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Refusing to Twist: Demonstration of a Line Hexatic Phase in DNA Liquid Crystals

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We report conclusive high resolution small angle x-ray scattering evidence that long DNA fragments form an untwisted line hexatic phase between the cholesteric and the crystalline phases. The line hexatic phase is a liquid-crystalline phase with long-range hexagonal bond-orientational order, long-range nematic order, but liquidlike, i.e., short-range, positional order. So far, it has not been seen in any other three dimensional system. By line-shape analysis of x-ray scattering data we found that positional order *decreases* when the line hexatic phase is compressed. We suggest that such anomalous behavior is a result of the chiral nature of DNA molecules.

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Is it surprising that liquid crystals of theoretically possible order and symmetry still remain unobserved? For example, the line hexatic or $N + 6$ phase was first predicted for nematic liquid crystals by Toner [1] and later for magnetic flux-line lattices in type-II high-T_c superconductors [2] but were never experimentally confirmed. Characterized by long-range bond-orientational order, long-range nematic order, and liquidlike positional order perpendicular to the nematic axis of the polymers, this phase is the three dimensional analog of the two dimensional hexatic phase that was first proposed by Halperin and Nelson [3]. In fact, any cut through the line hexatic phase perpendicular to the local director reveals a collection of points at which the individual polymers pass through the cutting plane exhibiting canonical 2D hexatic order. Remarkably, there is no twist in the location of these points as the cut is made at successive points along the nematic axis of the molecules. Our earlier suggestion that this phase was exhibited by chiral DNA molecules [4] was received as a puzzle [5] whose possible resolution was proposed only recently [6]. The experimental issue hinges on the comparative range of positional and bond-orientational order.

We now bring conclusive high resolution small angle x-ray scattering evidence that long DNA does pack into the untwisted line hexatic phase. It is located on the phase diagram where a columnar hexagonal phase was previously assumed [7]. We suggest that it emerges out of a competition between packing symmetry and local angular correlations between DNA molecules.

Oriented DNA sheets were prepared from calf thymus DNA (Pharmacia) with an average molecular weight (MW) of $\approx 10^7$ (corresponding to a contour length of ≈ 5 μm or some 100 persistence lengths of 50 nm) by wet-spinning [8] and then drying. Though the samples were polydisperse, they contained no detectable DNA with MW $\leq 10^6$. The dried DNA sheets of 0.7 mm thickness and 5 mm width were cut perpendicular to the principal axis of the DNA molecules into strips of approximately $l_x = 0.7$ mm; $l_y = 5$ mm; $l_z = 1$ mm, with DNA molecules pointing along the z direction. To set the density of the DNA in the samples, they were rehydrated and equilibrated against poly (ethylene glycol) (MW 8000, UCB) solutions containing 0.5M NaCl, 10 mM Tris, 1 mM EDTA, pH8. Poly (ethylene glycol) (PEG) concentrations were varied from 50 wt% PEG down to about 20 wt% PEG. Oriented DNA samples bathed in PEG solutions retain their rectangular shape while swelling only in two dimensions (x-y plane). The relation between PEG osmotic pressure and the concurrent density of the stressed DNA phase was established and explored before [9]. Preliminary x-ray scattering measurements were performed on a rotating anode x-ray generator. The synchrotron x-ray scattering reported here was performed at the National Synchrotron Light Source (NSLS) on Exxon's beam line X10A. The beam was defined by a pair of Ge(111) crystals ($\lambda = 1.5$ Å) and slits giving a spot size at the sample of 0.8 mm (vert) $\times$ 0.6 mm (hor). The sample was mounted on a four-circle goniometer (Huber, Germany). The scattering was measured both with an image plate area detector (Mar Research, Germany; 180 mm diam, 1200×1200 pixels) as well as a scintillation detector (Bicron, OH) mounted on the 2θ arm with slits defining the detector's angular resolution.

To measure the in-plane positional correlation length λ_{PO} the incoming x-ray beam is aimed perpendicular to the principal axis of the DNA molecules in the macroscopically oriented sample at 50 wt% PEG. The inset in Fig. 1(a) shows the scattering pattern, where the angular width of the arcs indicate a mosaic spread of about 40°. Such mosaic spread is quite reasonable considering that the sample dimensions are 10^5 times larger than the persistence length of DNA. Figure 1(a) displays the scattering

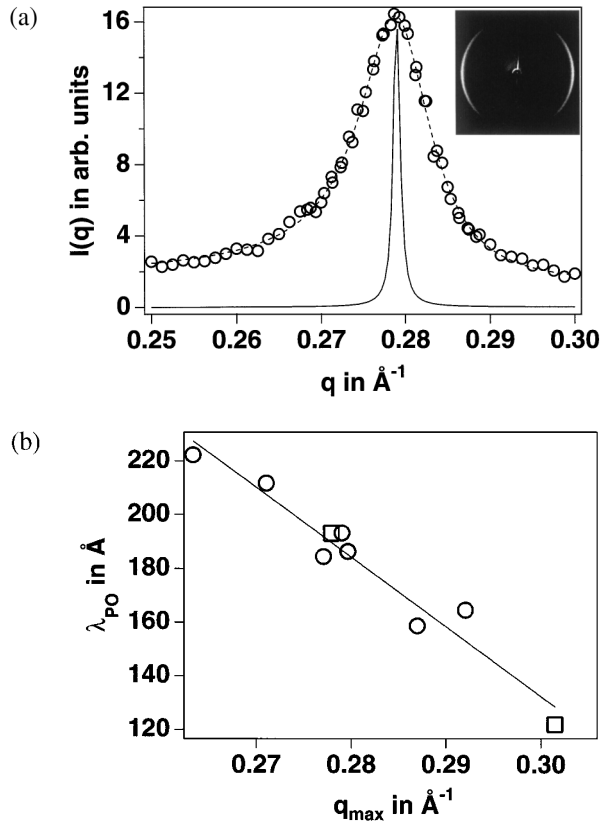

FIG. 1. (a) Scattering intensity versus momentum transfer q, measured perpendicular to the molecular axis. The resolution here is $\Delta q = 5 \times 10^{-3}$ Å^{-1} FWHM and is displayed as a solid line. The fit resulted in an in-plane positional correlation length of 160 Å. The peak corresponds to an interaxial distance between two DNA molecules of $d = 4\pi/\sqrt{3}\, q_{\max} = 25$ Å. Inset: X-ray detector image of an aligned DNA sample with perpendicular orientation. The angular width indicates a sample mosaic spread of approximately 40°. (b) Positional in-plane correlation length λ_{PO} versus inverse lattice spacing $q_{\max}$ for oriented (circles) and powder (squares) samples. Positional order becomes more liquidlike (shorter correlation length) as the DNA arrays get denser.

intensity versus momentum transfer q, measured perpendicular to the molecules. (The system resolution here is $\Delta q = 5 \times 10^{-3}$ Å^{-1} FWHM, solid line.) The intensity distribution was fitted (dashed line) using a symmetrized Lorentzian multiplied by the form factor of a solid cylinder with a radius $R = 10$ Å.

$$I(q) = A\left(\frac{\Gamma}{(q - q_{\max})^2 + \Gamma^2} + \frac{\Gamma}{(q + q_{\max})^2 + \Gamma^2}\right)\left(\frac{J_0(qR)}{qR}\right)^2.$$

The peak corresponds to an interaxial distance $d = 4\pi/\sqrt{3}\, q_{\max} = 25$ Å between two nearest neighbor DNA molecules. The width of the Lorentzian gives a positional correlation length of $\lambda_{PO} = 1/\Gamma = 160$ Å, or about six neighbors.

To verify that the measured correlation length is an equilibrium quantity, we repeated the experiment on several oriented and unoriented (powder) samples at different DNA densities [Fig. 1(b)] spanning the regime of the interaxial spacings between 27.5 to 24.0 Å which lies within the line hexatic part of the phase diagram. Regardless of the direction in which samples were hydrated or dehydrated, after sufficient equilibration against PEG solutions, the samples showed reproducible positional correlation lengths λ_{PO}. Powder samples [squares in Fig. 1(b)] showed the same correlation lengths as oriented samples [circles in Fig. 1(b)] at the same DNA density.

In addition, the variation of λ_{PO} as a function of DNA density shows that positional order within the sample is more liquidlike (shorter correlation length) the more DNA density is increased. In fact, the correlation length goes from about five neighbors at 24.0 Å interaxial spacing to about eight neighbors at 27.5 Å. This trend is surprising and counterintuitive; one would expect the DNA array to exhibit increasingly longer-ranged positional order approaching the crystalline phase where it becomes (ideally) infinite. We will argue that this puzzling progressive disordering of DNA packing at higher densities could be due to increasing frustration of the molecules as they try to satisfy both the positional and the angular constraints imposed by the interaction potential (see below).

To estimate the *bond*-orientational order correlation length λ_{BO}, we oriented the sample so that the principal axis of the DNA molecules was parallel to the incoming x-ray beam. Except for fluctuations, momentum transfer q was in the plane perpendicular to the molecules. The inset in Fig. 2 shows the 2D scattered intensity distribution with pronounced sixfold angular modulation. Because the width of the incoming beam was about 0.8 mm × 0.6 mm, the bond-orientational order correlations must have extended over at least 0.6 mm, i.e., over the area covered by the x-ray beam. With shorter-range correlations, the intensity distribution would have been

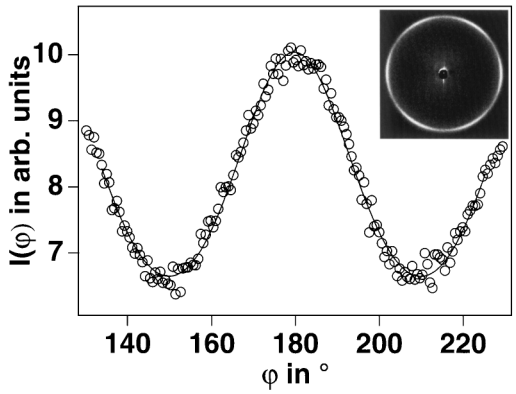

FIG. 2. Sixfold symmetric azimuthal intensity profile $I(\varphi)$ taken from x-ray detector image of an aligned DNA sample (see Fig. 1) with parallel orientation (inset) at $q_{\max}$. Earlier measurements and theoretical calculations on stacked hexatic (thick film of smectic $S_{B\text{-Hex}}$ or S_I) [16] suggested a particular angular intensity profile. In order to reconcile our data with this intensity profile we had to introduce a mosaic spread of about 10° in φ (shown as solid line).

smeared into a uniform ring and the fingerprint of a hexatic phase would be lost.

The bond-orientational order melts, i.e., all angular modulation in the diffraction pattern is lost, at lower DNA densities corresponding to the nearest neighbor DNA separation of ~36 Å [4]. Scattering from samples just prior to complete melting of the hexatic order showed a broad isotropic smaller-q liquidlike ring, which extends continuously into the cholesteric phase, coexisting with a sharper sixfold-modulated ring [9]. When DNA density decreased, the integrated intensity of the broad diffraction ring increased; at the same time the intensity of the sharper sixfold modulated diffraction ring decreased. Partial sixfold modulation spontaneously reappears when increasing the DNA density from just inside the fully melted cholesteric exhibiting one single broad isotropic ring. Recovery of the sixfold modulation was not possible for samples that had swelled deeply into the cholesteric phase, most probably because cholesteric twist had destroyed global alignment. From these findings, we conclude that the line hexatic-cholesteric transition is an equilibrium phenomenon.

According to recent theoretical arguments [5], the existence of a DNA line hexatic phase is surprising. In certain liquid crystals with liquidlike positional order, molecular chirality induces remarkable long-range nematic twist patterns, e.g., in the cholesteric phase [10]. Because the line hexatic phase also has liquidlike positional order, Kamien [5] predicted that its bond-orientational order should twist along its nematic axis, just as the nematic order twists along the cholesteric axis in the cholesteric phase. It thus seemed that chiral DNA molecules would prefer a twisted hexatic phase (the pitch of which should be on the same order of magnitude as the corresponding pitch in the DNA cholesteric phase, i.e., about 2 μm), wherein the bond-orientational order should rotate along the nematic director. In this case, of course, the sixfold angular modulation of the diffraction pattern would be smeared into a ring of equal intensity.

The clear sixfold angular modulation of the diffraction intensity clearly shows that in our samples there is no such twist; if it nevertheless exists, its pitch must be much larger than the 1 mm sample thickness—almost 3 orders of magnitude larger than the expected 2 μm.

In a typical cholesteric, the twist angle between neighboring molecules perpendicular to the cholesteric axis amounts only to a fraction of a degree. Harris *et al.* [11] recently argued that chiral interactions can be averaged out if molecules in a liquid crystalline phase are allowed to rotate independently around their long axes. They concluded that chiral interactions require rotational correlations between molecules. The twisting strength of the chiral interaction was found to be proportional to $\langle\cos(\Delta\varphi - \langle\Delta\varphi\rangle)\rangle$ [see Fig. 3(a)].

Rotational correlation results from an angular part of the DNA-DNA interaction potential that might exhibit an optimal orientation angle $\langle\Delta\varphi\rangle$ between two neighboring helices; its force is to lock the two molecules into a separation-dependent mutual angle. The sharper the minimum in angular potential, the stronger the rotational correlations and the more effective would be this angular locking mechanism.

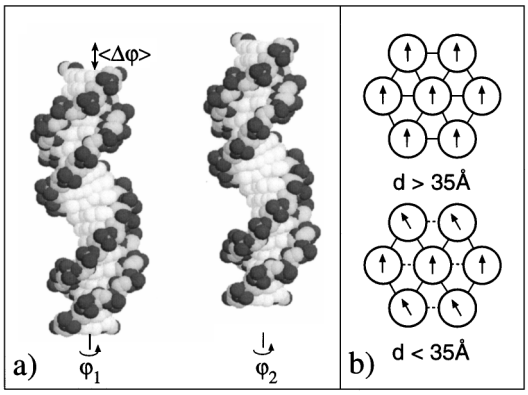

FIG. 3. (a) Illustration of an optimal orientation angle $\langle\Delta\varphi\rangle$ between two DNA molecules. For helical molecules, rotations translate into translations along the long axis. If two molecules can rotate independently their chirality averages out, and there will be no chiral interaction between them. Chiral interactions require nonzero rotational correlations $\langle\cos(\Delta\varphi - \langle\Delta\varphi\rangle)\rangle$. (b) Nonzero optimal angles between hexagonally packed DNA molecules lead to angular frustrations. One out of three pairwise interactions are frustrated. These frustrations could weaken rotational correlations and therefore suppress chiral interactions between DNA molecules.

The angular part of the interaction potential between DNA helices is finally becoming better understood. Separation-dependent optimal angles and angular potentials between two double helical molecules have been recently formulated by Kornyshev and Leikin [12] in the mean field approximation. They took into account helical pitch, the number of helical strands, the detailed positions of charges or other chemical groups along the helix, the number of base pairs per turn, and a model for the distribution of the counterions. Their calculation thus corresponds to a generalization of the Bjerrum-pairing model appropriate to helical polyelectrolytes. For nonsymmetric double helices like DNA, they found that for interaxial distances larger than the helical pitch the optimal mutual angle is 0°. Upon closer approach there is a critical distance, ≈36 Å for double stranded DNA in *B* conformation, from which separation down the optimal angle monotonically increases to almost 90° at close separations. Reassuringly, this critical 36 Å interaxial spacing almost coincides with the phase transition in DNA solutions from the cholesteric phase to the line hexatic phase (see above).

Large optimal angles between DNA molecules might be the reason why the bond-orientational order of DNA in the line hexatic phase does not twist. Consider the local hexagonal packing of DNA molecules in liquid crystalline arrays. If the optimal angles are large then there is no way to arrange the DNA molecules in a triangular lattice that satisfies all optimal angles. As illustrated in

Fig. 3(b), in a triangle two pairs of angular interactions can be satisfied, but the third pair will be always frustrated. Although the angular part of the pair potential sharpens as the molecules approach each other, rotational correlations can actually be weakened by angular frustrations due to the coupling between the angular and the positional parts of the interaction potential. Angular frustrations in the line hexatic phase resemble those in frustrated spin systems [13], such as in antiferromagnets on a triangular lattice. In alkyl-chain systems similar frustrations have been found to induce disorder in the hexagonal phase cooled toward the orthorhombic [14].

That optimal angles between DNA molecules exist was shown experimentally by Langridge *et al.* in 1960 [15]. At very high densities DNA forms several crystalline phases. Li-DNA at separations ≤ 25 Å interaxial spacing shows a phase transition from a hexagonal crystalline phase to an orthorhombic phase. The orthorhombic phase solves the angular frustration problem by distorting the hexagonal equilateral into the isosceles triangles. Two pairs of molecules are close to each other maintaining optimal angles while the third pair is farther apart and can be in a nonoptimal configuration. Angular frustration can thus substantially modify local packing symmetry. The question of exactly how angular frustrations could affect bond-orientational order has not yet been properly addressed.

The existence of a line hexatic phase poses additional questions that need to be resolved in the future. Is the line hexatic phase a "glass" or a "liquid"? Both have short-range positional order. How strong are angular frustrations compared to thermal energies? Do such angular frustrations suffice to trap DNA in a glassy state? Can one directly observe angular correlations in different phases?

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