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Physics Abstracts

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Statistical mechanics of defects in polymer liquid crystals

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Abstract. — We develop a continuum theory for the statistical mechanics of thermally activated point defects in the nematic and hexagonal phases of polymer liquid crystals. In the nematic phase, there are elementary splay defects (chain ends and hairpins), and in the hexagonal phase, there are both splay defects and twist defects. In the nematic phase, splay defects are free in the limit of large separation; i.e., their binding energy is finite. By contrast, in the hexagonal phase, both types of defects are bound in $+-$ pairs. We derive expressions for two correlation functions, the structure factor and the director fluctuation spectrum, in the presence of defects, and we use these correlation functions to define macroscopic Frank constants and elastic moduli. In the nematic phase, the presence of ionized splay defects causes the macroscopic splay constant \hat{K}_1 to be finite. It is large and strongly temperature-dependent in the low-temperature regime, but smaller and temperature-independent in the higher-temperature, Debye-Hückel regime. By contrast, in the hexagonal phase, the macroscopic splay and twist constants \hat{K}_1 and \hat{K}_2 are infinite, just as in harmonic theory. These effects should be observable in x-ray and light-scattering experiments on polymer liquid crystals.

1. Introduction.

Nematic liquid crystals support a variety of fascinating defects in their texture, such as disclination lines and noyaux. Because the cost in free energy to create these defects is normally large compared to $k_B T$, they do not play a significant role in the thermodynamic properties of ordinary nematics (at least not in three dimensions). For example, the director fluctuation spectrum—important for light scattering—can be satisfactorily computed within harmonic theory [1], which explicitly neglects defects.

It was first pointed out by de Gennes [2] that the harmonic theory of *polymer* nematics has strange anomalies in the long-chain limit. In long-chain polymer nematics, there is an intrinsic coupling between orientational and density fluctuations. This coupling leads to a divergence of the macroscopic Frank constant K_1 , which describes the elastic energy cost of a splay in the director field. In a recent paper [3], we extended this result and found that the x-ray structure factor is anomalous as well: it resembles a “butterfly” pattern as opposed to the structure factor of conventional nematics, which is more like that of isotropic liquids [1]. We also found that, in a number of ways, polymer nematics are similar to *smectic* liquid crystals. For example, a

splay deformation can only penetrate a finite distance into a defect-free polymer nematic. This "screening" of splay in polymer nematics is the analogue of the screening of twist and bend in smectics.

Meyer [4] has noted that defects *do* play an important role in the thermodynamics of polymer nematics. Polymer nematics support point-like defects that are unique to polymer liquid crystals and whose energy cost can be of order $k_B T$. The purpose of this paper is to investigate how these defects modify the anomalous predictions of the harmonic theory for the macroscopic Frank constant K_1 , the structure factor, and the screening of splay deformations.

Topological defects in aligned chain systems have been classified by Bouligand [5] and Kléman *et al.* [6]. Topological defects that are not point-like, such as disclination lines, have little chance of thermal excitation, so we can restrict ourselves to point-like defects. In particular, we will consider point-like "splay" defects, which are believed to play an important role in both dielectric and elastic properties [7]. Polymer nematics have two types of splay defects, which are illustrated in figure 1. We may either cut a polymer ("scission") and separate the endpoints, or we may fold a polymer over 180° ("hairpin") [7]. We will call the endpoint of a polymer attached to the top sample boundary ($z = L/2$) a "+" defect and an endpoint connected to the bottom sample boundary ($z = -L/2$) a "-" defect. Since hairpins can be treated as two combined endpoint defects, we simply give them a double "charge": ++ or --

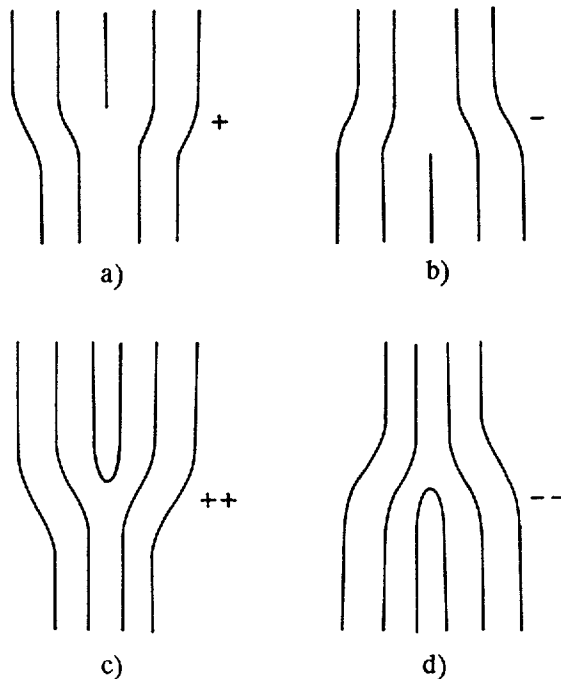


Fig. 1. — Side views of splay defects in polymer liquid crystals: (a), (b). Endpoint defects. (c), (d). Hairpin defects. In $D = 2$, the endpoint defects shown here are isomorphic to dislocations in smectic liquid crystals.

If we now assume that the energy cost of nucleating and ionizing a pair of endpoint defects is finite, then there must be a finite concentration of free defects. In figure 2, we show why K_1 is expected to be finite if there are indeed free endpoint defects. Hairpin defects have a similar

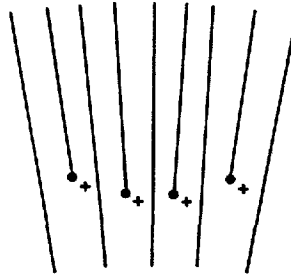


Fig. 2. — A splay in the nematic director field, in the presence of free endpoint defects.

effect, so even for polymer nematics that cannot be scissioned, we still expect K_1 to be finite.

The simplest description of polymer nematics with free splay defects would be to borrow the Flory-Huggins theory for “living” polymers [8]. Living polymers are materials consisting of rods that can be thermally scissioned (e. g., cylindrical micelles). Flory-Huggins theory completely neglects interaction between endpoints, with the result that the endpoints form an *ideal gas*. The length distribution of the rods is then found to be exponential. It is easy to show that under those conditions $K_1 \propto 1/n$, where n is the density of endpoints [7]. The weakness of Flory-Huggins theory is that the endpoints or hairpins induce elastic deformations in the surrounding medium, which lead to an interaction among the defects. For that reason, the splay defects do not constitute an ideal gas, as was noted already by Meyer [4]. Interactions among defects increase the defect ionization energy and therefore increase K_1 .

The importance of topological defects for chain-like liquid crystals is not limited to the nematic phase. If the density or the stiffness of the chains is increased, a polymer nematic can undergo a phase transition to a hexagonal lattice of positionally ordered chains. In reference [9] we developed a density-functional theory for the nematic-hexagonal transition, and in reference [3] we constructed a harmonic theory for the hexagonal phase, with the following results: (i) the macroscopic splay and twist constants K_1 and K_2 are now *both* infinite, (ii) there are sharp Bragg spots in the structure factor (i.e., there is long-range positional order), and (iii) the mean square of the chain displacement field $\langle |u|^2 \rangle$ is finite above the lower critical dimension $D_L = 2.5$. The divergence of K_2 is due to coupling between director twist and shear deformation of the hexagonal lattice. The fact that the lower critical dimension exceeds that of conventional crystals ($D_L = 2$) indicates that the hexagonal phase is not a true solid, and indeed the K_3 bending constant remains finite.

Like the nematic phase, the hexagonal phase can support splay defects. In addition, there is a second class of defects associated with director twist instead of splay. These defects are constructed by a ring exchange of two or more chains, as shown in figure 3. We will assign a + sign to a counterclockwise twist and a – sign to a clockwise twist.

In this paper, we present a continuum description of the statistical mechanics of point defects in both the nematic and hexagonal phases [10]. The basis of the calculation is the observation that two-dimensional (2D) polymer nematics are isomorphic to 2D smectic liquid crystals; the similarity in $D = 3$ becomes an identity in $D = 2$. As is clear from figure 1, an endpoint defect of a 2D polymer nematic is equivalent to a dislocation in a 2D smectic. Furthermore, the statistical mechanics of point defects in 2D smectics is well understood through the continuum theory of Toner and Nelson [11]. In section 2, we discuss the Toner-Nelson method and generalize it to 3D polymer nematics. In section 3, we apply the same method to the hexagonal phase. Our model applies to polymer systems in which splay defects (either endpoints or hairpins)

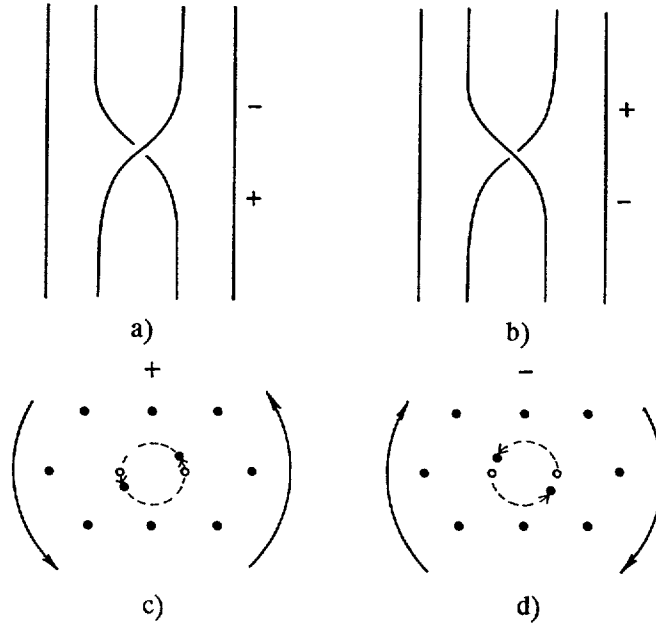


Fig. 3. — Twist defects in polymer liquid crystals: (a), (b). Side views of chain exchanges, which are +- and -+ dipoles of twist defects. (c), (d). Top views of + and - twist defects.

and twist defects are in thermal equilibrium. It also applies to analogous systems of long, semiflexible aggregates, such as worm-like micelles and columns of discotic liquid crystals, in which the analogous defects can be thermally excited.

Our principal results are as follows:

Polymer nematics must be grouped into two classes: those with defect core energy E_S large compared to the thermal energy $k_B T$ (“low-temperature regime”) and those with E_S comparable to or less than $k_B T$ (“Debye-Hückel regime”). In the low-temperature regime, polymer nematics support an exponentially low concentration of ionized splay defects, which are well described by the ideal gas picture. The defect pair ionization energy is not divergent, so the macroscopic splay constant \hat{K}_1 is large—but finite—and strongly temperature dependent. The wavevector-dependent splay constant $K_1(\mathbf{q})$, with $\hat{K}_1 = K_1(\mathbf{q} = 0)$, is found to be

$$K_1(\mathbf{q}) \approx \begin{cases} K_1 + \lambda q_z^{-2}, & \text{if } q_z \gg \xi^{-1}, \\ k_B T a^{-1} e^{F_{\text{bind}}/k_B T}, & \text{if } q_z \ll \xi^{-1}, \end{cases} \quad (1.1)$$

with K_1 the “bare” splay constant, λ the bulk modulus, ξ a length of order the mean spacing between free defects, and a the microscopic length scale. The defect binding energy F_{bind} is, as discussed in the text, in excess of $2E_S$ due to defect-defect elastic interaction. The structure factor of polymer nematics in this regime still contains the “butterfly pattern” of harmonic theory, except that the extinction line at $\mathbf{q}_\perp = 0$ is erased.

For polymer nematics in the Debye-Hückel regime, with $E_S \lesssim k_B T$, an ideal gas picture would be seriously in error. In this regime, the nematic phase is a dense plasma of defects. One of the consequences is that now \hat{K}_1 is smaller and no longer temperature-dependent,

$$\hat{K}_1 \approx \frac{E_S}{a}, \quad (1.2)$$

and has no relation at all with the bare splay constant. The structure factor no longer resembles a butterfly pattern but instead is similar to that of an ordinary uniaxial liquid. In fact, in many respects the properties of a polymer nematic in the Debye-Hückel regime resemble those of a short-chain nematic. In particular, we should not expect to encounter the peculiar duality with smectic-like properties predicted by harmonic theory.

The change from the low-temperature regime to the Debye-Hückel regime could be a gradual crossover or a first-order phase transition. In the latter case, it would be characterized by a very sharp increase in \hat{K}_1 accompanied by a dramatic reorganization of the structure factor.

In the hexagonal phase we find, beside the splay defects discussed above, a second type of point defects associated with a *twist* in the bundle of polymers. The exchange of two neighboring chains in the hexagonal lattice corresponds to a $+ -$ dipole of twist defects. Unlike the nematic phase, in the hexagonal phase we find that both splay and twist defects are confined by a linear restoring force: the hexagonal phase can support neither free splay nor free twist defects. Chain exchanges are closely localized.

The confinement of defects can be traced to the existence of a finite shear coefficient μ . As we increase the twist defect concentration, the shear coefficient is reduced and eventually goes to zero: the hexagonal phase cannot support large concentrations of twist defect pairs.

A consequence of the confinement is that the prediction of the harmonic theory that \hat{K}_1 and \hat{K}_2 are infinite remains valid. The gas of defect dipoles renormalizes the Lamé coefficients λ and μ but does not affect the basic description of the harmonic theory. The connection between the confinement potential and the shear coefficients suggest that a (hypothetical) hexatic phase, with $\hat{\mu} = 0$, would have finite values of \hat{K}_1 and \hat{K}_2 , but this goes beyond the scope of this paper.

2. Nematic phase.

In a continuum description of a condensed phase such as a nematic, we must begin by identifying the hydrodynamic variables that describe the low-energy excitations. The next step is to construct a fluctuation free energy for these variables consistent with the symmetry of the nematic phase. For a nematic, the position-dependent order parameter—the director $\hat{\mathbf{n}}(\mathbf{r})$ —provides one of these hydrodynamic variables. The other one is the fluctuation $\rho(\mathbf{r})$ around the average density ρ_0 . For polymer nematics, $\rho(\mathbf{r})$ and ρ_0 are really *area* densities of the chains in a plane perpendicular to $\hat{\mathbf{n}}$. If both $\hat{\mathbf{n}}(\mathbf{r})$ and $\rho(\mathbf{r})$ vary slowly with position, the the fluctuation free energy is the sum of the Frank free energy and the energy cost of density fluctuations:

$$H = \frac{1}{2} \int d^3\mathbf{r} \left[K_1(\nabla \cdot \hat{\mathbf{n}})^2 + K_2(\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}))^2 + K_3(\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}}))^2 + \lambda \left(\frac{\rho - \rho_0}{\rho_0} \right)^2 \right]. \quad (2.1)$$

The stiffness constants K_1 , K_2 , and K_3 are the Frank constants for, respectively, splay, twist, and bend of the director texture, while λ is the isothermal bulk modulus of the chains. We will assume that the fluid of chains plus solvent is incompressible, so an increase in ρ is accompanied by a reduction in solvent density, and vice versa.

Both the stiffness constants and λ are “bare” parameters; i.e., they are to be computed by a local cell average over a volume small compared to the system size but large compared to microscopic length scales. For the case of polymers with purely steric repulsion, it has been shown [3 12] that:

$$K_3 \approx k_B T P a^{-2}, \quad (2.2a)$$

$$K_1 \approx K_2 \approx k_B T P^{1/3} (a - b)^{2/3} a^{-2}, \quad (2.2b)$$

$$\lambda \approx k_B T P^{-1/3} (a - b)^{-2/3} a^{-2} \quad (2.2c)$$

Here, a is the inter-chain spacing (with $\rho_0 = 2/(\sqrt{3}a^2)$), and b is the chain diameter ($b < a$). The persistence length P is the distance over which a *free* polymer maintains its orientation.

2.1 HARMONIC APPROXIMATION. — In the harmonic approximation one treats $\hat{\mathbf{n}}(\mathbf{r})$ and $\rho(\mathbf{r})$ as smoothly varying, singularity-free fields. This assumption implies neglect of defects. We may identify the director $\hat{\mathbf{n}}$ with the tangent to the chains averaged over a small volume. As first shown by de Gennes [2], this leads to a coupling between the density and the director fields,

$$\hat{\mathbf{n}} \cdot \nabla \rho = -\rho_0 \nabla \cdot \hat{\mathbf{n}}. \quad (2.3)$$

Equation (2.3) can be regarded as a *continuity equation*. It expresses the fact that the number of chains entering a small region equals the number of chains leaving that region. In other words, in this approximation there are no chain ends.

The constraint of equation (2.3) can be conveniently incorporated by considering the two-component chain displacement field $\mathbf{u}(\mathbf{r})$, which gives the (x, y) displacement of the chains (see Ref. [3]). In the harmonic approximation, $\mathbf{u}(\mathbf{r})$ is related to $\hat{\mathbf{n}}(\mathbf{r})$ and $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$ by:

$$\hat{\mathbf{n}}_{\perp}(\mathbf{r}) = \frac{\partial \mathbf{u}}{\partial z}, \quad (2.4a)$$

$$\delta\rho(\mathbf{r}) = -\rho_0 \nabla_{\perp} \cdot \mathbf{u}, \quad (2.4b)$$

where the subscript \perp denotes the x and y components of a vector and $\hat{\mathbf{z}}$ is the average chain direction. Inserting equations (2.4) into (2.1) gives an effective Hamiltonian for the \mathbf{u} field:

$$H_{\text{H}} = \frac{1}{2} \int d^3\mathbf{r} \left[K_1 \left| \nabla_{\perp} \cdot \frac{\partial \mathbf{u}}{\partial z} \right|^2 + K_2 \left| \nabla_{\perp} \times \frac{\partial \mathbf{u}}{\partial z} \right|^2 + K_3 \left| \frac{\partial^2 \mathbf{u}}{\partial z^2} \right|^2 + \lambda \left| \nabla_{\perp} \cdot \mathbf{u} \right|^2 \right]. \quad (2.5)$$

(The subscript H will always indicate that we restrict ourselves to a harmonic theory.) Assuming $\mathbf{u}(\mathbf{r})$ to be a smooth function, we can expand it in a Fourier series:

$$\mathbf{u}(\mathbf{q}) = \Omega^{-1/2} \int d^3\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \mathbf{u}(\mathbf{r}), \quad (2.6)$$

with Ω the system volume. In terms of $\mathbf{u}(\mathbf{q})$, the effective Hamiltonian becomes

$$H_{\text{H}} = \frac{1}{2} \sum_{\mathbf{q}} \left[K_1 q_z^2 |\mathbf{q}_{\perp} \cdot \mathbf{u}(\mathbf{q})|^2 + K_2 q_z^2 |\mathbf{q}_{\perp} \times \mathbf{u}(\mathbf{q})|^2 + K_3 q_z^4 |\mathbf{u}(\mathbf{q})|^2 + \lambda |\mathbf{q}_{\perp} \cdot \mathbf{u}(\mathbf{q})|^2 \right]. \quad (2.7)$$

To analyze H_{H} , it is convenient to decompose \mathbf{u} into a longitudinal and a transverse part:

$$\mathbf{u}_{\text{L}} = \frac{\mathbf{q}_{\perp} (\mathbf{q}_{\perp} \cdot \mathbf{u})}{q_{\perp}^2}, \quad (2.8a)$$

$$\mathbf{u}_{\text{T}} = \mathbf{u} - \frac{\mathbf{q}_{\perp} (\mathbf{q}_{\perp} \cdot \mathbf{u})}{q_{\perp}^2} \quad (2.8b)$$

In terms of $\mathbf{u}_{\text{L}}(\mathbf{q})$ and $\mathbf{u}_{\text{T}}(\mathbf{q})$,

$$H_{\text{H}} = \frac{1}{2} \sum_{\mathbf{q}} \left[\epsilon_{\text{L}}(\mathbf{q}) |\mathbf{u}_{\text{L}}(\mathbf{q})|^2 + \epsilon_{\text{T}}(\mathbf{q}) |\mathbf{u}_{\text{T}}(\mathbf{q})|^2 \right], \quad (2.9)$$

where

$$\epsilon_{\text{L}}(\mathbf{q}) = \lambda q_{\perp}^2 + q_z^2 (K_1 q_{\perp}^2 + K_3 q_z^2), \quad (2.10a)$$

$$\epsilon_{\text{T}}(\mathbf{q}) = q_z^2 (K_2 q_{\perp}^2 + K_3 q_z^2). \quad (2.10b)$$

The harmonic mode spectrum thus consists of two branches. The transverse branch involves only the Frank elastic constants and is purely orientational in nature. It is unaffected by the director-density coupling. The longitudinal branch is a mixed density-orientational mode, called the "peristaltic mode" in reference [3].

2.2 POINT DEFECTS: SPLAY. — We argued in the introduction that in the nematic phase only point defects such as endpoint and hairpin defects need to be considered, at least as far as the thermodynamic properties are concerned. We will now develop the 3D analogue of the Toner-Nelson theory [11] for 2D smectics and apply it to the case of polymer nematics. The energy cost associated with adding or removing chains is partly due to a “core” energy—either the energy cost of scissioning a chain or the energy cost of a 180° bend—and partly due to a deformation energy in the surrounding medium. One can use continuum theory to compute the latter contribution and treat core energies as adjustable microscopic parameters. Note that the addition of a new chain does *not* lead to an energy cost proportional to the chain length. The fluid simply adjusts its density to the equilibrium value in the neighborhood of the new chain. Except near the endpoint, there is no energy cost associated with this adjustment. However, a new chain added to the sample does in fact introduce a *mathematical* singularity in the displacement $\mathbf{u}(\mathbf{r})$.

Assume we introduce a new chain at $\mathbf{r}_\perp = 0$ in the interval $z > 0$, as shown in figure 1a. At $\mathbf{r} = 0$, we have a “+” endpoint defect. The displacement field is then given by

$$\nabla_\perp \cdot \mathbf{u} = \rho_0^{-1} \delta(\mathbf{r}_\perp) \theta(z) + \{\text{non-singular terms}\}. \quad (2.11)$$

(The same expression would hold with a $-$ sign for a “-” endpoint defect, and with a factor of ± 2 for a “++” or “--” hairpin defect.) The resulting splay in the director field is given by equation (2.4a), which leads to

$$\nabla_\perp \cdot \hat{\mathbf{n}}_\perp = \rho_0^{-1} \delta(\mathbf{r}) + \{\text{non-singular terms}\}. \quad (2.12)$$

However, the density of chains is *not* given by equation (2.4b) anymore, because equation (2.4b) describes the reduction in density of the surrounding chains but does not include the central chain that has been added. Rather, fluctuations in the density of chains are now described by

$$\delta\rho(\mathbf{r}) = -\rho_0 \nabla_\perp \cdot \mathbf{u} + \delta(\mathbf{r}_\perp) \theta(z) + \rho_d(\mathbf{r}). \quad (2.13)$$

The first term on the right-hand side of this equation represents the reduction in density of the chains surrounding the central chain due to their outward splay. The second term gives the density of the central chain itself. Note that this term cancels the singular part of the first term, giving no singularity in the density field. The third term, $\rho_d(\mathbf{r})$, represents the local changes in the density near the endpoint defect. It is assumed to be a short-range function centered at $\mathbf{r} = 0$.

From equation (2.11), we can identify $\rho_0 \partial_z \nabla_\perp \cdot \mathbf{u}$ as the defect charge density. The volume integral of this quantity gives the topological quantum number Q_S , which is the total splay charge of the sample. This volume integral can be converted into the surface integral

$$Q_S = \rho_0 \int d^2s (\nabla_\perp \cdot \mathbf{u}) \Big|_{z=-L/2}^{z=L/2} \quad (2.14)$$

Thus, the topological quantum number Q_S of a sample associated with splay defects is simply the difference between the number of chains attached to the top surface ($z = L/2$) and to the bottom surface ($z = -L/2$).

To find the displacement field away from the singularity at $\mathbf{r}_\perp = 0$, $z > 0$, we minimize the induced elastic deformation energy

$$H_D \approx \frac{1}{2} \int' d^3\mathbf{r} \left[K_3 \left| \frac{\partial^2 \mathbf{u}}{\partial z^2} \right|^2 + \lambda |\nabla_\perp \cdot \mathbf{u}|^2 \right]. \quad (2.15)$$

In this equation, the K_1 term is omitted because it is small compared to the λ term for a slowly varying field \mathbf{u} (i.e., for $K_1 q_z^2 \ll \lambda$). The K_2 term is omitted because by symmetry there is no twist. The K_3 term must, however, be included because it is always dominant if \mathbf{u} depends on z only. The prime on the integral sign indicates that we exclude a thin tube around $\mathbf{r}_\perp = 0$, $z > 0$, from the integration interval to avoid the (unphysical) singularity in \mathbf{u} at $\mathbf{r}_\perp = 0$, $z > 0$.

Minimizing H_D with respect to \mathbf{u} gives

$$-\lambda_S^2 \frac{\partial^4 \mathbf{G}_S}{\partial z^4} + \nabla_\perp (\nabla_\perp \cdot \mathbf{G}_S) = \rho_0^{-1} \nabla_\perp \delta(\mathbf{r}_\perp) \theta(z), \quad (2.16)$$

where $\lambda_S = \sqrt{K_3/\lambda}$. We use the notation \mathbf{G}_S instead of \mathbf{u} because \mathbf{G}_S will play the role of a Green's function for the defects. The source term in equation (2.16) was chosen such that \mathbf{G}_S obeys equation (2.11).

Assuming that we have solved equation (2.16), we can now construct the displacement field for a whole collection of splay defects. For that purpose, we divide the sample into cells of volume a^3 , taking the inter-chain spacing a as the microscopic length of the problem. Define $a^3 m_S(\mathbf{r})$ to be the topological charge of a cell located at \mathbf{r} , allowing only $a^3 m_S(\mathbf{r}) = 0, \pm 1$. The full displacement field due to the defects is then

$$\mathbf{u}(\mathbf{r}) = \int' d^3 \mathbf{r}' m_S(\mathbf{r}') \mathbf{G}_S(\mathbf{r} - \mathbf{r}'). \quad (2.17)$$

The energy cost of the defects is found by inserting equation (2.17) into equation (2.15):

$$\begin{aligned} H_D = & \frac{\lambda}{2} \int' d^3 \mathbf{r} \int' d^3 \mathbf{r}' \int' d^3 \mathbf{r}'' m_S(\mathbf{r}') m_S(\mathbf{r}'') \\ & \left[\lambda_S^2 \frac{\partial^2 \mathbf{G}_S(\mathbf{r} - \mathbf{r}')}{\partial z^2} \cdot \frac{\partial^2 \mathbf{G}_S(\mathbf{r} - \mathbf{r}'')}{\partial z^2} + (\nabla_\perp \cdot \mathbf{G}_S(\mathbf{r} - \mathbf{r}')) (\nabla_\perp \cdot \mathbf{G}_S(\mathbf{r} - \mathbf{r}'')) \right] \\ & + E_S a^3 \int d^3 \mathbf{r} m_S^2(\mathbf{r}). \end{aligned} \quad (2.18)$$

Here we have added a microscopic energy cost E_S associated with each endpoint defect. It describes—in a phenomenological way—the contribution to the defect energy from the core region where continuum theory fails. If hairpins are less costly than chain scissioning, we should instead interpret $4E_S$ as the microscopic energy cost of a hairpin defect and restrict $a^3 m_S = 0, \pm 2$.

The subsequent calculation of H_D can be simplified by defining a conjugate Green's function \tilde{G}_S by the equation

$$\lambda_S \frac{\partial^2 \mathbf{G}_S}{\partial z^2} = \nabla_\perp \tilde{G}_S. \quad (2.19)$$

Away from the defects, the conjugate Green's function also satisfies

$$\lambda_S \frac{\partial^2 \tilde{G}_S}{\partial z^2} = \nabla_\perp \cdot \mathbf{G}_S. \quad (2.20)$$

In general, \tilde{G}_S obeys the equation

$$-\lambda_S^2 \frac{\partial^4 \tilde{G}_S}{\partial z^4} + \nabla_\perp^2 \tilde{G}_S = \frac{\lambda_S}{\rho_0} \delta(\mathbf{r}_\perp) \delta'(z). \quad (2.21)$$

After performing a partial integration in equation (2.18) and using equation (2.21), we find

$$H_D = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' m_S(\mathbf{r}) m_S(\mathbf{r}') U_S(\mathbf{r} - \mathbf{r}') + E_S a^3 \int d^3\mathbf{r} m_S^2(\mathbf{r}). \quad (2.22)$$

The function $U_S(\mathbf{r})$ is given by

$$U_S(\mathbf{r}) = \frac{\sqrt{K_3 \lambda} \partial \tilde{G}_S(\mathbf{r})}{\rho_0 \partial z} \quad (2.23)$$

According to equation (2.22), we can treat the collection of endpoint defects as constituting a *two-component plasma*—if we restrict $a^3 m_S = 0, \pm 1$ —with an effective Hamiltonian H_D . The function $U_S(\mathbf{r})$ can be interpreted as the pair potential between the charges. If $U_S(\mathbf{r}) > 0$, it provides an attractive potential between charges of opposite sign and a repulsive interaction between charges of the same sign. The core energy E_S plays the role of a (microscopic) chemical potential. This form for the defect Hamiltonian is completely analogous to corresponding defect Hamiltonians found in the theory of 2D melting, 2D smectics, and 2D superfluidity. As we shall see, computing the macroscopic correlation functions reduces to a calculation of the pair correlation function of this plasma.

The free energy cost of scissioning a chain and separating the two resulting chain endpoints to infinity is now

$$F_{\text{bind}} = 2E_S + U_S(0) - U_S(\infty). \quad (2.24)$$

To determine whether free endpoints are indeed possible, we must find the asymptotic behavior of $U_S(\mathbf{r})$. To compute this function, we first perform a Fourier transform in equation (2.21) and then use equation (2.23) to obtain

$$U_S(\mathbf{q}) = \frac{K_3}{\Omega^{1/2} \rho_0^2} \frac{q_z^2}{\lambda_S^2 q_z^4 + q_\perp^2}. \quad (2.25)$$

The inverse Fourier transform then gives

$$U_S(\mathbf{r}) = \frac{K_3}{2^{5/2} \pi \rho_0^2 \lambda_S^{3/2}} \int_0^{a^{-1}} q_\perp^{1/2} dq_\perp J_0(q_\perp r_\perp) \exp\left(-\sqrt{\frac{q_\perp z^2}{2\lambda_S}}\right) \left(\cos\sqrt{\frac{q_\perp z^2}{2\lambda_S}} - \sin\sqrt{\frac{q_\perp z^2}{2\lambda_S}}\right). \quad (2.26)$$

Note that we let a^{-1} be an ultraviolet cutoff on q_\perp . In the limit $\mathbf{r} \rightarrow 0$, we obtain

$$U_S(\mathbf{r} \rightarrow 0) \approx \frac{K_3}{3\pi \rho_0^2 (2\lambda_S a)^{3/2}}, \quad (2.27)$$

while for $\mathbf{r} \rightarrow \infty$, the function $U_S(\mathbf{r}) \rightarrow 0$. From equations (2.27) and (2.24), we conclude that F_{bind} is finite. As a consequence, *the chemical potential for free endpoints is finite, and hence the nematic phase will always contain free endpoints* (provided that E_S is finite). A similar argument applies to hairpin defects.

The asymptotic form of $U_S(\mathbf{r})$ depends on the direction of \mathbf{r} . For $|z| \ll \sqrt{\lambda_S r_\perp}$, $U_S(\mathbf{r})$ decays as

$$U_S(\mathbf{r}) \approx \frac{(\Gamma(\frac{3}{4}))^2}{2^{5/2} \pi^2} \frac{K_3}{\rho_0^2 (\lambda_S r_\perp)^{3/2}}, \quad (2.28)$$

while for $|z| \gg \sqrt{\lambda_S r_\perp}$, $U_S(\mathbf{r})$ passes through 0 around $|z| \approx \sqrt{\lambda_S a}$ and then vanishes as

$$U_S(\mathbf{r}) \approx -\frac{K_3}{\pi \rho_0^2 |z|^3}. \quad (2.29)$$

As a consequence, two charges of opposite sign with approximately the same r_\perp value will *repel* each other for $z \gtrsim \sqrt{\lambda_S a}$ and will attract each other for $z \lesssim \sqrt{\lambda_S a}$. This is a surprising result because in $D = 2$, $U_S(\mathbf{r}_\perp \neq 0, z)$ is always positive and $U_S(\mathbf{r}_\perp = 0, z) = 0$ [11]. It implies that if we create a collection of splay defects (for example, by applying a splay to the sample boundaries), then these defects would tend to organize themselves into strings parallel to the z -axis.

2.3 CORRELATION FUNCTIONS. — We claimed in the introduction that point defects should play an important role in the thermodynamic properties of polymer nematics. To investigate this role, we will now discuss experimentally accessible correlation functions. The first correlation function of interest is the structure factor $S(\mathbf{q}) \equiv \langle |\rho(\mathbf{q})|^2 \rangle$, which describes fluctuations in the density field. Second, there are the orientational correlation functions $I_L(\mathbf{q}) \equiv \langle |n_L(\mathbf{q})|^2 \rangle$ and $I_T(\mathbf{q}) \equiv \langle |n_T(\mathbf{q})|^2 \rangle$, which describe fluctuations in the nematic director field. The definition of the longitudinal and transverse components n_L and n_T of $\hat{\mathbf{n}}(\mathbf{r})$ is analogous to equations (2.8). The structure factor can be measured by x-ray scattering and the orientational correlation functions by depolarized light scattering.

The harmonic contribution to $S(\mathbf{q})$ and $I_{L,T}(\mathbf{q})$ is discussed in detail in reference [3]. It is found by using equations (2.4) to relate $\rho(\mathbf{q})$ and $\hat{\mathbf{n}}_\perp(\mathbf{q})$ to $\mathbf{u}(\mathbf{q})$, and then applying the equipartition theorem to H_H to obtain

$$\langle |\mathbf{u}_{L,T}(\mathbf{q})|^2 \rangle_H = \frac{k_B T}{\epsilon_{L,T}(\mathbf{q})}. \quad (2.30)$$

The resulting structure factor is

$$S(\mathbf{q})_H = \frac{k_B T \rho_0^2 q_\perp^2}{\lambda q_z^2 + K_1 q_\perp^2 q_z^2 + K_3 q_z^4}. \quad (2.31)$$

Thus, in the harmonic approximation, contours of constant intensity of $S(\mathbf{q})_H$ in \mathbf{q} -space exhibit a set of paraboloids $|q_\perp| \propto q_z^2$ in the limit $\mathbf{q} \rightarrow 0$. These paraboloids of revolution form the center of a butterfly-like pattern at larger \mathbf{q} values. This should be contrasted with the $S(\mathbf{q})$ of short-chain nematic liquid crystals, for which $S(\mathbf{q} \rightarrow 0)$ is always finite. Furthermore, in the harmonic theory for chains, the director fluctuation spectrum is

$$I_L(\mathbf{q})_H = \frac{k_B T}{\lambda q_z^{-2} q_\perp^2 + K_1 q_\perp^2 + K_3 q_z^2}, \quad (2.32a)$$

$$I_T(\mathbf{q})_H = \frac{k_B T}{K_2 q_\perp^2 + K_3 q_z^2}. \quad (2.32b)$$

In this approximation, there is a relationship between the correlation functions:

$$I_L(\mathbf{q})_H = \frac{q_z^2}{\rho_0^2 q_\perp^2} S(\mathbf{q})_H. \quad (2.33)$$

This relation between $I_L(\mathbf{q})_H$ and $S(\mathbf{q})_H$ results from the continuity equation (2.3). It is certainly not valid for short-chain liquid crystals, and it will turn out not to be valid beyond the harmonic approximation for polymer liquid crystals.

We can now define the macroscopic Frank constants and bulk modulus. To define the macroscopic Frank constants \hat{K}_1 , \hat{K}_2 , and \hat{K}_3 , we will fit long-wavelength expressions for $I_{L,T}(\mathbf{q})$ by the expressions for a conventional nematic phase of short-chain molecules:

$$I_L(\mathbf{q})_{\text{conv}} = \frac{k_B T}{\hat{K}_1 q_\perp^2 + \hat{K}_3 q_z^2}, \quad (2.34a)$$

$$I_T(\mathbf{q})_{\text{conv}} = \frac{k_B T}{\hat{K}_2 q_\perp^2 + \hat{K}_3 q_z^2} \quad (2.34b)$$

The resulting macroscopic Frank constants for splay and twist are

$$\hat{K}_1^{-1} = \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \frac{q_\perp^2 I_L(\mathbf{q})}{k_B T}, \quad (2.35a)$$

$$\hat{K}_2^{-1} = \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \frac{q_\perp^2 I_T(\mathbf{q})}{k_B T}, \quad (2.35b)$$

while \hat{K}_3 will always equal K_3 in the following. Thus, in the harmonic theory for polymer nematics, \hat{K}_1 diverges as λ/q_z^2 , while \hat{K}_2 is not renormalized from its bare value. Similarly, we will define the macroscopic bulk modulus $\hat{\lambda}$ by fitting a long-wavelength expression for $S(\mathbf{q})$ in the presence of defects to the harmonic approximation (2.31) for a polymer nematic phase. The resulting macroscopic bulk modulus $\hat{\lambda}$ is thus:

$$\hat{\lambda}^{-1} = \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \frac{S(\mathbf{q})}{k_B T \rho_0^2}. \quad (2.36)$$

To compute $S(\mathbf{q})$ and $I_{L,T}(\mathbf{q})$ in the presence of defects, we first decompose $\mathbf{u}(\mathbf{r})$ into a harmonic part and a defect contribution,

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}(\mathbf{r})_H + \int d^3 \mathbf{r}' \mathbf{G}_S(\mathbf{r} - \mathbf{r}') m_S(\mathbf{r}'). \quad (2.37)$$

In this expression, $\mathbf{u}(\mathbf{r})_H$ and $m_S(\mathbf{r}')$ are independent random variables. The resulting director field is

$$\hat{\mathbf{n}}_\perp(\mathbf{r}) = \frac{\partial \mathbf{u}(\mathbf{r})_H}{\partial z} + \int d^3 \mathbf{r}' \frac{\partial \mathbf{G}_S(\mathbf{r} - \mathbf{r}')}{\partial z} m_S(\mathbf{r}'). \quad (2.38)$$

Because \mathbf{G}_S is purely longitudinal, $I_T(\mathbf{q})$ is not affected by the defects, while $I_L(\mathbf{q})$ becomes

$$I_L(\mathbf{q}) = I_L(\mathbf{q})_H + \Omega q_z^2 |\mathbf{G}_S(\mathbf{q})|^2 \Sigma_S(\mathbf{q}). \quad (2.39)$$

In this equation,

$$\mathbf{G}_S(\mathbf{q}) = -\frac{\mathbf{q}_\perp}{\Omega^{1/2} \rho_0 q_z} \frac{1}{\lambda_S^2 q_z^4 + q_\perp^2} \quad (2.40)$$

is the Fourier-transformed Green's function. The quantity $\Sigma_S(\mathbf{q}) \equiv \langle |m_S(\mathbf{q})|^2 \rangle$ is the structure factor of the many-body system of splay defects as controlled by the Hamiltonian H_D . It is the Fourier transform of the pair-correlation function

$$\langle m_S(0) m_S(\mathbf{r}) \rangle \equiv \frac{\sum_{\{m_S\}} m_S(0) m_S(\mathbf{r}) e^{-H_D/k_B T}}{\sum_{\{m_S\}} e^{-H_D/k_B T}} \quad (2.41)$$

From equation (2.35a), the macroscopic Frank constant for splay becomes

$$\hat{K}_1^{-1} = \frac{1}{k_B T \rho_0^2} \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}). \quad (2.42)$$

To derive $S(\mathbf{q})$, we follow a similar argument. Applying equation (2.13) for the density field to the set of defects described by $m_S(\mathbf{r})$ gives

$$\begin{aligned} \delta\rho(\mathbf{r}) = & -\rho_0 \nabla_\perp \cdot \mathbf{u}(\mathbf{r})_{\text{H}+} \\ & + \int d^3\mathbf{r}' [-\rho_0 \nabla_\perp \cdot \mathbf{G}_S(\mathbf{r} - \mathbf{r}') + \delta(\mathbf{r}_\perp - \mathbf{r}'_\perp) \theta(z - z') + \rho_d(\mathbf{r} - \mathbf{r}')] m_S(\mathbf{r}'). \end{aligned} \quad (2.43)$$

The structure factor therefore becomes

$$S(\mathbf{q}) = S(\mathbf{q})_{\text{H}} + \Omega \left| i\rho_0 \mathbf{q}_\perp \cdot \mathbf{G}_S(\mathbf{q}) + \frac{i}{\Omega^{1/2} q_z} + \rho_d(\mathbf{q}) \right|^2 \Sigma_S(\mathbf{q}). \quad (2.44)$$

From equation (2.36), the macroscopic bulk modulus $\hat{\lambda}$ is given by

$$\hat{\lambda}^{-1} = \lambda^{-1} + \frac{1}{k_B T \rho_0^2} \left| \Omega^{1/2} \rho_d(\mathbf{q} = 0) \right|^2 \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}). \quad (2.45)$$

To compute $\Sigma_S(\mathbf{q})$ explicitly in the nematic phase, we will first use Debye-Hückel theory [11]. In the Debye-Hückel approximation, one treats $m_S(\mathbf{r})$ as an unrestricted, continuous field, which should be a good approximation if we have a *high* defect density, i.e., if $E_S \lesssim k_B T$. We begin by rewriting the splay defect Hamiltonian (2.22) as

$$H_D = \frac{1}{2} \sum_{\mathbf{q}} \left(E_S a^3 + \Omega^{1/2} U_S(\mathbf{q}) \right) |m_S(\mathbf{q})|^2, \quad (2.46)$$

where $U_S(\mathbf{q})$ is given by equation (2.25). We then apply the equipartition theorem to obtain

$$\Sigma_S(\mathbf{q}) = \frac{k_B T \rho_0^2 (\lambda_S^2 q_z^4 + q_\perp^2)}{E_S a^3 \rho_0^2 (\lambda_S^2 q_z^4 + q_\perp^2) + K_3 q_z^2}. \quad (2.47)$$

Hence,

$$\lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}) = \frac{k_B T}{E_S a^3}. \quad (2.48)$$

We conclude that

$$\hat{K}_1 = E_S a^3 \rho_0^2 \approx \frac{E_S}{a} \quad (2.49)$$

and

$$\hat{\lambda}^{-1} = \lambda^{-1} + \frac{1}{E_S a^3 \rho_0^2} \left| \int d^3\mathbf{r} \rho_d(\mathbf{r}) \right|^2 \quad (2.50)$$

Furthermore, for $\mathbf{q} \rightarrow 0$ and $\lambda_S q_z^2 \ll q_\perp$, we obtain

$$I_L(\mathbf{q}) = \frac{k_B T}{\hat{K}_1 q_\perp^2 + K_3 q_z^2} \quad (2.51)$$

Thus, the long-wavelength director fluctuation spectrum reduces to that of a conventional nematic phase, with the renormalized value of K_1 and the bare value of K_3 . The anomalous behavior of $I_L(\mathbf{q})$ for small q_z is cancelled by the effects of splay defects.

The structure factor described by equation (2.44) has very different constant intensity contours than those predicted by harmonic theory. In particular, for $\mathbf{q}_\perp = 0$ and q_z small, the harmonic theory gives $S(0, q_z) = 0$ while equation (2.44) gives $S(0, q_z) \approx k_B T \rho_0^2 \lambda_S^2 / K_3$. In the opposite order of limits, for $q_z = 0$ and \mathbf{q}_\perp small, equation (2.44) gives $S(\mathbf{q}_\perp, 0) \approx k_B T \rho_0^2 / \hat{\lambda}$. In general, the constant intensity contours resemble those of a liquid with a uniaxially anisotropic compressibility, such as a short-chain nematic. Thus, in the Debye-Hückel approximation, large defect concentrations modify the correlation functions $I_L(\mathbf{q})$ and $S(\mathbf{q})$ into forms similar to those of ordinary nematics.

We now consider the limit of $E_S \gg k_B T$. In this regime, the defect density is very low, and hence $m_S(\mathbf{r})$ cannot be regarded as a continuous field. For that reason, the Debye-Hückel approximation is no longer valid. The limiting value of $\Sigma_S(\mathbf{q})$ can now be written as

$$\lim_{\mathbf{q}_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}) = \frac{\langle Q_S^2 \rangle}{\Omega}, \tag{2.52}$$

which is simply the concentration of unbound defects. Because each finite chain is associated with two endpoint defects, this concentration is

$$\lim_{\mathbf{q}_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}) = \frac{2\rho_0}{\bar{l}}, \tag{2.53}$$

where \bar{l} is the average length of a chain. The defect concentration is then

$$\lim_{\mathbf{q}_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}) \approx a^{-3} e^{-F_{\text{bind}}/k_B T}, \tag{2.54}$$

where $F_{\text{bind}} = 2E_S + \Delta U$ is the binding free energy of equation (2.24). As a result, the macroscopic splay constant becomes

$$\hat{K}_1 = \frac{k_B T \rho_0 \bar{l}}{2} \approx \frac{k_B T}{a} e^{F_{\text{bind}}/k_B T}, \tag{2.55}$$

and the macroscopic bulk modulus becomes

$$\hat{\lambda}^{-1} \approx \lambda^{-1} + \frac{1}{k_B T \rho_0^2 a^3} \left| \int d^3 \mathbf{r} \rho_d(\mathbf{r}) \right|^2 e^{-F_{\text{bind}}/k_B T} \tag{2.56}$$

Note that this result for \hat{K}_1 is equivalent to the result of Meyer [4], which was derived by considering the entropy of packing rigid chains. This relation between \hat{K}_1 and \bar{l} has been confirmed experimentally by Lee and Meyer [13].

We should make several remarks about our results in the Debye-Hückel ($E_S \lesssim k_B T$) and low-temperature ($E_S \gg k_B T$) regimes. First, in the Debye-Hückel regime the results for \hat{K}_1 and $\hat{\lambda}$ are independent of temperature, while in the low-temperature regime \hat{K}_1 and $\hat{\lambda}$ depend exponentially on temperature. Indeed, this difference in temperature dependence would be the clearest experimental signature of the distinction between the two regimes. Second, in both regimes the renormalized splay constant \hat{K}_1 is independent of the bare value of K_1 . In the Debye-Hückel regime \hat{K}_1 is determined only by the microscopic energy cost E_S associated

with each splay defect, while in the low-temperature regime \hat{K}_1 is determined by the temperature and by the binding free energy. For that reason, measurements of \hat{K}_1 do not give any information about the value of K_1 that appears in the microscopic harmonic Hamiltonian, and this microscopic K_1 is not proportional to \bar{l} . Third, in both regimes the renormalization of λ is determined only by the local density changes $\rho_d(\mathbf{r})$ near the endpoints and hairpins, not by the rest of the chains. Because these density changes are short-ranged, the integral in equations (2.50) and (2.56) is convergent. Hence, the local density changes give only a finite reduction in λ . Finally, in both regimes the defect contributions to $S(\mathbf{q})$ and $I_{L,T}(\mathbf{q})$ dominate the harmonic contributions to these correlation functions in the long-wavelength limit, for $q_z^2 \lesssim \lambda_S \Sigma_S(0)/k_B T \rho_0^2$. However, in the low-temperature regime $\Sigma_S(0)$ is exponentially small. For that reason, the harmonic theory for the correlation functions applies down to an exponentially small crossover value of q_z , at which point the defect contribution begins to dominate. The structure factor thus remains very close to that predicted by the harmonic theory, with its characteristic butterfly pattern. By contrast, in the Debye-Hückel regime the defect contribution begins to dominate at a much larger value of q_z .

3. Continuum theory: hexagonal phase.

In the hexagonal phase, the chains maintain long-range positional order in addition to the orientational order. In the continuum free energy of such an ordered array, we must include a new term associated with the restoring force against a shear deformation. If μ is the isothermal shear coefficient of the hexagonal lattice, then the continuum free energy is

$$H = \frac{1}{2} \int d^3\mathbf{r} \left[K_1 (\nabla \cdot \hat{\mathbf{n}})^2 + K_2 (\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}))^2 + K_3 (\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}}))^2 + \lambda \left(\frac{\rho - \rho_0}{\rho_0} \right)^2 + \frac{\mu}{2} \left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} \right)^2 \right], \quad (3.1)$$

with $\alpha, \beta = x, y$. For the case of chains with purely steric repulsion, the shear coefficient $\mu = \lambda/3$ [3]. The existence of long-range positional order and a nonzero shear modulus have far-reaching effects. As before, we will begin with a review of the harmonic theory.

3.1 HARMONIC APPROXIMATION. — If we proceed along the same steps as in section 2.1, we find the following harmonic mode spectrum:

$$H_H = \frac{1}{2} \sum_{\mathbf{q}} \left[\epsilon_L(\mathbf{q}) |\mathbf{u}_L(\mathbf{q})|^2 + \epsilon_T(\mathbf{q}) |\mathbf{u}_T(\mathbf{q})|^2 \right], \quad (3.2)$$

where

$$\epsilon_L(\mathbf{q}) = (\lambda + 2\mu)q_1^2 + q_z^2 (K_1 q_1^2 + K_3 q_z^2), \quad (3.3a)$$

$$\epsilon_T(\mathbf{q}) = \mu q_1^2 + q_z^2 (K_2 q_1^2 + K_3 q_z^2). \quad (3.3b)$$

Thus, the longitudinal branch remains a mixed splay-density mode but the transverse branch is now a mixed shear-twist mode. The combination of Lamé coefficients $(\lambda + 2\mu)$ can be called the longitudinal modulus.

3.2 POINT DEFECTS: SPLAY. — We define splay defects in the same way as for a nematic. Proceeding as in section 2.2, we find the defect energy

$$H_D = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' m_S(\mathbf{r}) m_S(\mathbf{r}') U_S^H(\mathbf{r} - \mathbf{r}') + E_S a^3 \int d^3\mathbf{r} m_S^2(\mathbf{r}), \quad (3.4)$$

where

$$U_S^H(\mathbf{r} - \mathbf{r}') = U_S(\mathbf{r} - \mathbf{r}') + \tau_S |\mathbf{r} - \mathbf{r}'|. \quad (3.5)$$

In equation (3.5), $U_S(\mathbf{r})$ is given by equation (2.26) with λ replaced by $(\lambda + 2\mu)$ in the definition of λ_S . The mathematical origin of the linear term in equation (3.5) is the surface contribution to the partial integration of equation (2.18). For $\mu = 0$, the surface term vanishes, but for $\mu \neq 0$, the surfaces of the thin tubes surrounding the added or removed chains contribute a term which is proportional to the length of the excluded tubes. Thus, for $\mu \neq 0$ we must choose the location of the tubes to minimize the free energy. If the tube originating from a + defect at \mathbf{r} coincides with a tube originating from a - defect at \mathbf{r}' , then the terms cancel. However, as shown in figure 4, there is always a tube of length $|\mathbf{r} - \mathbf{r}'|$ left, which cannot be cancelled.

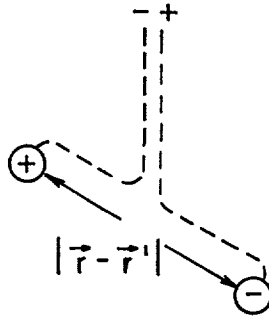


Fig. 4. — Defect line connecting + and - splay defects at \mathbf{r} and \mathbf{r}' in the hexagonal phase.

The physical origin of τ_S is readily understood. In the hexagonal phase, an added chain corresponds to a column of *interstitials* of the hexagonal lattice, while a removed chain corresponds to a column of *vacancies* [14]. Vacancies and interstitials are both stable defects. We cannot remove them by a density adjustment as we did in the case of the nematic phase [15]. *The mathematical singularity in the displacement field $\mathbf{u}(\mathbf{r})$ now corresponds to a physical singularity.* This physical singularity is equivalent to the lock-in fault line discussed by Prost [16]. We thus can interpret τ_S as the energy cost per unit length (line tension) of an interstitial or vacancy column. This line tension may depend on the direction of $\mathbf{r} - \mathbf{r}'$, but we will neglect this anisotropy here. Since τ_S is, like E_S , a microscopic quantity, it should be treated as an adjustable parameter. However, in the Appendix we estimate τ_S using continuum elastic theory, which gives $\tau_S \approx \mu a^2$. We will use this value as a rough estimate in the rest of this paper. In particular, $\tau_S = 0$ when $\mu = 0$.

It could be questioned whether τ_S should not be *negative* for a vacancy column if the interaction between chains is purely repulsive. However, if we remove a section of a chain to create a +− pair, we must insert this chain elsewhere in the sample, creating a +− pair, to conserve mass. We thus will interpret $2\tau_S$ as the cost per unit length of creating both the interstitial and the vacancy column. Under this construction, τ_S is always positive.

We can immediately conclude from equation (3.5) that, unlike the nematic phase, the splay defect ionization energy in the hexagonal phase is infinite. The existence of free splay defects is inconsistent with long-range hexagonal order. Consequently, we should expect from the preceding sections that splay defects necessarily come in $+-$ pairs and $\hat{K}_1 \rightarrow \infty$. Because of the linear attractive potential between $+-$ pairs, we could call the hexagonal phase a “confined” phase.

3.3 POINT DEFECTS: TWIST. — We noted in the introduction that the hexagonal phase supports a second class of defects, which are related to the positional ordering of the chains. In the simplest case, two chains may exchange positions by either a right-handed or a left-handed twist, as shown in figures 3a and 3b. More generally, we can cut out a tube containing two or more chains and rotate it over a lattice constant.

Consider a right-handed exchange of two chains around $z = 0$, $\mathbf{r}_\perp = 0$, as shown in figure 3a. Let $\phi(z)$ be the twist rotation angle of the pair of chains being exchanged. We have $0 \leq \phi(z) \leq \pi$, with $\phi(-\infty) = 0$ and $\phi(\infty) = \pi$. In the lower part of the chain exchange, where $\phi(z) \gtrsim 0$, the surrounding chains feel a *right*-handed torque, as shown in figure 3c. If $\mathbf{u}(\mathbf{r})$ is the displacement field of the neighboring chains, then $\hat{\mathbf{z}} \cdot \nabla \times \mathbf{u} > 0$ in this region. By contrast, in the upper part of the chain exchange, where $\phi(z) \lesssim \pi$, the two chains have almost switched places, so we have once more a nearly perfect hexagonal lattice. In this region, the neighboring chains feel a *left*-handed torque, with $\hat{\mathbf{z}} \cdot \nabla \times \mathbf{u} < 0$, as shown in figure 3d. The crossover from a right-handed to a left-handed torque on the neighboring chains occurs, by symmetry, at $\phi(z) = \pi/2$.

To compute $\mathbf{u}(\mathbf{r})$ far away from this chain exchange, we define the displacement field of a single “twist defect” at $\mathbf{r} = 0$ as

$$\hat{\mathbf{z}} \cdot \nabla_\perp \times \mathbf{u} = \pm \gamma \rho_0^{-1} \delta(\mathbf{r}_\perp) \theta(z) + \{\text{non-singular terms}\}. \quad (3.6)$$

A right-handed chain exchange now corresponds to a $+$ twist defect followed by a $-$ twist defect located at the same value of \mathbf{r}_\perp but a larger value of z . In other words, a right-handed chain exchange is a $+-$ dipole of twist defects. Similarly, a left-handed chain exchange consists of a $-$ twist defect followed by a $+$ twist defect; i.e., it is a $-+$ dipole. The constant $\gamma \approx 1$ depends on the rotation of the chains adjacent to our two exchanging chains and once again can only be estimated from a microscopic model. This is, of course, a simplified model of the exchange process. We would expect the ring of neighboring chains to have a twist that varies more smoothly than a pair of step functions. However, for distances large compared to the separation of the $+-$ pair, the error will be small.

From here on, the calculation of $\mathbf{u}(\mathbf{r})$ for twist defects is strictly analogous with the preceding calculation for splay defects. We first define a Green’s function $\mathbf{G}_T(\mathbf{r})$ for $+$ twist defects:

$$-\lambda_T^2 \frac{\partial^4 \mathbf{G}_T}{\partial z^4} + (\hat{\mathbf{z}} \times \nabla_\perp) (\hat{\mathbf{z}} \times \nabla_\perp \cdot \mathbf{G}_T) = \gamma \rho_0^{-1} (\hat{\mathbf{z}} \times \nabla_\perp) \delta(\mathbf{r}_\perp) \theta(z), \quad (3.7)$$

where $\lambda_T = \sqrt{K_3/\mu}$. If we define $a^3 m_T(\mathbf{r}) = 0, \pm 1$, as the twist defect density, then

$$\mathbf{u}(\mathbf{r}) = \int' d^3 \mathbf{r}' m_T(\mathbf{r}') \mathbf{G}_T(\mathbf{r} - \mathbf{r}') \quad (3.8)$$

is the displacement field due to a field of twist defects. The twist defect Hamiltonian is

$$H_D = \frac{1}{2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' m_T(\mathbf{r}) m_T(\mathbf{r}') U_T^H(\mathbf{r} - \mathbf{r}') + E_T a^3 \int d^3 \mathbf{r} m_T^2(\mathbf{r}). \quad (3.9)$$

Here, the interaction potential is

$$U_T^H(\mathbf{r} - \mathbf{r}') = U_T(\mathbf{r} - \mathbf{r}') + \tau_T |\mathbf{r} - \mathbf{r}'|, \tag{3.10}$$

with

$$U_T(\mathbf{r}) = \frac{\gamma^2 K_3}{2^{5/2} \pi \rho_0^2 \lambda_T^{3/2}} \int_0^{a^{-1}} q_\perp^{1/2} dq_\perp J_0(q_\perp r_\perp) \exp\left(-\sqrt{\frac{q_\perp z^2}{2\lambda_T}}\right) \left(\cos\sqrt{\frac{q_\perp z^2}{2\lambda_T}} - \sin\sqrt{\frac{q_\perp z^2}{2\lambda_T}}\right). \tag{3.11}$$

The line energy τ_T again must come from a microscopic calculation. If we estimate it in continuum elastic theory, we obtain $\tau_T \approx \mu a^2$. The asymptotic properties of $U_T(\mathbf{r})$ follow from equations (2.27)-(2.29), replacing λ_S by λ_T .

Since $U_T^H(\mathbf{r} - \mathbf{r}')$ again diverges as $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$, we should expect twist defects to remain confined in dipoles as well. The chain-exchange process discussed above does not spread out along the z direction.

3.4 CORRELATION FUNCTIONS. — To calculate the correlation functions $S(\mathbf{q}) \equiv \langle |\rho(\mathbf{q})|^2 \rangle$ and $I_{L,T}(\mathbf{q}) \equiv \langle |n_{L,T}(\mathbf{q})|^2 \rangle$, we follow a procedure similar to that in section 2.3. For the harmonic contribution, we use equations (2.4) to relate $\rho(\mathbf{q})$ and $\hat{\mathbf{n}}_\perp(\mathbf{q})$ to $\mathbf{u}(\mathbf{q})$, and then apply the equipartition theorem to the Hamiltonian (3.2). As a result, the structure factor is

$$S(\mathbf{q})_H = \frac{k_B T \rho_0^2 q_\perp^2}{(\lambda + 2\mu)q_\perp^2 + K_1 q_\perp^2 q_z^2 + K_3 q_z^4}, \tag{3.12}$$

and the director fluctuation spectrum is

$$I_L(\mathbf{q})_H = \frac{k_B T}{(\lambda + 2\mu)q_z^{-2} q_\perp^2 + K_1 q_\perp^2 + K_3 q_z^2}, \tag{3.13a}$$

$$I_T(\mathbf{q})_H = \frac{k_B T}{\mu q_z^{-2} q_\perp^2 + K_2 q_\perp^2 + K_3 q_z^2} \tag{3.13b}$$

Note that these expressions for $S(\mathbf{q})$ and $I_L(\mathbf{q})$ satisfy the relation (2.33), which expresses the continuity of the chains.

We can use these correlation functions to define macroscopic Frank constants and Lamé coefficients in the hexagonal phase. The macroscopic Frank constants can be defined by fitting long-wavelength expressions for $I_{L,T}(\mathbf{q})$ to the expressions (2.34) for a conventional, short-chain nematic, so \hat{K}_1 and \hat{K}_2 are still given by equation (2.35). As a result, in the harmonic theory for the hexagonal phase, \hat{K}_1 diverges as $(\lambda + 2\mu)/q_z^2$ and \hat{K}_2 as μ/q_z^2 . The macroscopic longitudinal modulus $(\hat{\lambda} + 2\hat{\mu})$ can be defined by fitting a long-wavelength expression for $S(\mathbf{q})$ in the presence of defects to the harmonic approximation (3.12) for the hexagonal phase. Hence, $(\hat{\lambda} + 2\hat{\mu})$ is given by

$$(\hat{\lambda} + 2\hat{\mu})^{-1} = \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \frac{S(\mathbf{q})}{k_B T \rho_0^2}. \tag{3.14}$$

Finally, the macroscopic shear modulus $\hat{\mu}$ can be defined by fitting a long-wavelength expression for $I_T(\mathbf{q})$ to the expression (3.13b) in the harmonic theory for the hexagonal phase. This procedure gives

$$\hat{\mu}^{-1} = \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \frac{q_\perp^2 I_T(\mathbf{q})}{q_z^2 k_B T} \tag{3.15}$$

From equations (2.35b) and (3.15), it follows that \hat{K}_2 and $\hat{\mu}$ cannot both be finite. If $\hat{\mu}$ is finite, as it should be for the hexagonal phase, then \hat{K}_2 must necessarily be infinite. Note that \hat{K}_1 does not, *a priori*, need to be infinite.

To derive $S(\mathbf{q})$ and $I_{L,T}(\mathbf{q})$ in the presence of defects, we follow the procedure of equations (2.37)–(2.45). We first decompose $\mathbf{u}(\mathbf{r})$ into a harmonic part and parts due to splay and twist defects,

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}(\mathbf{r})_H + \int d^3\mathbf{r}' \mathbf{G}_S(\mathbf{r} - \mathbf{r}') m_S(\mathbf{r}') + \int d^3\mathbf{r}' \mathbf{G}_T(\mathbf{r} - \mathbf{r}') m_T(\mathbf{r}'). \quad (3.16)$$

The director field is therefore

$$\hat{\mathbf{n}}_\perp(\mathbf{r}) = \frac{\partial \mathbf{u}(\mathbf{r})_H}{\partial z} + \int d^3\mathbf{r}' \frac{\partial \mathbf{G}_S(\mathbf{r} - \mathbf{r}')}{\partial z} m_S(\mathbf{r}') + \int d^3\mathbf{r}' \frac{\partial \mathbf{G}_T(\mathbf{r} - \mathbf{r}')}{\partial z} m_T(\mathbf{r}'). \quad (3.17)$$

As a result, the orientational correlation functions become

$$I_L(\mathbf{q}) = I_L(\mathbf{q})_H + \Omega q_z^2 |G_S(\mathbf{q})|^2 \Sigma_S(\mathbf{q}), \quad (3.18a)$$

$$I_T(\mathbf{q}) = I_T(\mathbf{q})_H + \Omega q_z^2 |G_T(\mathbf{q})|^2 \Sigma_T(\mathbf{q}). \quad (3.18b)$$

Here, $G_S(\mathbf{q})$ and $G_T(\mathbf{q})$ are the Green's functions for splay and twist, and $\Sigma_S(\mathbf{q}) \equiv \langle |m_S(\mathbf{q})|^2 \rangle$ and $\Sigma_T(\mathbf{q}) \equiv \langle |m_T(\mathbf{q})|^2 \rangle$ are the structure factors for splay and twist defects, respectively. Hence, the macroscopic Frank constants \hat{K}_1 and \hat{K}_2 are given by

$$\hat{K}_1^{-1} = \frac{1}{k_B T \rho_0^2} \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}), \quad (3.19a)$$

$$\hat{K}_2^{-1} = \frac{\gamma^2}{k_B T \rho_0^2} \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_T(\mathbf{q}), \quad (3.19b)$$

and the macroscopic shear modulus $\hat{\mu}$ is given by

$$\hat{\mu}^{-1} = \mu^{-1} + \frac{\gamma^2}{k_B T \rho_0^2} \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} q_z^{-2} \Sigma_T(\mathbf{q}). \quad (3.20)$$

These limits will be investigated below.

Fluctuations in the density field $\delta\rho(\mathbf{r})$ consist of a harmonic part and a part due to splay defects,

$$\begin{aligned} \delta\rho(\mathbf{r}) = & -\rho_0 \nabla_\perp \cdot \mathbf{u}(\mathbf{r})_H + \\ & + \int d^3\mathbf{r}' [-\rho_0 \nabla_\perp \cdot \mathbf{G}_S(\mathbf{r} - \mathbf{r}') + (1 + \alpha) \delta(\mathbf{r}_\perp - \mathbf{r}'_\perp) \theta(z - z') + \rho_d(\mathbf{r} - \mathbf{r}')] m_S(\mathbf{r}'). \end{aligned} \quad (3.21)$$

The density field is not affected by twist defects. Equation (3.21) for the density field in the hexagonal phase is identical to the corresponding equation (2.43) in the nematic phase except for the term involving α . This term describes the change in density along the vacancy or interstitial column that connects each pair of splay defects in the hexagonal phase. This term is absent in the nematic phase, because in the nematic phase there is no physical singularity away from the point defects themselves. With this extra term, the structure factor for the hexagonal phase becomes

$$S(\mathbf{q}) = S(\mathbf{q})_H + \Omega \left| i\rho_0 \mathbf{q}_\perp \cdot \mathbf{G}_S(\mathbf{q}) + \frac{i(1 + \alpha)}{\Omega^{1/2} q_z} + \rho_d(\mathbf{q}) \right|^2 \Sigma_S(\mathbf{q}). \quad (3.22)$$

We therefore obtain

$$(\hat{\lambda} + 2\hat{\mu})^{-1} = (\lambda + 2\mu)^{-1} + \frac{\alpha^2}{k_B T \rho_0^2} \lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} q_z^{-2} \Sigma_S(\mathbf{q}) \tag{3.23}$$

for the macroscopic longitudinal modulus. Note that the change in density along the vacancy or interstitial column controls the correction term.

To determine $(\hat{\lambda} + 2\hat{\mu})$ and \hat{K}_1 , we must again calculate the limiting behavior of $\Sigma_S(\mathbf{q})$. As a first step, note that in the hexagonal phase, splay defects only occur as bound pairs. For that reason, the net “charge” $Q_S = \int d^3\mathbf{r} m_S(\mathbf{r})$ is strictly zero. If the density of pairs is not too high, we can neglect the interaction between pairs. It is then straightforward to evaluate $\langle m_S(0)m_S(\mathbf{r}) \rangle$. For $|\mathbf{r}| \gg a$, $\langle m_S(0)m_S(\mathbf{r}) \rangle$ must be proportional to the Boltzmann distribution $\exp(-U_S^H(\mathbf{r})/k_B T)$. The integral $\int_{|\mathbf{r}| \gtrsim a} d^3\mathbf{r} \langle m_S(0)m_S(\mathbf{r}) \rangle$ must be minus the density of $+ -$ vortex pairs (with the negative sign because it describes dipoles). We will call this density y_S^2 . Finally, the total integral $\int d^3\mathbf{r} \langle m_S(0)m_S(\mathbf{r}) \rangle$ must be zero because, as we saw, $Q_S = 0$. Combining these requirements gives

$$\langle m_S(0)m_S(\mathbf{r}) \rangle = y_S^2 [\delta(\mathbf{r}) - N^{-1} \exp(-U_S^H(\mathbf{r})/k_B T)], \tag{3.24}$$

with $N = \int d^3\mathbf{r} \exp(-U_S^H(\mathbf{r})/k_B T)$ and $y_S^2 \approx a^{-3} \exp(-2E_S/k_B T)$. The defect structure factor is then

$$\Sigma_S(\mathbf{q}) = y_S^2 \int d^3\mathbf{r} e^{i\mathbf{q}\cdot\mathbf{r}} [\delta(\mathbf{r}) - N^{-1} \exp(-U_S^H(\mathbf{r})/k_B T)]. \tag{3.25}$$

We therefore obtain the limits

$$\lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_S(\mathbf{q}) = 0, \tag{3.26a}$$

$$\lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} q_z^{-2} \Sigma_S(\mathbf{q}) = \frac{1}{2} y_S^2 \langle z^2 \rangle_S, \tag{3.26b}$$

where $\langle z^2 \rangle_S$ is the mean-square displacement between splay defects in a bound pair. From equations (3.19a) and (3.23), we conclude that

$$\hat{K}_1^{-1} = 0, \tag{3.27a}$$

$$(\hat{\lambda} + 2\hat{\mu})^{-1} = (\lambda + 2\mu)^{-1} + \frac{\alpha^2 y_S^2 \langle z^2 \rangle_S}{2k_B T \rho_0^2} \tag{3.27b}$$

Because of the “confinement” of the defects, $\langle z^2 \rangle_S$ is finite in the hexagonal phase, so the renormalized longitudinal modulus $(\hat{\lambda} + 2\hat{\mu})$ must be finite as well. Furthermore, the renormalized splay constant \hat{K}_1 diverges as $1/q_z^2$, just as in the harmonic approximation.

The mean-square displacement

$$\langle z^2 \rangle_S = \frac{\int z^2 \exp(-U_S^H(\mathbf{r})/k_B T) d^3\mathbf{r}}{\int \exp(-U_S^H(\mathbf{r})/k_B T) d^3\mathbf{r}} \tag{3.28}$$

can be computed to be

$$\langle z^2 \rangle_S \approx 2 \left(\frac{k_B T}{\tau_S} \right)^2 \tag{3.29}$$

for small τ_S . It is determined by the line tension τ_S , as expected.

Our expression (3.27b) is really the first term in an expansion in y_S^2 . The small parameter of the perturbation theory is

$$\epsilon_S = \frac{(\lambda + 2\mu)y_S^2 \langle z^2 \rangle_S}{k_B T \rho_0^2} \quad (3.30)$$

Using $\tau_S \approx \mu a^2$ and $\alpha \approx 1$ gives $\epsilon_S \approx (\lambda + 2\mu)k_B T y_S^2 / \mu^2$. For the case of purely steric repulsion, we have $\lambda \approx \mu$, while the smallest allowed value of μ is of order $k_B T / P^{1/3} a^{3/3}$. For these values, $\epsilon_S \approx (P/a)^{1/3} \exp(-2E_S/k_B T)$, with P the single-chain persistence length. For $\epsilon_S \gtrsim 1$, the longitudinal modulus of the hexagonal phase will be very considerably lowered by thermal fluctuations.

To determine $\hat{\mu}$ and \hat{K}_2 , we must calculate the limiting behavior of $\Sigma_T(\mathbf{q})$. A completely analogous discussion gives

$$\lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} \Sigma_T(\mathbf{q}) = 0, \quad (3.31a)$$

$$\lim_{q_\perp \rightarrow 0} \lim_{q_z \rightarrow 0} q_z^{-2} \Sigma_T(\mathbf{q}) = \frac{1}{2} y_T^2 \langle z^2 \rangle_T, \quad (3.31b)$$

where now $y_T^2 \approx a^{-3} \exp(-2E_T/k_B T)$ is the concentration of "exchanges" (dipoles of twist defects), and $\langle z^2 \rangle_T$ is the mean-square separation between twist defects in a given exchange. Equations (3.19b) and (3.20) then imply

$$\hat{K}_2^{-1} = 0, \quad (3.32a)$$

$$\hat{\mu}^{-1} = \mu^{-1} + \frac{\gamma^2 y_T^2 \langle z^2 \rangle_T}{2k_B T \rho_0^2} \quad (3.32b)$$

Because $\langle z^2 \rangle_T \approx (k_B T / \tau_T)^2 \approx (k_B T / \mu a^2)^2$ is finite, the renormalized shear modulus $\hat{\mu}$ is also finite. Furthermore, the renormalized twist constant \hat{K}_2 diverges as $1/q_z^2$, just as in the harmonic approximation.

Could the hexagonal phase have a high density of twist dipoles? To see why this is not possible, note that equation (3.32b) can be interpreted as a self-consistency equation for $\hat{\mu}$. The renormalization of the shear modulus μ due to twist defect pairs is of order $\epsilon \approx k_B T y_T^2 / \mu$. The shear modulus is of course further reduced by other thermal fluctuations, such as anharmonic phonon modes and dislocation loops, so equation (3.32b) is only a lower bound for this reduction. If, however, chain exchange is the dominant reduction mechanism, then we have approximately

$$\hat{\mu}^{-1} - \mu^{-1} \approx k_B T y_T^2 \hat{\mu}^{-2} \quad (3.33)$$

On the right-hand side of equation (3.33), we have used the *renormalized* value $\hat{\mu}$ in $\tau_T \approx \hat{\mu} a^2$. If y_T^2 is too large, this self-consistency equation has no solution. The largest allowed value of y_T^2 is of order $\mu/k_B T$. We conclude that

$$y_T^2 \lesssim \frac{\mu}{k_B T} \quad (3.34)$$

is a stability requirement for the hexagonal phase. Not only does the hexagonal phase not support free splay or twist defects, but also the concentration of twist dipoles must remain modest. For purely steric repulsion, this stability requirement reads

$$\left(\frac{P}{a}\right)^{1/3} e^{-2E_T/k_B T} \lesssim 1. \quad (3.35)$$

Note that there is no such restriction on the concentration y_S^2 of splay defect pairs.

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Appendix

Line tension in the hexagonal phase.

In this appendix, we use continuum elastic theory to estimate the line tension τ_S of the defect line between two oppositely charged splay defects in the hexagonal phase. Suppose that an extra chain is added to the hexagonal lattice along the axis $\mathbf{r}_\perp = 0$ from $z = 0$ to $z = Z$. Thus, there is a + endpoint defect at $(0, 0, 0)$ and a - endpoint defect at $(0, 0, Z)$. If these defects are widely separated, then the displacement field \mathbf{u} becomes independent of z in the region between them. In that region, equation (2.11) gives

$$\nabla_\perp \cdot \mathbf{u} = \rho_0^{-1} \delta(\mathbf{r}_\perp), \quad (\text{A1})$$

which implies that

$$\mathbf{u} = \frac{\mathbf{r}_\perp}{2\pi\rho_0 r_\perp^2}. \quad (\text{A2})$$

We now insert this expression for \mathbf{u} and the corresponding expressions for the director field $\hat{\mathbf{n}}$ and the density ρ into the Hamiltonian (3.1) for the hexagonal phase. Only the μ term gives an energy that scales linearly with the defect separation Z . This line energy can be written as

$$E_{\text{line}} = \int_0^Z dz \int d^2\mathbf{r}_\perp \frac{\mu}{\pi^2 \rho_0^2 r_\perp^4}. \quad (\text{A3})$$

For a lower cutoff on the \mathbf{r}_\perp integral, we use the lattice constant a , because continuum elastic theory breaks down at that length scale. We therefore obtain

$$E_{\text{line}} = \frac{\mu Z}{\pi \rho_0^2 a^2}. \quad (\text{A4})$$

Thus, the line tension $\tau_S = E_{\text{line}}/Z$ is approximately

$$\tau_S \approx \mu a^2. \quad (\text{A5})$$

We emphasize that this calculation gives only a rough estimate of τ_S because continuum elastic theory breaks down at microscopic length scales. For a more precise estimate, one would need a microscopic model of the defect line, as in reference [16]. However, this calculation does show that τ_S is finite in the hexagonal phase, and that it vanishes as $\mu \rightarrow 0$.

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