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Robert A. Pelcovits[a][b]
[a] The Martin Fisher School of Physics, Brandeis University, Waltham, Massachusetts, U.S.A. [b] Department of Physics, Brown University, Providence, RI, U.S.A.

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Cholesteric pitch of rigid and semi-flexible chiral liquid crystals

by ROBERT A. PELCOVITS
The Martin Fisher School of Physics, Brandeis University, Waltham,
Massachusetts 02254, U.S.A. and Department of Physics, Brown University,
Providence, RI 02912, U.S.A.†

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We calculate using mean field theory, the cholesteric pitch in systems composed of chiral molecules, which we model as 'corkscrews'. We consider both the rigid and semi-flexible limits. Our result for the cholesteric pitch depends on the intrinsic molecular pitch length as well as the concentration of molecules, but does not depend on the flexibility of the molecule.

1. Introduction

Cholesteric liquid crystals are formed from chiral molecules which differ from their mirror images. Simple mechanical models for chiral molecules include threaded rods, twisted biaxial bodies, and corkscrews (which are threaded rods with a hollow core). The cholesteric pitch in a system of threaded rods was considered by Straley [1] using Onsager theory [2], and extended by Odijk [3] to the semi-flexible case using scaling arguments [4]. For rigid threaded rods of length L, diameter d (not including the threads), thread depth Δ, ($\Delta \ll L$) and number density ρ_L, Straley found the following expression for the pitch length p,

$$p \simeq (\Delta d \rho_L)^{-1}. \tag{1}$$

Surprisingly, there is no dependence in this expression on the intrinsic pitch of the molecule, i.e. the distance between the neighbouring threads. One would expect that a system of coarsely threaded rods has a shorter cholesteric pitch length, as compared with a system of finely threaded rods, because in the former case neighbouring rods will pack together with a larger angle between their long axes. Finely threaded rods can mesh their threads together and remain nearly parallel. We would expect then to have a cholesteric pitch length inversely proportional to the molecular pitch length. Odijk's result for the semi-flexible threaded molecule also has no dependence on the intrinsic molecular pitch.

Evans [5] was the first to consider the effect of the molecular pitch on the cholesteric pitch using a density functional theory applied to twisted rigid biaxial ellipsoids. He derived numerically the ratio of the chiral pitch to the molecular pitch in terms of the semi-axis lengths of the hard body and in the limit of small twist. For a fixed molecular biaxiality Evans found that the cholesteric pitch ratio is proportional to the pitch of the ellipsoid, and independent of concentration. However, a strong dependence on concentration has been observed experimentally [6] in cholesteric polymers. The proportionality of the cholesteric pitch and the molecular pitch is physically reasonable in a model of twisted ellipsoids which become nonchiral as the pitch of the twist goes to zero; for screw-like molecules we expect an inverse relationship, because the screw threads get more dense as the molecular pitch tends to zero.

In this paper we return to the model of screw-like molecules and calculate the cholesteric pitch within Maier–Saupe theory for chiral molecules modelled as corkscrews for both the rigid and semi-flexible limits. By modelling the chiral molecules as corkscrews and using Maier–Saupe theory we can calculate the pitch length analytically for the rigid case. We find the cholesteric pitch length to be inversely proportional to the molecular pitch length, in agreement with the intuitive arguments presented above. For strong nematic order our Maier–Saupe result can be readily transcribed to an Onsager form involving the concentration and molecular parameters. It has been hypothesized that semi-flexible molecules such as the fd virus are in fact corkscrew-like in structure [7]. Our analytic result for the rigid case is readily extended to the semi-flexible case using Odijk's scaling prescription [4]. We find a dependence of the cholesteric pitch on concentration different from that found by Odijk, and no dependence on molecular flexibility, in disagreement with Odijk's results.

2. Results

To calculate the cholesteric pitch we need to evaluate the elastic constant K_t, the coefficient of the term linear in the director gradient in the Frank free energy. The

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† Permanent address.

pitch length is then given by [8]

$$p = \frac{2\pi K_2}{K_t}, \tag{2}$$

where K_2 is the twist elastic constant. We follow the approach of Lo and Pelcovits [9] who evaluated elastic constants for non-chiral molecules by calculating within mean-field theory the free energy of a distorted nematic using the Maier–Saupe potential [10] (this potential is equivalent to Onsager theory for strong nematic order where the director angular distribution function becomes Gaussian). In the present case we consider a twist distortion, and calculate K_t and K_2 from the free energy of distortion,

$$-k_B T\rho_L \, ln(Z/Z_o) = K_t q(\delta n) + \frac{1}{2} K_2 q^2 (\delta n)^2 + O((\delta n)^4). \tag{3}$$

Here Z_o is the partition function of an undistorted nematic (with the director parallel to the z direction), Z is the partition function of the distorted nematic, and δn is the amplitude of the twist nematic distortion, i.e., the distorted director field obeys,

$$\hat{\mathbf{n}}(\mathbf{r}(s)) = \hat{\mathbf{z}} \cos \theta_n(\mathbf{r}(s)) + \hat{\mathbf{x}} \sin \theta_n(\mathbf{r}(s)), \tag{4}$$

and

$$\theta_n(\mathbf{r}(s)) = (\delta n) \sin qy(s), \tag{5}$$

for a cholesteric twist along the y axis. The position vector $\mathbf{r}(s)$ gives the location of a point on the molecule located an arc length from one end, $s = 0$, of the molecule, and is measured from a fixed laboratory origin. Equation (3) is evaluated in mean-field Maier–Saupe theory by writing the partition function for a single molecule with local tangent vector $\hat{\mathbf{u}}(s)$ as

$$Z = \int \mathrm{d}\mathbf{R} \int \mathscr{D}\hat{\mathbf{u}}(s) \times \exp\left\{ \frac{aS}{k_B T} \int_0^L \mathrm{d}s \left[\frac{3}{2} (\hat{\mathbf{u}}(s) \cdot \hat{\mathbf{n}}(\mathbf{r}(s)))^2 - \frac{1}{2} \right] \right\}, \tag{6}$$

where a is a phenomenological parameter, S is the nematic order parameter, and L is the chemical length of the molecule. The position vector $\mathbf{R}$ specifies the location of the end of the molecule parameterized by $s = 0$; the integration over $\mathbf{R}$ samples the full spatially varying director pattern. The undistorted partition function Z_o is given by equation (6) with $\hat{\mathbf{n}}(\mathbf{r}(s)) = \hat{\mathbf{z}}$ for all values of s. The position vector $\mathbf{r}(s)$ is related to $\hat{\mathbf{u}}(s)$ by

$$\mathbf{r}(s) = \int_0^s \mathrm{d}s' \, \hat{\mathbf{u}}(s'). \tag{7}$$

Equation (3) is readily evaluated if we introduce a primed coordinate system whose origin is at the molecular end $s = 0$, and whose z' axis is parallel to $\hat{\mathbf{n}}(\mathbf{R})$, the local director at $\mathbf{R}$ (i.e. we rotate the coordinate axes by an angle $\delta n \sin(\mathbf{q} \cdot \mathbf{R})$ about the y axis). In the present case of chiral molecules we evaluate equation (3) to leading order in δn to obtain K_t; we will use the results from [4] and [9] for K_2 for rod-like molecules and thus obtain the leading dependence of p on the molecular chirality. In the primed coordinate system the dot product appearing in equation (6) is given to first order in δn by

$$\begin{aligned} \hat{\mathbf{u}}(s) \cdot \hat{\mathbf{n}}(\mathbf{r}(s)) = u'_z(s) + u'_x(s)[&\sin \mathbf{q} \cdot \mathbf{R} \cos qy'(s) \\ &+ \cos \mathbf{q} \cdot \mathbf{R} \sin qy'(s) - \sin \mathbf{q} \cdot \mathbf{R}]\delta n \\ &+ O((\delta n)^2). \end{aligned} \tag{8}$$

Using equations (3)–(8) we then find

$$K_t = \int \mathrm{d}R \int_0^L \mathrm{d}s \langle (-3aSu'_z(s)u'_x(s)y'(s)) \rangle, \tag{9}$$

where the expectation value $\langle \cdots \rangle$ is evaluated in the undistorted ensemble specified by the partition function Z_o. For rod-like molecules (i.e. $\hat{\mathbf{u}}' = \hat{\mathbf{z}}'$), K_t would be identically zero. For a corkscrew molecule with pitch axis $\mathbf{p_m} = p_m \hat{\mathbf{p}}_\mathbf{m}$, wavevector $\mathbf{q_m} = (2\pi/p_m)\hat{\mathbf{p}}_\mathbf{m}$ and radius $A = d/2 + \Delta$, the tangent vector is given by

$$\begin{aligned} \hat{\mathbf{u}}' = c_1 \hat{\mathbf{p}}_\mathbf{m} + c_2(&\hat{\mathbf{u}}_o \cos(2\pi s/\ell + \psi) \\ &+ \hat{\mathbf{p}}_\mathbf{m} \times \hat{\mathbf{u}}_o \sin(2\pi s/\ell + \psi)), \end{aligned} \tag{10}$$

where $\hat{\mathbf{u}}_o$ is a unit vector perpendicular to $\mathbf{p_m}$,

$$c_1 = \frac{p_m}{\ell} \tag{11}$$

$$c_2 = \left(\frac{\ell^2 - p_m^2}{\ell^2} \right), \tag{12}$$

$\ell = p_m + 2\pi A$ is the arc length of a single turn of the corkscrew, and ψ is the phase of the corkscrew relative to the background nematic field.

We evaluate the expectation value in equation (9) by integrating over all orientations of $\mathbf{p_m}$ in the undistorted ensemble (using spherical coordinates in the primed frame) and integrating over ψ (to average over the rotation of the corkscrew about its long axis†) with the result

$$K_t = \frac{3}{4} LaSp_m \rho_L \frac{\ell^2 - p_m^2}{\ell^2}, \tag{13}$$

which has the following limits for corkscrews with small

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†The author is indebted to R. Kamien for pointing out the importance of averaging over this rotation.

and large pitches respectively,

$$K_t \simeq LaS\rho_L p_m, \quad p_m \ll A \tag{14}$$

$$K_t \simeq LaS\rho_L A, \quad p_m \gg A. \tag{15}$$

The result for K_2 in Onsager [4, 11] and Maier–Saupe [9] theories (zeroth-order in the molecular pitch) is

$$K_2 = k_B T \rho_L \frac{L^2}{6}, \tag{16}$$

and thus the pitch length is given by

$$p = \frac{4\pi k_B T L}{9aS} \left\{ \frac{\ell^2}{\ell^2 - p_m^2} \right\}. \tag{17}$$

We relate the phenomenological Maier–Saupe parameters to more realistic ones by using the correspondence between the Maier–Saupe and Onsager theories at strong nematic order. In this limit the orientational distribution function of the director, $f(\theta)$ is Gaussian, with a width $2k_B T/3aSL$ in Maier–Saupe theory. In the Onsager theory of rigid rods the width is $\pi/2(d/L\phi)^2$ [12], where ϕ is the volume fraction of polymer. Equating these two expressions for the width of the Gaussian we can rewrite equations (16) and (17) as follows

$$K_t = \frac{k_B T}{\pi} (L\phi/d)^2 p_m \rho_L \frac{\ell^2 - p_m^2}{\ell^2}, \tag{18}$$

$$p = \frac{\pi^2 d^2}{3 p_m \phi^2} \frac{\ell^2}{\ell^2 - p_m^2}. \tag{19}$$

These equations have the following limiting behaviour:

$$K_t \simeq k_B T \rho_L p_m (L\phi/d)^2, \quad p_m \ll A, \tag{20}$$

$$K_t \simeq k_B T \rho_L A (L\phi/d)^2, \quad p_m \gg A, \tag{21}$$

$$p \simeq \frac{d^2}{p_m \phi^2}, \quad p_m \ll A, \tag{22}$$

$$p \simeq \frac{d^2}{A\phi^2}, \quad p_m \gg A. \tag{23}$$

Equations (22) and (23) predict that the cholesteric pitch for a corkscrew with a large diameter and small molecular pitch will be larger than for one with molecular pitch large compared with the diameter.

We now consider the pitch for a solution of long, semi-flexible corkscrews using the scaling prescription of Odijk [4]. This prescription consists of the replacements: $L \rightarrow \lambda$, $\rho_L \rightarrow \rho_\lambda$, where λ is the deflection length of a nematic polymer, and ρ_λ is the number density of effective segments of the deflection length. In terms of the persistence length P and its associated number density ρ_P, we have [4, 11]

$$\lambda = (P^{1/2} d \rho_P)^{-2/3}, \tag{24}$$

and

$$\rho_\lambda = \frac{\pi}{4} (P^2 d)^{2/3} \rho_P^{5/3}. \tag{25}$$

We find then,

$$K_t \simeq k_B T p_m (\phi/d)^2 (P^2 \rho_P / d^2)^{1/3} \left\{ \frac{\ell^2 - p_m^2}{\ell^2} \right\}. \tag{26}$$

The pitch p is unchanged by this scaling.

Odijk's extension of the Straley calculation produced the following results for p, K_t and H_c:

$$p \simeq \Delta^{-1} P^{-4/3} d^{-5/3} \rho_P^{-5/3}, \tag{27}$$

$$K_t \simeq k_B T P^2 \Delta d \rho_P^2, \tag{28}$$

The experimental measurements on poly(γ-benzyl L-glutamate) solutions by Dupre and Duke [6] show power law behaviour for p with an exponent of $-1{\cdot}8$, whereas the present theory yields an exponent of -2 and Odijk finds $-1{\cdot}66$. Thus both theories show approximately the same degree of agreement with experiment and we cannot confirm the validity of either theory. More experimental measurements on a variety of materials, both rigid and semi-flexible, would clearly be very valuable.

Finally, we note that our mean-field theory, as all other mean-field theories of chiral systems, assumes that each molecule is in exactly the same field as every other[†]. In equation (6) we assumed that the interaction strength aS is independent of the molecular tangent field $\hat{\mathbf{u}}(s)$, i.e., that the neighbouring molecules creating the mean field have rotated along with the molecule we are integrating over. In fact, the interaction should vary in strength as the tangent vector $\hat{\mathbf{u}}(s)$ moves closer or farther from the tangent vectors of neighbouring molecules. Thus, a more complete theory (which we will not attempt here) might account for this effect with a phenomenological prefactor in the interaction strength.

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