

Chiral Polymer Hexatics: A New Twist on DNA

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Theories of the “ $N + 6$ ” hexagonally ordered phase of DNA are generally based on treatments of hexatic order in smectic systems. Thus $N + 6$ phases should be analogous to superconductors and should expel twist of the nematic director, in an analogy of the Meissner effect. However, in $N + 6$ systems there is no smectic order, hence a radically different mathematical description is required. Here I present the appropriate theory and show that, as $N + 6$ phases are not analogous to superconductors, they can exhibit twist in any direction, without forming any topological defects.

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Many liquid crystals and quasicrystals exhibit spontaneous orientational symmetry breaking, despite having no long-range positional order [1]. A wide range of different symmetries have been studied, varying from common systems, such as uniaxial nematics, to exotic phases with icosahedral, octahedral, or tetrahedral symmetry [2,3]. Recently, interest has focused on newly-discovered hexagonal systems formed from DNA molecules [4–8]. These “chiral polymer hexatics” exhibit both nematic and hexagonal bond-orientational order, the hexagonal part of which is similar to the conventional hexatic systems that occur in some materials between the smectic-*A* and crystalline phases [9]. Unsurprisingly therefore, theoretical models of these new “ $N + 6$ ” phases draw heavily on our understanding of smectic hexatics. Such models can make use of a powerful analogy to superconductors, which break the axial $U(1)$ gauge symmetry of electromagnetism, because hexatics break the axial D_∞ symmetry of the smectic state. Consequently, the most striking behaviors expected of the $N + 6$ phase are that it should expel the spontaneous twist of the chiral nematic state, just as the Meissner effect expels curl of the vector potential in superconductors, and that “Type-II” systems should exhibit a defect ridden “Abrikosov” or TGB (twist-grain boundary) phase between the cholesteric and $N + 6$ states [5]. The purpose of this Letter is to demonstrate that this is not the case; while the superconducting analogy provides a sound model for smectic hexatics, theories of the $N + 6$ phase require a radically different mathematical foundation. In particular, while the differential geometry of superconducting systems forces the exclusion of magnetic field, the corresponding geometry of $N + 6$ states readily accommodates nematic twist without forming topological defects, and in chiral systems, such as those formed from DNA molecules, the spontaneously twisted state is often the preferred energy minimum.

The superconducting analogy is successful in describing smectic hexatics because the preexisting flat smectic layers provide a uniaxial ground state about which to perform a Ginzburg-Landau type expansion of the hexatic energy. Crucially, the smectic order itself excludes the twist and bend distortions of the nematic state. However, when hex-

atic order forms in the $N + 6$ state, there is no positional order present to stop it either twisting or bending. Indeed, the lack of preexisting positional order means that the symmetry group broken by this hexagonal order is not the axial group D_∞ , but the full rotation group $O(3)$. In this respect, the $N + 6$ phase is, as the authors of Ref. [5] actually comment, “not terribly different from a biaxial-nematic phase.” Theories of uniaxial-biaxial phase transitions generally need to use a tensor order parameter [10], because it is not possible to describe the biaxial order in terms of a single orientational variable (e.g., ϕ , as in $|\psi|e^{i2\phi}$, where ϕ is the azimuthal angle with respect to the uniaxial axis) since the uniaxial axis changes its orientation as a function of position. Consequently, unless the uniaxial order can be assumed to be oriented in the same direction everywhere, the biaxial order can only be described by using both polar (θ) and azimuthal (ϕ) variables, and hence in terms of the basis functions of the group $O(3)$. Furthermore, whereas biaxial nematics can be, and are, described by the same irreducible second-rank Cartesian tensor (\mathbf{Q}) used to describe the uniaxial phase, the hexagonal orientational order requires a sixth-rank [2,11] Cartesian tensor (\mathbf{P}) to describe its properties fully. Thus, as the order parameters belong to entirely separate irreducible representations (irreps), one cannot even assume that the symmetry axis of the nematic order will remain parallel to the sixfold axis of the bond order. These degrees of freedom exist because the two types of order depend on physically distinct types of correlations: the nematic order on the orientation of the molecules with respect to each other; the hexagonal bond order on correlations of the centers of mass of the molecules with respect to each other (see Fig. 1). Consequently, it is essential to use two separate Cartesian-tensor order parameters to describe $N + 6$ ordering, for both physical and mathematical reasons.

It is easy to visualize twist in a biaxial nematic. However, while visualizing twist of hexatic order along the sixfold axis is straightforward [6], it is much harder to visualize conventional, and defect-free, nematic twist within a hexagonally ordered state. To achieve such a visualization, we must first determine the structure of the relevant tensor order parameter (\mathbf{P}) and then show that for chiral

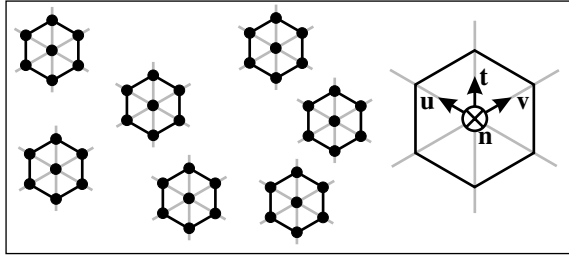


FIG. 1. Hexatic systems consist of hexagonally coordinated clusters of molecules. Correlations of the positions of the centers of mass of the molecules (the black dots) decay exponentially, but the orientation of the clusters possess true long-range order. Four unit vectors are used here to describe the geometry of the system: \mathbf{n} (directed out of the paper) points along the sixfold symmetry axis; \mathbf{t} , \mathbf{u} and \mathbf{v} point along the directions of maximum bond density.

phases, the Ginzburg-Landau free-energy density favors spontaneous nematic twist. Fundamental group-theoretical analysis of the little groups of the irreps of $O(3)$ [2,11] reveals that the lowest order irrep to exhibit the required D_6 symmetry is the thirteen-dimensional irrep ($J = 6$). In this case, the irrep can be written explicitly as the sum of two tesseral harmonic functions [11], such that the order-parameter \mathbf{P} is isomorphic to $uZ_0^6 + hZ_{6+}^6$. The tesserals are defined as normal:

$$Z_0^6 = \frac{1}{32} \sqrt{\frac{13}{\pi}} (231 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5), \quad (1)$$

$$Z_{6+}^6 = \frac{1}{64} \sqrt{\frac{6006}{\pi}} (\cos 6\phi) (\sin^6 \theta), \quad (2)$$

where θ and ϕ are the polar and azimuthal angles, and the scalars u and h determine, respectively, the amplitudes of the uniaxial and hexagonal parts of the irrep. By identifying three orthonormal vectors, \mathbf{n} (the uniaxial director), \mathbf{m} , and \mathbf{k} , with the angles θ and ϕ , in the usual way (i.e., $\mathbf{n} = \cos \theta$, $\mathbf{m} = \sin \theta \cos \phi$, $\mathbf{k} = \sin \theta \sin \phi$), it is possible to map these tesseral harmonics into their irreducible Cartesian tensor counterparts:

$$\begin{aligned} Z_0^6 \rightarrow \frac{1}{32} \sqrt{\frac{13}{\pi}} \{ & 231 \mathbf{n}_i \mathbf{n}_j \mathbf{n}_p \mathbf{n}_q \mathbf{n}_r \mathbf{n}_s \\ & - 21 (\mathbf{n}_i \mathbf{n}_j \mathbf{n}_p \mathbf{n}_q \delta_{rs} + 14 \text{ permutations}) \\ & + \frac{7}{3} (\mathbf{n}_i \mathbf{n}_j \delta_{pq} \delta_{rs} + 44 \text{ permutations}) \\ & - \frac{1}{3} (\delta_{ij} \delta_{pq} \delta_{rs} + 14 \text{ permutations}) \}, \quad (3) \end{aligned}$$

$$\begin{aligned} Z_{6+}^6 \rightarrow \frac{1}{64} \sqrt{\frac{6006}{\pi}} \{ & \mathbf{m}_i \mathbf{m}_j \mathbf{m}_p \mathbf{m}_q \mathbf{m}_r \mathbf{m}_s - \mathbf{k}_i \mathbf{k}_j \mathbf{k}_p \mathbf{k}_q \mathbf{k}_r \mathbf{k}_s \\ & - (\mathbf{m}_i \mathbf{m}_j \mathbf{m}_p \mathbf{m}_q \mathbf{k}_r \mathbf{k}_s + 14 \text{ permutations}) \\ & + (\mathbf{m}_i \mathbf{m}_j \mathbf{k}_p \mathbf{k}_q \mathbf{k}_r \mathbf{k}_s + 14 \text{ permutations}) \}, \quad (4) \end{aligned}$$

where δ_{ij} is the Kronecker delta tensor, and where the ‘‘other permutations’’ include all permutations of the indices, such that the resulting object is symmetric with respect to the interchange of any index pair, as required for

an irreducible tensor [12]. Using this sixth-rank tensor, it is straightforward to show that, as for the second-rank nematic order-parameter [9], there is only a single chiral term in the lowest (second) order Landau-de Gennes expansion: $\mathbf{P}_{impqrs} \varepsilon_{ijk} \nabla_j \mathbf{P}_{kmpqrs}$, where ε_{ijk} is the alternating tensor. It is a lengthy, though essentially trivial, exercise to contract these tensors together, assuming that the amplitudes u and h are constant, to produce the corresponding orientational elastic-energy density in terms of the standard twist invariants:

$$\begin{aligned} \mathbf{P}_{impqrs} \varepsilon_{ijk} \nabla_j \mathbf{P}_{kmpqrs} = & - \frac{3003}{128\pi} \left(\frac{559}{198} u^2 - h^2 \right) (\mathbf{n} \cdot \nabla \times \mathbf{n}) \\ & - \frac{273273}{2048\pi} h^2 [(\mathbf{m} \cdot \nabla \times \mathbf{m}) \\ & + (\mathbf{k} \cdot \nabla \times \mathbf{k}) - (\mathbf{n} \cdot \nabla \times \mathbf{n})]. \quad (5) \end{aligned}$$

The orientational elasticity of hexagonal systems has already been studied [13] by combinatorial methods. Although Ref. [13] does not use the convenient orthonormal basis set employed here (preferring instead a set of complex vectors), transformation from one notation to the other is not difficult. There are eight independent quadratic terms and two independent chiral terms in the energy according to Ref. [13]. The two chiral terms can be identified as those shown in Eq. (5), while the quadratic energy contains two corresponding quadratic twist terms: $K_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2$ and $K_{66} [(\mathbf{m} \cdot \nabla \times \mathbf{m}) + (\mathbf{k} \cdot \nabla \times \mathbf{k}) - (\mathbf{n} \cdot \nabla \times \mathbf{n})]^2$, where K_{22} is the ordinary nematic twist elastic constant and K_{66} is the elastic constant for twist of the hexagonal order along the \mathbf{n} direction. It follows from (5) that the free energy will be minimized by ordinary nematic twist when the following inequality is satisfied:

$$\frac{16}{91K_{22}} \left| \frac{559}{198} u^2 - h^2 \right| > \frac{h^2}{K_{66}}, \quad (6)$$

otherwise, the system will prefer to twist along the \mathbf{n} direction. At the nematic- $(N+6)$ phase transition the elastic constant K_{66} must vanish, and in this limit one may expect it to be proportional to h^2 , so that the h dependence of the right-hand side of (6) vanishes. Therefore, close to the phase transition, whether the inequality is satisfied will depend on the values of the other parameters. However, the system is still far more likely to exhibit nematic twist, as one must also consider the chiral term derived from the second-rank order-parameter: $\mathbf{Q}_{il} \varepsilon_{ijk} \nabla_j \mathbf{Q}_{kl} = -s^2 (\mathbf{N} \cdot \nabla \times \mathbf{N})$ (where \mathbf{N} is the nematic director). This matters as the high symmetry axes of \mathbf{Q} and \mathbf{P} (\mathbf{N} and \mathbf{n} , respectively) are coupled together by terms in the homogeneous Landau expansion such as $\mathbf{Q}_{ij} \mathbf{Q}_{kl} \mathbf{Q}_{mn} \mathbf{P}_{ijklmn} \propto s^3 u P_6 (\mathbf{N} \cdot \mathbf{n})$ (where P_6 denotes the sixth Legendre polynomial). Consequently, any deformation of one order-parameter field will tend to induce the same deformation in the other.

This demonstrates that spontaneous nematic twist does correspond to the elastic-energy minimum in some circumstances. However, it does not make clear the fact that a twisted hexagonal state may exist without a proliferation of defects. In order to describe such a state, it is helpful

to introduce an analog of the Frank-Oseen theory of uniaxial nematics, instead of the Cartesian tensor treatment used above. Thus, we may describe the local orientational order, below the nematic- $(N + 6)$ phase transition, with a set of unit vector fields (see Fig. 1): $\mathbf{n}(\mathbf{r})$, which points along the sixfold symmetry axis, and which will be contained in the plane perpendicular to the twist axis; $\mathbf{t}(\mathbf{r})$, which points along one of the six twofold axes of the D_6 state, and along the twist axis; $\mathbf{u}(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$, which point along two of the remaining twofold axes such that they are both at 60° to $\mathbf{t}(\mathbf{r})$ and at 120° to each other. This description does contain some redundancy: only three noncoplanar vectors are required to uniquely specify the orientation of any object in three-dimensional space. Descriptions that use an orthonormal triad have some advantages, but the set $(\mathbf{n}, \mathbf{t}, \mathbf{u}, \mathbf{v})$ provides a more intuitive description of the $N + 6$ phase. If the twist axis is assumed to be along the z direction of a three-dimensional space, then the spatial distribution of the first two vectors will be:

$$\mathbf{t}(\mathbf{r}) = \hat{\mathbf{z}}, \quad (7)$$

$$\mathbf{n}(\mathbf{r}) = [\cos(\frac{z}{b})]\hat{\mathbf{x}} + [\sin(\frac{z}{b})]\hat{\mathbf{y}}, \quad (8)$$

where the pitch is $2\pi b$. The tools needed to discover the distribution of the other two vectors are well established, and belong to the discipline of differential geometry. Since we assume that these vector fields fill the whole of space, without any topological defects, we may immediately use the equivalence relation between such a smooth set of (tangent) vectors and their corresponding integral curves [14]. The integral curves of $\mathbf{t}(\mathbf{r})$ are all straight lines along the z direction, while the integral curves of $\mathbf{n}(\mathbf{r})$ are straight lines that lie in the x - y plane. Evidently, the integral curves of $\mathbf{u}(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$ must be “lines of constant slope” [i.e., they must always be at a constant angle ($\alpha = 60^\circ$) to the twist axis]. Therefore, they must be left and right handed 60° circular helices. The general equation of such lines is well known [14]:

$$\mathbf{R} = a(\cos\xi)\hat{\mathbf{x}} + a(\sin\xi)\hat{\mathbf{y}} + b\xi\hat{\mathbf{z}}, \quad (9)$$

where \mathbf{R} indicates position; $a, b \neq 0, \xi \in \mathbb{R}; \xi (-\infty < \xi < \infty)$ parametrizes the curve; and $\cos\alpha = b(a^2 + b^2)^{-1/2}$. From Eq. (9) it is a simple matter [14] to find the corresponding tangent vectors:

$$\mathbf{u}, \mathbf{v}(\mathbf{r}) = (a^2 + b^2)^{-1/2} \{ \mp a[\sin(\frac{z}{b})]\hat{\mathbf{x}} \pm a[\cos(\frac{z}{b})]\hat{\mathbf{y}} + b\hat{\mathbf{z}} \}. \quad (10)$$

It is trivial to verify that these distributions obey the necessary symmetry constraints: $\mathbf{n} \cdot \mathbf{t} = \mathbf{n} \cdot \mathbf{u} = \mathbf{n} \cdot \mathbf{v} = 0$, $\mathbf{t} \cdot \mathbf{u} = \mathbf{t} \cdot \mathbf{v} = \cos\alpha$, and $\mathbf{u} \cdot \mathbf{v} = \cos 2\alpha$, at all points in space. Since this set of vectors is smooth (without topological defects) we may conclude that there is absolutely no geometric prohibition of nematic twist in the $N + 6$ phase. To aid visualization, several members of the set of integral curves relevant to the description of twisted hexagonal order are shown in Fig. 2. Furthermore, since the

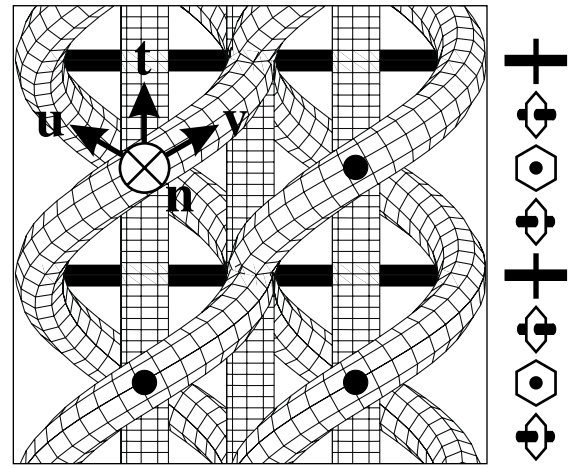


FIG. 2. Representative integral curves from the complete set that describes twisted hexagonal order. The curves are plotted as “fat lines” to aid visualization of the structure. The integral curves of \mathbf{n} , the sixfold axis, are drawn in solid black, the other curves show three of the twofold axes, the straight one of which corresponds to \mathbf{t} (which is also the twist axis), while the \mathbf{u} and \mathbf{v} curves form pairs of counter-rotating 60° circular helices. The orientation of \mathbf{n} , and the directions of maximum bond density (\mathbf{t} , \mathbf{u} , and \mathbf{v}), are indicated, at various positions along the twist axis, to the right of the figure.

above reasoning holds for vectors at any angle α to the twist axis, it is possible to conclude that there is no prohibition of twist for orientationally ordered systems of any symmetry; for example, a twisted icosahedral quasicrystal can be described by a set of six integral curves through each point in space, one along each of the fivefold symmetry axes of the icosahedral order (as illustrated in Fig. 3).

While it seems clear that the foundational theory of the $N + 6$ phase needs to be formulated in terms of $O(3)$ symmetry breaking, rather than by analogy to superconductors,

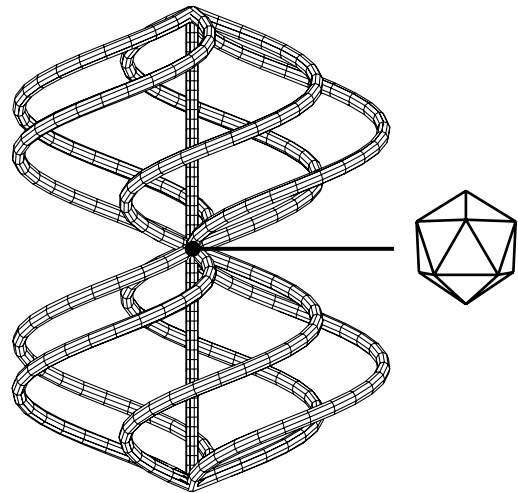


FIG. 3. As for Fig. 2, but for a twisted icosahedral system. Here, all of the integral curves, including the twist axis, correspond to the fivefold symmetry axes of icosahedral order, the orientation of which is indicated at one point by the icosahedron shown.

it is also clear that one situation exists where the conventional theory is acceptable. If the nematic director (\mathbf{N}) is spatially uniform, and if fluctuations of the sixfold axis of the hexatic order away from the \mathbf{N} direction are neglected, then the hexatic symmetry breaking does occur from an axial state. Kamien and Levine [5] assume that such a state is forced into existence by boundary conditions. They then succeed in explaining the puzzling observation [4] that a chiral $N + 6$ phase of DNA molecules exhibits a sixfold x-ray diffraction pattern, when naive arguments suggest that the pattern should be smeared out by a precession of the hexagonal order along the nematic axis. The present theory will always agree with such “uniaxial-ground-state” calculations, but stark disagreement occurs when deviations away from uniform \mathbf{N} states are considered. For example, experiments [4] show that when a system of DNA molecules is hydrated up, out of the $N + 6$ phase, deep into the cholesteric phase, and then dehydrated back down into the $N + 6$ phase again, the sixfold x-ray diffraction pattern fails to return. In this situation, the conventional theory suggests that the diffraction pattern should return, because the reappearance of hexatic order is assumed to unwind the cholesteric helix, thus returning the system to its original state. However, the empirical situation is readily explained given the present work: once the ordered phase “melts,” upon hydration, the boundary conditions disappear, thereby allowing a conventionally twisted cholesteric phase to form. Since this twist is actually compatible with defect-free hexatic order, it will remain upon reentry into the $N + 6$ phase, so the liquid crystals will possess sixfold order, but it will be oriented in different directions at different points in the sample. Consequently, an x-ray diffraction experiment would detect only a smeared out average, as reported in Ref. [4].

Lorman, Podgornik, and Žekš also assume a uniaxial-ground-state as a starting point for their treatment of $N + 6$ phases that develop spontaneous polar order [8]. Consequently, their basic analysis seems fundamentally sound. However, they do not consider elastic deformations away from the ground state. Such an extension of the theory

will be necessary if it is to describe $N + 6$ phases in general, and not just special cases where boundary conditions prevent any distortions of \mathbf{N} away from uniformity. This presents an interesting challenge because, as the arguments detailed above show, $N + 6$ phases actually have far greater freedom, in the types of defect-free elastic distortions that they can support, than the superconducting analogy would allow.

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