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Fluctuation-entanglement mechanism for director anchoring at nematic polymer surfaces

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The existence of polymeric entanglements in a polymer nematic liquid crystal modifies the Frank elastic description governing director deformation. We present a calculation of the director fluctuation contribution to polymer nematic surface tension, in which we supplement the usual Frank terms with a damping term due to entanglements. We infer an effective surface anchoring potential, going to zero as $n \ln n$ in the limit of low entanglement density n. The anchoring easy axis depends on the relative magnitudes of the Frank constants governing director elasticity. We comment on generalizing the approach to take into account polydomain structure.

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I. INTRODUCTION

The details of the boundary conditions on the director $\mathbf{n}_s$ at a nematic surface, the so-called ''anchoring'' conditions, are of considerable importance in liquid crystal applications [1]. They are often adequately represented by the Rapini-Papoular potential

$$W(1-|\mathbf{n}_s\cdot\mathbf{n}_e|^2), \tag{1}$$

describing preferential orientation of $\mathbf{n}_s$ along an ''easy axis'' $\mathbf{n}_e$, according to a positive anchoring strength W. Several microscopic approaches exist which give $\mathbf{n}_s$ and W explicitly within the framework of the Maier-Saupe and Onsager theories of nematic ordering [2]. These involve mean-field approximation and need to be qualified by their neglect of fluctuations $\delta\mathbf{n}_s$, which might be important since they occur in a quasi-two-dimensional space for which mean-field theory is vulnerable [3]. However, for models pertaining to the traditional low-molecular-weight thermotropic nematics, $\delta\mathbf{n}_s$ fluctuations appear to manifest themselves as well-behaved corrections to the mean-field predictions, well within the range of validity of simple Ginzburg criteria [3,4].

The statistical mechanical procedure for calculating such corrections generally involves expanding in a harmonic approximation about some ''bare'' anchoring potential, which one can identify with the mean-field result. For low-molecular-weight nematics, all fluctuation-induced anchoring effects disappear in the limit in which the bare potential goes to zero. In this paper we present a departure from this state of affairs. We argue that in the general case of *polymer* nematics there remains, by contrast, a residual surface anchoring potential which is entirely due to fluctuations.

The effect is engendered by introducing a bulk anchoring term into the fluctuation Hamiltonian. In the next section we discuss how, physically, this term expresses coupling between director fluctuations and an entanglement matrix. Section III calculates the associated contribution to surface tension. In Sec. IV, we interpret the anisotropy of the surface tension according to the Rapini-Papoular scheme. Section V discusses modifications to the calculation due to the polydomain characteristics of polymer nematics.

II. DIRECTOR FLUCTUATIONS IN POLYMER NEMATICS

Consider a main-chain polymer liquid crystal in which the persistence length P of the chains is much smaller than their length L. The isotropic phase conforms to the standard bulk polymer scenario, in which each molecule is a spherical coil and there is a degree of entanglement between the coils. With the onset of nematic ordering, however, the sphere becomes elongated (see Fig. 1). The entanglements accommodate this new equilibrium structure by relaxing and reforming in lower stress configurations. Once mechanical equilibrium is established, it is clear that any attempt to inhomogeneously deform the director will be accompanied by a short-time stress coupling to the entanglements.

This is similar to the physical picture presented by Warner and Terentjev [5] in their discussion of the hydrostatic coupling between cross-links and Frank elasticity in nematic elastomers. We now make the ansatz that in polymer nematics, thermal director fluctuations $\delta\mathbf{n}(\mathbf{r})$ over the space $\mathbf{r}$ of the system take place on time scales shorter than the characteristic reptation times associated with the entanglements, such that we can adopt the hydrostatics of a nematic elastomer wholesale. That is, we assume that a fluctuation interacts with an entanglement in the same way as it would with a permanent cross-link. The fluctuation Hamiltonian then includes, in addition to the usual Frank terms, a term

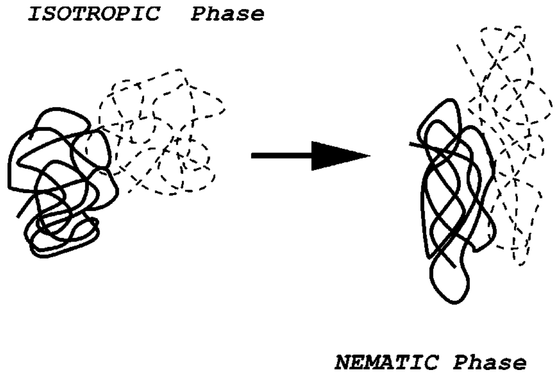

FIG. 1. Schematic conformation of two entangled molecules in the bulk of a main-chain polymer liquid crystal in the isotropic and nematic phases, respectively.

$\sim \delta\mathbf{n}^2$ expressing local anchoring to the entanglement matrix:

$$H=\tfrac{1}{2}\int d\mathbf{r}\{K_1(\operatorname{div}\delta\mathbf{n})^2+K_2(\mathbf{n}\cdot\operatorname{curl}\delta\mathbf{n})^2 +K_3(\mathbf{n}\times\operatorname{curl}\delta\mathbf{n})^2+D\,\delta\mathbf{n}^2\}. \tag{2}$$

Note that this choice of Hamiltonian remains phenomenologically relevant as P/L increases from the limit $P\ll L$, since the polymeric ‘‘shape’’ continues to mold itself around nematic order in the system and, as stressed in [5], it is this basic facility which underpins the term in D. Clearly, however, the argument no longer applies beyond $P\sim L$, when the chains are fully extended

In the case of side-chain polymer nematics, it is the backbone order (i.e., the degree of elongation of the sphere), rather than the side-chain mesogens, which couples to entanglements. Since the backbone is flexible, we may surmise that there is always entanglement coupling, independently of the rigidity of the mesogens.

III. SURFACE TENSION

To derive surface tension from H, we consider the partition function for a system h, consisting of a polymer nematic confined between two flat parallel surfaces at $z=0$ and $z=h$ in Cartesian coordinates $\mathbf{r}=(x,y,z)$,

$$Z_h=\int d[\delta\mathbf{n}(\mathbf{r})]\exp(-H_h/k_BT). \tag{3}$$

The surface tension γ per unit area A of the surfaces is the nonbulk part of the Helmholtz free energy $F_h=-k_BT\ln Z_h$ in the limit $h\rightarrow\infty$, i.e.,

$$\gamma=\lim_{h\rightarrow\infty}\partial F_h/\partial A. \tag{4}$$

Our strategy in the following will be, rather than calculating Z_∞ directly, to calculate F_h for arbitrary h, and then take $h\rightarrow\infty$. The advantage of this approach is that it allows us to exploit a mathematically useful analogy with the 1D quantum oscillator, pointed out by Ajdari *et al.* [6] in their calculation of the pseudo-Casimir interaction between walls bounding ordinary nematics.

Let us consider first the case of fluctuations about a uniform ground state in which the director is everywhere perpendicular ($\perp$) to the surfaces, following closely the analysis of [6]. We expand $\delta\mathbf{n}(\mathbf{r})\simeq(\delta n_x(\mathbf{r}),\delta n_y(\mathbf{r}),1)$ in Fourier components over surface area A, separating longitudinal (l) and transverse (t) modes:

$$\delta\mathbf{n}(\mathbf{r})=\frac{1}{A}\sum_{\mathbf{q}}[\tilde{n}_l(\mathbf{q},z)+\tilde{n}_t(\mathbf{q},z)]\exp(i\mathbf{q}\cdot\mathbf{R}),$$

where $\mathbf{R}=(x,y)$ and the wave vectors $\mathbf{q}$ lie parallel to the surfaces.

The l and t modes can be treated separately. We focus on the l modes, defining for notational convenience $\phi(\mathbf{q},z)=\tilde{n}_l(\mathbf{q},z)$.

Each l mode contributes a partition function factor

$$Z_{h,\mathbf{q}}=\int d[\phi(\mathbf{q},z)]\exp(-H_{h,\mathbf{q}}/k_BT), \tag{5}$$

where, using Eq. (2), the Hamiltonian for the mode is

$$H_{h,\mathbf{q}}=\tfrac{1}{2}\int_0^h dz[(D+K_1q^2)\phi^2+K_3(\partial_z\phi)^2]. \tag{6}$$

Equation (5) may be cast in the form

$$Z_{h,\mathbf{q}}=\int d\phi_0 d\phi_1 G_h(\phi_1,\phi_0), \tag{7}$$

with

$$G_h(\phi_1,\phi_0)=\int_{\phi(0)=\phi_0}^{\phi(h)=\phi_1} d[\phi(z)]\exp\Bigg\{-(2k_BT)^{-1} \times\int_0^h dz[(D+K_1q^2)\phi^2+K_3(\partial_z\phi)^2]\Bigg\}. \tag{8}$$

The kernel G_h satisfies

$$\frac{\partial}{\partial h}G_h(\phi,\phi_0)=\frac{1}{2}\left[\left(\frac{k_BT}{K_3}\right)\frac{\partial^2}{\partial\phi^2}-\left(\frac{D+K_1q^2}{k_BT}\right)\phi^2\right]G_h(\phi,\phi_0), \tag{9}$$

with the initial condition

$$G_0(\phi,\phi_0)=\delta(\phi-\phi_0). \tag{10}$$

The solution for G_h is well known in the context of the 1D quantum oscillator,

$$G_h(\phi,\phi_0)=\sum_{p=0}^{\infty}e^{-\omega_{\mathbf{q}}(p+1/2)h}\psi_p(\phi)\psi^*(\phi_0), \tag{11}$$

with eigenfunctions

$$\psi_p(\phi)=\frac{1}{\sqrt{2^p p!}}\left(\frac{\beta_{\mathbf{q}}}{\pi}\right)^{1/4}e^{-\beta_{\mathbf{q}}\phi^2/2}\mathcal{H}_p(\sqrt{\beta_{\mathbf{q}}}\phi). \tag{12}$$

Here $\mathcal{H}_p$ is the pth Hermite polynomial, and we have defined

$$\omega_{\mathbf{q}}=\sqrt{\left(\frac{D+K_1q^2}{K_3}\right)},\qquad \beta_{\mathbf{q}}=(K_BT)^{-1}\sqrt{K_3(D+K_1q^2)}. \tag{13}$$

Substituting Eq. (11) into Eq. (7), and performing the integration, Ajdari *et al.* obtain

$$Z_{h,\mathbf{q}}=\left[\frac{\beta_{\mathbf{q}}}{4\pi}\left(\frac{1-e^{-2\omega_{\mathbf{q}}h}}{e^{-\omega_{\mathbf{q}}h}}\right)\right]^{-1/2}. \tag{14}$$

This gives the total Helmholtz free energy according to $F_h = -k_BT\Sigma_{\mathbf{q}} \ln Z_{h,\mathbf{q}}$:

$$F_h = \frac{k_BT}{2}\sum_{\mathbf{q}} \left[h\omega_{\mathbf{q}} + \ln(1-e^{-2\omega_{\mathbf{q}}h}) + \ln(\beta_{\mathbf{q}}/4\pi)\right]. \tag{15}$$

To obtain the surface tension, we take the derivative with respect to surface area A. Only the third term contributes to the $h\rightarrow\infty$ limit, i.e.,

$$\gamma = \lim_{h\rightarrow\infty} \partial F_s/\partial A = \frac{k_BT}{2}\partial/\partial A \sum_{\mathbf{q}} \ln(\beta_{\mathbf{q}}/4\pi), \tag{16}$$

where we identify as the surface excess part of F_h,

$$F_s = \frac{k_BT}{2}\sum_{\mathbf{q}} \left[\ln(1-e^{-2\omega_{\mathbf{q}}h}) + \ln(\beta_{\mathbf{q}}/4\pi)\right]. \tag{17}$$

IV. SURFACE ANCHORING

Adding to the above the contribution due to transverse fluctuations, we calculate in the thermodynamic limit $A\rightarrow\infty$,

$$\begin{aligned}\gamma(\perp) &= k_BT(2\pi)^{-2}\int^{q_c} dq \int^{\pi/2} q\,d\phi \left(\frac{D}{K_1q^2+D} + \frac{D}{K_2q^2+D}\right) - \frac{k_BT}{2\pi}q_c^2 \\ &= \frac{k_BT}{16\pi}\left\{\frac{\ln(\xi_1^2q_c^2+1)}{\xi_1^2} + \frac{\ln(\xi_2^2q_c^2+1)}{\xi_2^2}\right\} - \frac{k_BT}{2\pi}q_c^2,\end{aligned} \tag{18}$$

where q_c is a high-wave number cutoff, and we define $\xi_\alpha = \sqrt{K_\alpha/D}$ with dimensions of length.

Repeating the analysis for the case of a uniform ground state in which the director is everywhere *parallel* ($\|$) to the surface, we arrive at

$$\begin{aligned}\gamma(\|) &= k_BT(2\pi)^{-2}\int^{q_c} dq \int^{\pi/2} q\,d\phi \\ &\quad\times\left(\frac{D}{(K_1\sin^2\phi + K_3\cos^2\phi)q^2+D} + \frac{D}{(K_2\sin^2\phi + K_3\cos^2\phi)q^2+D}\right) - \frac{k_BT}{2\pi}q_c^2.\end{aligned} \tag{19}$$

Equations (18) and (19) establish a basic anchoring potential of the Rapini-Papoular type, with anchoring strength

$$W = |\gamma(\|) - \gamma(\perp)|, \tag{20}$$

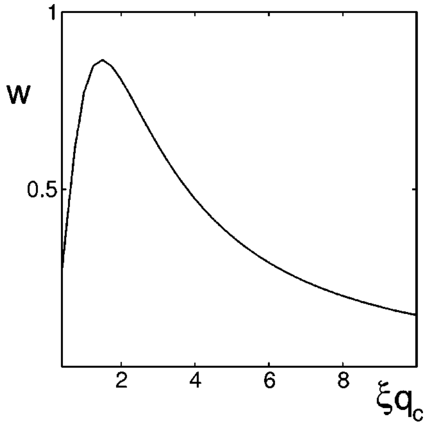

FIG. 2. The reduced planar anchoring potential of Eq. (23), $w[\xi q_c] = 4\ln(1+\xi^2q_c^2)/(\xi q_c)^2 - 4(1+\xi^2q_c^2)^{-1}$.

and an easy axis $\mathbf{n}_e$ which is either planar or perpendicular, according to the relative magnitudes of the Frank constants K_1, K_2, and K_3.

By way of illustration, consider the example of ''Onsager-like'' anisotropy $K_1 = K_2 = K$, $K_3 = K + \Delta K$ [7]. Then

$$\gamma(\perp) = \frac{k_BT}{8\pi}\left(\frac{\ln[\xi^2q_c^2+1]}{\xi^2}\right) - \frac{k_BT}{2\pi}q_c^2 \tag{21}$$

and, to lowest order in $\Delta K = K_3 - K$,

$$\gamma(\|) \simeq \frac{k_BT}{8\pi}\left(\frac{\ln[(\xi' q_c)^2+1]}{\xi'^2}\right) - \frac{k_BT}{2\pi}q_c^2, \tag{22}$$

where $\xi' = \sqrt{(K+\Delta K/2)/D}$.

The difference between the two constitutes a *planar* anchoring potential, of strength

$$W = \gamma(\perp) - \gamma(\|) \simeq \frac{k_BT}{16\pi}q_c^2\left(\frac{\Delta K}{K}\right)w[\xi q_c]. \tag{23}$$

Figure 2 shows the dimensionless quantity $w[\xi q_c]$ near the strong entanglement limit in which ξ approaches the cutoff length q_c^{-1}.

In the weak-entanglement limit ($D\rightarrow 0$, $\xi\rightarrow\infty$), W goes to zero as

$$W = \frac{k_BT\ln\xi q_c}{2\pi\xi^2}\left(\frac{\Delta K}{K}\right) \quad (\xi\rightarrow\infty). \tag{24}$$

An interpretation of this expression at the microscopic level is revealing. We write $q_c \sim d^{-1}$, $K \sim k_BT/d$, with d an effective mesogen dimension, and, following [5], $D \sim nk_BT$, where n is the entanglement density. Hence, $\xi^{-2} = D/K \sim nd$ and

$$\frac{W/d}{nk_BT} \sim \ln(nd^3), \tag{25}$$

which relates the anchoring free energy to the distributional entropy of entanglements over the mesogen ''lattice.''

V. POLYDOMAIN CORRECTIONS

Experimentally, polymer nematics exhibit a polydomain structure. To take this into account, let us assume that there exists a well-defined length scale ζ characterizing domain size. More specifically, we will interpret ζ as a length scale over which director-director correlations persist. This is to be distinguished from the alternative [8] in which ζ is understood as an average separation between topological defects of sheetlike character (which would also have anchoring properties).

Two modifications to the surface tension calculation suggest themselves: (i) In the summations over **q**, Eqs. (18) and (19), we implement an effective low-wave-number cutoff $\sim\zeta^{-1}$, replacing the thermodynamic limit. (ii) We set $h=\zeta$ in Eq. (16), rather than $h\rightarrow\infty$, and absorb into our definition of surface tension the resulting excess free energy due to the quasi-Casimir effect, the second term on the right in the definition of F_s, Eq. (17).

With these modifications, the fluctuation part of the surface tension splits into two parts, i.e., $\gamma=\gamma_\infty-\gamma_\zeta$, with γ_ζ the finite-domain correction. For the case of the weak Onsager-like elastic anisotropy invoked above (i.e., $K=K_1=K_2$, $K_3=K+\Delta K$), the leading order corrections to the planar anchoring potential of Eq. (23) are

$$W_\zeta=\tilde{\gamma}_\zeta(\|)-\tilde{\gamma}_\zeta(\perp)\simeq-\frac{k_BT}{4\pi\zeta\xi}\left(\frac{\Delta K}{K}\right)\quad(\xi\ll\zeta)$$

$$\simeq-\frac{3k_BT}{8\pi\zeta^2}\left(\frac{\Delta K}{K}\right)\quad(\xi\gg\zeta).\qquad(26)$$

The $\xi\ll\zeta$ limit of W_ζ is negligible by comparison with Eqs. (23) and (24), and can be disregarded. In the $\xi\gg\zeta$ limit, however, W_ζ dominates. Hence there is a transition to *homeotropic* anchoring in passing between these limits.

VI. CONCLUSION

In summary, we have argued that in polymer nematics in which the backbones of the molecules are not fully extended, interference of entanglements with director fluctuations generates an effective surface anchoring potential, the easy axis and strength of which depend on the relative magnitudes of the bulk Frank elastic constants.

Our analysis is illustrative in character, the emphasis being on making explicit the fundamental contrast with the role of director fluctuations at low-molecular-weight nematic surfaces. We are not able to say at present whether the contrast is actually experimentally significant. This would require a simultaneous appraisal of both mean-field and fluctuation effects. Although it is feasible that the mean-field mechanisms which have had some success in describing low-molecular-weight nematic anchoring may also have some relevance to polymer nematics, experimental data for the latter are currently lacking.

We stress that, except for extended side-chain polymers, our approach does not apply to fully extended polymers. In this sense, we are describing systems which are not in general covered by the well-known argument (see [9]) predicting planar anchoring on the basis of the high free energy cost of packing chain ends in a homeotropic configuration at the surface.

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[8] The polydomain structure has been interpreted variously as a consequence of long relaxation times for nematic defects and as a random anisotropy effect originating from entanglements (see [5]).

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