-\; \tfrac{1}{3}\delta_{\alpha\beta}. \tag{1}$$

The greek indices represent the components x, y and z. A pair interaction between the molecules i and j can be constructed by the contraction of two of these tensors

$$
\begin{aligned}
H_{ij}^{(1)} \;&=\; -\tfrac{3}{2}J_{ij}\Lambda_{\alpha\beta i}\Lambda_{\alpha\beta j} \\
&=\; -J_{ij}P_2(\mathbf{a}_i \cdot \mathbf{a}_j).
\end{aligned} \tag{2}
$$

The coupling constant J_{ij} depends on the distance vector $\mathbf{r}_{ij}$ between the centres of mass of the molecules i and j and P_2 is the second Legendre polynomial. This interaction is of the form found by Maier and Saupe for the induced dipole–dipole interaction [2]. It is well known that this model leads to a first order phase transition from the nematic to the isotropic phase.

For the construction of a twist producing interaction tensor (1) must be contracted with an odd rank tensor. Since first rank tensors are not compatible with the absence of polarity, these tensors are of rank three at least. A third rank tensor representing the chirality of the molecule is

$$\Lambda_{\alpha\beta\gamma} \;=\; a_\alpha \varepsilon_{\beta\gamma\mu}a_\mu, \tag{3}$$

where ε is the Levi–Civita tensor. The simplest twist interaction can now be obtained by the contraction of this tensor with $\Lambda_{\alpha\beta}$ and the unit distance vector **u**

$$
\begin{aligned}
H_{ij}^{(2)} \;&=\; -\tfrac{1}{2}K_{ij}\Lambda_{\alpha\beta\gamma i}\Lambda_{\alpha\beta j}u_{\gamma ij} \;-\; \tfrac{1}{2}K_{ji}\Lambda_{\alpha\beta\gamma j}\Lambda_{\alpha\beta i}u_{\gamma ji} \\
&=\; -\tfrac{1}{2}(K_{ij} + K_{ji})(\mathbf{a}_i \cdot \mathbf{a}_j)(\mathbf{a}_i \times \mathbf{a}_j) \cdot \mathbf{u}_{ij}.
\end{aligned} \tag{4}
$$

This interaction is of the same form as the induced dipole–quadrupole interaction following from a generalization of the Maier–Saupe approach using cylindrically symmetric chiral molecules [1, 3].

The purpose of this paper is to present the thermodynamic properties of a system of identical molecules subject to both the Maier–Saupe interaction (2) and the twist interaction (4). The model hamiltonian is thus given by

$$H \;=\; -\frac{1}{2}\sum_{i \neq j} \{J_{ij}P_2(\mathbf{a}_i \cdot \mathbf{a}_j) \;+\; K_{ij}(\mathbf{a}_i \cdot \mathbf{a}_j)(\mathbf{a}_i \times \mathbf{a}_j) \cdot \mathbf{u}_{ij}\}. \tag{5}$$

The influence of the twist producing term has previously been investigated with the aid of perturbation theory: Analytically, for the spherical version of the Maier–Saupe model [4, 7] and numerically, for the original model [5]. In this paper the full range of the coupling constants is investigated (without the use of perturbation theory) for the original model.

Before proceeding, we would like to point out that, in spite of the fact that both the nematic and twist producing term can be interpreted in terms of a multipole expansion of the dispersion interaction, and explicit expressions for the coupling

constants J_{ij} and K_{ij} can be given, the chosen hamiltonian should be considered to represent a phenomenological model, because there is no reason to assume that the terms in the expansion, that are not taken into account, can be neglected.

3. The order parameters

Because of the cylindrical symmetry of the molecules, assumed in §2, the order parameters can only be constructed from the position dependent unit vectors $\mathbf{a}(\mathbf{r})$. The absence of polarity limits the discussion to tensors of even rank. For simplicity we will restrict our attention to the following tensor of second rank

$$\Gamma_{\alpha\beta}(\mathbf{r}) = \langle a_\alpha(\mathbf{r})a_\beta(\mathbf{r})\rangle, \tag{6}$$

where the brackets denote the statistical average. The trace of Γ is equal to one.

The chiral nematic phase is further characterized by a helix of wave vector $\mathbf{q}$, which can be taken without loss of generality in the $\mathbf{x}$ direction. Therefore we can express the tensor $\Gamma(\mathbf{r})$ in terms of the tensor $\Gamma(\mathbf{o})$

$$\Gamma_{\alpha\beta}(\mathbf{r}) = \mathfrak{R}_{\alpha\mu}(qr_x, \mathbf{x})\mathfrak{R}_{\beta\nu}(qr_x, \mathbf{x})\Gamma_{\mu\nu}(\mathbf{o}), \tag{7}$$

where the matrix $\mathfrak{R}(\phi, \mathbf{v})$ represents a rotation over the angle ϕ around the axis $\mathbf{v}$.

The chosen pair interaction has the lowest energy for two molecules i and j having an angle of 45 degrees between their directions $\mathbf{a}_i$ and $\mathbf{a}_j$ with the intermolecular distance vector $\mathbf{r}_{ij}$ being perpendicular to both $\mathbf{a}_i$ and $\mathbf{a}_j$. Thus it is natural to assume that the direction $\mathbf{x}$ of the helix is compatible with the choice of a locally diagonal Γ

$$\Gamma_{\mu\nu}(\mathbf{o}) = \frac{1}{3}\begin{pmatrix} 1 - S + R & 0 & 0 \\ 0 & 1 - S - R & 0 \\ 0 & 0 & 1 + 2S \end{pmatrix} \tag{8}$$

such that

$$S = -\tfrac{1}{2} + \tfrac{3}{2}\langle a_z^2(\mathbf{o})\rangle \tag{9}$$

and

$$R = \tfrac{3}{2}(\langle a_x^2(\mathbf{o})\rangle - \langle a_y^2(\mathbf{o})\rangle). \tag{10}$$

The order parameters S and R measure the local nematic order and the biaxiality respectively.

4. The molecular field equations

It is straightforward to determine the molecular field hamiltonian for the particle at the origin

$$H_0 = \frac{J}{8}(S - R)(S - R - 2) + \frac{JA(q)}{24}(3S + R)^2$$

$$+ \frac{3J}{4}(S - R)a_x^2(\mathbf{o}) + \frac{JA(q)}{4}(3S + R)(a_y^2(\mathbf{o}) - a_z^2(\mathbf{o})), \tag{11}$$

where

$$J = \sum_{j \neq 0} J_{0j} \tag{12}$$

and

$$JA(q) \ = \ \sum_{j \neq 0} \{ J_{0j} \cos{(2qr_{xj})} + \tfrac{2}{3} K_{0j} u_{x0j} \sin{(2qr_{xj})} \}. \tag{13}$$

Extrema of the Helmholtz free energy per particle, $f = -1/\beta \cdot \ln Z$, where $Z = \int da^2(\mathbf{o}) \exp{(-\beta H_0)}$ is the partition function, with respect to the parameters S, R and the wave number q, can be shown to obey the selfconsistent equations

$$\tfrac{1}{3}(1 + 2S) \ = \ \frac{1}{Z} \int d^2 a(\mathbf{o}) a_z^2(\mathbf{o}) \exp{(-\beta H_0)} \tag{14}$$

and

$$\tfrac{2}{3} R \ = \ \frac{1}{Z} \int d^2 a(\mathbf{o}) (a_x^2(\mathbf{o}) - a_y^2(\mathbf{o})) \exp{(-\beta H_0)} \tag{15}$$

and the wave number equation

$$\frac{dA(q)}{dq} \ = \ 0. \tag{16}$$

5. The wave number equation

In order to solve the wave number equation (16) we have to make our model more explicit. The summation in the expression (13) for $A(q)$ can be evaluated by assuming random positions for the molecules and introducing a continuous pair distribution function $g(\mathbf{r})$. Therefore we replace the summation over a function $f(j)$, depending on j by way of $\mathbf{r}_{0j}$, by the following integration:

$$\sum_{j \neq 0} f(j) \ = \ \varrho \int d^3 r f(\mathbf{r}) g(\mathbf{r}), \tag{17}$$

where $\varrho = (3/4\pi) R_0^{-3}$ is the density of the system and R_0 is an intermolecular distance. The function $g(\mathbf{r})$ is taken to be

$$g(\mathbf{r}) \ = \ \Theta(r - R_0), \tag{18}$$

where $\Theta(x)$ is the Heaviside step function.

In addition to these assumptions the position dependences of J_{0j} and K_{0j} have to be known. Following the analogy between the proposed model hamiltonian and the original theory as mentioned in §2, we take

$$J_{0j} \ = \ \frac{\bar{J}}{r_{0j}^6} \tag{19}$$

and

$$K_{0j} \ = \ \frac{\bar{K}}{r_{0j}^7}. \tag{20}$$

Using the replacement (17) it is straight forward to derive the equalities

$$J \ = \ \frac{\bar{J}}{R_0^6} \tag{21}$$

and

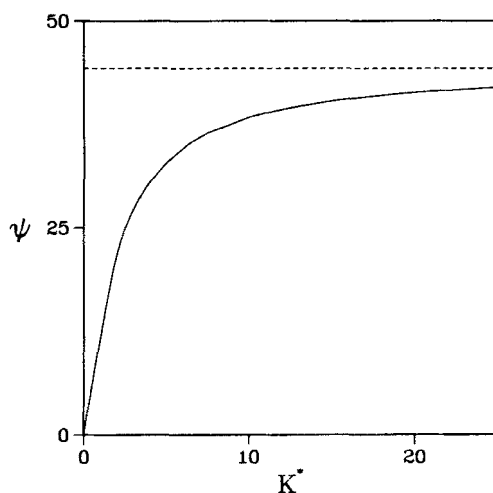$$K \ = \ \sum_{j \neq 0} K_{0j} \ = \ \frac{\bar{K}}{R_0^7}. \tag{22}$$

Figure 1. The twist angle ψ over the distance R_0 as a function of the relative strength K^*. The dashed curve represents the asymptotic value $\psi = 44 \cdot 29$ degrees where K^* goes to infinity.

Now the expression (13) for $A(q)$ can also be evaluated and gives

$$A(q^*) = \frac{3}{(q^*)^3} \left[q^* \cos(q^*) + (5 + K^* q^*) \sin(q^*) \right.$$
$$\left. - (30 + 5K^* q^*) \int_1^\infty dy \, \frac{\sin(q^* y)}{y^7} \right], \qquad (23)$$

where $q^* = 2qR_0$ and $K^* = (8K/9J)$. With the help of this expression the wave-number equation (16) was solved numerically for the full range of the relative coupling strength K^*. The solutions will be denoted by q_0^*. In the limit of small K^* values it can be shown that $q_0^* = \frac{1}{3}K^*$ and $A(q_0^*) = 1 + \frac{1}{2}(q_0^*)^2$. In the limit of K^* going to infinity the solution approaches asymptotically the value $q_0^* = 1 \cdot 546$. The twist angle ψ over the intermolecular distance R_0, $\psi = R_0 q_0 = \frac{1}{2}q_0^*$, is plotted as a function of K^* in figure 1.

The limiting value of ψ, $\psi = 44 \cdot 29$ degrees for K^* going to infinity, can be understood by inspection of the twist producing pair interaction. This interaction favours angles of 45 degrees between molecules. If more than nearest neighbours are taken into account this leads to frustration since there is no way all molecules can make angles of 45 degrees with one another. The fact that the limiting value is so close to 45 degrees reflects the short range characeter (r_{ij}^{-7}) of the position dependent coupling strength K_{ij}.

6. The selfconsistent equations

The solution of the selfconsistent equations for S and R has been determined numerically for several values of K^*. For all cases we find a first order phase transition. The results show a qualitative difference for $K^* < K_0^*$, and $K^* > K_0^*$, where K_0^* is approximately equal to five. For $K^* < K_0^*$ both S and R are monotonic functions of the temperature. For $K^* > K_0^*$ the biaxiality, R, exhibits a maximum for some temperature T smaller than the critical temperature T_c. The temperature dependence of S and R is shown in figure 2 for three representative values of
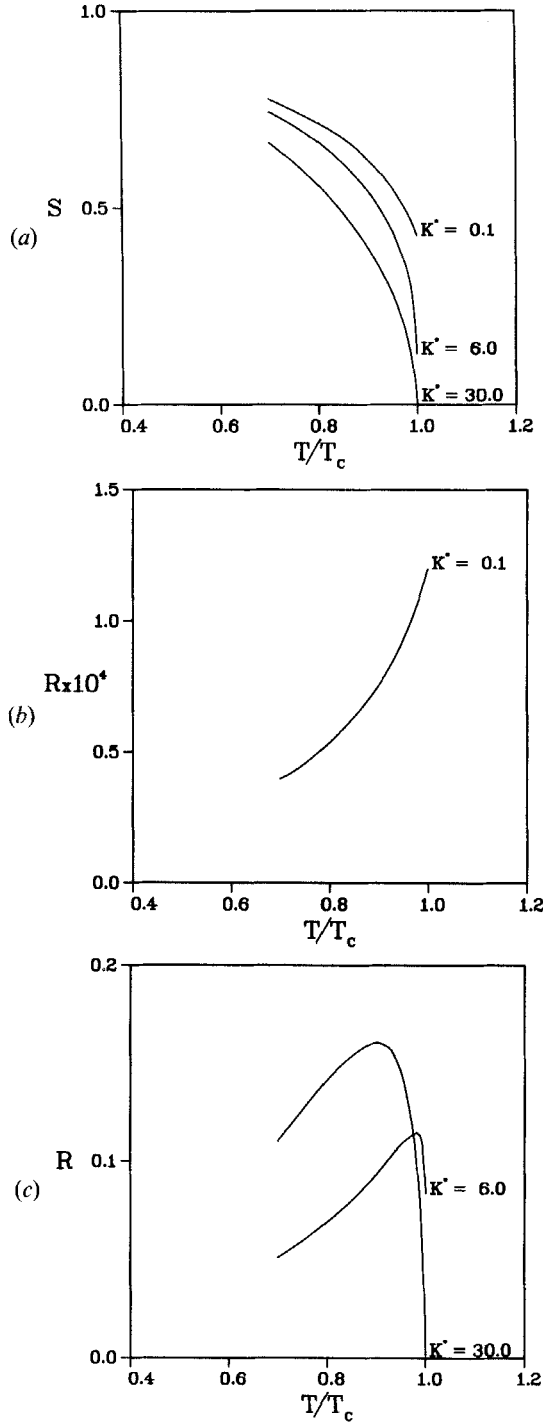
Figure 2.   (a) The order parameter S for the local nematic order as a function of the reduced
temperature T/T_c for the values $K^* = 0.1$, $K^* = 6$ and $K^* = 30$. The transition values
for S are $S_c = 0.429$, $S_c = 0.129$ and $S_c = 0.00115$ respectively. (b) The order parameter
R for the biaxiality as a function of the reduced temperature T/T_c for the value $K^* = 0.1$.
The transition value for R is $R_c = 0.000120$. (c) The order parameter R for the biaxiality
as a function of the reduced temperature T/T_c for the values $K^* = 6$ and $K^* = 30$. The
transition values for R are $R_c = 0.0838$ and $R_c = 0.00115$ respectively.

K^*: $K^* = 0 \cdot 1$, $K^* = 6$ and $K^* = 30$. For $K^* = 0 \cdot 1$ the S curve is very similar to the one found for the Maier–Saupe model. The biaxiality parameter R is still very small (note the different scales of the plotted R curves for $K^* = 0 \cdot 1$ and both other values). This result is in agreement with the perturbation calculation of Scholte and Vertogen, namely the critical value of S changes according to $(q_0^*)^4$ and the critical value of R is of the order of $(q_0^*)^2$ [4] and is also in agreement with the numerical result of Lin–Liu and Lee [5]. For $K^* = 30$ the first order transition is very weak and resembles a second order transition as shown by the smallness of the critical values S_c and R_c.

7. The case $J = 0$

In case only the twist producing term is present the Helmholtz free energy per molecule with respect to the isotropic phase, f, appears to depend on the order parameter $\tilde{S} = S + R/3$ and is given by

$$f = \tfrac{1}{2}K(q)(\tilde{S})^2 - \frac{1}{\beta}\ln\left[\frac{1}{4\pi}\int d^2a(\mathbf{o})\exp\{\beta K(q)\tilde{S}(a_z^2(\mathbf{o}) - a_y^2(\mathbf{o}))\}\right], \quad (24)$$

with

$$K(q) = \frac{1}{2}\sum_{j\neq0} K_{0j}u_{0jx}\sin(2qr_{xj}). \quad (25)$$

The selfconsistent equation for $\tilde{S}$ and the wave number equation $[dK(q)/dq] = 0$ have to be solved numerically. As expected from the behaviour for $K^* = 30$, the system appears to exhibit a second order phase transition. The critical temperature satisfies the relation $\beta_c K(q_0) = 3 \cdot 750$, where q_0 is the solution of the wavenumber equation. It can easily be shown that the wave number equation $[dK(q)/dq] = 0$ is equivalent to the corresponding equation (16) for $A(q)$ in the limit of K^* going to infinity. Thus, the solution of the wave number equation is already known from §5, i.e. we find $2q_0 R_0 = 1 \cdot 546$. The curves of S and R are nearly identical to those for $K^* = 30$. Therefore we do not show them separately. Finally we demonstrate analytically that the purely chiral model has a second order phase transition. For this purpose we expand the free energy (24) in terms of $\tilde{S}$ giving

$$f = \tfrac{1}{2}K(q)[1 - \tfrac{4}{15}\beta K(q)]\tilde{S}^2 + \tfrac{4}{1575}\beta^3 K^4(q)\tilde{S}^4 + O(\tilde{S}^6). \quad (26)$$

As the term proportional to $\tilde{S}^4$ is positive and thus stabilizes the chiral nematic phase, the phase transition is a second order one with a critical temperature determined by $\beta_c K(q_0) = \tfrac{15}{4} = 3 \cdot 750$, in perfect agreement with the numerical result from the previous section.

8. Conclusion

The present analysis of the simplest molecular model for the chiral nematic phase shows that the biaxiality of this phase must be taken into account even if the pitch is large, i.e. from a molecular statistical point of view the chiral nematic phase is always biaxial. The temperature dependence of the parameter R, which describes the biaxiality, is quite remarkable for relatively strong twist interactions, where it shows a maximum. New is the result that the model has a second order phase transition, if the nematic term is absent.

It must be mentioned, that the occurrence of blue phase is neglected here. Such phases are found intermediate between the chiral nematic and the isotropic phase for

small values of the pitch and can be described indeed by the present model. Finally it should be noted that the artefact of a temperature independent pitch can easily be removed by the introduction of additional nematic and/or twist producing interactions [8, 9].

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