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# Weak Chirality in Ordered Dna Phases

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# WEAK CHIRALITY IN ORDERED DNA PHASES

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Abstract Recent experiments[1] on aligned DNA show hexatic order with no sign of macroscopic chirality. I make the analogy between smectic liquid crystals and chiral hexatics and show how the absence of chirality cannot occur in a thermodynamic phase of chiral molecules. In addition, I discuss the microscopic origin of chiral mesophases in liquid crystals and show that, within the context of central forces between "atoms" on "molecules", chiral interactions can occur only if there are biaxial correlations between the mesogens. Weak biaxial correlations can therefore lead to small cholesteric pitches.

## INTRODUCTION

Experimental realizations of the liquid crystalline hexatic, a phase with broken orientational but not translational order[2], are difficult to find[3]. More exotic hexatic structures have been proposed[4] in three dimensions in which there is nematic order and, simultaneously, hexatic order in the plane perpendicular to the director $\hat{\mathbf{n}}$. Until recently, only the liquid state (the regular nematic) and the hexagonal state (the hexagonal columnar phase) had been observed, typically in long, chiral molecules such as DNA[5]. In fact, the liquid-like phase of chiral polymers is cholesteric – the nematic phase will always start to twist in the presence of chirality. The hexagonal columnar phase, however, need not twist: there is a thermodynamic region of elastic constants in which twist is expelled. The twist can come in either via a tilt-grain-boundary state in which the nematic order twists or via a moiré state in which the polymers braid about each other and the local crystalline axes rotate along the polymer axis[6].

In a new set of experiments[1] a phase with both nematic and hexatic order was found in DNA, in addition to a cholesteric phase at lower concentration. In the first section of this talk I will argue that this is rather surprising: in an "N+6" phase Landau theory predicts that, unless a microscopic parameter is precisely tuned, either the nematic order or the bond-orientational order must twist. If that were the case, the X-ray scattering in the plane perpendicular to the nematic director would be a powder average over many different, rotated hexatic regions. Thus one might expect that there should be a ring in the $q_\perp$ plane, rather than the observed $\cos 6\theta$ modulation as shown in Figure 1.

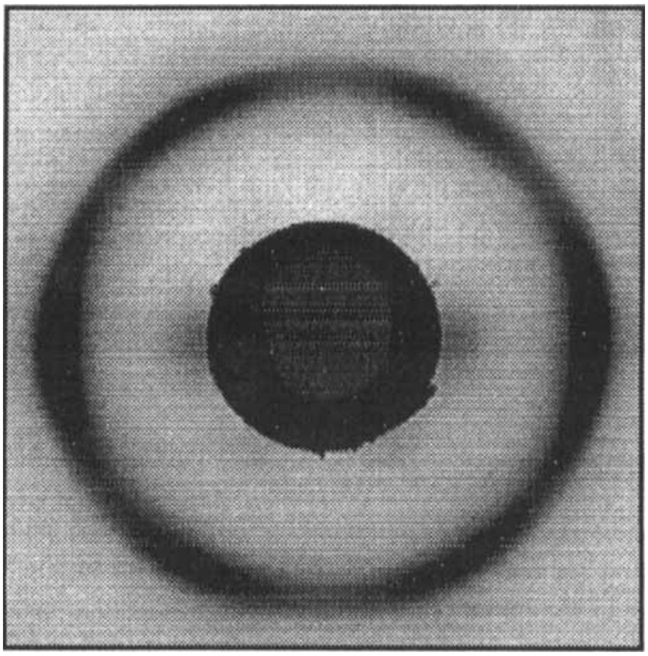

FIGURE 1. X-ray structure function in the plane perpendicular to the nematic direction[1]. This diffraction pattern contains a non-zero $\cos 6\theta$ component and no measurable $\cos 6n\theta$ for $n \geq 2$. The small amount of $\cos 2\theta$ can be attributed to the misalignment of the X-ray beam. (Figure provided courtesy of R. Podgornik).

If the chiral interactions are small, however, the hexatic order may not twist. Fortunately, there are reasons to believe that this may be the case: in the last section of this talk I will argue that molecular chirality manifests itself as mesoscopic chirality (*i.e.*, cholesteric pitch) via a subtle short-range correlation of molecular orientation. Naïvely, one might expect that the cholesteric pitch should be on the order of the molecular scale divided by a fraction of a radian, $P \approx 20\text{Å}/(0.1\pi)$. Typically pitches are *much* longer, on the order of microns. The necessity of intramolecular correlations may shed some light on the "naturalness" of observed cholesteric structures.

## CHIRAL BOND ORDER AND EXPULSION OF CHOLESTERIC TWIST

Based on symmetry let us construct a Landau free energy to describe the phases of chiral molecules with nematic and hexatic phases[6,7]. In the non-chiral nematic phase, orientational fluctuations are controlled via the Frank free energy density:

$$\mathcal{F}_n = \frac{K_1}{2}(\nabla\cdot\hat{\mathbf{n}})^2 + \frac{K_2}{2}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \frac{K_3}{2}[\hat{\mathbf{n}}\times(\nabla\times\hat{\mathbf{n}})]^2 . \tag{1}$$

If there is hexatic order, there will also be a spin stiffness for the hexatic bond-angle $\theta_6$. When determining the free energy for $\theta_6$, one must take into account the transformation properties of $\theta_6$ under the nematic symmetry $\hat{\mathbf{n}} \to -\hat{\mathbf{n}}$. Since angular changes must be measured with respect to some vector (via a "right-hand" rule), under nematic inversion $\theta_6 \to -\theta_6$. This does not change the sense of any twisting present in $\theta_6$ since the angular change is measured with respect to $\hat{\mathbf{n}}$. Taking into account the local nematic anisotropy, the elasticity for $\theta_6$ is:

$$\begin{aligned}\mathcal{F}_6 = \frac{K_A^{||} - K_A^{\perp}}{2}[\hat{\mathbf{n}}\cdot\nabla\theta_6]^2 + \frac{K_A^{\perp}}{2}[\nabla\theta_6]^2 \\ + K_6\nabla\times\hat{\mathbf{n}}\cdot\nabla\theta_6 + K_6'(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})(\hat{\mathbf{n}}\cdot\nabla\theta_6) .\end{aligned} \tag{2}$$

These terms are invariant under the simultaneous change $(\hat{\mathbf{n}},\theta_6) \to -(\hat{\mathbf{n}},\theta_6)$. The combined free energies have been considered before and constitute the elasticity theory for the "N+6" phase[4,8].

In a system composed of chiral molecules (such as DNA), one expects additional chiral terms invariant under nematic inversion but which change sign under spatial inversion. Since nematic symmetry already forces all terms to have even powers of $\hat{\mathbf{n}}$ and $\theta_6$, a character need not be assigned to these variables (*i.e.* vector or pseudovector, pseudoscalar or scalar, respectively). Thus I include the following chiral terms, quadratic in the fields:

$$\mathcal{F}^* = K_2 q_0 \hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}} + K_A^{||}\tilde{q}_0\hat{\mathbf{n}}\cdot\nabla\theta_6 . \tag{3}$$

The first term is the usual chiral term which favors a cholesteric texture $\hat{\mathbf{n}} = [\cos q_0 z, \sin q_0 z, 0]$ while the second term favors the twisting of the hexatic order[7]. The second term has been considered before in cholesteric melts[9] and chiral polymer crystals[6]. Similar theories could be constructed for molecules or molecular packings with other sorts of in-plane symmetries, for instance tetrahedral molecules[10].

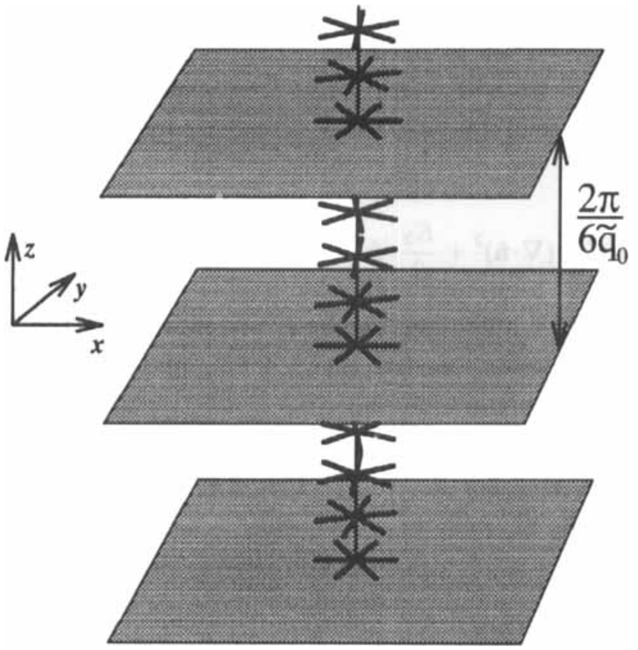

FIGURE 2. A chiral hexatic. In each plane the bond-angle order parameter is $\theta_6 = \theta_6^0 \bmod 2\pi/6$. The bond-angle rotates smoothly between the planes. Each plane of constant bond-angle is analogous to a smectic layer. This phase has no density modulations

In the following I simplify to the case $K_A^{\perp} = K_A^{\|} = K_A$, $K_6 = K_6' = 0$ and employ the *ansatz* first considered by Meyer[11] for a nematic in a magnetic field: $\hat{\mathbf{n}} = [\cos\phi\cos qz, \cos\phi\sin qz, \sin\phi]$, with $\phi$ constant. Minimizing the total free energy $F = \int d^3x\,[\mathcal{F}_n + \mathcal{F}_6 + \mathcal{F}^*]$ with respect to $\theta_6$ yields an effective free energy for $\hat{\mathbf{n}}$ (note that the mean-field equations only allow constant $\nabla\theta_6$):

$$\mathcal{F}_{\text{eff}} = \mathcal{F}[\hat{\mathbf{n}};\tilde{q}_0] - \frac{K_A}{2}\tilde{q}_0^2\,(\hat{z}\cdot\hat{\mathbf{n}})^2\,. \tag{4}$$

This is precisely the free energy considered by Meyer for a nematic with negative magnetic susceptibility in a magnetic field. It is straightforward to show that for $K_2 < K_3$ the cholesteric phase ($\phi = 0$) is the lowest energy state (within this class of solutions[12] when $K_2 q_0^2 > K_A \tilde{q}_0^2$ and that the nematic phase ($\phi = \pi/2$) is lowest in energy otherwise. When $K_2 > K_3$ an intermediate conical phase with $0 < \sin\phi < 1$ is allowed[11,7], though typically this inequality of the Frank constants is not satisfied.

We have just seen that the presence of hexatic order can act as a field. In fact, the chiral coupling to the hexatic bond-order field makes this system identical to that of a smectic liquid crystal composed of chiral mesogens with a layer spacing of $2\pi/(6\tilde{q}_0)$. The hexatic "wave" plays the role of the smectic layers. Each "layer" is a place where the bond-angle is $\theta_6 = 0 \bmod 2\pi/6$. This is illustrated in Figure 2. As in smectics, there will be a myriad of phases, though, in analogy with a type-II superconductor[13], the simplest phases will be the cholesteric phase which has no chiral bond order (normal metal), the chiral hexatic phase with no cholesteric twist (Meissner phase), and finally the twist-grain-boundary (TGB) phase[14] (Abrikosov flux lattice phase).

This analogy can be made precise[7] by introducing the hexatic order parameter $\psi_6$. The Landau theory which describes the liquid-to-hexatic transition is:

$$\mathcal{F}_6 = |\nabla\psi_6|^2 + r|\psi_6|^2 + u|\psi_6|^4, \tag{5}$$

where $r \propto (T - T_c)$. In the ordered phase ($T < T_C$) $\psi_6 = |\psi_6|e^{i\theta_6}$ and $|\psi_6|^2 = K_A/72$. Adding the second term of (3) as well as the Frank free energy for a nematic with pitch $q_0$ ($\mathcal{F}[\hat{\mathbf{n}}; q_0]$) yields:

$$\mathcal{F}_6^* = |\nabla\psi_6|^2 + r|\psi_6|^2 + u|\psi_6|^4 - 6i\tilde{q}_0\hat{\mathbf{n}}\cdot(\psi^*\nabla\psi - \psi\nabla\psi^*) + \mathcal{F}[\hat{\mathbf{n}}; q_0]. \tag{6}$$

Completing the square, this leads to:

$$\mathcal{F}_6^* = |(\nabla + 6i\tilde{q}_0\hat{\mathbf{n}})\psi|^2 + \left(r - 36\tilde{q}_0^2\right)|\psi|^2 + u|\psi|^4 + \mathcal{F}[\hat{\mathbf{n}}; q_0], \tag{7}$$

which is precisely the free energy of a smectic-A liquid crystal with layer spacing[13] $a = 2\pi/(6\tilde{q}_0)$.

Drawing upon the smectic-A analogy, one would expect that cholesteric twist will be excluded in favor of *chiral* hexatic order. In particular, this means that from plane to plane the sixfold order should rotate if there is nematic alignment. This is not what is seen experimentally – there are six distinct spots in the scattering perpendicular to the nematic director[1]. While the molecular symmetry suggests that the chiral terms in (3) must be present, they may nonetheless be small. In the next section I will analyze the origin of chiral interactions among molecules and argue that they could be anomalously small. It should be pointed out that if all the chiral terms were set to zero there is no a *priori* reason why the phase sequence nematic–N+6–hexagonal-columnar-phase could not exist[15].

## THE MICROSCOPIC BASIS OF CHIRAL INTERACTIONS

A molecule is chiral if its symmetry group does not contain the element $\mathbf{S_n}$: a rotation around a $C_n$-axis by $2\pi/n$ followed by a mirror through the perpendicular plane[16]. Moreover, all chiral molecules must have $n$-axial order around some axis since the groups $\mathcal{C}_\infty$ and $\mathcal{D}_\infty$ are not allowed for any real objects[17]: the only infinite subgroups of the rotation group in three dimensions are $\mathcal{C}_{\infty v}$ and $\mathcal{D}_{\infty h}$, both of which contain $\mathbf{S_1}$. As we shall see, the lack of uniaxial symmetry plays a crucial role in the chiral interactions. Let us first concentrate on calculating the cholesteric pitch $q_0$, or, more accurately, $K_2q_0$ the coefficient of $(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})$, and return later to estimating $\tilde{q}_0$. The following will only be a sketch of the main results presented elsewhere[18]. To this end, let us consider two planes of molecules separated along the $x$-axis by $R$, the first aligned along the $\hat{z}$ axis, the second along $(\hat{z}\cos\theta+\hat{y}\sin\theta)$. Expanding for $\theta \ll 1$ yields:

$$F=\int d^3x\, K_2q_0\partial_x\delta n_y+\mathcal{O}(\theta^2)\approx K_2q_0L_yL_z\theta, \tag{8}$$

where $L_y$ and $L_z$ are the sample dimensions. There is a famous expression for the coefficient of $\theta$ in this expansion–the torque. Thus $L_yL_zK_2q_0$ is the torque that one plane of molecules exerts on the next plane of molecules when they are aligned along a common axis. In the simplest case, let us consider weakly interacting molecules and thus build the torque up out of nearest neighbor, pairwise interactions across the planes. If there are $N$ molecules per plane then the torque between two of the molecules is $AK_2q_0$, where $A$ is the free area of each molecule.

We see that the problem of calculating $K_2q_0$ reduces to the problem of calculating the torque between two molecules separated by a distance $R$ when they are aligned with each other and perpendicular to their separation. For simplicity, let us assume that the atoms on the molecules all interact via the same central potential. This analysis necessarily excludes quantum interactions which can be non-local and which do produce chiral terms in the Landau theory of liquid crystals[19], but does include, as a limiting case, hard-core steric interactions which can be built up out of short range central forces. The relevant component of the torque is along $\hat{\mathbf{R}} \equiv \mathbf{R}/|\mathbf{R}|$, where $\mathbf{R}$ is the separation between the centers of mass of each molecule and $\mathbf{R}\cdot\hat{\mathbf{n}} = 0$. The atoms on each molecule are at a position $\mathbf{r}_\alpha$ relative to the center of mass and $\alpha$ runs over the atoms on the molecule. Assuming a central potential $V(\mathbf{R})$, the relevant component of the torque is:

$$\hat{\mathbf{R}}\cdot\tau = -\frac{1}{|\mathbf{R}|}\sum_{\alpha\beta} R^i \epsilon_{ijk} r^j_\beta \partial^k V(\mathbf{R}+\mathbf{r}_\beta-\mathbf{r}_\alpha), \tag{9}$$

where $\alpha$ runs over the atoms on the first molecule and $\beta$ runs over the atoms on the second molecule. An expansion in powers of $(|\mathbf{r}|/|\mathbf{R}|)$ is certainly reasonable in

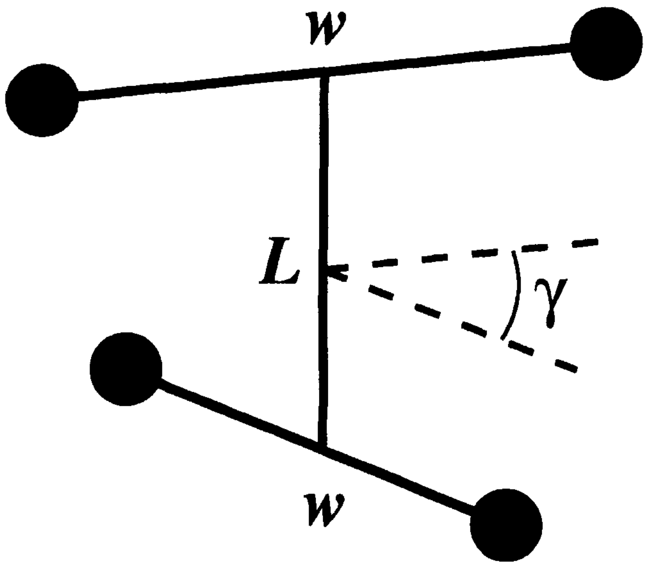

FIGURE 3. Prototypical chiral molecule. The spheres indicate the positions of the atoms. When the angle $\gamma$ is $n\pi/2$ this molecule is not chiral. The chiral order parameter for this molecule is $\psi = -(1/8)w^4 L\sin(2\gamma)$, where $L$ and $w$ are the dimensions shown and $L > w$ (not drawn to scale).

the dilute limit and the general symmetry of the interaction should not be significantly altered at higher densities. Note that terms in the expansion which are *even* in $\mathbf{r}$ must vanish: under $\mathbf{r}\to-\mathbf{r}$ both molecules will change their handedness and thus the chiral pitch will change sign. Note that $\partial^k V(\mathbf{R}) \propto R^k$ and thus from the antisymmetry of $\epsilon_{ijk}$ the first order term will vanish. The third order term is:

$$\left(\hat{\mathbf{R}}\cdot\tau\right)_3 = -\frac{1}{2!}\frac{1}{|\mathbf{R}|}\sum_{\alpha\beta} R^i\epsilon_{ijk}r^j_\beta\left(r^m_\beta - r^m_\alpha\right)\left(r^l_\beta - r^l_\alpha\right)\partial^k\partial^m\partial^l V(\mathbf{R}). \tag{10}$$

The potential term $\partial^k\partial^m\partial^l V(\mathbf{R})$ will, by symmetry, have only two types of terms: those proportional to 1) $R^kR^mR^l$ and 2) $\left(R^k\delta^{ml} + R^m\delta^{kl} + R^l\delta^{km}\right)$. Again, due to the antisymmetry of $\epsilon_{ijk}$, terms of the first type will vanish and the only part of (10) which survives is:

$$\left(\hat{\mathbf{R}}\cdot\tau\right)_3 \propto \sum_{\alpha\beta} R^i\epsilon_{ijk}r^j_\beta r^k_\alpha \mathbf{R}\cdot\left(\mathbf{r}_\beta - \mathbf{r}_\alpha\right). \tag{11}$$

Note that every term in (11) will contain the single sum $\sum_\mu r^i_\mu$ which is identically 0 since the $\mathbf{r}_\mu$ are measured from the center of mass. Thus, the third order term will vanish.

Fortunately, perseverance will pay off and the fifth order term will not identically vanish. At fifth order there are a variety of terms. Again, any term which is a sum over a single factor of $r^i_\mu$ will vanish. This leaves only terms with three $r^i$ on one molecule and two $r^j$ on the other. Taking the average yields[18]:

$$\left(\hat{\mathbf{R}}\cdot\tau\right)_5 = U(R)Q^{il}\epsilon_{ijk}\left\{S^{jlm}_2 B^{km}_1 + S^{jlm}_1 B^{km}_2\right\}, \tag{12}$$

where $U(R) = \{\frac{1}{8}R^3 f^{(4)}(R^2/2) - \frac{1}{2}Rf^{(3)}(R^2/2)\}$ is a function of $R = |\mathbf{R}|$, $V(R) = f(R^2/2)$, $Q^{il} \equiv \left[n^in^l - (1/3)\delta^{il}\right]$ is the nematic alignment tensor (equal for both molecules), the two tensors $S^{jlm}_p$ and $B^{km}_p$ are defined on molecule $p = 1, 2$ via

$$\begin{aligned} S^{jlm}_p &\equiv \sum_{\mu\in p}\left\{r^j_\mu r^l_\mu r^k_\mu - \frac{1}{9}|\mathbf{r}_\mu|^2\left[\delta^{jl}r^k_\mu + \delta^{jk}r^l_\mu + \delta^{kl}r^j_\mu\right]\right\} \\ B^{km}_p &\equiv \sum_{\mu\in p} r^s_\mu r^t_\mu\left\{\tilde{\delta}^{sk}\tilde{\delta}^{tm} - \frac{1}{2}\tilde{\delta}^{km}\tilde{\delta}^{st}\right\}, \end{aligned} \tag{13}$$

and $\tilde{\delta}^{ij} = \left[\delta^{ij} - n^in^j\right]$ is the transverse projection operator. The tensor $B^{km}$ measures the biaxial orientation of the molecules in the plane perpendicular to the nematic direction, which is assumed to be the principal axis of the molecule with the largest moment. The other tensor $S^{jlm}$ is some measure of the chirality of the molecule, but is not a measure by itself: indeed, some components of $S^{jlm}$ will be non-zero for achiral molecules and zero for chiral molecules. Consider, however, the order parameter $\psi_p = S_p^{jlm}\epsilon_{ijk}Q^{il}B_p^{km}$ on a single molecule $p$: in the coördinate system of the principal axes, $\psi = (\lambda_y - \lambda_x)\sum_\mu r_\mu^x r_\mu^y r_\mu^z$ where $\lambda_x$ and $\lambda_y$ are the eigenvalues along the $\hat{x}$ and $\hat{y}$ directions of the single-molecule moment of inertia tensor and $\hat{z}$ is the nematic axis. This order parameter vanishes identically for achiral molecules, since under inversion the principal axes do not change but the sum will change sign. Solving for $S_p^{jlm} = \psi_p\epsilon_{ijk}Q^{il}B_p^{km}/(2B_p^2) +$ (symmetric permutations), (12) reduces to:

$$\left(\hat{\mathbf{R}}\cdot\tau\right)_5 = \psi\, U(R)\frac{B_1^{km}B_2^{km}}{B^2}. \tag{14}$$

where $B^2 = B_1^2 = B_2^2$ is the same on the two identical molecules. Up to this point, the average over the $n$-axial direction has not been performed. In any mean field theory $\langle B^{km}\rangle$ will either be zero (uniaxial) or non-zero. In the latter case the entire phase will be *biaxial*, with long-range biaxial order. If the same mesogens in racemic mixtures have only uniaxial nematic phases then $\langle B^{km}\rangle = 0$ (*i.e.*, no long-range biaxial order). Thus if the molecules rotate *independently* around their nematic axes then the average $\langle B_1^{km}B_2^{km}\rangle = \langle B_1^{km}\rangle\langle B_2^{km}\rangle = 0$. Thus in a uniaxial phase, chiral interactions will come about only via *short-range* correlations of biaxial order. In other words, upon averaging, (14) becomes

$$\left\langle \hat{\mathbf{R}}\cdot\tau\right\rangle_5 = \psi\, U(R)\frac{\langle B_1^{km}B_2^{km}\rangle}{B^2} \equiv \psi\, U(R)g_B(R), \tag{15}$$

where $g_B(R) \sim e^{-R/\xi_B}$ is the normalized biaxial correlation function, and $\xi_B$ is the biaxial correlation length, which one might naïvely expect to be on the scale of the intramolecular spacing.

The previous discussion shows that there are two factors which lead to a large chiral parameter $q_0$: the strength of the chiral order parameter $\psi$ on the molecule and the range of the biaxial correlations. If either is small, it is reasonable to expect a very long pitch. Note that almost cylindrical, corkscrew-like molecules are *not* very biaxial and thus $\psi$ would be small. In addition, in the DNA system studied at NIH, the molecules are on the order of 40Å apart (center-to-center) and are each roughly 20Å wide. Moreover, the Debye screening length at the typical salt concentrations investigated is on the order of 5Å and thus one might expect that the biaxial interactions would be weak and hence $\xi_B$ to be small. Together, the smallness of both factors suggests that the chirality might be very small. In fact, it is even possible that in the hexatic phase biaxial correlations are *smaller* than in the cholesteric phase, despite the higher molecular density.

Since the cholesteric phase picks out a preferred, biaxial direction (the pitch axis) the biaxial correlations could be longer-ranged (even possibly long-range). In a hexatic phase, however, the biaxial order parameter might be suppressed due to the 6-fold "crystal" field of the hexatic. Note that if the biaxial correlations are removed there could still be "6-axial" correlations. In that case, however, the analogous order parameter to $\psi$ would be more complicated and would include higher geometric moments. Moreover, the expansion of $\hat{\mathbf{R}}\cdot\tau$ in powers of $(|\mathbf{r}|/|\mathbf{R}|)$ would vanish, upon averaging, even at fifth order, and one would have to go to, at least, *ninth* order which would lead to a very small interaction at dilute separations.

Finally, let us estimate the amount of twisting of the hexatic order by considering a simplified two-polymer model. Consider one polymer helically winding its way around another straight polymer at a mean separation $a$: the rate at which the separation vector rotates along the straight polymer axis is a simple estimate of $\tilde{q}_0$ and will be precisely equal to the pitch of the helical polymer trajectory. There are two major contributions to the energy of the helical polymer: the first is the usual bending energy of a stiff polymer, while the second is the "nematic" free energy for the two molecules which includes the cholesteric term proportional to $q_0$. Take the first polymer to follow the curve $\mathbf{r}(z) = [a\cos\tilde{q}_0 z, a\sin\tilde{q}_0 z, z]$ and the second to lie along the $\hat{z}$-axis at $x = y = 0$. In this case $\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}} \approx (a\tilde{q}_0)/a = \tilde{q}_0$, and so the free energy of the second polymer is:

$$F = \int dz \left\{ \frac{\kappa}{2}\left\{1 + (a\tilde{q}_0)^2\right\}^{-3/2} a^2(\tilde{q}_0)^4 + \frac{K_2}{2}a^2\left[\tilde{q}_0 + q_0\right]^2 \right\}. \tag{16}$$

Minimizing for small $a\tilde{q}_0$ and taking the bending stiffness $\kappa = k_{\mathrm{B}}TL_P$, where $L_P$ is the persistence length, yields:

$$2L_P(\tilde{q}_0)^3 + \frac{K_2}{k_{\mathrm{B}}T}\tilde{q}_0 = -\frac{K_2}{k_{\mathrm{B}}T}q_0. \tag{17}$$

Taking the typical DNA values for $K_2 = 10^{-6}$ *dyne*, $q_0 = 2\pi/\mu m$ and $L_P = 600$Å, I expect that at room temperature $\tilde{q}_0 \approx -q_0$. It should be noted, however, that as $L_P \to \infty$, $\tilde{q}_0 \to 0$, in accord with one's intuition – as the polymers become infinitely stiff there can be no hexatic twisting. More generally, the elastic constant $K_2$ has been estimated for semi-flexible polymers with mean spacing $a$ (roughly 40Å in the DNA samples) to be[20] $K_2 \approx k_{\mathrm{B}}TL_P^{1/3}/a^{4/3}$. Substituting into (17) I find $\tilde{q}_0 \sim -q_0$ for pitches $P = 2\pi/\tilde{q}_0 > 2\pi\left(L_P a^2\right)^{1/3} \approx 600$Å, which is almost always the case. Thus, because the typical pitches are much longer than any intrinsic molecular length, the polymer stiffness plays no significant role in reducing $\tilde{q}_0$.

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