Chiral Mesophases of DNA

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In the hexagonal columnar phase of chiral polymers a bias towards cholesteric twist competes with braiding along an average direction. When the chirality is strong, topological defects proliferate, leading to either a tilt grain boundary phase or a new “moiré state” with twisted bond order. This moiré phase can melt leading to a new phase: the chiral hexatic. I will discuss some recent experimental results from the NIH on DNA liquid crystals in the context of these theories.

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1. Introduction and Summary

Chiral molecules are ubiquitous in nature [1]. It is remarkable, in fact, that cellular processes can produce copious amounts of chiral molecules of the same handedness, while, by comparison, standard synthetic techniques usually produce racemic mixtures in which there are an equal number of left- and right-handed molecules. While each molecule in a racemic mixture can be chiral, from the point of view of coarse-grained, effective models these systems are not chiral. Thus studying biologically produced materials is intriguing: it allows one to consider macroscopic chiral structures composed of regular, sometimes monodisperse, molecules. It is already known that these materials have remarkable elastic properties – for instance, they become more viscous on dilution [2] and have remarkable viscoelastic properties because of their rigidity [3]. Moreover, to a theorist these biomaterials offer a significantly cleaner environment since they can be produced with greater regularity and monodispersity [4,5] than is possible for conventional polymers. Thus theoretical discussions and predictions of the effects of polydispersity, chirality and interaction types (i.e. steric, van der Waals, screened Coulomb, etc.) can be made, for the first time, in the context of experiment. Because biomolecules are the building blocks of ultrastrong materials, such as silkworm and spider silk, theoretical understanding of the allowed and preferred structures is an essential element in the design of strong materials based on molecular constituents. In addition, DNA-lipid complexes [6] show promise as therapeutic DNA transfection systems that do not require virus vectors [7]. Again, the detailed structure and packing of the biomolecules in these complexes is crucial for advances in successful DNA delivery.

In the following, I shall describe three new chiral liquid crystalline phases, which one might expect to observe in these relatively pure, biomolecular materials. First I will describe two new defect phases, akin to the Renn-Lubensky twist-grain-boundary (TGB) phase of chiral smectics [8], the polymer TGB phase and the moiré phase [9]. In the next section I will describe a three-dimensional hexatic phase with chiral bond order [10]. Finally, I will discuss recent experiments on DNA [11] which might be interpreted as true, three-dimensional hexatic phases.
2. Novel Phases of Chiral Liquid Crystalline Polymers

A notable feature of biological materials is the profusion of long polymer molecules with a definite handedness. DNA, polypeptides (such as poly-γ-benzyl-glutamate) and polysacharides (such as xanthan) can all be synthesized with a preferred chirality. Long polymers in dense solution often crystallize into a hexagonal columnar phase. When the polymers are chiral this close packing into a triangular lattice competes with the tendency for the polymers to twist macroscopically \[12\] as in cholesteric liquid crystals. Similar to the twist grain boundary phase of chiral smectics \[8\], macroscopic chirality can proliferate when screw dislocations enter the crystal. Like flux lines in a type II superconductor, dislocations only appear provided the free energy reduction from the chiral couplings exceeds the dislocation core energy. If the chirality is weak, a defect free hexagonal columnar phase persists, as in the Meissner phase of superconductors \[9\].

The hexagonal columnar phase of liquid crystals has broken rotational invariance around all three coördinate axes. The associated Goldstone modes are simply the deviations in the nematic director field away from the \(\hat{\mathbf{z}}\)-axis, \(\delta\hat{n} \equiv \hat{n} - \hat{z}\) and the hexatic \[13\] bond-angle field \(\theta_6\) defined in the \(xy\)-plane \[10\]. Fluctuations of the nematic director are controlled by the Frank free energy:

\[
\mathcal{F}_{\delta\hat{n}} = \frac{K_1}{2} (\nabla \cdot \delta\hat{n})^2 + \frac{K_2}{2} [\hat{z} \cdot (\nabla \times \delta\hat{n}) - q_0]^2 + \frac{K_3}{2} [\partial_z \delta\hat{n}]^2
\]

where \(K_i\) are the Frank elastic constants and \(2\pi/q_0\) is the equilibrium cholesteric pitch. The hexatic director is governed by the anisotropic free energy:

\[
\mathcal{F}_{\theta_6} = \frac{K_A^\parallel}{2} (\partial_\theta \theta_6)^2 + \frac{K_A^\perp}{2} (\nabla \theta_6)^2 - K_A^\parallel \tilde{q}_0 \hat{z} \cdot \nabla \theta_6
\]

where \(K_A^\parallel\) and \(K_A^\perp\) are the spin-stiffnesses parallel and perpendicular to the nematic axis, respectively. Note that the last term is chiral and is allowed by symmetry: the sign of changes in \(\theta_6\) must be measured with respect to a vector (the right-hand-rule requires a thumb) which we choose as the nematic director \(\hat{n} \approx \hat{z}\). Under the nematic inversion \(\hat{n} \rightarrow -\hat{n}\) the sign of \(\theta_6\) will likewise change and thus \(\hat{n} \cdot \nabla \theta_6\) respects the symmetry of the phase. In addition there are are additional non-chiral couplings between \(\delta\hat{n}\) and \(\theta_6\) \[14,15\]:

\[
\mathcal{F}_{\delta\hat{n}\theta_6} = C (\partial_\theta \theta_6) [\hat{z} \cdot (\nabla \times \delta\hat{n})] + C' \nabla \theta_6 \cdot \nabla \times \delta\hat{n}
\]

In addition, the hexagonal columnar phase is a two-dimensional crystal and thus has a two-dimensional displacement field \(\vec{u}\) arising from the broken translational invariance.
Rotational invariance dictates the allowed couplings and terms in the free energy density $F$:

$$F_{\text{crystal}} = \mu (\partial_i u_j - \epsilon_{ij} \theta_6)^2 + \frac{\lambda}{2} u_{ii}^2 + \mu' (\partial_z u_i - \delta n_i)^2$$

(2.4)

where $u_{ij} \equiv \frac{1}{2} (\partial_i u_j + \partial_j u_i)$ is the two-dimensional strain tensor, $\mu$ is the two-dimensional shear modulus, $\lambda$ the two-dimensional bulk modulus, $\mu'$ is the tilt modulus and $\epsilon_{ij}$ is the two-dimensional anti-symmetric symbol. The total free energy density is thus

$$F = F_{\text{crystal}} + F_{\delta \vec{n}} + F_{\theta_6} + F_{\delta \vec{n} \theta_6}.$$  

(2.5)

By minimizing the total free energy with respect to $\delta \vec{n}$ and $\theta_6$ we find $\delta \vec{n} \approx \partial_z \vec{u}$ and $\theta_6 \approx \frac{1}{2} \epsilon_{ij} \partial_i u_j$ so that the achiral free energy density is (to lowest order in derivatives):

$$F_{\text{eff}} = \mu (u_{ij})^2 + \frac{\lambda}{2} u_{ii}^2 + \frac{K_3}{2} (\partial_z^2 u_i)^2.$$  

(2.6)

The chiral contribution is subtle: in terms of the displacement field $\vec{u}$ the two chiral terms are

$$F^*_{\text{eff}} = -\gamma (\partial_x \partial_z u_y - \partial_y \partial_z u_x) - \gamma' (\partial_z \partial_x u_y - \partial_y \partial_x u_x),$$

(2.7)

where $\gamma = K_2 q_0$ and $\gamma' = \frac{1}{2} K_{A1} |q_0|$. The only difference between the two allowed chiral terms is the order of differentiation – integration by parts on the boundary of the sample will make these two terms identical! Moreover, both terms are total derivatives and thus one may think that they are unimportant. However, topological defects provide boundaries inside the sample and thus boundary conditions become important in non-uniform structures.

When dislocations are introduced $\vec{u}$ is no longer single valued. To account for this, one may introduce a new variable $w_{\gamma i}$ which is equal to $\partial_\gamma u_i$ away from the defects [16]. The free energy becomes

$$F = \int d^3 x \mu \left( \frac{w_{ij} + w_{ji}}{2} \right) + \frac{\lambda}{2} (w_{ii})^2 + \frac{K_3}{2} (\partial_z w_{zi})^2 - \gamma \epsilon_{ij} \partial_i w_{zj} - \gamma' \partial_z \left( \frac{1}{2} \epsilon_{ij} w_{ij} \right),$$

(2.8)

where $\theta_6 = \frac{1}{2} \epsilon_{ij} w_{ij}$ and $\delta n_i = w_{zi}$.

Dislocations are restricted so that the Burger’s vector, $\vec{b}$ must lie in the $xy$ plane. We introduce the density tensor $\alpha_{\gamma i}(\vec{r}) = \int dt d\vec{b} t_\gamma b_i \rho(t, \vec{b}, \vec{r})$, where $\rho(t, \vec{b}, \vec{r})$ is the volume density of dislocations at the point $\vec{r}$ with Burger’s vector $\vec{b}$ pointing in the $\vec{t}$ direction. Since the dislocations do not end, $\nabla \cdot \vec{t} = 0$, and $\partial_\gamma \alpha_{\gamma i} \equiv 0$. Following [16] it is straightforward to show that:

$$\epsilon_{\mu \nu \gamma} \partial_\nu w_{\gamma i} = -\alpha_{\mu i}.$$  

(2.9)
This relation can be manipulated to show that:

\[ 2 \partial_z \theta_6 - \hat{z} \cdot \nabla \times \delta \vec{n} = - \text{Tr}[\alpha]. \]  

(2.10)

This relation shows that screw dislocations, which only contribute to the symmetric part of \( \alpha \) require either a twisting of the director \( \delta \vec{n} \) or the hexatic director \( \theta_6 \).

Using the effective free energy (2.4) one can calculate the energetic penalty for screw and edge dislocations in the crystal. The free energy per unit length of a screw dislocation is finite (independent of the system size). Thus if the desire to twist is large enough defects will proliferate to allow the system to twist. We have proposed two new defect phases: the polymer tilt-grain-boundary phase in which the director twists discretely across grain-boundaries (this phase is nearly identical in morphology to the Renn-Lubensky twist-grain-boundary phase [10]) and the moiré phase in which the bond-order rotates along the polymer axis. We show a portion of this structure in Figure 1 and the phase diagram for our system in Figure 2. Recently, the morphology of the moiré phase has been proposed as the steady-state structure of flux-lines in superconductors in a current parallel to the magnetic field [18].

3. The Polymer Hexatic

When the crystalline order melts, the Goldstone modes of broken rotational invariance, \( \delta \vec{n} \) and \( \theta_6 \) become the interesting degrees of freedom. The N+6 [14] phase of liquid crystals is thus very similar to a biaxial nematic phase, although instead of having two-fold symmetry perpendicular to the nematic director, the N+6 phase has six-fold symmetry. Recently, in a DNA system, the NIH group [11] has seen the first evidence of a nematic phase with hexatic order. I will argue that this is rather surprising: unless the tendency to twist around the nematic axis (\( \tilde{q}_0 \)) is small, Landau theory predicts that 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 3.

We can recast the hexatic free energy in terms of the hexatic order parameter \( \psi_6 \). When there is no hexatic order, \( \psi_6 = 0 \), and when there is hexatic order \( \psi_6 = |\psi_6| \exp 6i\theta_6 \). For simplicity I take \( K_\perp = K_\parallel = K_A \). The free energy density can be recast as [10]:

\[
\mathcal{F} = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_2 [\hat{n} \cdot \nabla \times \hat{n} - q_0]^2 + \frac{1}{2} K_3 [\hat{n} \times (\nabla \times \hat{n})]^2 \\
+ |(\partial - i\tilde{q}_0 \hat{n}) \psi_6| + r |\psi_6|^2 + u |\psi_6|^4,
\]  

(3.1)
where \( r \) is the reduced temperature and \( u \) is an interaction parameter. Note that this theory is identical to that for a smectic-A liquid crystal composed of chiral molecules, first proposed by de Gennes [19]. The phenomenology of this model can be borrowed from the theory of superconductors: there are two possible uniform phases of this system. There is a cholesteric phase (normal metal) in which \( \psi_6 \) vanishes and \( \hat{n} \cdot \nabla \times \hat{n} = q_0 \) and the chiral hexatic phase (Meissner phase) in which \( \psi_6 \) is non-zero and the nematic director points along a single axis. Note that in this phase the hexatic director must rotate about the nematic axis with an inverse pitch \( 2\pi/\tilde{q}_0 \), as shown in Figure 4.

Finally we note that if the system has a stable defect phase (i.e., it is like a type-II superconductor) then it can have a Renn-Lubensky TGB phase in which grain-boundaries separate regions of perfect chiral hexatic order.

4. Where Is The Twist?

Unfortunately, the above analysis suggests that when chiral molecules form \( N+6 \) phases, either the hexatic order must twist or the nematic director must twist. The data presented in Figure 3 is contrary to this result – if the hexatic order were twisting, the 6-fold modulation would be washed out and turned into a ring. Since this same DNA system, at lower concentrations, forms a cholesteric with a micron-sized pitch, it is hard to imagine that the hexatic order does not also twist at the micron scale. The illuminated area in the X-ray experiment is on the order of one millimeter, so one would expect many twists of the hexatic order.

One possibility is that the DNA stiffness makes twisting difficult [20]. Unfortunately, since the persistence length is 50 nanometers, DNA molecules can easily bend around each other on the micron length scale. Another possibility is that fluctuations can reduce the chiral strength. This is known to happen in polymer cholesterics [21,22]. However, even with the most optimistic estimates, this effect produces only a factor of two increase of the pitch. Finally, one might calculate the values of \( q_0 \) and \( \tilde{q}_0 \) via a microscopic approach [23]. This work is in progress.

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Figure Captions

Fig. 1. The moiré state. The thick tubes running in the $\hat{z}$ direction are polymers, while the dark lines are stacked honeycomb arrays of screw dislocations. The intersection of these polymers with any constant $z$ cross section away from the hexagonal defect arrays has the topology of a triangular lattice.

Fig. 2. Phase diagram of a chiral polymer crystal. Insets are representative tilt (TGB) and moiré grain boundaries. Shaded lines are screw dislocations. In the TGB phase the solid lines are the polymers in front of the grain-boundary, while the dashed ones are behind it. In the moiré phase the crosses are the heads of polymers beneath the grain-boundary and the circles are the tails of the polymers above it.

Fig. 3. X-ray structure function in the plane perpendicular to the nematic direction $[11]$. 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).

Fig. 4. Model of a chiral hexatic. In each plane the bond-order parameter is $\theta_6 = \theta_6^0 \mod 2\pi/6$. Between the planes the bond order uniformly precesses along the average nematic director, $\hat{\mathbf{n}} = \hat{z}$. The planes are analogous to smectic planes, though there is no density wave in this liquid crystalline phase.
Figure 4