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Micellar shape dependence of cholesteric pitch in lyotropic liquid crystals

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A generalized Landau–Ginzburg–de Gennes theory of cholesteric pitch in lyotropic chiral liquid crystals is presented. Using the non-critical order parameter, introduced by Toledano and Figueiredo Neto, the question of pitch dependence on micellar shape is addressed. This extra order parameter accounts for the shape change of the micelles. The predictions agree qualitatively with the unique experimental observations of Lopes and Figueiredo Neto.

The cholesteric phase appears in materials composed of chiral molecules or in mixtures of the latter with ordinary nematogenic compounds, and is known for both thermotropic and lyotropic liquid crystals [1–5]. It is locally very similar to the nematic phase where the centres of mass of the molecules or micelles are disordered, while their orientations are, on average, parallel to the director, $\hat{\mathbf{n}}$. The director, however, is not constant in space, but rotates uniformly about a helical axis, perpendicular to $\hat{\mathbf{n}}$. The periodicity of the structure often lies in the optical region, which results in the Bragg scattering of visible light. As in nematics, the states $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ of the director are equivalent, implying that the spatial periodicity (wavelength) of the cholesterics is one half of the magnitude of the pitch [1–3].

The cholesteric phase of lyotropic cholesteric liquid crystals (i.e. mixtures of amphiphilic compounds, water, and chiral molecules) [4, 5], has been studied intensively over the last decade [4–7]. In particular, it was shown, that for small concentration M_α of optically active material dissolved in a nematic matrix, the wavelength of the helical distortion is inversely proportional to M_α. While this observation is analogous to what we know for thermotropic cholesterics [1], an experiment that showed the influence of the shape anisotropy of the micelles on the pitch [8] seems to be unique to lyotropic systems. More specifically, it was observed that an increase in the microscopic shape anisotropy of the micelles lowers the cholesteric pitch. The system studied was a mixture of potassium laurate, decanol, water, and brucine sulphate. For a fixed molar concentration of the chiral material, the shape anisotropy of the micelles was controlled by the balance between the molar concentrations of the alcohol and the soap. Identification of the pitch and of the micellar shape anisotropy followed from optical and X-ray diffraction techniques, respectively.

A purpose of this paper is to look at the shape anisotropy dependence of the pitch from a theoretical point of view. We shall generalize the order parameter description of cholesterics by incorporating the non-critical order parameter of Toledano and Figueiredo Neto [9, 10], which measures the shape anisotropy of the micelles.

To start with, let us recall that the leading order parameter describing orientational properties of mesophases is an alignment tensor $\mathbf{Q}(\mathbf{r})$. The tensor is symmetric and traceless, and of second rank. Therefore it has five independent components. The spatial dependence of $\mathbf{Q}$ takes into account the possibility of non-uniform configurations of the orientational degrees of freedom, like those observed for cholesterics. In general, it describes locally three structures: (a) the isotropic reference structure, where $\mathbf{Q}(\mathbf{r})=0$; (b) the uniaxial structure in which case $\mathbf{Q}(\mathbf{r})$ has two equal eigenvalues; and (c) the biaxial structure, where all three eigenvalues of $\mathbf{Q}(\mathbf{r})$ are different. In the case of the cholesteric phase $\mathbf{Q}(\mathbf{r})$ takes the general

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form of a biaxial helix [11]

$$\mathbf{Q}_{\mathrm{Ch}}(\mathbf{r}) = \frac{-Q_0}{\sqrt{6}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \frac{\sqrt{2}Q_2}{2}\begin{pmatrix} \cos(u) & -\sin(u) & 0 \\ -\sin(u) & -\cos(u) & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (1)$$

where u stands for $qz + \psi_2$, q for wave vector, ψ_2 for an arbitrary phase reflecting a freedom of choosing the coordinate orgin and Q_0, Q_2 for magnitudes of the uniaxial and biaxial parts of $\mathbf{Q}_{\mathrm{Ch}}$, respectively.

It was de Gennes who first proposed the Landau–Ginzburg type of expansion in terms of the alignment tensor $\mathbf{Q}(\mathbf{r})$ [1]. He aimed to describe fluctuations of the order parameter in the isotropic phase, close to the nematic (cholesteric) phase transition. Therefore, the free energy, $\mathscr{F}_{\mathrm{deGL}}$, that he proposed, contains $\mathcal{O}(3)$ (or $\mathcal{SO}(3)$ for the cholesteric case) symmetric invariants, which can be constructed from the order parameter $\mathbf{Q}(\mathbf{r})$ and its derivatives. $\mathscr{F}_{\mathrm{deGL}}$ consists of two parts: the *gradient* free energy, which includes terms in derivatives of the order parameter, and the *bulk* part, containing powers of the order parameter itself. Stability of the expansion demands keeping at least the terms up to second order in the gradient and up to fourth order in the bulk free energy. In the absence of external fields and in the reduced units of Grebel *et al.* [11, 12] the original expression of de Gennes reads [13]:

$$\mathscr{F}_{\mathrm{deGL}} = v^{-1}\int_v \mathrm{d}^3\mathbf{x}\left\{\frac{1}{4}[t\,\mathrm{Tr}(\mathbf{Q}^2) - 2\kappa\varepsilon_{ijk}Q_{\mathrm{in}}Q_{jn,k} + (Q_{ij,l})^2 + \rho Q_{ij,j}^2] - \sqrt{6}\beta\,\mathrm{Tr}(\mathbf{Q}^3) + \gamma[\mathrm{Tr}(\mathbf{Q}^2)]^2\right\} \qquad (2)$$

where the symbol ε_{ijk} denotes the totally antisymmetric Levi–Civita tensor and the summation over repeated indices is to be understood. The mixed term containing the Levi–Civita tensor is different from zero *only* in the cholesteric phase, which has no mirror symmetry. The stability of the expansion (2) requires that $\rho > -3/2$ and $\gamma > 0$.

The meaning of all the parameters in the expansion (2) has been explained by Grebel *et al.* [11, 12]. For example, κ is the dimensionless chirality parameter, t is the dimensionless reduced temperature and ρ is the relative elastic constant. Distance and pitch, when expressed in reduced units, are dimensionless with the bare correlation length at the istropic–nematic (racemic) phase boundary serving as a unit of length. The remaining two parameters β and γ are redundant. Due to the choice of units and due to the prolate–oblate symmetry of $\mathscr{F}_{\mathrm{deGL}}$ one may take $\beta = \gamma = 1$ [11, 12].

The free energy (2), when supplemented with fifth and sixth order terms in $\mathbf{Q}$, describes qualitatively the main features of phase diagrams of nematic and cholesteric liquid crystals, i.e. all observed nematic phases are classified properly and the topologies of phase diagrams are reproduced correctly for thermotropic liquid crystals and partly for lyotropic systems. However, there are generic observations that cannot be accounted for by the free energy functional $\mathscr{F}_{\mathrm{deGL}}$. One of them is temperature behaviour of the cholesteric pitch. The Landau–Ginzburg–de Gennes model predicts that the cholesteric pitch does not depend on temperature. To see this, let us note that the explicit q-dependence appears only in the elastic part of $\mathscr{F}_{\mathrm{deGL}}$. The direct substitution of $\mathbf{Q}_{\mathrm{Ch}}$, equation (1), into $\mathscr{F}_{\mathrm{deGL}}$ and simple minimization over q yields $q_{\min} = \kappa$, which is in clear contradiction with experiments on cholesterics, where the wave vector depends strongly on temperature [14].

The experimentally observed temperature dependence of the pitch clearly suggests that the higher order elastic terms, which are usually disregarded in the standard theory (2), must be relevant. In a series of publications [15–17] a systematic way of studying the general properties of the higher order elastic free energy expansion was proposed. This generalized theory, as we will show below, allows for a qualitative description of the temperature dependence of the pitch and it will be a starting point of our discussion of the shape anisotropy dependence of the pitch.

Owing to the first order nature of the isotropic–cholesteric phase transition and the weakness of the spatial modulation of $\mathbf{Q}$, it seems justified to consider only elastic terms that are linear and quadratic in the derivatives of $\mathbf{Q}$. Therefore we shall restrict ourselves to the elastic invariants built up from the tensors $Q_{ij}Q_{lk}\ldots Q_{st}(Q_{mn,o})$ and $Q_{ij}Q_{lk}\ldots Q_{st}(Q_{mn,o})(Q_{rw,p})$ by means of contractions with the Kronnecker deltas and the Levi–Civita tensors.

A major difficulty in the analysis of higher order elastic terms is their huge number. Also, not all of them are independent as the constraints: $Q_{ii} = 0$ and $Q_{ii,j} = 0$ must be taken into account. Using the method of integrity basis, it was shown that the general elastic free energy up to quadratic order in $\partial\mathbf{Q}$ is composed of 39 invariants [15], which are multiplied by arbitrary polynomials in $\mathrm{Tr}\,\mathbf{Q}^2$ and $\mathrm{Tr}\,\mathbf{Q}^3$. The leading higher order invariants are cubic terms of the form $Q_{ij}Q_{lm,n}Q_{st,o}$. For the stability of the free energy expansion we must additionally retain some $Q_{gk}Q_{ij}Q_{lm,n}Q_{st,o}$ terms. The Cartesian form of these invariants has been given by Longa *et al.* [17]. There are six cubic invariants, 13 quartic invariants and one chiral invariant of third order, which introduce, besides the terms already present in equation (2), 20 more elastic terms. Although three surface relaxations eliminate three invariants, a study of the free energy expansion with an extra 17 adjustable parameters is hardly worthwhile. It is thus important to identify the relevant terms. Interestingly, due to the properties of the cholesteric tensor field $\mathbf{Q}_{\mathrm{Ch}}(\mathbf{r})$, equation (1), the majority of these new elastic terms just disappear leaving only one reduced elastic constant of third order, two elastic constants of fourth order and one third order chiral coupling constant. Gathering all non-vanishing terms of cubic and quartic order and adding the next-to-leading, chiral cubic invariant we get the following additional contribution $\mathscr{F}_{\mathrm{el}}$ to $\mathscr{F}_{\mathrm{deGL}}$ [17]

$$\begin{aligned}\mathscr{F}_{\mathrm{el}} = {} & L_4^{(3)} Q_{\alpha\beta} Q_{\alpha\mu,\nu} Q_{\beta\mu,\nu} + L_7^{(4)} Q_{\alpha\rho} Q_{\beta\rho} Q_{\alpha\mu,\nu} Q_{\beta\mu,\nu} \\ & + L_1^{(4)}\,\mathrm{Tr}(\mathbf{Q}^2) Q_{\alpha\mu,\nu} Q_{\alpha\mu,\nu} \\ & + 2L_7^{(3)} \varepsilon_{\alpha\beta\gamma} Q_{\alpha\mu} Q_{\beta\nu} Q_{\mu\gamma,\nu},\end{aligned} \tag{3}$$

where the notation follows that of [17].

We may safely assume that the weight of the higher order terms (3) should be smaller than that of the leading ones present in the expansion (2). Observing symmetry of various terms, this would imply that

$$L_1^{(4)} \lesssim 1,\ L_7^{(4)} \lesssim 1,\ L_7^{(4)} \lesssim |L_4^{(3)}| \lesssim 1 \quad \text{and} \quad |L_7^{(3)}| \lesssim \kappa. \tag{4}$$

Additionally, the stability of the combined expansion $\mathscr{F}_{\mathrm{deGL}} + \mathscr{F}_{\mathrm{el}}$ requires that $L_1^{(4)} > 0$ and $L_7^{(4)} > 0$.

Now, substitution of equation (1) into (2) and (3) yields

$$\begin{aligned}&\mathscr{F}_{\mathrm{deGL}} + \mathscr{F}_{\mathrm{el}} \\ &= \left(-3 - \frac{1}{2} bq + \frac{1}{4} gq^2\right) Q_0 Q_2^2 + \left(2 + \frac{1}{4} aq^2\right) Q_0^2 Q_2^2 \\ &\quad + Q_0^3 + Q_0^4 + \left(1 + \frac{1}{4} hq^2\right) Q_2^4 + \frac{1}{4} t Q_0^2 \\ &\quad + \left(\frac{1}{4} q^2 - \frac{1}{2} \kappa q + \frac{1}{4} t\right) Q_2^2\end{aligned} \tag{5}$$

where $a = 2L_1^{(4)} + (1/3)L_7^{(4)}$, $h = 2L_1^{(4)} + L_7^{(4)}$, $b = (2\sqrt{6}/3)L_7^{(3)}$, and where $g = (2\sqrt{6}/3)L_4^{(3)}$. That is, instead of 17 new coupling constants, we get for cholesterics only one reduced elastic constant of third order, denoted g, and two elastic constants a and h of fourth order, where $a \leqslant h$. There is also a third order chiral coupling constant b. In the majority of cases they should obey the relations: $a \lesssim 7/3$, $h \lesssim 3$, $|b| \lesssim (2\sqrt{6}/3)\kappa$ and $\sqrt{6}(h - a) \lesssim |g| \lesssim 2\sqrt{6}/3$, which follow from equation (4).

Minimization of equation (5) with respect to q yields the equilibrium value of the wave vector

$$\frac{q}{\kappa} = \frac{\left(\dfrac{b}{\kappa}\right) Q_0 + 1}{g Q_0 + a Q_0^2 + h Q_2^2 + 1}. \tag{6}$$

It depends on the amplitudes Q_0 and Q_2, which are also found from the minimization of the free energy (5). Note that cholesteric wave vector q depends on temperature in an indirect way, i.e. through equilibrium values of Q_0 and Q_2. For a weak higher order chiral term (small b) the increase of the order parameters Q_0 and Q_2 (decrease of temperature) causes a decrease of the wave vector. This general behaviour predicted by the model is illustrated in figure 1 (dashed lines). Some other possibilities, e.g. with a maximum at intermediate temperatures, also exist [18].

The theoretical results are in line with experimental data for thermotropic cholesterics [14], although very strong temperature variation of the pitch for some temperatures, e.g. close to a smectic phase or in the vicinity of the isotropic–cholesteric phase transition, most probably cannot be understood exclusively in terms of temperature variation of the order parameters. In these regimes short range smectic ordering or fluctuations seem to affect the cholesteric helix much more strongly than the predictions of equation (6).

Now we turn to lyotropic systems. The most important new aspect here is changes in the form of the micellar aggregates that directly couple to the resulting orientational order. This means that in any microscopic or phenomenological descriptions of lyotropics it is necessary to take into account the modification of the average micellar shape anisotropy with temperature

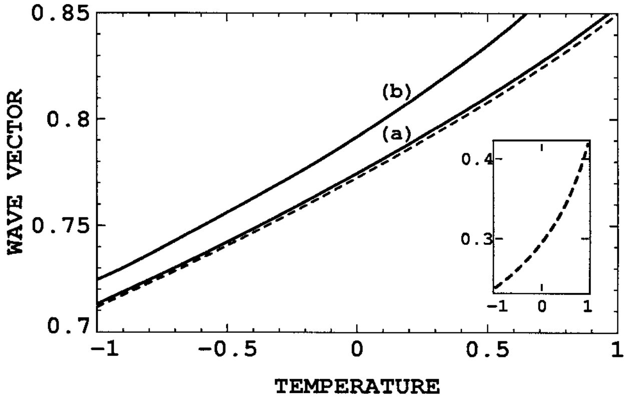

Figure 1. Temperature variation of the wave vector q/κ disregarding (dashed lines) and regarding (solid lines) shape parameter of the micelles for $\kappa = 1$, $b = -0.5$, $g = -0.5$ $a = 0.3$, $h = 0.4$ and for (*a*) $x_1 = -0.5$; $x_2 = 2$ and (*b*) $x_1 = -1$; $x_2 = 1$. Inset corresponds to $\kappa = 1$, $b = -0.3$, $g = 1.6$ $a = 2.4$ and $h = 3$. All quantities are plotted dimensionless.

and relative concentrations in the mixture compounds [9, 10]. One possibility is to introduce a non-critical, scalar order parameter, τ, in addition to $\mathbf{Q}$, as proposed by Toledano and Figueiredo Neto [9, 10]. One could interpret τ as measuring a relative variation in the population of different types of micelle. For instance, the description of a biaxial nematic phase sandwiched between two isotropic phases would require τ, which measures the relative population of predominantly biaxial and almost spherical micellar aggregates [9, 10]. In the case of phase transition between isotropic and cholesteric discotic phases, τ would measure the relative balance between predominantly discotic and almost spherical micelles.

The minimal coupling theory describing isotropic, uniaxial and biaxial phases observed in lyotropic systems was shown to be a series expansion in terms of the three independent invariants [9, 10]: τ, $\mathrm{Tr}(\mathbf{Q}^2)+\tau^2$ and $\mathrm{Tr}(\mathbf{Q}^3)$ instead of just $\mathrm{Tr}(\mathbf{Q}^2)$ and $\mathrm{Tr}(\mathbf{Q}^3)$ as in equation (2). The modified expansion has the same mathematical structure as that in $\mathrm{Tr}(\mathbf{Q}^2)$ and $\mathrm{Tr}(\mathbf{Q}^3)$. The expansion in τ is dropped at the τ_2 term. In the case of biaxial micellar systems the expansion runs up to sixth order in $\mathbf{Q}$.

Interestingly, the theory so constructed classifies properly the phase diagrams observed in lyotropic nematics. In particular, it accounts for re-entrant behaviour [9, 10, 19–21], which for many years was an unsolved problem.

Now the question that arises is whether a combination of de Gennes theory and higher order elastic terms with the ideas of the microscopic shape anisotropy of the micelles as a function of τ can explain qualitatively the pitch behaviour of cholesteric lyotropic liquid crystals [8]. Applying the transformation: $\mathrm{Tr}(\mathbf{Q}^2)\rightarrow \mathrm{Tr}(\mathbf{Q}^2)+\tau^2$ to $\mathscr{F}_{\mathrm{deGl}}+\mathscr{F}_{\mathrm{el}}$ and adding *independently* terms in τ (up to quadratic order) [9, 10] yields the free energy, equation (5), supplemented by extra terms

$$\mathscr{F}_\tau = x_1\tau + \frac{1}{4}t\tau^2 + x_2\tau^2 + 2(Q_0^2+Q_2^2)\tau^2 + \frac{1}{4}a_1 q^2 Q_2^2\tau^2 + \tau^4 \tag{7}$$

where x_1, x_2 and $a_1 = 1/2(3a-h)$ are additional phenomenological parameters. Note that the terms depending exclusively on τ are allowed by symmetry. Their presence is necessary as they take into account the modification of the micellar shape anisotropy [9, 10]. The only new term appearing in equation (7), as compared with the work by Toledano *et al.* [9, 10], is that proportional to a_1. It accounts for the direct coupling between elastic deformations and τ.

The minimization of $\mathscr{F} = \mathscr{F}_{\mathrm{deGL}} + \mathscr{F}_{\mathrm{el}} + \mathscr{F}_\tau$ with respect to q now yields

$$\frac{q}{\kappa} = \frac{\left(\dfrac{b}{\kappa}\right)Q_0 + 1}{gQ_0 + aQ_0^2 + hQ_2^2 + a_1\tau^2 + 1} \tag{8}$$

which is similar to the one given by equation (6) except for the extra term proportional to a_1. In addition to Q_0 and Q_2, now also τ must be found from the miminization of the free energy. The temperature variation of the pitch in the case when we account for the change in the shape of the micelles ($|\tau| < 0.5$) and restrict phenomenological parameters to those previously discussed, is shown in figure 1 (solid lines). We note that although micellar shape clearly changes the wave vector of cholesterics, the curves follow strictly those where the micellar shape was not included. The relative contribution from micellar shape change is of the order of 10% and is strongest in the vicinity of the isotropic–cholesteric phase transition. Again this prediction is quite general and practically independent of the values of phenomenological parameters. Also note that due to the prolate–oblate symmetry of the Landau–Ginzburg description [13], the results hold both for cholesteric discotic and cholesteric calamitic phases. In the first case τ measures relative population of predominantly discotic and almost spherical micelles, while in the second case discotic micelles are replaced by prolate ones.

Now we turn to the case studied experimentally in [8]. As already mentioned, the experiments were carried out for the mixture of potassium laurate, decanol, water, and brucine sulphate. Temperature and molar concentration of the chiral component were kept fixed (or nearly so), while the shape anisotropy of the micelles was controlled by the balance between the molar concentrations of the alcohol and the soap. In all cases studied the stable phase observed was cholesteric discotic, positioned a few degrees above the isotropic phase or polyphasic region.

In our phenomenological description this is equivalent to minimization of $\mathscr{F}$ with respect to q, Q_0 and Q_2 for given τ keeping t, κ, and all remaining parameters fixed. Note that x_1 and x_2 are irrelevant in this case. The generic prediction of such minimization is shown in figure 2. Generally, we find that increases of micellar shape anisotropy shifts q towards higher values, i.e. *lowers the pitch.* For moderate values of τ ($|\tau| \leqslant 0.5$) and for a chosen set of the parameters, the relative increase in q is 10–20%. Within the theory presented, the micellar shape affects the cholesteric wave vector both directly via coupling with higher order elastic terms and indirectly through its influence on the equilibrium value of the order parameters Q_0 and Q_2.

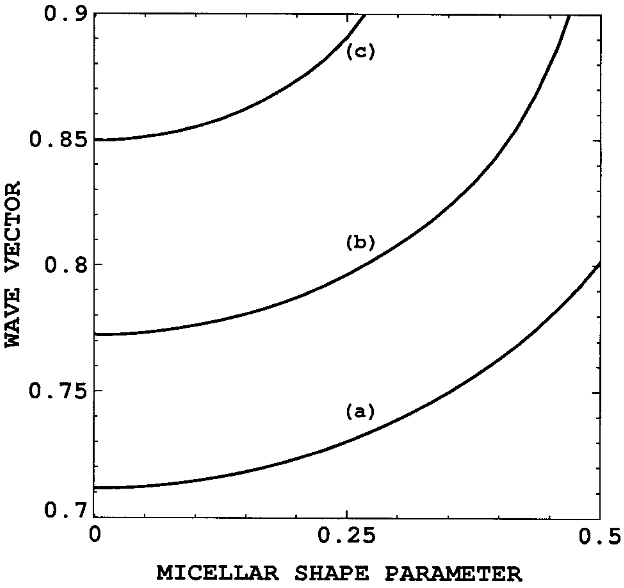

Figure 2. Variation of the wave vector q/κ in micellar systems as a function of the shape parameter τ for $\kappa = 1$, $b = -0.5$, $g = -0.5$ $a = 0.3$, $h = 0.4$ and for (*a*) $t = -1$, (*b*) $t = 0$ and (*c*) $t = 1$.

In order to make a qualitative comparison between theory and experiment we need a relation between the experimental shape anisotropy parameter and τ. First we note that in the experiment [8], the change in shape of the micelles was quantified in terms of the dimensionless parameter A, defined as the ratio of the average micellar disk diameter, s_x^{-1}, to the average distance between the neighbouring disks s_y^{-1}: $A = s_x^{-1}/s_y^{-1}$, where s_y^{-1} was nearly constant for all the samples studied. With this definition, the inverse pitch was found to vary linearly with A. Secondly, following the ideas of Toledano *et al.* [9, 10] the microscopic definition of τ should be connected with the relative change in the average micellar shape. Combining the above observations we find that one possible definition reads

$$\tau \approx \tau_0 + \frac{s_x^{-1} - s_y^{-1} + s_0}{s_x^{-1} + s_y^{-1} - s_0} = \tau_0 + \frac{A - 1 + s_1}{A + 1 - s_1} \qquad (9)$$

where $s_y^{-1} - s_0$ is the average height of the micellar disk ($s_1 < 1$) and τ_0 is the adjustable parameter. Clearly, an increase of A implies an increase of τ, which means that the trends found theoretically indeed agree qualitatively with *unique* experimental observations [8]. Although the results are presented for a specific set of model parameters, we found that the increase of the wave vector with τ, as shown in figure 2, is practically independent of these parameters provided that the wave vector increases with increasing temperature (figure 1), in the absence of τ-terms.

In summary, we have developed a generalized Landau–Ginzburg–de Gennes theory of cholesteric liquid crystals, specially applied to lyotropics where the shape anisotropy of the micelles is a function of the temperature and the relative concentrations of the different compounds. The theory describes qualitatively the experimental behaviour of the cholesteric pitch as a function of the temperature and the relative concentrations of the different compounds in lyotropic cholesterics. As the formalism used makes no distinction between prolate and oblate symmetry, it would also be of interest to carry out analogous experiments for the cholesteric calamitic phase.

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