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## Liquid Crystals

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L. Varichon<sup>a</sup>; A. Ten Bosch<sup>a</sup>

<sup>a</sup> Laboratoire de physique de la matière condensée, Nice Cedex2, France

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## Molecular model for cholesteric polymers including biaxiality and chain flexibility

by L. VARICHON\* and A. TEN BOSCH

Laboratoire de physique de la matière condensée, U.A. CNRS No. 190,  
Parc Valrose, 06018 Nice Cedex2, France

A mean field theory for cholesteric polymers based on the elastic model is presented. The effect of flexibility and the biaxial order and nematic order parameters are studied. The biaxial order and nematic order parameters are increasing functions of chirality and vary slightly with flexibility. Biaxiality is shown to be important for the transition temperature and the cholesteric pitch as well as the latent heat of transition.

### 1. Introduction

The literature devoted to biaxial liquid crystals is extensive [1–3]. It has been shown that biaxiality becomes important near the isotropization temperature [4–5] and measures of biaxial order are a way to determine the possibility of a blue phase [6]. But, because of the difficulty of interpretation of deuterium NMR spectral patterns, measurements are very rare [7–8]. Nevertheless two conclusions arise: biaxiality increases with increasing temperature and decreasing pitch length and the mechanism for biaxiality is almost entirely a consequence of the anisotropy of the orientational distribution along the molecular axis rather than due to the helical texture of cholesterics [9]. Some molecular theories have been proposed [10–12] and as emphasized by Gelbart [13], these models are based upon the particular interaction deemed to be dominant: (i) attractive forces of dispersion (for example Maier–Saupe [14]); (ii) repulsive steric forces (for example Onsager [15], Flory [16]); or (iii) a combination of both where the dominant interaction depends on temperature (for example Alben [17]). At least two deficiencies have been found to explain the poor quantitative agreement with experimental results: the breakdown of the mean field concept and the effect of flexibility. One way to take into account the rigidity is to deal with the continuum elastic chain model [18] widely used for polymers [19–24] and recently for liquid crystalline polymers [25–28]. We report the conjugate effects of flexibility and biaxiality on the usual order parameters  $S_2$ ,  $S_4$  and on the transition temperature in a thermotropic system. And we predict the possibility for the biaxiality to become zero without affecting the pitch behaviour.

### 2. Molecular field theory for rigid rods

Considering uniaxial molecular symmetry and a chiral interaction only, the simplest potential that gives a cholesteric structure with order parameters  $S_2$ ,  $S_4$  and  $\Delta$  is [29–31].

$$V(1, 2) = V_0(\mathbf{r}_{12}) + V_2(\mathbf{r}_{12})P_2(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) + (\mathbf{r}_{12} \cdot \boldsymbol{\Omega}_1 \times \boldsymbol{\Omega}_2)(V_1(\mathbf{r}_{12})P_1(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) + V_3P_3(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2)), \quad (1)$$

\* Author for correspondence.

where  $P_m$ ,  $m=1,2,3$  are the Legendre polynomials,  $\Omega$  is a unit vector indicating the molecular orientation, and  $\mathbf{r}_{12}$  is a unit vector joining the centres of gravity of molecules 1 and 2. Coupling between orientation and position are not required by symmetry arguments and will be neglected here.

In a second order term in the virial expansion, the Helmholtz free energy for the one particle distribution function  $F(f(\Omega, \mathbf{r}), \rho, T)$ , can be derived as [32]

$$F(f(\mathbf{r}, \Omega)/T, \rho) = F_0(T, \rho) + \frac{1}{2} \rho^2 \int f(\mathbf{r}_1, \Omega_1) f(\mathbf{r}_2, \Omega_2) V(1, 2) d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1 d\Omega_2 \\ + \rho kT \int f(\mathbf{r}, \Omega) \ln 4\pi f(\mathbf{r}_2, \Omega_2) d\mathbf{r} d\Omega, \quad (2)$$

with  $\rho = N/V$ , the average number density.

We introduce the usual second and fourth order parameter tensor dependent on position

$$Q_{\alpha\beta}(\mathbf{r}) = \int d\Omega f(\mathbf{r}, \Omega) \left( \frac{3}{2} \Omega_\alpha \Omega_\beta - \frac{1}{2} \delta_{\alpha\beta} \right), \\ Q_{\alpha\beta\gamma\zeta}(\mathbf{r}) = \int d\Omega f(\mathbf{r}, \Omega) \left( \begin{array}{l} \frac{35}{8} \Omega_\alpha \Omega_\beta \Omega_\gamma \Omega_\zeta \\ -\frac{30}{8} (\Omega_\alpha \Omega_\beta \delta_{\gamma\zeta} + 5 \text{ distinct index permutations}) \\ +\frac{3}{8} (\delta_{\alpha\beta} \delta_{\gamma\zeta} + 2 \text{ distinct index permutations}) \end{array} \right). \quad (3)$$

It is now straightforward to express more conveniently the three anisotropic intermolecular contributions in the free energy development.

$$\langle (\mathbf{r}_{12} \cdot \Omega_1 \times \Omega_2) P_1(\Omega_1 \cdot \Omega_2) \rangle_\Omega = \frac{4}{9} \varepsilon_{\alpha\beta\gamma} \mathbf{r}_{12\alpha} Q_{\beta\zeta}(\mathbf{r}_1) Q_{\gamma\zeta}(\mathbf{r}_2), \\ \langle P_2(\Omega_1 \cdot \Omega_2) \rangle_\Omega = \frac{2}{3} Q_{\alpha\beta}(\mathbf{r}_1) Q_{\alpha\beta}(\mathbf{r}_2), \\ \langle (\mathbf{r}_{12} \cdot \Omega_1 \times \Omega_2) P_3(\Omega_1 \cdot \Omega_2) \rangle_\Omega = -\frac{2}{3} \varepsilon_{\alpha\beta\gamma} \mathbf{r}_{12\alpha} Q_{\beta\zeta}(\mathbf{r}_1) Q_{\gamma\zeta}(\mathbf{r}_2) + \frac{5}{2} \varepsilon_{\alpha\beta\gamma} \mathbf{r}_{12\alpha} \\ \times \left\{ \frac{8}{35} Q_{\alpha\beta\gamma\phi}(\mathbf{r}_1) + \frac{1}{7} \int d\Omega_1 f(1) [\Omega_{1\alpha} \Omega_{1\beta} \delta_{\gamma\phi} + 5 \text{ perm.}] - \frac{1}{35} [\delta_{\alpha\beta} \delta_{\gamma\phi} + 2 \text{ perm.}] \right\} \\ \times \left\{ \frac{8}{35} Q_{\alpha\beta\gamma\kappa}(\mathbf{r}_1) + \frac{1}{7} \int d\Omega_2 f(2) [\Omega_{2\alpha} \Omega_{2\beta} \delta_{\gamma\kappa} + 5 \text{ perm.}] - \frac{1}{35} [\delta_{\alpha\beta} \delta_{\gamma\kappa} + 2 \text{ perm.}] \right\}. \quad (4)$$

It is possible to express the traceless symmetric tensor  $Q_{\alpha\beta}(\mathbf{r})$  in a position dependent coordinate system  $B(\mathbf{r}) = \{\mathbf{l}(\mathbf{r}), \mathbf{m}(\mathbf{r}), \mathbf{n}(\mathbf{r})\}$  characteristic of the cholesteric structure in which the diagonal elements:  $Q_{\alpha\beta} = \{S_{xx}, S_{yy}, S_{zz}\}$  are position independent. We will consider that biaxiality is dominantly contained in  $Q_{\alpha\beta}(\mathbf{r})$ , so  $Q_{\alpha\beta\gamma\zeta}(\mathbf{r})$  will be taken to be dependent on  $\theta$  only.  $B(\mathbf{r})$  does not diagonalize  $Q_{\alpha\beta\gamma\zeta}(\mathbf{r})$ , but each component can be

expressed in terms of  $Q_{zzzz}$ . Then, for a macroscopic pitch  $P$  defined along the  $x$  axis, in the ideal cholesteric representation [33]

$$\mathbf{l}(\mathbf{r}) = (1, 0, 0); \mathbf{m}(\mathbf{r}) = (0, \cos xh, \sin xh); \mathbf{n}(\mathbf{r}) = (0, -\sin xh, \cos xh) \text{ and } P = 2\Pi/h$$

the orientational part of the free energy can be rewritten as

$$\begin{aligned} \frac{F}{N} = & kT \langle \ln 4\Pi f \rangle_{\Omega} + \frac{\rho}{3} \int d\mathbf{r} V_2(\mathbf{r}) [S_{xx}^2 + (S_{yy}^2 + S_{zz}^2) \cos^2 hx + 2S_{yy}S_{zz} \sin^2 hx] \\ & + \frac{1}{12} \rho \int d\mathbf{r} \left( \frac{V_3(\mathbf{r})}{r} + \frac{2V_1(\mathbf{r})}{3r} \right) [(S_{yy} - S_{zz})^2 x \sin 2hx] \\ & + \frac{5}{4} \rho \int d\mathbf{r} \frac{V_3(\mathbf{r})}{r} \times Q_{zzzz} \left[ \frac{9}{392} \sin 2hx + \frac{5}{64} \sin 4hx \right] \end{aligned} \quad (5)$$

and in the limit of the long wavelength ( $hx \ll 1$ ), we obtain finally

$$\frac{F}{N} = kT \langle \ln 4\Pi f \rangle_{\Omega} - \frac{A}{2} \left[ S_2^2 + \frac{\Delta^2}{3} \right] + Bh^2 \left[ S_2 + \frac{\Delta}{3} \right]^2 - 2h \left( \left( S_2 + \frac{\Delta}{3} \right)^2 (C + D) + \frac{25}{21} S_4^2 D \right), \quad (6)$$

with the density energy expressions of 'nematic' types  $A$  and  $B$  of chiral contributions  $C$  and  $D$

$$\left. \begin{aligned} A &= -\rho \int V_2(\mathbf{r}) d\mathbf{r}, & B &= -\frac{3}{4} \rho \int V_2(\mathbf{r}) x^2 d\mathbf{r}, \\ C &= -\frac{\rho}{4} \int V_1(\mathbf{r}) \frac{x^2}{r} d\mathbf{r}, & D &= -\frac{3}{16} \rho \int V_3(\mathbf{r}) \frac{x^2}{r} d\mathbf{r} \end{aligned} \right\} \quad (7)$$

and the definition of the order parameters

$$\left. \begin{aligned} S_{zz} = S_2 &= \int f(\Omega) P_2(\cos \theta) d\Omega, \\ S_{xx} - S_{yy} = \Delta &= \int f(\Omega) \frac{3}{2} \sin^2 \theta \cos 2\phi d\Omega, \\ Q_{zzzz} = S_4 &= \int f(\Omega) P_4(\cos \theta) d\Omega, \end{aligned} \right\} \quad (8)$$

where  $\Delta$  is the measure of the biaxiality of the system, and  $S_2$  and  $S_4$  are the usual nematic order parameters.

Minimization of the interactions with respect to  $h$  yields for an equilibrium value for the inverse of the pitch

$$h_0 = \frac{C + D \left( 1 + \frac{25}{21} \left( \frac{S_4}{S_2 + \frac{\Delta}{3}} \right)^2 \right)}{B}, \quad (9)$$

which reintroduced in the free energy expansion gives

$$\frac{F}{N} = kT \langle \ln 4\Pi f \rangle_{\Omega} - \frac{A}{2} \left[ S_2^2 + \frac{\Delta^2}{3} \right] - \frac{1}{B} \left[ S_2 + \frac{\Delta}{3} \right]^2 \left( C + D \left( 1 + \frac{25}{21} \left( \frac{S_4}{S_2 + \frac{\Delta}{3}} \right)^2 \right) \right)^2. \quad (10)$$

By minimization of the functional free energy with respect to  $f(\Omega)$  and taking into account the normalization condition,

$$f(\theta, \phi) = \frac{\exp\left(-\frac{V_{\text{mf}}(\theta, \phi)}{kT}\right)}{Z} \quad \text{with} \quad \int f(\theta, \phi) \, d\Omega = 1, \quad (11)$$

we obtain the mean field potential expression

$$\begin{aligned} V_{\text{mf}}(\theta, \phi) = & -P_2(\cos \theta) \left[ AS_2 + \frac{2}{B} Ch1 Ch2 \left( S_2 + \frac{\Delta}{3} \right) \right] \\ & - \frac{3}{2} \sin^2 \theta \cos 2\phi \left[ A \frac{\Delta}{3} + \frac{2}{3B} Ch1 Ch2 \left( S_2 + \frac{\Delta}{3} \right) \right] \\ & - P_4(\cos \theta) \left[ \frac{100D}{21B} Ch1 S_4 \right], \end{aligned} \quad (12)$$

with coefficients

$$Ch1 = C + D \left( 1 + \frac{25}{21} \alpha(T) \right), \quad Ch2 = C + D \left( 1 - \frac{25}{1} \alpha(T) \right), \quad (13)$$

where temperature dependence is realized through the ratio of order parameters  $\alpha(T)$

$$\alpha(T) = \left( \frac{S_4}{S_2 + \frac{\Delta}{3}} \right)^2. \quad (14)$$

We find two characteristic values when  $Ch1$  and  $Ch2$  become zero. The first case is the classical one which has been reported previously [34–37]: when chiral contributions  $C$  and  $D$  are close, but with opposite sign, then it could happen that at a certain critical temperature  $Ch1$  cancels, the pitch diverges and the handedness of the macroscopic helix changes. Moreover we have verified that  $\Delta$  becomes zero and changes sign as well at the transition, like the pitch. This is due to the mean field approximation for cylindrically symmetric molecules, where biaxiality for a nematic is not allowed [2]. More interesting is the case where  $Ch2$  becomes zero: the pitch is not affected, but  $\Delta$  can become zero again. It can be noticed that because the ratio of the order parameters is a decreasing function with temperature,  $Ch1$  and  $Ch2$  cannot cancel simultaneously for two specified chiral interactions  $C$  and  $D$  when the temperature changes. Calculations on this phenomenon and on the order parameter  $S_4$  are currently in progress.

### 3. Functional integral description of flexible molecules

Liquid crystalline polymers possess some conformational flexibility due to the cumulative effect of internal vibrations, bond bending and degrees of freedom. In the continuum elastic chain model, a chain is characterized by its bending constant  $\kappa$  and the extended chain length  $L$ . The end to end distribution function for a single chain in the mean field approximation can be expressed in a functional integral representation. [27]

$$G(\Omega', \Omega''; 0, L) = \int_{\Omega(0)=\Omega'}^{\Omega(L)=\Omega''} \delta(\Omega) \exp - \left( \int_0^L ds \left[ \frac{1}{2} \beta \kappa \left( \frac{\delta \Omega}{\delta s} \right)^2 + V_{\text{mf}}(\Omega) \right] \right). \quad (15)$$

This model neglects end effects [38] and assumes slow variations on the atomic scale.  $G(\mathbf{\Omega}', \mathbf{\Omega}(s); s)$  satisfies a Schrödinger-like equation

$$\left[ \frac{\delta}{\delta s} - \frac{1}{2\beta\kappa} \Delta_{\mathbf{\Omega}} + V_{\text{mf}}(\mathbf{\Omega}) \right] G(\mathbf{\Omega}', \mathbf{\Omega}; 0, s) = \delta(\mathbf{\Omega} - \mathbf{\Omega}') \delta(s). \quad (16)$$

The curvilinear abscissa  $s$  playing the role of an imaginary time,  $G(\mathbf{\Omega}', \mathbf{\Omega}(s); s)$  is analogous to the space-time propagator for a particle in an external field [39] and can be expanded in eigenfunctions  $\psi_j(\mathbf{\Omega}, s)$

$$G(\mathbf{\Omega}', \mathbf{\Omega}(s); 0, s) = \frac{1}{2} \sum_j [\psi_j^*(\mathbf{\Omega}') \psi_j(\mathbf{\Omega}(s)) + \psi_j(\mathbf{\Omega}') \psi_j^*(\mathbf{\Omega}(s))] \quad (17)$$

and  $\psi_j(\mathbf{\Omega}, s)$  can always be developed in spherical harmonics when decoupling in  $\mathbf{\Omega}$  and  $s$  is true

$$\psi_j(\mathbf{\Omega}(s)) = \sum_l \sum_m r_j^l {}^m Y_l^m(\mathbf{\Omega}) \exp(-E_j s) \quad (18)$$

Calculation of order parameter  $\Delta$  implies  $m$  being not always equal to zero.

Flexibility can be estimated by the ratio  $L/q$ , where  $q$ , the persistence length, indicates the correlation length of two tangent vectors  $\mathbf{\Omega}(s)$  and  $\mathbf{\Omega}(t)$  when  $s$  and  $t$  describe distances along the chain (40)

$$\langle \mathbf{\Omega}(s) \cdot \mathbf{\Omega}(t) \rangle \propto \exp\left(-\frac{s-t}{q}\right). \quad (19)$$

In an isolated polymer molecule,  $q$  is given by  $\beta\kappa$  [18].

When inserting the cholesteric mean field (12) in the diffusion-type equation (14), one obtains a secular equation

$$\sum_k \sum_{n=-k}^k [A_{l,k}^{m,n} - a_j \delta_{m,n} \delta_{k,l}] r_j^k {}^n = 0, \quad (20)$$

where  $\mathbf{A}_{l,k}^{m,n}$ , a real square symmetric matrix of dimension  $(2l+1)^2$ ,  $a_j$  and  $r_j^k {}^m$  are given in the Appendix.

With a sufficient number of spherical harmonics (at least 7 when considering  $S_2$  or both  $S_2$  and  $S_4$  and  $S_5$  when we consider  $\Delta$ ), calculation of eigenvectors  $r_j^k {}^m$  and eigenvalues  $a_j$  allows us to solve numerically the self-consistent system constituted by the three order parameter equations (8).

#### 4. Results and discussion

When the chiral interaction of second order  $D$  is small compared to the other interaction terms, then the pitch is almost constant with temperature. In this case we report some new results implying flexibility effects. When we solve the self-consistent system, the physical behaviour is determined by the values of  $kTc/AL$  and  $\varepsilon_1$  at the transition with

$$\varepsilon_1 = \frac{C^2}{AB}. \quad (21)$$

From equation (7), an approximation, using a Lennard-Jones-like potential, yields  $B = r_c^2 A$  where  $r_c$  is an intermolecular length. Thus we have only two independent parameters:  $A$  and  $C$ . In the visible range, the magnitude of  $\varepsilon_1$  can be estimated to be

$10^{-5}$ , consistent with estimations made from values of the twist elastic constant [11]. But in the following, we will see that  $\varepsilon_1$  must be much greater than this estimated value so that the chiral part becomes significant compared to the nematic behaviour. One possible interpretation of this discrepancy could be that fluctuations should be collective and should be scaled by the number of correlated molecules [11]. Another explanation could be that chiral contribution  $D$ , as previously shown, can be very close to  $C$  [31, 37] and cannot be dropped from equation (9). Then taking  $D = \lambda C$ , we estimate

$$\varepsilon_1 \approx \left(2\pi \frac{r_c}{P}\right)^2 \frac{1}{(1+\lambda)^2}.$$

When  $\lambda$  approaches  $-1$ ,  $\varepsilon_1$  can reach values reported for numerical calculations.

Because we have no information on the exact magnitude of  $A$ ,  $B$  and  $C$  we will assume that they are in a constant ratio, whatever is the chain rigidity given by the ratio  $L/q$ . Then, we verify that biaxiality increases with chirality and decreases slightly with the rigidity until it reaches a plateau (see figure 1). The order parameter  $S_2$  decreases with chirality and reaches a minimum which is a function of chirality. This minimum takes place at lower rigidity when the chirality increases (see figure 2). The fluctuations observed for high chirality are due to numerical precision which has to be very important when chirality is not a small perturbation. The ratio of order parameters confirms that the effect of flexibility is small with respect to  $L/q$ . The effect of temperature is given (see figures (3–5)): the ratio  $\Delta/S_2$  decreases less with  $T/T_c$  than reported [9], especially close to the transition, and we see that flexibility at a given chirality does not play an important role even though it reduces the ratio of the order parameters and decreases slightly the effects of temperature (the slopes in figure 4 are more sensitive to temperature than those in figure 5).

The ratio  $kT_c/AL$  implying both energy term and length (we cannot isolate just one of these two variables) increases with chirality (see figure 6). When  $\varepsilon_1$  is not negligible, we add a strong contribution to the dominant  $A$  in the mean field potential; the

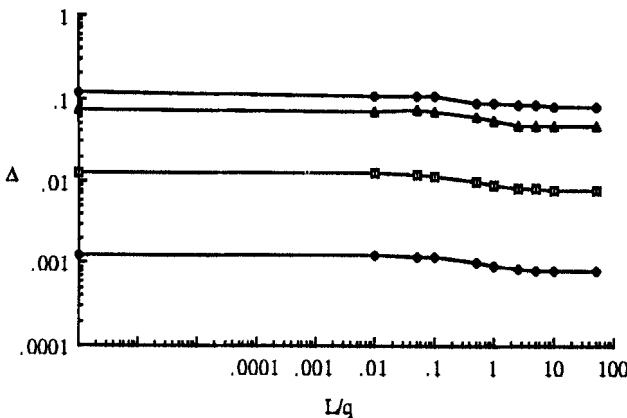


Figure 1. Evolution of the biaxial order parameter  $\Delta$ , at the transition temperature, with chain rigidity  $L/q$  ( $L$ , total chain length contour;  $q$ , persistence length) for different chiralities.  $\Delta$  is an increasing function of the chirality  $\varepsilon_1$  and varies slightly with flexibility. For a given  $\varepsilon_1$  the minimum of  $\Delta$  increases with decreasing biaxiality.  $\blacklozenge$ ,  $\varepsilon_1 = 0.0022$ ;  $\square$ ,  $\varepsilon_1 = 0.023$ ;  $\blacktriangle$ ,  $\varepsilon_1 = 0.183$ ;  $\diamond$ ,  $\varepsilon_1 = 0.6445$ .

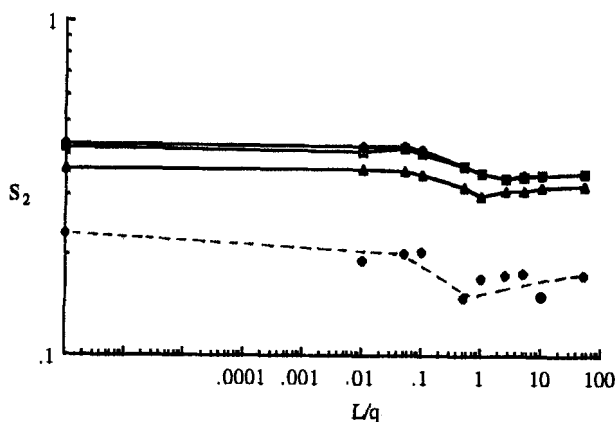


Figure 2. Evolution of the order parameter  $S_2$ , at the transition temperature, with chain rigidity for different chiralities. The behaviour of  $S_2$  is essentially affected when  $\varepsilon_1$  increases. When  $\varepsilon_1 = 0.6445$ , chirality is not a perturbation and the self-consistent system is more sensitive to numerical precision.  $\blacklozenge$ ,  $\varepsilon_1 = 0.0022$ ;  $\square$ ,  $\varepsilon_1 = 0.023$ ;  $\blacktriangle$ ,  $\varepsilon_1 = 0.183$ ;  $\diamond$ ,  $\varepsilon_1 = 0.6445$ .

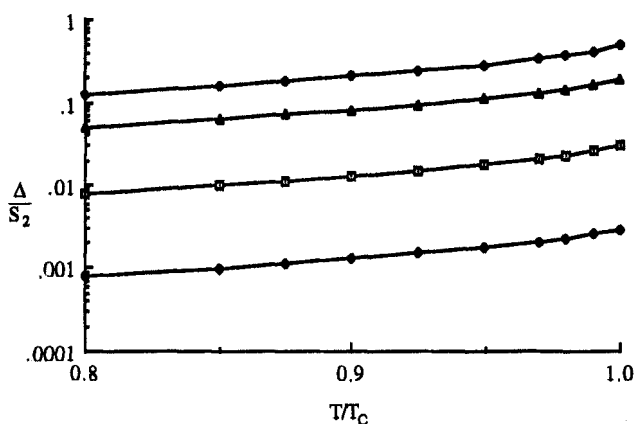


Figure 3. Evolution of the ratio of order parameters  $\Delta/S_2$ , with reduced temperature for rod-like molecules ( $L/q = 10^{-7}$ ).  $\blacklozenge$ ,  $\varepsilon_1 = 0.0022$ ;  $\square$ ,  $\varepsilon_1 = 0.023$ ;  $\blacktriangle$ ,  $\varepsilon_1 = 0.183$ ;  $\diamond$ ,  $\varepsilon_1 = 0.6445$ .

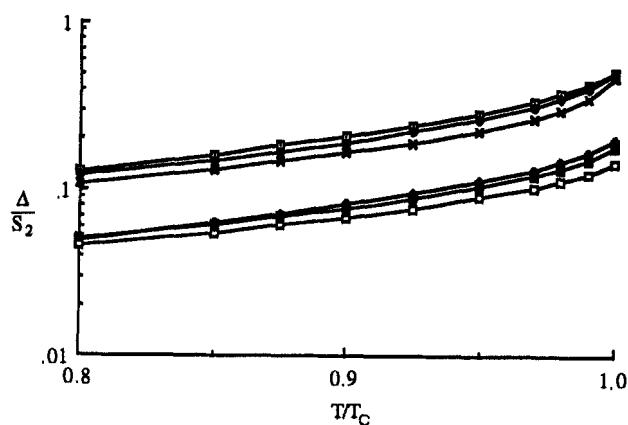


Figure 4. Evolution of the ratio of order parameters  $\Delta/S_2$ , with reduced temperature for 2 different high chiralities when flexibility is zero ( $L/q = 10^{-7}$ ), in the intermediate range of flexibility ( $L/q = 1$ ), and for flexible molecules ( $L/q = 50$ ).  $\square$ ,  $\varepsilon_1 = 0.6445$ ,  $L/q = 10^{-7}$ ;  $\blacklozenge$ ,  $\varepsilon_1 = 0.6445$ ,  $L/q = 1$ ;  $\times$ ,  $\varepsilon_1 = 0.6445$ ,  $L/q = 50$ ;  $\diamond$ ,  $\varepsilon_1 = 0.183$ ,  $L/q = 10^{-7}$ ;  $\blacksquare$ ,  $\varepsilon_1 = 0.183$ ,  $L/q = 1$ ;  $\square$ ,  $\varepsilon_1 = 0.183$ ,  $L/q = 50$ .



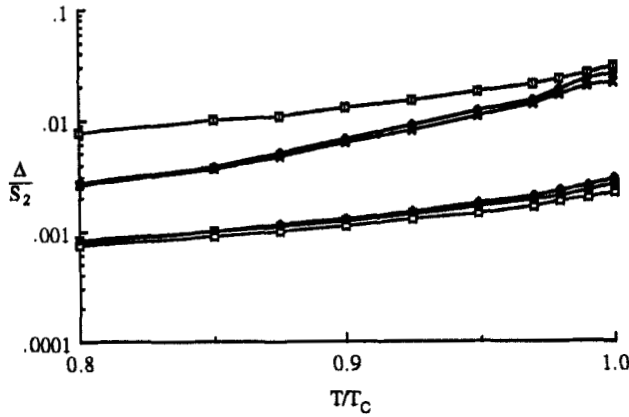


Figure 5. Evolution of the ratio of order parameters  $\Delta/S_2$ , with reduced temperature for 2 different low chiralities when flexibility changes.  $\square$ ,  $\epsilon_1=0.023$ ,  $L/q=10^{-7}$ ;  $\blacklozenge$ ,  $\epsilon_1=0.023$ ,  $L/q=1$ ;  $\times$ ,  $\epsilon_1=0.023$ ,  $L/q=50$ ;  $\diamond$ ,  $\epsilon_1=0.0022$ ,  $L/q=10^{-7}$ ;  $\blacksquare$ ,  $\epsilon_1=0.0022$ ,  $L/q=1$ ;  $\square$ ,  $\epsilon_1=0.0022$ ,  $L/q=50$ .

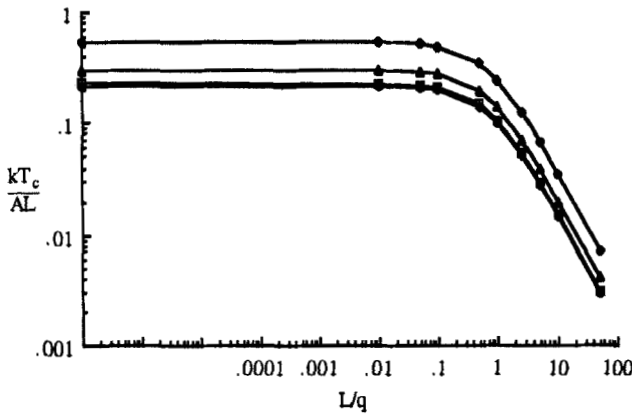


Figure 6. Evolution of the ratio  $kT_c/AL$  for the transition temperature  $T_c$ , for different chiralities. When  $\epsilon_1$  increases we allow the uniaxial nematic structure to show a biaxial behaviour.  $\diamond$ ,  $\epsilon_1=0.6445$ ;  $\blacktriangle$ ,  $\epsilon_1=0.183$ ;  $\square$ ,  $\epsilon_1=0.023$ ;  $\blacklozenge$ ,  $\epsilon_1=0.0022$ .

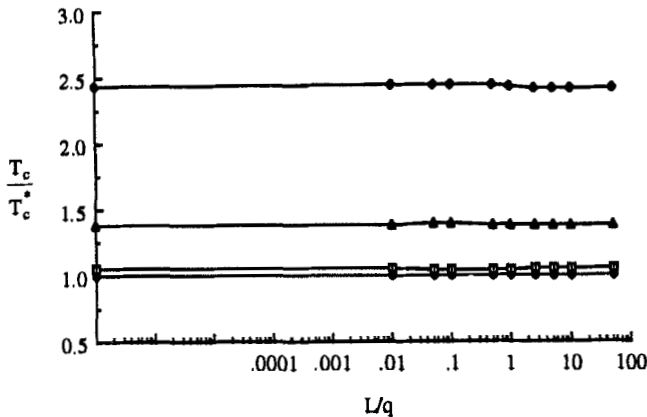


Figure 7. Evolution of the ratio  $T_c/T_c^*$  for different chiralities, where  $T_c^*$  is the transition temperature at zero chirality. The ratio  $T_c/T_c^*$  is almost a constant function of flexibility.  $\diamond$ ,  $\epsilon_1=0.6445$ ;  $\blacktriangle$ ,  $\epsilon_1=0.183$ ;  $\square$ ,  $\epsilon_1=0.023$ ;  $\blacklozenge$ ,  $\epsilon_1=0.0022$ .

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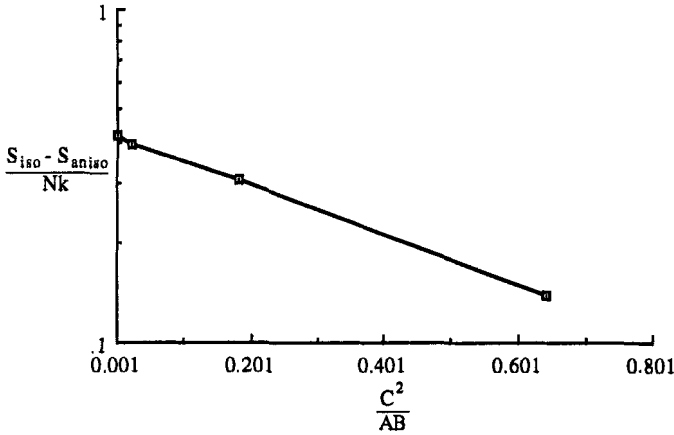


Figure 8. Evolution of the differential of entropy between the isotropic and the anisotropic phases for rod-like molecules with chirality  $\epsilon_1$ .

consequence is to lower, for a negative contribution, and to increase, for a positive contribution, the ratio  $kT_c/AL$ . We observe that the transition temperature increases with increasing biaxiality, but remains constant with chain flexibility (see figure 7). We also calculate the differential orientational entropy at the transition between the isotropic and the anisotropic phases in the limit of high rigidity (see figure 8).

$$\frac{S_{iso} - S_{aniso}}{Nk} = \int f(\Omega) \ln f(\Omega) d\Omega, \tag{22}$$

$S_{iso} - S_{aniso}/Nk$  decreases with chirality which indicates that the system can reach a second order phase transition when  $\epsilon_1$  increases. This is in good agreement with other theories [12, 17].

### Appendix

With the help of the recurrence relation for spherical harmonics defined in [41] for example, the components  $A_{l,k}^{m,n}$  are easily obtained with the following relation:

$$A_{l,k}^{m,n} = \int d\Omega Y_k^n(\theta, \phi) \left( \sum_{l',m'} [l(l+1) - c_2 \cos^2 \theta - c_4 \cos^4 \theta - c_d \sin^2 \theta \cos 2\phi] r_j^{l'} Y_{l'}^{m'}(\theta, \phi) \right)$$

with coefficients

$$c_2 = 3q \left( E_2 - \frac{5}{2} E_4 \right), \quad c_4 = \frac{35}{4} q E_4, \quad c_d = 3q E_c$$

and energy terms

$$E_2 = AS_2 + \frac{2}{B} Ch1 Ch2 \left( S_2 + \frac{\Delta}{3} \right),$$

$$E_d = A \frac{\Delta}{3} + \frac{2}{3B} Ch1 Ch2 \left( S_2 + \frac{\Delta}{3} \right),$$

$$E_4 = \frac{100D}{21B} Ch1 S_4.$$

The eigenvalues are

$$a_j = \left[ \frac{2q}{L} E_j - qA + \frac{3}{4} qC \right],$$

where  $A$ ,  $B$ ,  $C$ ,  $D$  are the basic energy contributions defined in (7).

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