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Microscopic Origin of Cholesteric Pitch

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Abstract
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Microscopic Origin of Cholesteric Pitch

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We present a microscopic analysis of the instability of the nematic phase to chirality when molecular chirality is introduced perturbatively. We show that for central-force interactions the previously neglected short–range biaxial correlations play a crucial role in determining the cholesteric pitch. We propose a pseudoscalar strength which quantifies the chirality of a molecule. [S0031-9007(97)02460-5]

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Chirality in molecules leads to a myriad of macroscopic chiral structures, including life itself [1]. A molecule is chiral if its mirror image cannot be rotated to replicate itself [2]. Equivalently it is chiral if its symmetry group does not contain the element $\mathbf{S}_n$—a rotation around an S_n axis by $2\pi/n$ followed by a mirror through a plane perpendicular to that axis. A chiral molecule cannot be uniaxial: the only infinite point groups are $\mathcal{C}_{\infty v}$ and $\mathcal{D}_{\infty h}$ [3] which both contain $\mathbf{S}_1$. Thus if the molecular orientations are averaged independently (even if the distribution is uniaxial about a common molecular axis), the interactions will be identical to those of molecules with a C_∞ axis and will therefore not be chiral. Figure 1 shows a schematic representation of two interacting chiral molecules whose degree of chirality can be varied continuously as we will discuss below.

Molecular chirality induces chiral interactions that produce intermolecular torques of a given sign and can give rise to equilibrium chiral structures such as the cholesteric phase of liquid crystals. There are two common analyses of this effect. The first is purely classical [4–8], while the second invokes a generalized chiral dispersion force whose origin is quantum mechanical [6]. One can argue that there are systems for which the dominant interaction is a classical one, involving two-point, central forces between atoms or interaction centers on molecules, and accordingly in this paper we consider only this classical mechanism. In a more detailed paper [9], we will consider the quantum interaction and compare its strength with the classical one studied here. Our primary focus will be the calculation of cholesteric pitch from these interactions. The usual classical picture of the origin of intermolecular twist considers two screwlike molecules with excluded-volume interactions [4,5]. In order for the vanes of the screws to interleave, the molecules must have a nonzero angle between their screw axes. A similar picture arises via the tangent-tangent interactions of chiral molecules [6,7] or via surface-nematic interactions of chiral dopants [8].

The above mechanism produces a preferred nonzero rotation angle between long axes of neighboring chiral molecules (such as two screws) only if there is correlation between the directions of their short axes, e.g., between ϕ_A and ϕ_B in Fig. 1. To our knowledge, no previous attempt to calculate the cholesteric pitch has treated this properly. If neighboring molecules are spun freely about their long axes, they become effectively nonchiral, and interactions favoring twist are washed out [10]. Thus, the pitch of a cholesteric depends critically on the degree of intermolecular correlation of short-axes directions: a vanishing correlation leads to an infinite pitch, and complete correlation, as would be produced by long-range biaxial order, leads to the shortest pitch. In a uniaxial phase, mean-field theory does not treat these short-axes correlations and cannot predict a finite cholesteric pitch from molecular shape. Thus it will either lead to a phase with long-range order in the short-axes directions (a biaxial phase) or to a uniaxial phase without chirality [11]. Although the results presented here are only methodological, they have crucial implications for numerical simulations [12] since such calculations are often based on excluded-volume hard-core or other

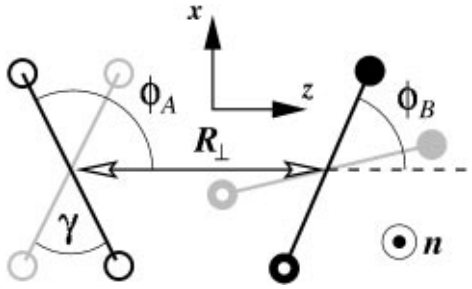

FIG. 1. Schematic representation of two chiral molecules. The atoms are represented by both the filled and unfilled circles, while the lines serve only as a guide to the eye. Each line on each molecule lies in an xz plane parallel to the page. The arms and atoms in the plane at $y = L/2$ are black, and those in the plane at $y = -L/2$ are grey. The angle γ between the projection of the two arms onto the same xz plane determines the degree of chirality. As examples, we consider two versions of this molecule. In the first, all atoms are identical, while in the second, the atoms with a hollow center carry a negative charge and those with a filled center carry a positive charge. In the nematic phase, the molecules spin freely about the nematic axis normal to the page so that $\langle \sin \phi_X \rangle = \langle \cos \phi_X \rangle = 0$. There are, however, orientational correlations between ϕ_A and ϕ_B.

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central classical interactions of the type we consider. In what follows, we will focus on molecules with biaxial symmetry and biaxial correlations, though our results can be generalized to molecules with n-axial symmetry. Cholesteric phases are, of course, biaxial. We are not discussing the higher order effect due to the biaxial order induced by the cholesteric pitch axis, but rather, the reverse mechanism in which biaxial order is needed to produce chiral phases.

The physics of many chiral liquid crystalline phases can be captured via the phenomenological Frank free energy density for the unit vector $\mathbf{n}$,

$$f = \tfrac{1}{2} K_1[\nabla \cdot \mathbf{n}]^2 + \tfrac{1}{2} K_2[\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + \tfrac{1}{2} K_3[\mathbf{n} \times (\nabla \times \mathbf{n})]^2 + h\mathbf{n} \cdot (\nabla \times \mathbf{n}), \quad (1)$$

where K_1, K_2, and K_3 are the Frank elastic constants for splay, twist, and bend, respectively, and h is a chiral parameter. This free energy is invariant under the inversion $\mathbf{n} \rightarrow -\mathbf{n}$, consistent with the symmetry of the nematic phase. The calculation of h is the focus of this paper.

The most common manifestation of the preferred packing angle of chiral molecules is the cholesteric liquid crystal phase in which a particular axis of each molecule lies along the nematic director $\mathbf{n} = [\cos kz, \sin kz, 0]$. The $\hat{z}$ axis is the pitch axis, and the pitch is $P = 2\pi/k$, the distance over which the nematic director rotates by 2π. In this uniform twisted state $\mathbf{n} \cdot \nabla \times \mathbf{n} = -k$, and the Frank free energy density reduces to $f = \frac{1}{2} K_2 k^2 - hk$ so that $h = -\partial f/\partial k|_{k=0}$. The equilibrium value of k is $k_0 = h/K_2$. Using standard statistical mechanical procedures, the chiral parameter can be expressed as

$$h = -\frac{\partial f}{\partial k}\bigg|_{k=0} = -\frac{1}{\Upsilon}\left\langle \frac{\partial U}{\partial k} \right\rangle\bigg|_{k=0}, \quad (2)$$

where the brackets denote a thermodynamic average in a nematic state in which there is a spatially uniform director $\mathbf{n}$, Υ is the sample volume, and U is the total potential energy. We denote the center-of-mass coordinate of molecule A by $\mathbf{R}_A$ and the coordinate relative to the center of mass of particle α in molecule A by $\mathbf{r}_{A\alpha}$. In general, α should run over all interaction centers (usually atoms and nuclei) in molecule A. The potential energy U is a function of all the coordinates. To determine h, we introduce an infinitesimal twist in a nematic state in which the molecules are aligned along a uniform director $\mathbf{n}$. Under such a twist, atomic coordinates within molecule A will undergo a rotation $\delta r^i_{A\alpha} = \epsilon_{ijk} \delta\omega^j_A r^k_{A\alpha}$ where $\delta\omega^j_A = k e^j(\mathbf{e} \cdot \mathbf{R}_A)$ is a rotation angle about an arbitrary unit vector $\mathbf{e}$ perpendicular to $\mathbf{n}$. The magnitude of $\delta\omega_A$ increases linearly with the projection of the center-of-mass position $\mathbf{R}_A$ along $\mathbf{e}$. Using (2) and the invariance of the system with respect to arbitrary rotations about the $\mathbf{n}$ axis, we obtain $h = -\frac{1}{4}\Upsilon^{-1}\sum_{BA} T_{BA}$, where $T_{BA} = \langle \mathbf{R}_\perp \boldsymbol{\tau}_{BA} \rangle$ is the projected torque, $\boldsymbol{\tau}_{BA}$ is the torque exerted on molecule B by molecule A, $\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$, and $\mathbf{R}_\perp$ is the projection of $\mathbf{R}$ onto the plane perpendicular to $\mathbf{n}$.

The chiral parameter h must be zero in achiral systems that have an equilibrium nematic phase. To see that our formulation leads to this result, consider evaluating $\sum_A T_{BA}$ for a system in which all molecules are achiral. The thermodynamic average is carried out over all configurations $\boldsymbol{\Omega}$ of the molecules consistent with the assumed nematic order. If, and only if, the molecules are achiral, the average may equivalently be carried out over all configurations $\overline{\boldsymbol{\Omega}}$, where $\overline{\boldsymbol{\Omega}}$ is obtained from $\boldsymbol{\Omega}$ by a reflection through a plane perpendicular to $\mathbf{n}$. But $\mathbf{R}_\perp \cdot \boldsymbol{\tau}_{BA}$ in $\boldsymbol{\Omega}$ is the negative of $\mathbf{R}_\perp \cdot \boldsymbol{\tau}_{BA}$ in $\overline{\boldsymbol{\Omega}}$, so $h = -h = 0$.

Our expression for h is perfectly general: it applies to quantum as well as classical systems. Note that hard-core interactions can be viewed as the limiting case of central forces between atoms of a single kind that mutually interact via central forces, and thus we begin our analysis for such systems. The projected torque is then

$$T_{BA} = \left\langle \sum_{\beta\alpha} \epsilon_{ijk} R^i_\perp r^j_\beta \partial^k V(\mathbf{R} + \mathbf{r}_\beta - \mathbf{r}_\alpha) \right\rangle, \quad (3)$$

where $\mathbf{r}_\alpha = \mathbf{r}_{A\alpha}$ and $\mathbf{r}_\beta = \mathbf{r}_{B\beta}$ are, respectively, the coordinates of atoms α and β in molecules A and B. To facilitate our analysis, we will now consider an expansion of T_{BA} in powers of relative atomic distance over center-of-mass separation, i.e., in $r_{\beta,\alpha}/R$. We expect, however, that the conclusions we draw from this analysis are more generally valid and apply, in particular, to hard-core interactions. In such an expansion, only terms that are odd in the atomic coordinates $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ are sensitive to reflections and thus to chirality. Furthermore, terms that are even in $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ are necessarily odd in $\mathbf{R}$ and will, therefore, not survive the average over the nematic distribution function. Thus, if we assume an achiral distribution characteristic of a nematic phase, we can restrict our attention to terms odd in $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$. (We will, however, reconsider this point later.) Since $\mathbf{r}_\beta$ measures the position relative to the center of mass, $\sum_\beta \mathbf{r}_\beta = 0$, and thus the linear and third order terms vanish. The first nonvanishing chiral term is the fifth order term

$$T^5_{BA} = \frac{1}{4!}\left\langle \sum_{\beta\alpha} \epsilon_{ijk} R^i_\perp r^j_\beta r^l_{\beta\alpha} r^m_{\beta\alpha} r^p_{\beta\alpha} r^s_{\beta\alpha} \partial^k \partial^l \partial^m \partial^p \partial^s V(\mathbf{R}) \right\rangle, \quad (4)$$

where $\mathbf{r}_{\beta\alpha} = \mathbf{r}_\beta - \mathbf{r}_\alpha$. This quantity can be reexpressed in terms of the second and third rank mass moment tensors on molecules $X = A, B$, $M^{jl}_X = \sum_{\chi\in X}(r^j_\chi r^l_\chi - \frac{1}{3} r^2_\chi \delta^{jl})$, and $S^{jlm}_X = \sum_{\chi\in X} r^j_\chi r^l_\chi r^m_\chi$. M^{jl} is the usual

quadrupole tensor describing nematic order, which can be decomposed into a uniaxial and a biaxial part. If we assume that there is perfect alignment of the longest principal axis along the nematic direction, then $M^{jl} = M_1(n^j n^l - \frac{1}{3}\delta^{jl}) + B^{jl}$, where B^{jl} is the symmetric traceless biaxial tensor with no components along **n**. The third rank tensor S^{ijk} is symmetric. In general, there are correlations between the direction of the vector **R** connecting two molecules and the respective orientations of these molecules. The important effects we consider are present even if these correlations are absent, and we will ignore them. This permits us to evaluate the orientational average of products of R^i with respect to a distribution that is isotropic in the plane perpendicular to **n**. For example, $\langle R^i R^j \rangle = R_{||}^2 n^i n^j + \frac{1}{2}R_\perp^2(\delta^{ij} - n^i n^j)$. Setting $V(\mathbf{R}) = g(R^2/2)$, expanding the derivatives of V, and performing the above average, we obtain

$$T_{BA}^5 = \tfrac{1}{2}\,\epsilon_{ijk} Q^{ip} \langle (B_B^{jl} S_A^{kpl} + B_A^{jl} S_B^{kpl}) K(\mathbf{R}) \rangle , \quad (5)$$

where $Q^{ip} = n^i n^p - \frac{1}{3}\delta^{ip}$ and

$$K(\mathbf{R}) = R_\perp^2 \{ g^{(3)} + R_{||}^2 g^{(4)} + \tfrac{1}{4} R_\perp^2 [g^{(4)} + R_{||}^2 g^{(5)}] \} , \quad (6)$$

where $g^{(n)}(x) = d^n g(x)/dx^n$. We see then, that only the traceless part of S^{kpl} contributes to T^5, and so we may take it to be traceless.

As we have already discussed, T_{BA} is nonzero only if the molecules are chiral. How is this fact manifested in (5)? Since both Q^{ip} and B^{jl} can be nonzero for achiral molecules, it would seem that the tensor S^{kpl} is a measure of chirality. This is not true, however, because S^{kpl} also has components that can be nonzero for achiral molecules. Though there are many possible definitions of a *molecular* chiral strength, when a molecule has a unique long axis we propose the pseudoscalar $\psi = S^{klm}\epsilon_{ijk} Q^{il} B^{jm}$ as a measure of the chiral strength of a molecule. This definition is useful because, as we shall see, h is proportional to ψ. If the molecule is not biaxial (i.e., $B^{km} = 0$), ψ will vanish. In addition, since ψ is a rotational invariant *odd* in **r**, it will also vanish if the molecule is achiral. It is possible that even for a chiral molecule, ψ vanishes. If this were the case, however, there would still be nonvanishing contributions to (3) at higher order in the expansion in powers of r/R. Indeed, a complete description of chiral interactions requires the knowledge of *all* the chiral moments of the molecules. In the basis of the principal axes of the molecule with **n** along $\hat{z}$, $\psi = S^{xyz}(B^{xx} - B^{yy})$. Only the components of S^{kpl} with three different indices in this basis contribute to ψ. We can, therefore, replace S^{kpl} in (5) with the tensor $\overline{S}^{kpl}$ whose only nonvanishing component in the principal axis basis is S^{xyz}.

The projected torque T_{BA}^5 is an average over fluctuations in the aligned nematic phase. It will be zero unless biaxial directions on pairs of molecules are correlated. If we were to spin the molecules independently, then $\langle B^{km} \rangle$ would be zero, and both terms in (5) would vanish. However, when there are biaxial correlations, this term will not vanish. To see this explicitly, we can use the identity $\overline{S}_A^{kpl} = -\psi_A \epsilon_{prs} B_A^{kr} Q^{sl}/2B^2 +$ (5 symmetric permutations), where $B^2 = \mathrm{Tr}(B^2)$. Inserting this into (5), we come to (assuming identical molecules)

$$T_{BA} = \frac{\psi}{B^2} \langle K(\mathbf{R}) B_A^{ij} B_B^{ij} \rangle \equiv \psi \langle K(\mathbf{R}) \Gamma_b(\mathbf{R}) \rangle , \quad (7)$$

where $\Gamma_b(\mathbf{R}) \propto \langle \cos[2(\phi_B - \phi_A)] \rangle$ is the biaxial correlation function for two molecules separated by a distance R. We would expect in a uniaxial phase that $\Gamma_b(R) \propto e^{-R/\xi}$ where ξ is the biaxial correlation length. Naively, one would expect ξ to be of the order of the molecular spacing. Thus we conclude that at the very least chirality requires biaxial correlations among the nematogens. We tabulate ψ for a number of chiral molecules in Table I.

Equation (7) gives the dominant contribution to T_{BA} to linear order in ψ in the nematic phase. There is an additional contribution linear in ψ arising from the chiral part of the equilibrium probability distribution ($e^{-U/k_B T}/\mathcal{Z}$ where $\mathcal{Z}$ is the partition function) and those terms with even powers of **r** arising in $r_\beta^j \partial_k V$ that are averaged in (3). In the isotropic phase, our analysis can be extended to show that this term cancels the contribution to T_{BA} from (4) and (5) to produce $h = 0$ as required. In the ordered phase, this other term is *higher order* in correlation functions and is subdominant to our result [9].

We have shown that the projected torque T_{BA} and hence $K_2 k_0$ will be proportional to the molecular chiral strength ψ. We note that there are a number of chiral liquid crystals, such as solutions of the viruses FD and TMV as well as of DNA, that show very small, if any, macroscopic chirality [13,14]. We believe the ideas presented here explain these observations, although a complete understanding will require a thorough investigation of the quantum dispersion force. Helical molecules have very small biaxiality and hence small values of ψ (see Table I). The chiral contribution to ψ comes from S^{kpl} and is inversely proportional to the number of turns per unit length, which is consistent with one's geometric intuition. In addition, since the molecular chiral strength depends on the degree of molecular biaxiality, we see that for *fixed* turn density (or equivalently, fixed S^{kpl}) ψ falls off as the total

TABLE I. Value of ψ for molecules made of atoms located at the coordinates given in the first column. The first molecule is shown in Fig. 1, and the second is a helix of uniform density.

Atomic coordinates	ψ
$L > 2w$: $\{(\pm w, 0, -L/2),$ $(\pm w\cos\gamma, \pm w\sin\gamma, L/2)\}$	$2w^4 L \sin(2\gamma)$
$L \gg r, n \in \mathbb{Z}$: $\{s \in [-1/2, 1/2]$ $(r\cos(2\pi n s), r\sin(2\pi n s), Ls)\},$	$\sim -\frac{3r^4 L}{(2\pi n)^3}\left[1 - \frac{24}{(\pi n)^2}\right]$

length *squared.* In addition, these molecules can easily rotate independently and are far apart (tens of angstroms). Hence we believe the biaxial correlation length ξ will be small compared to the intermolecular spacing. Our classical analysis should be valid especially for FD and TMV since these molecules are thought to interact sterically. Alternatively, short-molecule, thermotropic liquid crystals show very strong chirality, with pitches on the order of 5000 Å. These molecules are generally quite flat and thus quite biaxial. Typical molecular densities would not allow the molecules to rotate independently of each other, and thus we expect the biaxial correlations at the molecular separation to be reasonably large. The combined effect of a large biaxial component to ψ and of a large ξ should lead to relatively short pitches. In both cases we note that naively one would expect on dimensional grounds that k_0 would be on the order of π/a where a is the intermolecular spacing, which is certainly not a typical inverse pitch. Pitches are typically on the scale of *microns,* not *angstroms.* Our expression (7) for the leading term of T_{BA} is consistent with all of the above observations. We also note that in all but the most dilute solutions we do not expect any universal dependence of pitch on concentration or temperature: the details of the interactions and correlations should be different from system to system.

We briefly mention a number of generalizations to be discussed later [9]. We have considered here only the interactions between a pair of perfectly aligned, identical molecules. In the nematic state, the molecules are not perfectly aligned and the Maier-Saupe order parameter S is less than 1. We can incorporate these fluctuations into the calculation of T_{BA}. Indeed, we find, as discussed above, that when there is no nematic order there is no net torque. Since (5) involves the product of S^{kpl} on one molecule and B^{jl} on the other, our results easily generalize to chiral molecules interacting with achiral, biaxial molecules. More generally, we find that including correlations between the intermolecular direction and the molecular orientation leads to chiral interactions between chiral molecules and uniaxial molecules.

Additionally, we note that atomic identity may be relaxed. In this case, there is an interaction V_c between pairs of atoms leading to a potential energy $U = \frac{1}{2}\sum q_\alpha q_\beta V_c(\mathbf{R} + \mathbf{r}_{B\beta} - \mathbf{r}_{A\alpha})$, where q_α and q_β are the "charges" of atoms α and β. A chiral molecule such as that shown in Fig. 1 can carry a dipole moment $\mathbf{p}_A = \sum_\alpha q_\alpha \mathbf{r}_{A\alpha}$ perpendicular to its long axis. We then find a third order contribution to the projected torque of the form $\epsilon_{ijk} p_A^l C_B^{jm} R_\perp^i \partial^k \partial^l \partial^m V_c$, where $C_B^{jm} = \sum_\beta q_\beta (r_\beta^j r_\beta^m - \frac{1}{3} r_\beta^2 \delta^{jm})$ is the charge quadrupole moment tensor. The molecular chiral strength analogous to ψ for this system is $\psi_c = \epsilon_{ijk} p^i C^{jm} Q^{km}$. With this definition, T_{BA} is proportional to $\psi_c \Gamma_p(\mathbf{R})$ where $\Gamma_p(\mathbf{R})$ is the dipole-moment pair correlation function, which, like $\Gamma_b(\mathbf{R})$, measures angular correlations in the plane perpendicular to $\mathbf{n}$. Adding charges q and $-q$ to the molecules shown in Fig. 1 (and using the atomic positions specified in Table I), we have $\psi_c = 4q^2 w^2 L \sin\gamma$. We believe that chiral interactions of this type play a role in those liquid crystals which can form ferroelectric phases (i.e., Sm-C^*, TGB$_C^*$, etc.).

We close with some observations concerning the relation of our work to previous treatments of chiral interactions. An intermolecular potential of the form $V_{BA}^{\rm ch} = M_A^{ij} \epsilon_{jkl} R^k M_B^{il} V_p(R) + (A \leftrightarrow B)$ remains chiral and nonzero upon spinning about the local nematic director. It leads automatically to a free energy of the form of (1) with h proportional to V_p. Thus, this potential or ones similar to it are often used as a starting point for the description of chiral liquid crystals. Our analysis shows that this potential *cannot* be obtained from classical central forces between atoms on molecules, though it can arise through quantum dispersion forces [6]. The potential corresponding to (5) has the form $V_{BA} = \sum_{BA}[S_A^{ijk} M_B^{lm} \partial^i \partial^j \partial^k \partial^l \partial^m V + (A \leftrightarrow B)]$. S^{ijk} is a symmetric tensor—it cannot be expressed in terms of ϵ_{ijk} and M^{kl} to produce $V_{BA}^{\rm ch}$.

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