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Theoretical prediction of the cholesteric pitch in thermotropic and lyotropic systems

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The expression for the cholesteric pitch given by the theory of Lin-Liu *et al.* is extended by explicit consideration of the orientational entropy terms. The temperature dependence, as well as the dependence on the mole fraction in non-mesogenic solutions and on the degree of polymerization in polymer cholesterics can be obtained. In some cases helical inversion can be induced by variation of concentration as well as temperature.

1. Introduction

Some years ago, a molecular statistical theory for cholesteric liquid crystals was proposed in which the intermolecular potential contained chiral contributions [1, 2]. It was shown that a cholesteric phase is the consequence of chirality of the potential and the temperature dependence of the cholestric pitch was calculated. Both an increase as well as a decrease of the cholesteric pitch on increasing temperature was found and in a particular pure cholesteric, the helicity could be reversed by variation of temperature. Mixtures with a nematic phase were also studied.

Recent experiments on polymer liquid crystals have shown new effects [3, 4]. For example, cellulose derivatives can exhibit both left and right handed twist and sense inversion can be induced not only by the variation of temperature but also by the variation of the concentration in lyotropic systems. The pitch has also been shown to depend on the degree of polymerization [3, 5] and on the degree of substitution [6]. Such effects are not obtained in [1, 2]. In this paper we present an extension of the formula for the cholesteric pitch to include the effects of concentration in non-mesogenic and non-chiral solvents and of molecular weight in rigid polymer systems. Several numerical examples are given.

2. Contribution of the orientational entropy

For liquid crystals in the mean field approximation [2], the Helmholtz free energy functional F is

$$\begin{aligned} F\{f(\mathbf{r},\boldsymbol{\Omega})T,\rho\} = {} & F_0(T,\rho)+\rho kT\int f(\mathbf{r}_1\boldsymbol{\Omega}_1)\ln 4\pi f(\mathbf{r}_1\boldsymbol{\Omega}_1)\mathrm{d}\mathbf{r}_1\,\mathrm{d}\boldsymbol{\Omega}_1 \\ & +\tfrac{1}{2}\rho^2\int f(\mathbf{r}_1\boldsymbol{\Omega}_1)f(\mathbf{r}_2\boldsymbol{\Omega}_2)V(\mathbf{r}_1\boldsymbol{\Omega}_1,\mathbf{r}_2\boldsymbol{\Omega}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\boldsymbol{\Omega}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\boldsymbol{\Omega}_2, \end{aligned} \qquad (1)$$

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where ρ is the average number density of liquid crystal. The one particle distribution function $\rho f(\mathbf{r}, \boldsymbol{\Omega})$ at position $\mathbf{r}$ for orientation $\boldsymbol{\Omega}$ fulfils the condition

$$\int_V f(\mathbf{r}, \boldsymbol{\Omega})\, \mathrm{d}\mathbf{r}\, \mathrm{d}\boldsymbol{\Omega} = NL \tag{2}$$

for N rods with degree of polymerization L in volume V. Following the calculations given in detail in [2], the potential between particles, $V(\mathbf{r}_1, \boldsymbol{\Omega}_1, \mathbf{r}_2, \boldsymbol{\Omega}_2)$ is decomposed into two parts

$$V(\mathbf{r}_1, \mathbf{r}_2, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) = V_N(\mathbf{r}_{12}, \boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) + V_x(\mathbf{r}_{12}, \boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2)(\boldsymbol{\Omega}_1 x \boldsymbol{\Omega}_2 \cdot \mathbf{r}_{12}). \tag{3}$$

The V_N term is the usual orientation dependent nematic interaction and given by an expansion in spherical harmonics

$$V_N(\mathbf{r}_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2) = V_2(\mathbf{r}_{12}) P_2(\boldsymbol{\Omega}_1 \boldsymbol{\Omega}_2) + V_4(r_{12}) P_4(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) + \dots. \tag{4}$$

We limit the expansion to order four. The V_x term in equation (3) is the chiral component of the interaction,

$$V_x(\mathbf{r}_{12}, \boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) = V_1(r_{12}) \cdot P_1(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2) + V_3(r_{12}) P_3(\boldsymbol{\Omega}_1 \cdot \boldsymbol{\Omega}_2). \tag{5}$$

We limit the expansion at order three.

The distribution function $f(\mathbf{r}, \boldsymbol{\Omega})$ is expanded in Legendre polynomials in the angle Ψ between the director $\mathbf{n}(r)$ and $\boldsymbol{\Omega}$

$$f(\mathbf{n}(r) \cdot \boldsymbol{\Omega}) = \frac{1}{4\Pi}\left(1 + \sum_l (2l + l)\sigma_l P_l(\mathbf{n}(r) \cdot \boldsymbol{\Omega})\right). \tag{6}$$

The usual ansatz for $\mathbf{n}(r)$ is made, namely

$$\mathbf{n}(r) = (\cos qz, \sin qz, 0).$$

Here, the director is uniformly twisted along the z axis with pitch $p = 2\Pi/q$. The order parameters are defined as

$$\sigma_{2l} = \int f(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\Omega}) P_{2l}(\mathbf{n}(\mathbf{r})) \cdot \boldsymbol{\Omega}) \quad l = 1, 2, 3. \tag{7}$$

Equations (3)–(7) are inserted in expression (1) to obtain

$$F = F_{\mathrm{I}} + F_{\mathrm{N}} + F_{\mathrm{T}}(Q), \tag{8}$$

where F_{I} is the isotropic energy which contains the isotropic interactions and the mixing entropy, is of no further interest for the calculation of the pitch. F_{N} is the nematic energy including the orientational entropy and the interaction terms

$$F_{\mathrm{N}} = 4\pi x \mathrm{k} T \int_{-1}^{1} \tfrac{1}{2} f(\cos\psi) \ln 4\pi f(\cos\psi))\, \mathrm{d}\cos\psi + \tfrac{1}{2} x^2 (\sigma_2^2 \gamma_2 + \sigma_2^2 \gamma_4). \tag{9}$$

In order to study solutions in simple non-mesomorphic solvents, we introduce at this point the mole fraction or volume concentration x of cholesteric component. This can be written as $x = (NLv_0)/V$ where v_0 is the volume occupied by a single liquid crystal unit. F_{N} contains, as usual, the symmetric mean field given by $(l = 2, 4)$

$$\gamma_l = \frac{1}{v_0} \int V_l(\mathbf{r})\, \mathrm{d}\mathbf{r}.$$

In the following we will renormalize lengths relative to the intermolecular distance d leading to $Q=dq$, $\boldsymbol{\eta}=\mathbf{r}/d$ and $\zeta=z/d$. Then, $F_{\mathrm{T}}(Q)$ is the chiral mean field and depends on the pitch of the cholesteric

$$F_{\mathrm{T}}(Q)=\tfrac{1}{2}x^2(\sigma_2^2G_2(Q)+\sigma_4^2G_4(Q)), \tag{10}$$

with

$$G_2(Q)=\tfrac{3}{4}\lambda_2(2Q)-\tfrac{1}{2}\mu_1(2Q)+\tfrac{3}{14}\mu_3(2Q),$$
$$G_4(Q)=\tfrac{20}{64}\lambda_4(2Q)+\tfrac{35}{64}\lambda_4(4Q)-\tfrac{5}{56}\mu_3(2Q)-\tfrac{5}{16}\mu_3(4Q).$$

The interaction parameters $\lambda_l(Q)$ and $\mu_m(Q)$ are given as averages of the intermolecular potential,

$$\lambda_l(Q)=\frac{d^3}{v_0}\int d\boldsymbol{\eta}\, V_l(\eta)(\cos Q\xi-1),\quad l=2,4 \tag{11}$$

$$\mu_m(Q)=\frac{d^3}{v_0}\int d\boldsymbol{\eta}\, V_m(\eta)\,(\sin Q\xi)\xi/\eta,\quad m=1,3. \tag{12}$$

In order to derive an analytical expression for $Q\ll 1$, an expansion to order Q^2 is made

$$\lambda_l(Q)=\tfrac{1}{2}\lambda_l''(0)Q^2 \tag{13}$$

with

$$\lambda_l''(0)=-\left(\frac{d^3}{v_0}\int \xi^2V_l(\eta)d\boldsymbol{\eta}\right)$$
$$=\lambda_l, \tag{14}$$

and

$$\mu_m(Q)=\mu_m'(0)Q$$

with

$$\mu_m'(0)=\left(\frac{d^3}{v_0}\int \frac{\xi^2}{\eta}V_m'(\eta)d\boldsymbol{\eta}\right)$$
$$=\mu_m.$$

If, as in [2] only the twist interaction $F_T(Q)$ is expanded to order Q^2 and minimized with respect to Q, we obtain the equilibrium solution Q_0 for the inverse pitch, as in [2]

$$Q_0=\frac{\tfrac{1}{2}\mu_1\sigma_2^2-\tfrac{3}{14}\mu_3\sigma_2^2+\tfrac{5}{7}\mu_3\sigma_4^2}{\tfrac{3}{2}\lambda_2\sigma_2^2+5\lambda_4\sigma_4^2}. \tag{15}$$

We remark that in this approximation

(i) the pitch is independent of concentration as well as the degree of polymerization;
(ii) the dependence on temperature is given by σ_4^2/σ_2^2 and so an expansion in spherical harmonics at least to order four is necessary to reproduce the temperature dependence;
(iii) for $\lambda_2\gg\lambda_4$, the temperature gradient of the pitch is given by the sign of $R=\mu_1/\mu_3$ which can be positive or negative;
(iv) the pitch is given by a ratio of the (space) averages of the symmetric ($l=2,4$) and antisymmetric ($m=1,3$) interactions.

In the following we will show that the orientational entropy (the first term in F_N) also contributes to the calculation of the pitch. Supplementary factors appear leading to a dependence on concentration and a richer range of possible behaviour.

By minimization of the total free energy in equation (8) with respect to the orientational distribution we obtain

$$f(\cos\psi)=\frac{1}{Z}\exp\left(\frac{-Lx}{\mathrm{k}T}\right)[\sigma_2P_2(\cos\psi)(\gamma_2+G_2(Q))+\sigma_4P_4(\cos\psi)(\gamma_4+G_4(Q))], \quad (16)$$

where Z is determined by normalization (see equation (2)). The supplementary terms in the free energy are then calculated by inserting (16) in equation (9). Using the usual approximation $\lambda_2 \gg \lambda_4$ and $\gamma_2 \gg \gamma_4$, the equilibrium pitch is obtained as

$$Q_0=\frac{n_0+\dfrac{\hat{x}n_1+\hat{x}^2n_2}{n}}{\dfrac{\lambda_2}{\gamma_2}+\dfrac{\hat{x}d_1+\hat{x}^2d_2}{n}}, \quad (17)$$

with

$$n_0=m_1+m_2S^2(T),$$

$$n_1=4/5m_1,$$

$$n_2=-2\sigma_2(T)[m_1\tfrac{4}{35}+m_2\tfrac{4}{35}S(T)],$$

$$d_1=2\left[\left(\frac{\lambda_2}{\gamma_2}+3m_1^2\right)\tfrac{2}{5}+m_2^2S(T)^2\tfrac{2}{3}\right],$$

$$d_2=-2\sigma_2(T)\left[\tfrac{4}{35}\left(\frac{\lambda_2}{\gamma_2}+6m_1^2\right)+12S(T)\tfrac{4}{35}m_1m_2+6S(T)^2\tfrac{40}{693}m_2^2\right],$$

$$n=2+\frac{\hat{x}^2}{5}\sigma_2^2(T).$$

The important parameters of the theory are $\hat{x}$, $S(T)$, m_1 and m_2,

$$\hat{x}=x\frac{L\gamma_2}{\mathrm{k}T_c}\frac{T_c}{T}, \quad S(T)=\left(\frac{\sigma_4}{\sigma_2}\right), \quad m_1=\left(\frac{\mu_1}{3}-\frac{\mu_3}{7}\right)\frac{1}{\gamma_2}, \quad m_2=\tfrac{10}{21}\mu_3/\gamma_2.$$

Here T_C is the anisotropic–isotropic transition temperature of the pure cholesteric and in mean field theory for rigid nematic rods $L\gamma_2/\mathrm{k}T_C$ is a numerical constant. The pitch is found to be a ratio of polynominals in concentration x and the inverse reduced temperature. The temperature dependence is not solely determined by the ratio $S(T)$ of the order parameters. For $\hat{x}=0$, we recover the expression given in [2].

3. Discussion

We find that the pitch is a ratio of predominantly symmetric to predominantly chiral average interactions. In consequence, the concentration dependence can be given either by dilution of the chiral interactions (leading to an increase of the pitch on dilution) or by dilution of the symmetric interactions (leading to a decrease of the pitch on dilution) or by a rather delicate balance between the two.

From the expression for the pitch, we can immediately see the existence of poles for which $Q_0=0$. If these poles fall in the temperature or concentration range of observation, strong variations of the pitch will be observed. On the other hand, these poles can appear or disappear as the order of the expansion in $\hat{x}$ is increased. It is found that consistency between the results given by the first and second order expansion occurs for $\mu_3 \ll \mu_1$ (or $|R| \ll 1$) for which convergence of the expansion in $\hat{x}$ is sufficiently rapid.

We explore the dependence of the cholesteric pitch on the chiral interaction parameters μ_1 and μ_3 in figures 1–3. In these numerical examples of equation (15), $\gamma_2<0$ was eliminated by use of the Maier–Saupe relation [7]:

$$\frac{kT_C}{-L\gamma_2}=0{\cdot}22.$$

The order parameters $\sigma_2(T)$ and $S(T)$ were fitted to experimental data [8],

$$\sigma_2(T)=0{\cdot}28(T_C-T)^{0{\cdot}26}(1{\cdot}15^{1/(T_C-T)}), \quad T<T_C-0{\cdot}65$$

$$S(T)=0{\cdot}42\exp\left(-\frac{7{\cdot}31}{T_C-T}\right).$$

The ratio λ_2/γ_2 was estimated using a Lennard-Jones model potential for $V_2(r)$. If $|R| \ll 1$, we find two main types of behaviour.

(i) For $\mu_1>0$, $\mu_3>0$, the concentration dependence shows a decrease in the pitch with increasing concentration x (see figure 1 (*a*)). Here $R>0$ and the pitch is found to increase with increasing temperature (see figure 1 (*b*)).

(ii) If $\mu_1>0$ but $\mu_3<0$, an increase in the pitch is found as the concentration is increased (see figure 2 *a*)). $R<0$ and the pitch decreases with increasing temperature (see figure 2 (*b*)).

The case $\mu_1<0$, $\mu_3<0$ resembles (i), $\mu_1<0, \mu_3>0$ resembles (ii).

The pitch is, therefore, a sensitive measure of the relative strength of nematic type and chiral type interactions. For small μ_1 the sign of the concentration gradient is the inverse of that of the temperature gradient and both are determined by R. Strong concentration dependence is found at low concentrations $x \approx 0{\cdot}3$–$0{\cdot}4$, which will be usually in or near the biphasic gap. For somewhat larger values of $|R|$, a positive gradient in concentration and temperature is found (see figures 3 (*a*) and (*b*)). But note that the expression $p(2)$ using the second order expansion in $\hat{x}$ inverts the sense of the temperature gradient as compared to the first order expansion $p(1)$. This problem can be avoided by use of a self-consistent equation for Q instead of an expansion and will be explored in a future publication.

In a polymer liquid crystal the degree of polymerization (L) can be varied. This will cause a variation of Q through the transition temperature T_C. Experimental measurements of T_C generally show an initial increase with increasing L followed by a flattening of the curve [5]. The pitch then also varies with L in a cholesteric polymer and again the variation will be given by the sign and value of μ_1 and μ_3. For the range of parameters considered we find behaviour similar to the variation with concentration, i.e. a negative concentration gradient will lead to a decrease of the pitch on increase of molecular weight. This is in agreement with recent measurements but further experiments are needed, and the effect of chain flexibility, not included here, should be considered [9].

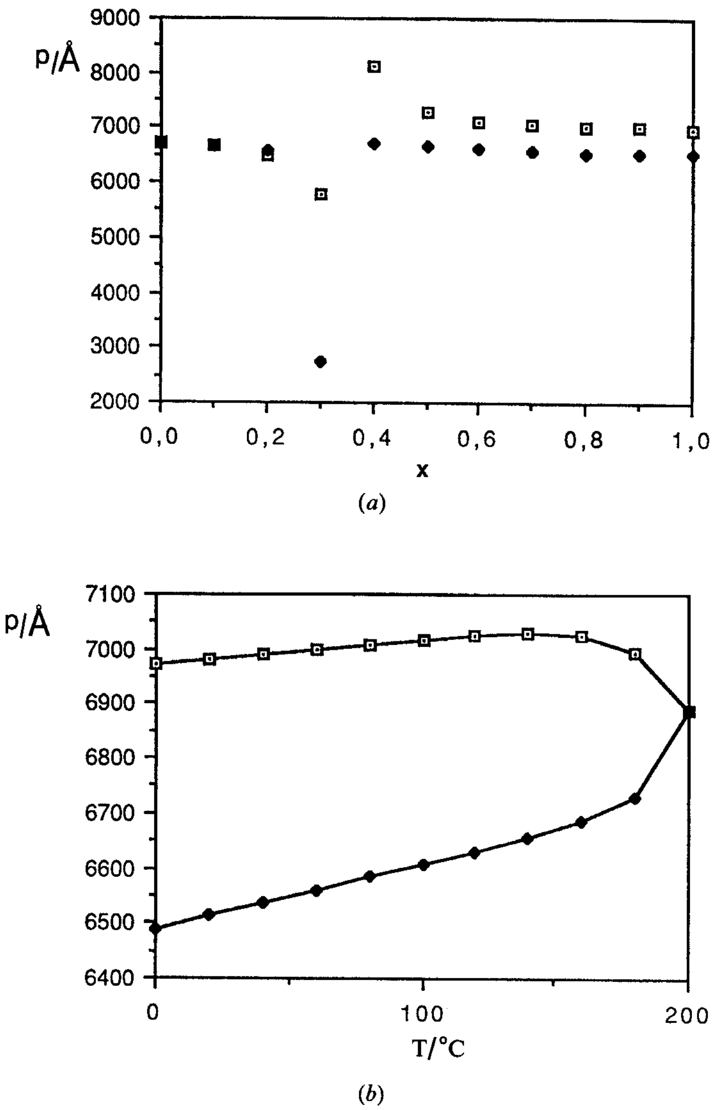
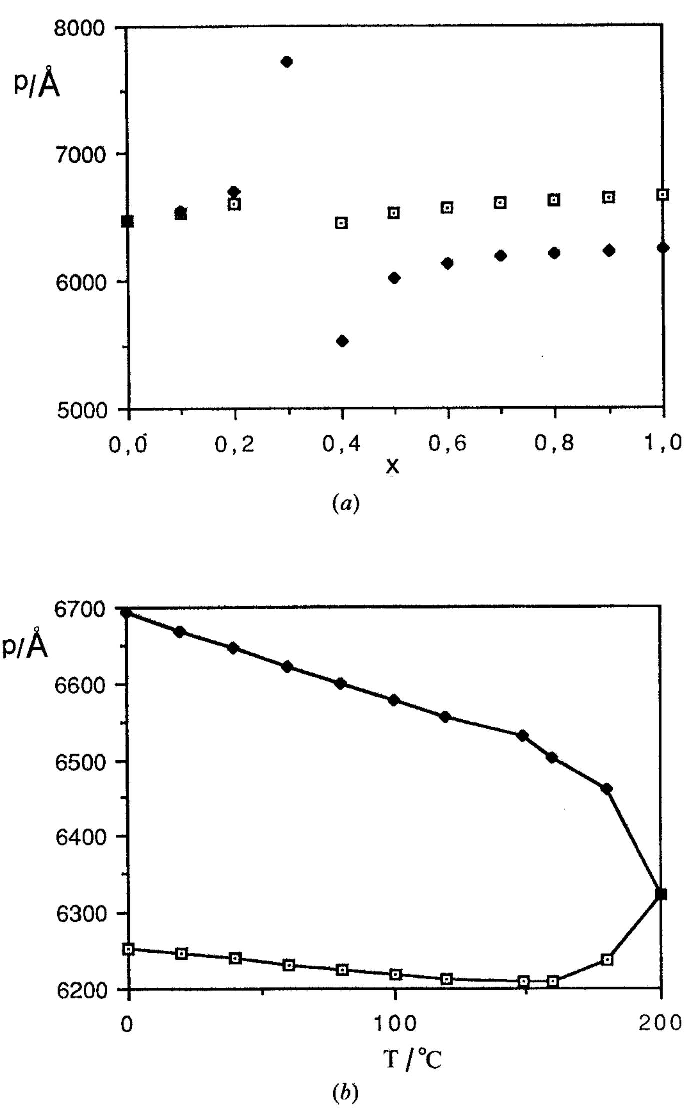


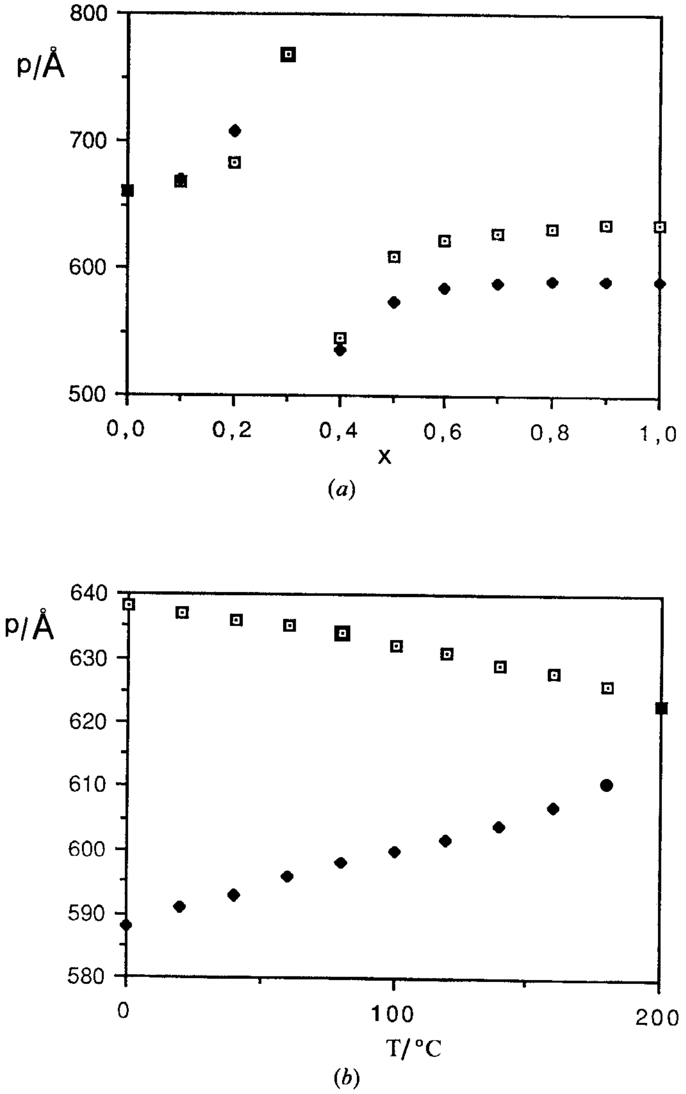
Figure 1. Pitch p for $T_C = 200°C$, $\lambda_2/\gamma_2 = -2$, $\mu_1/\gamma_2 = -0{\cdot}04$, $\mu_3/\gamma_2 = -0{\cdot}004$ (*a*) as a function of concentration (wt%) x at 180°C (*b*) as a function of temperature in the pure cholesteric $x = 1$. For $p(1)$ (□) the expansion of equation (14) was used to order one, for $p(2)$ (◆) to order two.



(a)

(b)

Figure 2. Pitch p for $T_C = 200°C$, $\lambda_2/\gamma_2 = -2$, $\mu_1/\gamma_2 = -0{\cdot}04$, $\mu_3/\gamma_2 = 0{\cdot}004$ (a) as a function of concentration (wt%) x at 180°C (b) as a function of temperature in the pure cholesteric. For $p(1)$ (□) the expansion of equation (14) was used to order one for $p(2)$ (◆) to order two.



(a)

(b)

Figure 3. Pitch p for $T_C = 200°C$, $\lambda_2/\gamma_2 = -2$, $\mu_1/\gamma_2 = -1$, $\mu_3/\gamma_2 = -0{\cdot}1$ (*a*) as a function of concentration (wt%) x at 180°C (*b*) as a function of temperature in the pure cholesteric. For $p(1)$ (□) the expansion of equation (14) was used to order one, for $p(2)$ (◆) to order two.

In conclusion, the present theory exhibits a large diversity of behaviour in agreement with experiments on polymer liquid crystals [3–6]. A change of helicity is shown to be not necessarily an effect of the solvent dielectric constant [10] nor a change in the structure of the liquid crystal chain but possibly due to a balance between attractive and repulsive forces at a certain concentration or temperature. Quantitative comparison between theory and experiment is hindered by lack of knowledge of the interaction parameters for a given liquid crystal. The sign of μ_1 and μ_3 plays an important role and will be determined by the dominance of repulsive (positive μ_i) or attractive (negative μ_i) interactions. It is as yet, difficult to relate the λ_l and μ_m parameters to specific interactions, for example to high order terms in a multipole expansion of the electrostatic potential between molecules [11]. These will be sensitive to chemical structure and to chain conformation and possibly also to the local ordering due, for example, to hydrogen bonding with the solvent. We could simply consider λ_l and μ_m as phenomenological parameters for a given system and study the influence of various quantities such as the characteristics of the solvent, the degree of substitution, the polarisability, anisotropy or the molecular shape. Ideally, a physically consistent picture should emerge and is currently under investigation.

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