

## Coupling between Smectic and Twist Modes in Polymer Intercalated Smectics

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We analyze the elastic energy of an intercalated smectic where orientationally ordered polymers with an average orientation varying from layer to layer are intercalated between smectic planes. The lowest order terms in the coupling between polymer director and smectic layer curvature are added to the smectic elastic energy. Integration over the smectic degrees of freedom leaves an effective polymer twist energy that has to be included into the total polymer elastic energy leading to a fluctuational renormalization of the intercalated polymer twist modulus. If the polymers are chiral, this, in its turn, leads to a renormalization of the cholesteric pitch. [S0031-9007(97)04961-2]

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Recent elucidation of the structure of DNA–cationic lipid (CL) complexes [1,2] has brought forth quite a few unsuspected features of this macromolecular aggregate. It appears that cationic lipids in the complex retain their preferred packing characterized by a multilamellar 3D smectic order, while the oppositely charged DNA gets intercalated in between the lipid bilayer smectic planes. The intercalated DNA appears to be packed with a 2D smectic order of relatively large domain sizes that are probably coupled to the order in the neighboring intercalated DNA layers [2]. The careful x-ray diffraction studies leave no ambiguity as to the fact that both components of the complex–cationic lipids as well as DNA are ordered.

The ordering tendencies giving rise to this complex aggregate structure are due partly to the fairly well understood interactions between lipid bilayers in aqueous solutions, where van der Waals attraction competes with electrostatic and hydration forces, augmented by entropic repulsion forces originating in elastic fluctuations of the lipid bilayers constrained to a multilamellar stack [3]. Similarly, interactions between DNA molecules in the bulk that have only recently come under closer experimental as well as theoretical scrutiny appear to be dominated by repulsive forces of electrostatic as well as hydration origin, this time also augmented through an entropic mechanism very similar to the one operating in multilamellar lipid systems [4]. The interaction between the two constituents of the complex are probably dominated by the electrostatic attraction between DNA and cationic lipids, possibly modified by elastic shape fluctuations of the DNAs intercalated between positively charged layers of lipids and possibly by the forces mediated by the lipid bilayer elasticity due to local deformations induced by the close proximity of intercalated DNA. More work is certainly needed to assess the relative importance of all of these mechanisms in bringing about the stability of the DNA-CL complex.

Compared to the phases existing in the bulk, the lipid subphase does not appear to be substantially modified. It

has the same structural geometry as the one found with other lipids in the bulk. DNA is in this respect very much modified. At effective interhelical spacings found in the DNA-CL complex [2], DNA in the bulk would be either in the line hexatic phase or within the cholesteric phase [5]. Very little of this bulk order persists in intercalated DNA that is forced effectively into 2D layers intercalated between lipid bilayers. The positional order does not change qualitatively if we consider only DNA intercalated within a single layer. They are both short ranged [2]. The orientational order is changed more drastically if the state of affairs in the bulk and in the DNA-CL complex are compared. It is nevertheless the apparent total absence of the cholesteric order in the complex that has motivated our study. Apart from very tentative statements [6] that cholesteric structures of extremely large pitch ( $\sim$ mm) can sometimes be detected in the complex, the chiral nature of the DNA molecule makes no imprint on the structure of this macromolecular aggregate.

It is our goal in this contribution to investigate the interaction between the orientational order of intercalated polymers and the smectic degrees of freedom of intercalating lipid bilayers. We propose a simple theory on the effect that the coupling between polymer (i.e., DNA) orientational ordering within the intercalated layers and the smectic order of these layers can have on the effective twist elastic constant of the polymer layers. If, in addition, the intercalated polymers are chiral, this theory, for the first time, introduces a comprehensive mechanism for coupling between smectic and twist degrees of freedom leading eventually to a fluctuational renormalization of the cholesteric pitch of the polymer subsystem.

We will consider a simplified model of an intercalated smectic phase, where long polymers within a *single* layer are supposed to be completely orientationally ordered (see Fig. 1). This is not unrealistic as the domains of order in this and a similar system, where only a single layer of DNA is adsorbed to a cationic lipid bilayer, are quite large [7]. We will presume that the director of the polymers  $\mathbf{n}(m; \rho)$

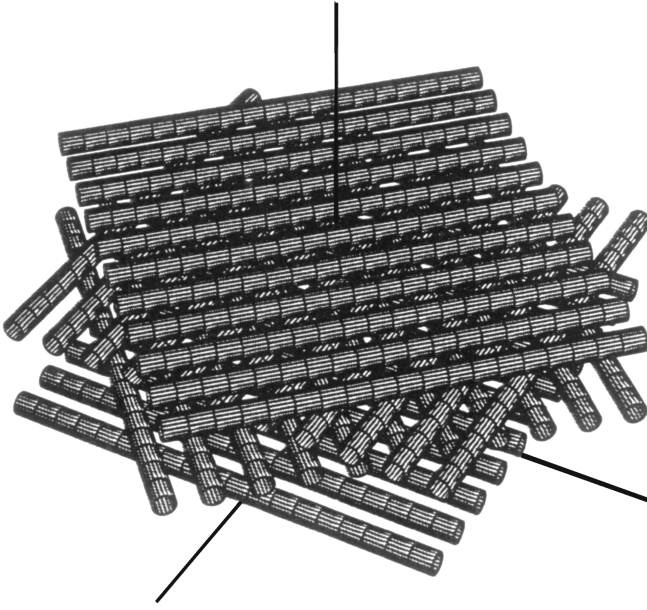


FIG. 1. A schematic representation of a part of a polymer intercalated smectic system. The smectic layers are not shown explicitly. The direction of the intercalated polymers changes from layer to layer. It has been arbitrarily assumed to change by  $\pi/4$  between two neighboring layers. The smectic interactions tend to orient the neighboring polymer layers in a parallel direction.

within an intercalated layer is a constant. We introduced  $m$  as the height index of the layer (layers are assumed to have the average positions at  $z_m = m \times d$ , where  $d$  is

the average layer-layer separation), while  $\boldsymbol{\rho} = (x, y)$  is the transverse radius vector. We have, thus, effectively limited ourselves to a mean-field approximation within a single layer.

We will construct an elastic free energy of this system, assuming a general dependence of the polymer director on the position, i.e., height index  $m$ , of the layer. Since the polymer orientational order can interact with the curvature energy of each layer, we first have to construct all of the scalar invariants that can be composed with  $\mathbf{n}$  and the second fundamental form of a single smectic layer.

If one defines the second fundamental form of Gauss of the  $m$ th layer with local displacement described within the Monge parametrization  $(x, y, \zeta_m(x, y))$  as

$$K_{ik}(m; \boldsymbol{\rho}) = \frac{\partial^2 \zeta_m(\boldsymbol{\rho})}{\partial x_i \partial x_k}, \quad (1)$$

where the indices  $i, k$  can have values  $i, k = 1, 2$ , with  $x_1 = x$  and  $x_2 = y$ , then the lowest order scalar invariants which can be built from the director  $\mathbf{n}$  and the tensor [Eq. (1)] of that layer are three [8]:  $K_{ii}K_{ik}n_i n_k$ ,  $K_{li}K_{ik}n_l n_k$ , and  $K_{ik}K_{lm}n_i n_k n_l n_m$ . Only two of these invariants are linearly independent if we ignore the terms containing Gaussian curvature. These terms could become important only if, instead of long polymers, the intercalated molecules would be short, anisotropic particles [9] or if the intercalated layers or the lipid bilayers themselves would show crystalline (or hexatic) order [10]. The curvature elastic energy of  $n$ th surface, assuming that within each layer the director of the polymers is a constant  $\mathbf{n}(m; \boldsymbol{\rho}) = \mathbf{n}(m)$ , can be written as

$$H_m(K_{ik}; \mathbf{n}) = \frac{1}{2} K_c \int [\text{Tr } K_{ik}(m; \boldsymbol{\rho})]^2 d^2 \boldsymbol{\rho} + \frac{1}{2} a \int K_{li}(m; \boldsymbol{\rho}) K_{ik}(m; \boldsymbol{\rho}) n_l(m) n_k(m) d^2 \boldsymbol{\rho} + \frac{1}{2} b \int K_{ik}(m; \boldsymbol{\rho}) K_{lr}(m; \boldsymbol{\rho}) n_i(m) n_k(m) n_l(m) n_r(m) d^2 \boldsymbol{\rho}. \quad (2)$$

In a stack of layers, the total elastic energy is composed of curvature elastic energy [Eq. (2)] and the deformation energy due to smectic dilations/compressions of the layers in the transverse direction, characterized by a smectic compressibility modulus  $\mathcal{B}$  [11]. The formal limits of this *ansatz* are well known and will not be discussed here. Introducing Fourier transform of the local displacement in the directions  $\boldsymbol{\rho}$  with wave vector  $\mathbf{Q}$ , we thus obtain, for the total smectic elastic energy, the expression

$$H = \frac{1}{2} \sum_{\mathbf{Q}} \int dm \left[ (K_c Q^4 + a Q^2 [\mathbf{Qn}(m)]^2 + b [\mathbf{Qn}(m)]^4) |\zeta_m(\mathbf{Q})|^2 + \mathcal{B} \left( \frac{\partial \zeta_m(\mathbf{Q})}{\partial m} \right)^2 \right] = \frac{1}{2} \sum_{\mathbf{Q}} \int dm \zeta_m(\mathbf{Q}) \mathcal{H}(m, m'; \mathbf{Q}) \zeta_m(-\mathbf{Q}), \quad (3)$$

where we have defined the operator  $\mathcal{H}(m, m'; \mathbf{Q})$  and used the shorthand  $\sum_{\mathbf{Q}} = [S/(2\pi)^2] \int d^2 \mathbf{Q}$ , with  $S$  being the area of the layer. If the intercalated polymers are chiral, we have to add to Eq. (3) the standard cholesteric elastic energy which depends in the lowest order only on the derivatives of the polymer director with respect to the stack index [11].

*Free energy of smectic fluctuations.*—We now proceed by integrating the smectic fluctuations from the free energy defined through the elastic Hamiltonian [Eq. (3)]

and, thus, obtaining an effective intercalated polymer free energy that will depend only on the director field of the polymers. We start by setting

$$\phi(m; \mathbf{Q}) = a Q^2 [\mathbf{Qn}(m)]^2 + b [\mathbf{Qn}(m)]^4 \quad (4)$$

and writing the operator explicitly that we introduced above Eq. (3):

$$\mathcal{H}(m, m'; \mathbf{Q}) = \left( -\mathcal{B} \frac{\partial^2}{\partial m^2} + K_c Q^4 + \phi(m; \mathbf{Q}) \right) \times \delta(m - m'), \quad (5)$$

which allows us to express the part of the free energy that depends explicitly on the polymer director field as

$$\begin{aligned}\mathcal{F}(\mathbf{n}(m)) &= -kT \ln \Xi = -kT \ln \left( \Pi_{\mathbf{Q}} \int \cdots \int \mathcal{D}\zeta_m(\mathbf{Q}) \exp(-\beta H) \right) \\ &= \frac{kT}{2} \sum_{\mathbf{Q}} \ln \text{Det } \mathcal{H}(m, m'; \mathbf{Q}) = \mathcal{F}_0 + \frac{1}{2} \sum_{\mathbf{Q}} \text{Tr } \phi(m; \mathbf{Q}) \int_0^1 d\mu \mathcal{G}_{\mu}(m, m'; \mathbf{Q}),\end{aligned}\quad (6)$$

where  $\mathcal{F}_0$  is the part of the free energy that does not explicitly contain  $\mathbf{n}(m)$ . The Green function  $\mathcal{G}_{\mu}(m, m'; \mathbf{Q})$  entering the above equation can be obtained as a solution of [12]

$$\left( -\mathcal{B} \frac{\partial^2}{\partial n^2} + K_c Q^4 + \mu \phi(m; \mathbf{Q}) \right) \mathcal{G}_{\mu}(m, m'; \mathbf{Q}) = \delta(m - m'). \quad (7)$$

Introducing, now,  $\mathcal{G}_0(m, m'; \mathbf{Q}) = \mathcal{G}_0(|m - m'|; \mathbf{Q}) = \mathcal{G}_{\mu=0}(m, m'; \mathbf{Q})$  in the form  $\mathcal{G}_0(m - m'; \mathbf{Q}) = \frac{1}{2} \mathcal{B}^{-1} \sqrt{-\mathcal{B}/K_c} Q^{-2} \exp(-\sqrt{K_c/\mathcal{B}} Q^2 |m - m'|)$ , we can expand  $\mathcal{G}_{\mu}(m, m'; \mathbf{Q})$  perturbatively up to the first order in  $\phi(m; \mathbf{Q})$ , thus obtaining the free energy to the second order in this quantity:

$$\begin{aligned}\mathcal{F}(\mathbf{n}(m)) &= \mathcal{F}_0 + \frac{kT}{2} \sum_{\mathbf{Q}} \int_0^1 d\mu \\ &\times \left[ \int dm \phi(m; \mathbf{Q}) \mathcal{G}_0(m, m; \mathbf{Q}) - \mu \iint dm dm' \phi(m; \mathbf{Q}) \mathcal{G}_0^2(m, m'; \mathbf{Q}) \phi(m'; \mathbf{Q}) + \dots \right].\end{aligned}\quad (8)$$

Since the zero order Green function is obviously of short range, we can expand the expression for the free energy [Eq. (8)] for a slowly varying  $\phi(m; \mathbf{Q})$  field in a standard fashion, obtaining the following approximate form of the free energy:

$$\begin{aligned}\mathcal{F}(\mathbf{n}(m)) &= \mathcal{F}_0 + \frac{kT}{2} \sum_{\mathbf{Q}} \left[ \mathcal{G}_0(0; \mathbf{Q}) \int dm \phi(m; \mathbf{Q}) - \frac{kT}{4} \left( \int dt \mathcal{G}_0^2(t; \mathbf{Q}) \right) \int dm \phi^2(m; \mathbf{Q}) \right. \\ &\quad \left. + \frac{kT}{8} \left( \int dt t^2 \mathcal{G}_0^2(t; \mathbf{Q}) \right) \int dm \left( \frac{\partial \phi(m; \mathbf{Q})}{\partial m} \right)^2 \right].\end{aligned}\quad (9)$$

The summation over the Fourier space also intends integration over the different directions of the  $\mathbf{Q}$  vector. Denoting this orientational integration with  $\langle \cdots \rangle_{\omega}$ , it is easy to see that  $\langle \phi(m; \mathbf{Q}) \rangle_{\omega}$ , as well as  $\langle \phi^2(m; \mathbf{Q}) \rangle_{\omega}$ , do not depend on the orientational angles at all and are, thus, independent of the director field  $\mathbf{n}(m)$ . The dependence on the director field remains only in the derivative terms, i.e., terms of the form  $(\frac{\partial \phi(m; \mathbf{Q})}{\partial m})^2$ . These terms contain  $\frac{d[\mathbf{Qn}(m)]}{dm} = \mathbf{Q} \frac{d\mathbf{n}(m)}{dm} = \mathbf{Q}\dot{\mathbf{n}}(m) = \mathbf{Q}[\mathbf{n}(m) \times \mathbf{\Omega}(m)]$ , where  $\mathbf{\Omega}(m)$  is the vector of the “angular velocity” of rotation of the director from layer to layer. If the average normal to the layers is in the  $z$  direction then  $\mathbf{\Omega}(m) = (0, 0, \Omega_z(m))$ ; also  $\dot{\mathbf{n}}(m)$  is within each layer and in direction perpendicular to  $\mathbf{n}(m)$  with magnitude  $|\dot{\mathbf{n}}(m)| = \Omega_z(m)$ . As can be easily seen, the only terms that survive the integration  $\langle \cdots \rangle_{\omega}$  and still depend on the director field are those depending quadratically on  $|\dot{\mathbf{n}}(m)|$ . From the free energy [Eq. (9)], these terms can be obtained in the form

$$\begin{aligned}\mathcal{F}(\mathbf{n}(m)) &= \mathcal{F}_0(a, b) + \frac{kT}{8} \frac{S}{2\pi} \int_0^{\infty} Q^9 dQ \\ &\times \left( \int dt t^2 \mathcal{G}_0^2(t; \mathbf{Q}) \right) \left[ (a + b)^2 + \left( \frac{b}{2} \right)^2 \right] \\ &\times \int |\dot{\mathbf{n}}(m)|^2 dm,\end{aligned}\quad (10)$$

where  $\mathcal{F}_0(a, b)$  is the part of the free energy that after the  $\langle \cdots \rangle_{\omega}$  integration does not depend explicitly on the

director anymore. Evaluating the last integral over  $Q$  and taking into account the fact that the minimal value of  $Q$  is set by the domain size, assumed to be a square of side  $l$ , while the maximal value is set by the molecular dimension  $\alpha$ , we obtain finally

$$\begin{aligned}\mathcal{F}(\mathbf{n}(m)) &= \mathcal{F}_0(a, b) + \frac{kTS}{256} \frac{1}{\mathcal{B}^2} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} \\ &\times \left[ (a + b)^2 + \left( \frac{b}{2} \right)^2 \right] \\ &\times \ln \frac{l}{\alpha} \int |\dot{\mathbf{n}}(m)|^2 dm.\end{aligned}\quad (11)$$

Thus, we see that, in an intercalated smectic, the smectic interactions between layers of orientationally ordered polymer molecules tend to renormalize the twist elastic modulus of intercalated oriented polymers to  $K_2 \rightarrow K_2 + \frac{kT}{128} \frac{1}{\mathcal{B}^2} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} [(a + b)^2 + (\frac{b}{2})^2] \ln \frac{l}{\alpha}$ , where  $K_2$  is the “bare” polymer twist modulus, i.e., the twist elastic modulus of the polymer subphase if the smectic interactions are not taken into account. This renormalization is of purely fluctuational origin. If the polymers are, in addition, chiral, the renormalization of the twist modulus obviously leads to unwinding of the cholesteric pitch of the intercalated polymers to a new equilibrium value of  $P \rightarrow P(1 + \frac{kT}{128K_2} \frac{1}{\mathcal{B}^2} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} [(a + b)^2 + (\frac{b}{2})^2] \ln \frac{l}{\alpha})$ .

The mean-field model introduced above led in a very straightforward way to a renormalization of the twist

modulus of intercalated polymers. The effect itself is a very intuitive one. If there exists a deformational “easy axis” within each smectic layer, which according to Eq. (3) represents a deformational wave whose direction is perpendicular to  $\mathbf{n}(m)$  within a single layer, the smectic compressibility term would tend to twist the directors of the neighboring layers towards a colinear position. This would introduce a coupling term  $[\mathbf{n}(m) - \mathbf{n}(m+1)]^2$  in the free energy of two neighboring layers. The continuum version of this effect would lead exactly to Eq. (11).

The coupling constants  $a$  and  $b$ , cf. Eq. (2), between the orientational ordering of intercalated polymers and effective elastic properties of the layers depend, in general, on the orientational order parameter of the polymer chain  $S$ , the elastic modulus of the chains defined as  $kT\mathcal{L}_p$ , where  $\mathcal{L}_p$  is the persistence length and the polymer surface density  $\rho$ . The orientational order parameter of the polymer chains is defined through the 2D orientational tensor  $\sigma_{ik}$  of the intercalated chains as  $\sigma_\alpha = \frac{\rho}{2}(1 \pm S)$ , where  $\alpha$  is the index of the two eigenvalues [13]. For  $S$  close to 1, i.e., close to complete orientational order where all of the chains point in the same direction, the scaling form for  $a$  and  $b$  should be  $a, b \sim kTS(\mathcal{L}_p/\ell_\perp)$ , where  $\ell_\perp$  is the separation between the chains perpendicular to their long axis. This is the form appropriate for our assumption of complete ordering of chains within each smectic layer.

We can now assess the magnitude of the contribution of smectic modes to the twist elastic modulus of the smectic layers. Assuming the above scaling form for constants  $a$  and  $b$ , we obtain for the ratio between the renormalized fluctuation and the bare value of the twist modulus

$$\sim \frac{(kT)}{K_2\mathcal{B}^2} \left( \frac{\mathcal{B}}{K_c} \right)^{5/2} \left( kTS \frac{\mathcal{L}_p}{\ell_\perp} \right)^2 \ln \frac{\ell}{\alpha}. \quad (12)$$

Since the dominant interactions determining  $\mathcal{B}$  are electrostatic attractions between DNA and cationic lipid headgroups, the smectic modulus has to be quite large, while  $\mathcal{L}_p/\ell_\perp$  is on the order of 10. Assuming that the bare DNA twist modulus can be estimated by invoking only steric interactions [11], we obtain the values between 10 and 100 for the ratio [Eq. (12)], depending on the exact value of  $\mathcal{B}$ . If the intercalated polymers are chiral, it would, thus, come as no surprise if the effective cholesteric pitch surviving in this system would be orders of magnitude larger than in the pure polymer system [6].

We have not included the possible direct modification of the chiral interactions (the details of which in condensed DNA arrays are not yet fully understood [14]) by

smectic fluctuations in this analysis, an effect that would act in the direction opposite to the smectic fluctuation renormalization of the polymer twist modulus. As this effect would tend to make the effective pitch smaller, which apparently has never been observed in this system, we assume that it is small.

In conclusion, we have shown how the smectic degrees of freedom couple to orientational modes of orientationally ordered polymers intercalated between smectic layers leading to fluctuation renormalization of the polymer twist modulus. We propose this as one of the possible reasons why no cholesteric structures have been observed in the DNA-CL system.

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