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Free energy of semiflexible polymers and structure of interfaces

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Abstract. The free energy of semiflexible polymers is calculated as a functional of the compositional scalar order parameter ϕ and the orientational order parameter of second-rank tensor S_{ij} on the basis of a microscopic model of wormlike chains with variable segment lengths. We use a density functional theory and a gradient expansion to evaluate the entropic part of the free energy, which is given in a power series of $Q_{ij} = S_{ij}/\phi$. The interaction term of the free energy is derived with a random phase approximation. For the rigid rod limit, the nematic-isotropic transition point is given by $Nw\phi = 4.05141$, N and w being the degree of polymerization and the anisotropic interaction parameter, respectively, and the degree of ordering at the transition point is 0.33448. We also find that the contour length of polymer chains becomes larger in a nematic phase than in an isotropic phase. Interface profiles are obtained numerically for some typical cases. In the neighborhood of isotropic-isotropic interfaces, polymer chains tend to align parallel to the interface on the polymer-rich side and perpendicular on the poor side. When an isotropic region and a nematic region coexist, orientational order parallel to the interface is preferred in the nematic region.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 61.30.Cz Theory and models of liquid crystal structure – 64.70.Md Transitions in liquid crystals

1 Introduction

Much attention has been paid to liquid crystalline polymers [1,2] because of the potential of industrial applications such as fibers with high tensile strength, synthetic membranes, nonlinear optics and electro-optical devices. Many liquid crystalline polymers are stiff due to mesogenic units incorporated into the backbone of the polymer and form a nematic ordered phase in suitable conditions. Extensive experimental [3–5] and theoretical [6–19] studies have been focused on liquid crystalline polymers and their mixtures. They exhibit a wide variety of phase behaviors depending on temperature (thermotropic case), volume fraction of liquid crystalline polymers (lyotropic case), degree of polymerization, stiffness of the polymer chains and their interactions. The richness of the phase behaviors arises from the coupling between compositional and orientational order and isotropic and anisotropic interactions between the components. Various types of phase diagrams have been shown theoretically and experimentally, the shape of which is quite complex and sensitively depends on physical properties of each system. As well as phase transition between isotropic and nematic phases, phase separation has been observed into isotropic and nematic phases, two nematic phases with different polymer concentrations, and two isotropic phases.

One of the aims of this article is to calculate the free energy of semiflexible polymers with inhomogeneous fluctuations. Despite numerous papers on such systems, not enough theoretical studies have been devoted to the properties of inhomogeneous states with interfaces between phase-separated domains [13,18,20,21]. In order to describe the properties of the phase behavior, orientational order as well as compositional order must be specified and the free energy is given as a functional of two order parameters: a scalar order parameter representing the volume fraction of polymers ϕ and an orientational order parameter of second-rank tensor S_{ij} which will be defined below. Inhomogeneity is taken into account by making a gradient expansion up to the second order in the free energy. We assume that only fluctuations of long wavelength are relevant to the morphology. Previous calculations of the free energy of liquid crystalline polymers or their mixtures in terms of the compositional and the orientational order parameters used a microscopic model of completely rigid rods and freely jointed chains [15], or that of inextensible wormlike chains [14,16]. Our calculation is similar to that of Liu and Fredrickson [16] and uses a density functional theory to calculate the entropic part of the free energy. A significant difference between our calculation and that of Liu and Fredrickson is that we use a microscopic model of wormlike chains without the constraint of constant segment length [22–24], while the calculation of Liu and Fredrickson is based on inextensible wormlike chains. As discussed below, one of the advantages of dealing with such extensible wormlike chains is that calculations can be performed systematically by using the techniques of field theory [25] because we can

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utilize the Gaussian property of the single chain Hamiltonian. The result holds for arbitrary concentration ϕ and is given by a Landau-de Gennes expansion with respect to the orientational order per segment, $Q_{ij} = S_{ij}/\phi$, not S_{ij}. The expansion coefficients can be calculated for arbitrary rigidity of the chain and are a function of the ratio of the dimensionless elastic constant (or persistence length) to the degree of polymerization. Although the expansion is truncated up to fourth order in Q_{ij} in evaluating the bulk part for arbitrary rigidity, rigorous expression for the bulk part can be obtained for the rigid rod limit because the expansion can be performed to infinite order in Q_{ij}. The obtained energy for rigid rod limit can be used to investigate the deep quench into the nematic phase in contrast to the Landau-de Gennes free energy. The interaction energy is calculated with a simple random phase approximation and we incorporate the isotropic interaction which favors demixing and the anisotropic Maier-Saupe interaction [8] which tends to orient the segments parallel to each other.

By using the free energy, we will investigate the structure of interfaces between phase-separated domains. Since the free energy is quite complicated, we calculate the interface profile numerically and restrict ourselves to the following typical cases: interfaces between two isotropic regions and between an isotropic region and a nematic region.

This paper is organized as follows: We define the order parameters and the single chain Hamiltonian and calculate the free energy in Section 2. Section 3 is devoted to a discussion on the bulk properties by using the free energy obtained in Section 2. In Section 4, we discuss the properties of interfaces between polymer-rich and polymer-poor regions and show the profiles of the interface. We make a brief conclusion in Section 5.

2 Calculation of the free energy

2.1 Order parameters and single chain Hamiltonian

We consider a system composed of homopolymers and denote the polymer species by K = A, B, and so on. We specify the state of the system by the following two order parameters. One is the volume fraction defined by

$$\phi_K(\mathbf{r}) = \frac{v_0}{b} \sum_{\alpha\in \mathrm{K}} \int_0^{N_K b} ds\,\delta(\mathbf{r} - \mathbf{R}^\alpha(s)). \tag{1}$$

Here N_K is the degree of polymerization, v_0 is the monomer volume and b is the average distance between adjacent monomers. $\mathbf{R}^\alpha(s)$ represents the configuration of the αth chain where s parameterizes the chain and runs from 0 to $N_K b$. We assume for simplicity that v_0 and b are common for all the monomer species.

The other is the orientational order parameter of second-rank tensor

$$S_{Kij}(\mathbf{r}) = \frac{v_0}{b} \sum_{\alpha\in \mathrm{K}} \int_0^{N_K b} ds \left[\dot{R}_i^\alpha(s)\dot{R}_j^\alpha(s) - \frac{1}{d}\delta_{ij}\right] \delta(\mathbf{r} - \mathbf{R}^\alpha(s)), \tag{2}$$

where overdots denote derivative with respect to s and d is the spatial dimension of the system. From the definition S_{Kij} is symmetric and $S_{Kij} = 0$ in the isotropic state. Notice that S_{Kij} is dimensionless and represents the orientational order per unit volume.

The single chain Hamiltonian of polymer species K is taken to be

$$\mathcal{H}^K\{\mathbf{R}(s)\} = \mathcal{H}_0^K\{\mathbf{R}(s)\} + \mathcal{H}_1^K\{\mathbf{R}(s)\}. \tag{3}$$

Here $\mathcal{H}_0^K\{\mathbf{R}(s)\}$ is the Hamiltonian of an unperturbed chain and we take the following form [22–24]:

$$\beta\mathcal{H}_0^K\{\mathbf{R}(s)\} = \int_0^{N_K b} ds \left\{\frac{d}{2l_K b}\dot{\mathbf{R}}(s)^2 + \frac{\epsilon_K b}{2}\ddot{\mathbf{R}}(s)^2\right\}, \tag{4}$$

where β is the inverse temperature. The first term and the second term in equation (4) represent the penalty for the stretching and the bending of the chain, respectively. We stress here that we do not impose the constraint of $|\dot{\mathbf{R}}| = 1$, that is, the chains are stretchable and S_{Kij} defined in equation (2) is not necessarily traceless. Imposing the constraint

$$\langle\dot{\mathbf{R}}(s)^2\rangle_0 \equiv \frac{\int \mathcal{D}\mathbf{R}\dot{\mathbf{R}}(s)^2 e^{-\beta\mathcal{H}_0^K}}{\int \mathcal{D}\mathbf{R} e^{-\beta\mathcal{H}_0^K}} = 1, \tag{5}$$

we obtain the relation [24] (see Appendix, Eq. (A.5))

$$l_K = \frac{4\epsilon_K}{d}\cdot \tag{6}$$

All the calculations below are done under the condition of equation (6).

The $\mathcal{H}_1^K$ is the source term given by

$$\beta\mathcal{H}_1^K\{\mathbf{R}(s)\} = \int d\mathbf{r} \int_0^{N_K b} ds \left\{h_{\phi_K}(\mathbf{r}) + h_{S_{Kij}}(\mathbf{r}) \times \left[\dot{R}_i(s)\dot{R}_j(s) - \frac{1}{d}\delta_{ij}\right]\right\} \frac{v_0}{b}\delta(\mathbf{r} - \mathbf{R}(s)), \tag{7}$$

where we have introduced the fields $h_{\phi_K}(\mathbf{r})$ and $h_{S_{Kij}}(\mathbf{r})$. Hereafter summation over repeated indices are implied.

2.2 Free energy of non-interacting chains (entropic part)

2.2.1 Density functional theory

We consider here the free energy of the ideal system composed of non-interacting chains. We take the density functional approach similar to that of Tang and Freed [26] for the Gaussian chain system with no rigidity. The grand partition function for the ideal system is

$$\Xi_{ideal} = \prod_K \Xi^K_{ideal}, \tag{8}$$

where the grand partition function for the component K is

$$\Xi^K_{ideal} = \sum_{n_K=0}^{\infty} \frac{1}{n_K!} {z_{0K}}^{n_K} = \exp(z_{0K}). \tag{9}$$

The z_{0K} is the partition function of a single chain

$$\begin{aligned} z_{0K} &= \tilde{\mathcal{Z}}_K \int \mathcal{D}\mathbf{R}(s) \exp(-\beta(\mathcal{H}^K_0\{\mathbf{R}(s)\} + \mathcal{H}^K_1\{\mathbf{R}(s)\})) \\ &= \mathcal{Z}_K \left\langle \exp\left(-\frac{v_0}{b} \int_0^{N_K b} ds\, (h_{\phi_K}(\mathbf{R}(s)) \right.\right. \\ &\quad \left.\left. + \left[\dot{R}_i(s)\dot{R}_j(s) - \frac{1}{d}\delta_{ij}\right] h_{S_{Kij}}(\mathbf{R}(s))\Big)\right)\right\rangle_0, \end{aligned} \tag{10}$$

where $\tilde{\mathcal{Z}}_K$ is the contribution from the kinetic energy and $\mathcal{Z}_K = \tilde{\mathcal{Z}}_K \int \mathcal{D}\mathbf{R}(s) \exp(-\beta\mathcal{H}^K_0\{\mathbf{R}(s)\})$.

The free energy of the ideal system is given by the following Legendre transform

$$\begin{aligned} \beta F_{ideal}\{\phi_K, S_{Kij}\} &= -\ln \Xi_{ideal} \\ &+ \sum_K \int d\mathbf{r} \left(h_{\phi_K}(\mathbf{r}) \frac{\delta \ln \Xi_{ideal}}{\delta h_{\phi_K}(\mathbf{r})} + h_{S_{Kij}}(\mathbf{r}) \frac{\delta \ln \Xi_{ideal}}{\delta h_{S_{Kij}}(\mathbf{r})} \right) \\ &= \sum_K \left(-z_{0K} + \int d\mathbf{r} \left(h_{\phi_K}(\mathbf{r}) \frac{\delta z_{0K}}{\delta h_{\phi_K}(\mathbf{r})} + h_{S_{Kij}}(\mathbf{r}) \frac{\delta z_{0K}}{\delta h_{S_{Kij}}(\mathbf{r})} \right) \right). \end{aligned} \tag{11}$$

We identify the order parameters ϕ_K and S_{Kij} with the average value, *i.e.*,

$$\phi_K(\mathbf{r}) = -\frac{\delta \ln \Xi_{ideal}}{\delta h_{\phi_K}(\mathbf{r})} = -\frac{\delta z_{0K}}{\delta h_{\phi_K}(\mathbf{r})}, \tag{12}$$

$$S_{Kij}(\mathbf{r}) = -\frac{\delta \ln \Xi_{ideal}}{\delta h_{S_{Kij}}(\mathbf{r})} = -\frac{\delta z_{0K}}{\delta h_{S_{Kij}}(\mathbf{r})} \cdot \tag{13}$$

From equations (7, 10, 12) we obtain

$$\begin{aligned} \phi_K(\mathbf{r}) = \tilde{\mathcal{Z}}_K \int &\mathcal{D}\mathbf{R}(s) \exp(-\beta(\mathcal{H}^K_0\{\mathbf{R}(s)\} + \mathcal{H}^K_1\{\mathbf{R}(s)\})) \\ &\times \frac{v_0}{b} \int_0^{N_K b} ds\, \delta(\mathbf{r} - \mathbf{R}(s)). \end{aligned} \tag{14}$$

Hence

$$\int d\mathbf{r} \phi_K(\mathbf{r}) = v_0 N_K z_{0K}. \tag{15}$$

By using equations (11, 12, 13, 15) the free energy F_{ideal} is finally expressed in terms of ϕ_K, S_{Kij}, h_{ϕ_K} and $h_{S_{Kij}}$ as

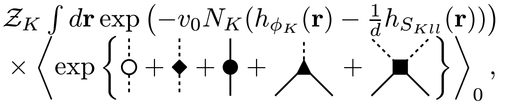
$$\begin{aligned} \beta F_{ideal}\{\phi_K, S_{Kij}\} = -\sum_K \int d\mathbf{r} \Big(&\frac{1}{v_0 N_K} \phi_K(\mathbf{r}) \\ &+ h_{\phi_K}(\mathbf{r})\phi_K(\mathbf{r}) + h_{S_{Kij}}(\mathbf{r}) S_{Kij}(\mathbf{r}) \Big). \end{aligned} \tag{16}$$

Our remaining task to obtain the functional form of $F_{ideal}\{\phi_K, S_{Kij}\}$ is to express h_{ϕ_K} and $h_{S_{Kij}}$ in terms of ϕ_K and S_{Kij} through inverting equations (12, 13).

Calculation of z_{0K} is necessary to obtain the expression of ϕ_K and S_{Kij} in terms of h_{ϕ_K} and $h_{S_{Kij}}$. However, we cannot calculate equation (10) for the Hamiltonian (4) analytically. Therefore we make a gradient expansion up to second order for the evaluation of equation (10) because we are interested only in the long-wavelength fluctuations.

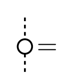
We make a gradient expansion for $h_{\phi_K}(\mathbf{R}(s))$ and $h_{S_{Kij}}(\mathbf{R}(s))$ around the center of gravity of the chain $\mathbf{R}_G \equiv (1/N_K b) \int_0^{N_K b} ds \mathbf{R}(s)$ [16]. Then equation (10) becomes

$$z_{0K} \simeq \mathcal{Z}_K \int d\mathbf{r} \exp\left(-v_0 N_K (h_{\phi_K}(\mathbf{r}) - \tfrac{1}{d} h_{S_{Kll}}(\mathbf{r}))\right)$$

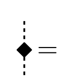


(17)

where we have defined the following graphs for brevity:



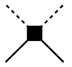
$$= -\frac{1}{2}\frac{v_0}{b} \partial_i \partial_j h_{\phi_K} \int_0^{N_K b} ds (\mathbf{R}(s) - \mathbf{R}_G)_i (\mathbf{R}(s) - \mathbf{R}_G)_j, \tag{18}$$



$$= \frac{1}{2}\frac{v_0}{b}\frac{1}{d} \partial_i \partial_j h_{S_{Kll}} \int_0^{N_K b} ds (\mathbf{R}(s) - \mathbf{R}_G)_i (\mathbf{R}(s) - \mathbf{R}_G)_j, \tag{19}$$

$$= -\frac{v_0}{b} h_{S_{Kij}} \int_0^{N_K b} ds \dot{\mathbf{R}}_i(s) \dot{\mathbf{R}}_j(s), \tag{20}$$

$$= -\frac{v_0}{b} \partial_k h_{S_{Kij}} \int_0^{N_K b} ds (\mathbf{R}(s) - \mathbf{R}_G)_k \dot{\mathbf{R}}_i(s) \dot{\mathbf{R}}_j(s), \tag{21}$$



$$\begin{aligned} = -\frac{1}{2}\frac{v_0}{b} \partial_k \partial_l h_{S_{Kij}} \int_0^{N_K b} &ds (\mathbf{R}(s) - \mathbf{R}_G)_k (\mathbf{R}(s) \\ &- \mathbf{R}_G)_l \dot{\mathbf{R}}_i(s) \dot{\mathbf{R}}_j(s). \end{aligned} \tag{22}$$

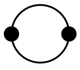
In the above graphs open vertex and filled vertices denote h_{ϕ_K} and $h_{S_{Kij}}$, respectively. Dashed lines imply taking derivatives of the fields h_{ϕ_K} and $h_{S_{Kij}}$ and that $\mathbf{R}(s) - \mathbf{R}_G$ appears in the integrands. Solid lines imply that $\dot{\mathbf{R}}$ appears in the integrands.

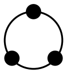
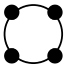
2.2.2 Zeroth order calculation in the gradients

We consider the zeroth order terms in the gradients in equation (17), that is, we retain only the graph (20) in equation (17). Since $\ln\langle\exp(\cdots)\rangle_0$ is equal to the sum of the connected graphs [25], we obtain

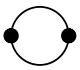
$$z_{0K}^{(0)} = \mathcal{Z}_K \int d\mathbf{r} \exp(\eta_0\{h_{\phi_K}(\mathbf{r}), h_{S_{Kij}}(\mathbf{r})\}), \tag{23}$$

with

$$\eta_0\{h_{\phi_K}(\mathbf{r}), h_{S_{Kij}}(\mathbf{r})\} = -v_0 N_K h_{\phi_K}(\mathbf{r}) +$$ 

$$+\frac{4}{3}$$  $$+2$$  $$+\cdots, \tag{24}$$

where

 $$= \left(-\frac{v_0}{b}\right)^2 \tilde{h}_{S_{Kij}} \tilde{h}_{S_{Kij}} \int_0^{N_K b} ds_1 \int_0^{N_K b} ds_2 c_1(s_1, s_2) c_1(s_1, s_2), \tag{25}$$

and so on. Here $\tilde{h}_{S_{Kij}} \equiv (h_{S_{Kij}} + h_{S_{Kji}})/2$ is the symmetric part of $h_{S_{Kij}}$ and we have defined the two point correlation function

$$\text{——} = c_1(s_1, s_2)\delta_{ij} = \langle \dot{\mathbf{R}}_i(s_1) \dot{\mathbf{R}}_j(s_2) \rangle_0. \tag{26}$$

In equation (A.5) we give the explicit form of $c_1(s_1, s_2)$. Note that when equation (6) holds, $h_{S_{Kll}}$ appearing in the first line of equation (17) is cancelled out by the first order graph in $h_{S_{Kij}}$.

We truncate the calculation of equation (23) up to fourth order in $\tilde{h}_{S_{Kij}}$. After some calculations we obtain from equations (12, 13, 23)

$$\begin{aligned}
&\ln\left(\frac{\phi_K(\mathbf{r})}{v_0 N_K \mathcal{Z}_K}\right) = -v_0 N_K h_{\phi_K}(\mathbf{r}) \\
&+ \left(-v_0 \frac{N_K}{d}\right)^2 D_2(dN_K/\epsilon_K) \tilde{h}_{S_{Kij}}(\mathbf{r}) \tilde{h}_{S_{Kij}}(\mathbf{r}) \\
&+ \frac{4}{3}\left(-v_0 \frac{N_K}{d}\right)^3 D_3(dN_K/\epsilon_K) \tilde{h}_{S_{Kij}}(\mathbf{r}) \tilde{h}_{S_{Kjk}}(\mathbf{r}) \tilde{h}_{S_{Kki}}(\mathbf{r}) \\
&+ 2\left(-v_0 \frac{N_K}{d}\right)^4 D_4(dN_K/\epsilon_K) \tilde{h}_{S_{Kij}}(\mathbf{r}) \tilde{h}_{S_{Kjk}}(\mathbf{r}) \tilde{h}_{S_{Kkl}}(\mathbf{r}) \tilde{h}_{S_{Kli}}(\mathbf{r}),
\end{aligned} \tag{27}$$

$$\begin{aligned}
&d\ Q_{Kij}(\mathbf{r}) = 2\left(-v_0 \frac{N_K}{d}\right) D_2(dN_K/\epsilon_K) \tilde{h}_{S_{Kij}}(\mathbf{r}) \\
&+ 4\left(-v_0 \tfrac{N_K}{d}\right)^2 D_3(dN_K/\epsilon_K) \tilde{h}_{S_{Kik}}(\mathbf{r}) \tilde{h}_{S_{Kkj}}(\mathbf{r}) \\
&+ 8\left(-v_0 \tfrac{N_K}{d}\right)^3 D_4(dN_K/\epsilon_K) \tilde{h}_{S_{Kik}}(\mathbf{r}) \tilde{h}_{S_{Kkl}}(\mathbf{r}) \tilde{h}_{S_{Klj}}(\mathbf{r}),
\end{aligned} \tag{28}$$

where

$$Q_{Kij}(\mathbf{r}) \equiv S_{Kij}(\mathbf{r})/\phi_K(\mathbf{r}) \tag{29}$$

is the orientational order per segment (notice that S_{ij} is the orientational order per volume) and D_2, D_3 and D_4 are defined by

$$D_2(dN_K/\epsilon_K) = \mathcal{I}_2(dN_K/\epsilon_K), \tag{30}$$

$$D_3(dN_K/\epsilon_K) = 3\mathcal{I}_2(dN_K/\epsilon_K) - 2\mathcal{I}_3(dN_K/\epsilon_K), \tag{31}$$

$$\begin{aligned}
D_4(dN_K/\epsilon_K) &= \frac{5}{2}\mathcal{I}_4(dN_K/\epsilon_K) - 6\mathcal{I}_3(dN_K/\epsilon_K) \\
&\quad + 4\mathcal{I}_2(dN_K/\epsilon_K) + \frac{1}{2}(\mathcal{I}_2(dN_K/\epsilon_K))^2.
\end{aligned} \tag{32}$$

Here we have defined

$$\mathcal{I}_n(x) = \frac{n!}{(-x)^n}\left(e^{-x} - \sum_{k=0}^{n-1} \frac{(-x)^k}{k!}\right). \tag{33}$$

Inversion of equations (27, 28) gives

$$\begin{aligned}
v_0 N_K h_{\phi_K}^{(0)}(\mathbf{r}) &= -\ln\left(\frac{\phi_K(\mathbf{r})}{v_0 N_K \mathcal{Z}_K}\right) \frac{d^2}{4D_2} Q_{Kij}(\mathbf{r}) Q_{Kij}(\mathbf{r}) \\
&- \frac{d^3 D_3}{3D_2^3} Q_{Kij}(\mathbf{r}) Q_{Kjk}(\mathbf{r}) Q_{Kki}(\mathbf{r}) \\
&+ \frac{3d^4(2D_3^2 - D_2 D_4)}{8D_2^5} Q_{Kij}(\mathbf{r}) Q_{Kjk}(\mathbf{r}) Q_{Kkl}(\mathbf{r}) Q_{Kli}(\mathbf{r}),
\end{aligned} \tag{34}$$

$$\begin{aligned}
-\frac{2v_0 N_K}{d} \tilde{h}_{S_{Kij}}^{(0)}(\mathbf{r}) &= \frac{d}{D_2} Q_{Kij}(\mathbf{r}) - \frac{d^2 D_3}{D_2^3} Q_{Kik}(\mathbf{r}) Q_{Kkj}(\mathbf{r}) \\
&+ \frac{d^3(2D_3^2 - D_2 D_4)}{D_2^5} Q_{Kik}(\mathbf{r}) Q_{Kkl}(\mathbf{r}) Q_{Klj}(\mathbf{r}).
\end{aligned} \tag{35}$$

The superscripts (0) denote the zeroth order part in the gradients.

Substituting equations (34, 35) into equation (16), we finally obtain the ideal free energy to the zeroth order in the gradients (or the ideal bulk energy)

$$\beta v_0 F_{ideal}^{(0)} = \sum_K \int d\mathbf{r} f_K^{(0)}\{\phi_K(\mathbf{r}), Q_{Kij}(\mathbf{r})\}, \tag{36}$$

with

$$\begin{aligned}
f_K^{(0)}\ &\{\phi_K(\mathbf{r}), Q_{Kij}(\mathbf{r})\} = \frac{\phi_K(\mathbf{r})}{N_K}(\ln\phi_K(\mathbf{r}) - \ln v_0 N_K \mathcal{Z}_K - 1) \\
+\ &\phi_K(\mathbf{r})\left\{\frac{1}{2} A_{K2} Q_{Kij}(\mathbf{r}) Q_{Kij}(\mathbf{r})\right. \\
+\ &\frac{1}{3} A_{K3} Q_{Kij}(\mathbf{r}) Q_{Kjk}(\mathbf{r}) Q_{Kki}(\mathbf{r}) \\
+\ &\left.\frac{1}{4} A_{K4} Q_{Kij}(\mathbf{r}) Q_{Kjk}(\mathbf{r}) Q_{Kkl}(\mathbf{r}) Q_{Kli}(\mathbf{r})\right\},
\end{aligned} \tag{37}$$

where

$$A_{K2} = \frac{d^2}{2D_2 N_K}, \tag{38}$$

$$A_{K3} = -\frac{d^3 D_3}{2D_2^3 N_K}, \tag{39}$$

$$A_{K4} = \frac{d^4(2D_3^2 - D_2D_4)}{2D_2^5 N_K}\,. \tag{40}$$

We conclude this subsection by noting that η_0 defined in equation (24) can be evaluated rigorously in the rigid rod limit ($N_K/\epsilon_K \to 0$) and that we obtain the following results:

$$\begin{aligned} v_0 N_K h^{(0)}_{\phi_K} &= -\ln\left(\frac{\phi_K}{v_0 N_K \mathcal{Z}_K}\right) - \frac{1}{2}\mathrm{Tr}\ln(\mathbf{1} + dQ_{Kij}) \\ &\quad - \frac{1}{2}(1+dQ_K)^{-1}_{ik} dQ_{Kki}, \end{aligned} \tag{41}$$

$$-\frac{2v_0N_K}{d}\tilde{h}^{(0)}_{S_{Kij}} = (1+dQ_K)^{-1}_{ik} dQ_{Kkj}, \tag{42}$$

$$\begin{aligned} &f^{(0)}_K\{\phi_K(\mathbf{r}), Q_{Kij}(\mathbf{r})\} = \\ &\quad \frac{\phi_K(\mathbf{r})}{N_K}(\ln\phi_K(\mathbf{r}) - \ln v_0 N_K \mathcal{Z}_K - 1) \\ &\quad + \frac{\phi_K(\mathbf{r})}{2N_K}\left\{-\mathrm{Tr}\ln(\mathbf{1} + dQ_{Kij}) + dQ_{Kii}\right\}, \end{aligned} \tag{43}$$

where $\mathbf{1}$ is a $d \times d$ unit matrix and $(1 + dQ_K)^{-1}_{ij}$ is the element of the inverse matrix of $\mathbf{1} + dQ_{Kij}$. Tr implies taking the trace of a matrix. Equation (43) can be used for the evaluation of the order parameter for a deep quench into a nematic phase in contrast to the free energy in a Landau expansion such as equation (36).

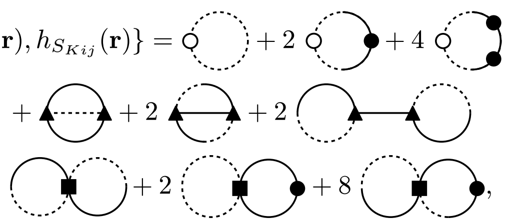
2.2.3 Second order calculation in the gradients

We can straightforwardly extend the calculation of z_{0K} to the second order in the gradients. We have

$$\begin{aligned} z_{0K} \simeq \mathcal{Z}_K \int d\mathbf{r}\exp(&\eta_0\{h_{\phi_K}(\mathbf{r}), h_{S_{Kij}}(\mathbf{r})\} \\ &+ \eta_2\{h_{\phi_K}(\mathbf{r}), h_{S_{Kij}}(\mathbf{r})\}). \end{aligned} \tag{44}$$

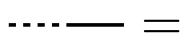
Here $\eta_0\{h_{\phi_K}(\mathbf{r}), h_{S_{Kij}}(\mathbf{r})\}$ is defined in equation (24) and

$\eta_2\{h_{\phi_K}(\mathbf{r}), h_{S_{Kij}}(\mathbf{r})\} =$

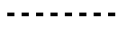


(45)

where we have retained only the terms up to second order in $h_{S_{Kij}}$ and

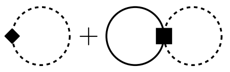


$= c_2(s_1, s_2)\delta_{ij} = \langle(\mathbf{R}(s_1) - \mathbf{R}_G)_i \dot{\mathbf{R}}_j(s_2)\rangle_0, \quad (46)$

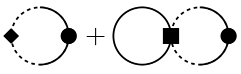


$= c_3(s_1, s_2)\delta_{ij} = \langle(\mathbf{R}(s_1) - \mathbf{R}_G)_i(\mathbf{R}(s_2) - \mathbf{R}_G)_j\rangle_0. \quad (47)$

Explicit forms of $c_2(s_1, s_2)$ and $c_3(s_1, s_2)$ are given in equation (A.5). Note that

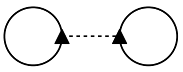


$= 0, \quad (48)$

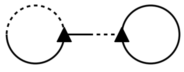


$= 0, \quad (49)$

when equation (6) holds and that



$= 0, \quad (50)$



$= 0. \quad (51)$

We write the fields h_{ϕ_K} and $h_{S_{kij}}$ as

$$h_{\phi_K} = h^{(0)}_{\phi_K} + h^{(2)}_{\phi_K} + \cdots, \tag{52}$$

$$h_{S_{Kij}} = h^{(0)}_{S_{Kij}} + h^{(2)}_{S_{Kij}} + \cdots \tag{53}$$

Here $h^{(0)}_{\phi_K}$ and $h^{(0)}_{S_{Kij}}$ are given in equations (34, 35), respectively, and $h^{(2)}_{\phi_K}$ and $h^{(2)}_{S_{Kij}}$ are the second order terms in the gradients. Then we obtain, after some calculations,

$$\begin{aligned} \exp(\eta_0 + \eta_2) \simeq &\frac{\phi_K}{v_0 N_K \mathcal{Z}_K}(1 + \eta_2\{h^{(0)}_{\phi_K}, h^{(0)}_{S_{Kij}}\}) \\ &- \frac{1}{\mathcal{Z}_K}(\phi_K h^{(2)}_{\phi_K} + S_{Kij} h^{(2)}_{S_{Kij}}). \end{aligned} \tag{54}$$

Here use has been made of equations (27, 28). Equation (12) together with equation (44) yields

$$\frac{\phi_K}{v_0 N_K \mathcal{Z}_K} = \exp(\eta_0 + \eta_2) + \partial_i\partial_j G_{ij}\{h_{\phi_K}, h_{S_{Kij}}\}. \tag{55}$$

The explicit form of G_{ij} is not necessary in the discussion below. Equations (54, 55) yield

$$\phi_K h^{(2)}_{\phi_K} + S_{Kij} h^{(2)}_{S_{Kij}} = \frac{\phi_K}{v_0 N_K}\eta_2\{h^{(0)}_{\phi_K}, h^{(0)}_{S_{Kij}}\} - \mathcal{Z}_K \partial_i\partial_j G_{ij}. \tag{56}$$

From equations (16, 36, 52, 53, 56) we can write the ideal free energy up to the second order in the gradients as

$$\begin{aligned} \beta v_0 F_{ideal} = \sum_K \int d\mathbf{r}(&f^{(0)}_K\{\phi_K(\mathbf{r}), Q_{Kij}(\mathbf{r})\} \\ &+ f^{(2)}_K\{\phi_K(\mathbf{r}), Q_{Kij}(\mathbf{r})\}), \end{aligned} \tag{57}$$

$$
\begin{aligned}
f_K^{(2)}\{\phi_K(\mathbf{r}),Q_{Kij}(\mathbf{r})\} = {} & \frac{1}{2\phi_K}\left(C_{K00}\delta_{ij}+C_{K01}Q_{Kij}+\frac{1}{2}C_{K02}Q_{Kik}Q_{Kkj}\right)(\partial_i\phi_K)(\partial_j\phi_K) \\
& +(\partial_i\phi_K)\partial_j\left(L_{K0}Q_{Kij}+\frac{1}{2}L_{K01}\delta_{ij}Q_{Kkl}Q_{Kkl}+\frac{1}{2}L_{K02}Q_{Kik}Q_{Kkj}\right) \\
& +\frac{1}{2}L_{K1}\phi_K\partial_k Q_{Kij}\partial_k Q_{Kij} \\
& +\frac{1}{2}\phi_K(L_{K21}\partial_i Q_{Kij}\partial_k Q_{Kkj}+L_{K22}\partial_k Q_{Kij}\partial_i Q_{Kjk}).
\end{aligned}
\qquad (59)
$$

Table 1. Coefficients in $f_K^{(2)}$ for the rigid rod limit($N/\epsilon \to 0$) and the flexible limit($N/\epsilon \to \infty$). The subscripts K's are omitted.

	rigid rod limit	flexible limit
C_{00}	$Nb^2/12d$	$2b^2\epsilon/3d^2$
C_{01}	$Nb^2/12$	$4b^2\epsilon/3d$
C_{02}	$O((N/\epsilon)^2)$	$4b^2\epsilon/3$
L_1	$dNb^2/24$	$b^2\epsilon/6$
L_{21}	$dNb^2/12$	$O(\epsilon^2)$
L_{22}	$dNb^2/12$	$4b^2\epsilon/3$
L_0	$Nb^2/12$	$b^2\epsilon/d$
L_{01}	$O((N/\epsilon)^2)$	$-b^2\epsilon/12$
L_{02}	$O((N/\epsilon)^2)$	$b^2\epsilon$

with the second order term in the gradients

$$
f_K^{(2)}\{\phi_K(\mathbf{r}),Q_{Kij}(\mathbf{r})\} = -\frac{\phi_K(\mathbf{r})}{N_K}\eta_2\{h^{(0)}_{\phi_K}(\mathbf{r}),h^{(0)}_{S_{Kij}}(\mathbf{r})\}. \qquad (58)
$$

The calculation of η_2 is cumbersome but straightforward. Here we give only the final result of the calculation.

See equation (59) above.

The coefficients appearing in equation (59) are the functions of N_K/ϵ_K and can be calculated for arbitrary N_K/ϵ_K. However the explicit form of the coefficients is quite complicated. Thus we present the results separately in Appendix B and in Table 1 we show the values of the coefficients for the two limiting cases: the rigid rod limit ($N_K/\epsilon_K \to 0$) and the flexible limit ($N_K/\epsilon_K \to \infty$).

2.3 Free energy of interacting chains

In order to incorporate the interaction terms into the free energy, we employ here a simple random phase approximation (RPA). In the RPA response of polymers to external fields is considered to be the same as that of ideal polymers, however the fields acting on polymers are corrected to take into account monomer interactions.

The effective fields acting on polymers are taken to be

$$
h^{eff}_{\phi K} = h_{\phi K} - \frac{1}{2v_0}\sum_{K'}\epsilon_{KK'}\phi_{K'} + V, \qquad (60)
$$

$$
h^{eff}_{S_{Kij}} = h_{S_{Kij}} - \frac{1}{2v_0}\sum_{K'}w_{KK'}\tilde{S}_{K'ij}, \qquad (61)
$$

where $\epsilon_{KK'}$ is the isotropic interaction parameter between polymer species K and K' and $w_{KK'}$ is the Maier-Saupe anisotropic interaction parameter. The $\tilde{S}_{Kij}$ is the traceless part of S_{Kij}. Note that the "true" orientational order is expressed by the traceless part of S_{Kij}. Although we can incorporate interactions associated with the trace of S_{Kij} (or the fluctuation of the segment length), we do not consider them here. The field V should be added to equation (60) if the system is considered to be incompressible ($\sum_K \int d\mathbf{r}\phi_K(\mathbf{r}) = 1$). The fields $h_{\phi K}$ and $h_{S_{Kij}}$ appearing in the right hand side of equations (12, 13) are replaced by $h^{eff}_{\phi K}$ and $h^{eff}_{S_{Kij}}$ and the final expression for the free energy is

$$
\begin{aligned}
\beta v_0 F = \sum_K \int & d\mathbf{r}(f_K^{(0)}\{\phi_K(\mathbf{r}),Q_{Kij}(\mathbf{r})\} \\
& + f_K^{(2)}\{\phi_K(\mathbf{r}),Q_{Kij}(\mathbf{r})\}) \\
& + \int d\mathbf{r} f_{int}\{\phi_K(\mathbf{r}),Q_{Kij}(\mathbf{r})\},
\end{aligned}
\qquad (62)
$$

where $f_K^{(0)}$ and $f_K^{(2)}$ are given in equations (37) (or (43) for the rigid rod limit) and (59), respectively and

$$
\begin{aligned}
f_{int}\{\phi_K(\mathbf{r}),Q_{Kij}(\mathbf{r})\} = -\frac{1}{2}\sum_K\sum_{K'} & (\epsilon_{KK'}\phi_K(\mathbf{r})\phi_{K'}(\mathbf{r}) \\
& + w_{KK'}\tilde{S}_{Kij}(\mathbf{r})\tilde{S}_{K'ij}(\mathbf{r})).
\end{aligned}
\qquad (63)
$$

For an incompressible blend equation (63) can be written, by setting $\phi_A = \phi$ and $\phi_B = 1-\phi$,

$$
\begin{aligned}
f_{int} = {} & \chi\phi(1-\phi) - \frac{1}{2}(\epsilon_{AA}\phi + \epsilon_{BB}(1-\phi)) \\
& - \frac{1}{2}(w_{AA}\tilde{S}_{Aij}\tilde{S}_{Aij} + 2w_{AB}\tilde{S}_{Aij}\tilde{S}_{Bij} + w_{BB}\tilde{S}_{Bij}\tilde{S}_{Bij}),
\end{aligned}
\qquad (64)
$$

where $\chi = (\epsilon_{AA}+\epsilon_{BB}-2\epsilon_{AB})/2$ is the usual Flory interaction parameter.

3 Bulk behavior

3.1 Orientational order

We discuss here the isotropic-nematic phase transition of rigid rods without density modulation (ϕ is constant throughout the sample during the phase transition). We also suppose here that only one component can have an orientational order, thus we omit the subscript K in this section. We assume that the orientational order can be described by the following uniaxial form:

$$Q_{ij} = Q\left(n_i n_j - \frac{1}{d}\delta_{ij}\right). \tag{65}$$

Here n_i is a unit vector of arbitrary direction and Q represents the degree of nematic ordering. For the rigid rod limit ($N/\epsilon \to 0$), the free energy is given by equations (43, 64) as

$$f = \frac{\phi}{2N}\{-\mathrm{Tr}\ln(\mathbf{1} + dQ_{ij}) + dQ_{ii}\} - \frac{1}{2}w\phi^2 Q_{ij}Q_{ij}, \tag{66}$$

where the part of the free energy independent of Q_{ij} is omitted. Substituting equation (65) into equation (66), we obtain for $d = 3$

$$f = \frac{\phi}{2N}\left\{-\ln((1-Q)^2(1+2Q)) - \frac{2Nw\phi}{3}Q^2\right\}, \tag{67}$$

and the orientational order Q is the solution of $\partial f/\partial Q = 0$, which is equivalent to

$$Q\left(\frac{9}{2Nw\phi} - (1-Q)(1+2Q)\right) = 0. \tag{68}$$

Equation (68) can be easily solved and has an obvious solution $Q = 0$ and

$$Q = \frac{1}{4} \pm \frac{3}{4}\sqrt{1 - \frac{4}{Nw\phi}} \tag{69}$$

for $Nw\phi > 4$. We show in Figure 1 the orientational order Q as a function of $Nw\phi$. The upper branch with positive Q corresponds to normal nematic phase. Negative Q implies that polymers are oriented perpendicular to $\mathbf{n}$ and represents the discotic phase. Similar result has been obtained in reference [17]. Metastable nematic phase appears at

$$(Nw\phi)^* = 4 \tag{70}$$

and the corresponding order parameter is

$$Q^* = \frac{1}{4}\cdot \tag{71}$$

Isotropic state becomes unstable at

$$(Nw\phi)^{**} = \frac{9}{2}\cdot \tag{72}$$

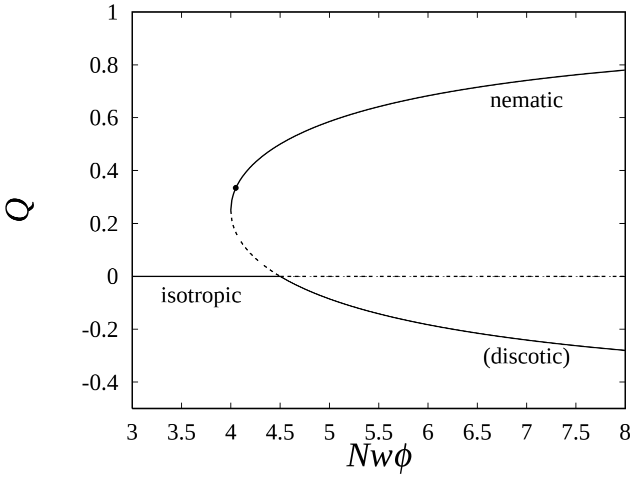


Fig. 1. Dependence of the orientational order Q on the parameter $Nw\phi$. Dotted lines are unstable branches. Filled circle implies the nematic-isotropic transition point.

At the nematic-isotropic transition point, the free energy of the nematic phase is equal to that of the isotropic phase (= 0) and the transition point is given by

$$(Nw\phi)^c = 4.05141, \tag{73}$$

which is shown by a filled circle in Figure 1. When w is independent of N or ϕ, lyotropic transition point ϕ_c is proportional to N^{-1}, which reproduces qualitatively the results of Onsager [6,28] and Flory [7,28]. The degree of ordering Q for the nematic phase at the transition point is

$$Q^c = 0.33448, \tag{74}$$

which is independent of N, w and ϕ and smaller than the value obtained by Onsager ($Q \simeq 0.84$) [6,28] or that by Maier and Saupe ($Q \simeq 0.44$) [8,28]. Finally we note that the width of the coexisting region of nematic and isotropic phases is proportional to N^{-1} and that the phase coexistence becomes more difficult with increasing the degree of polymerization.

3.2 Fluctuation of contour length

So far we have neglected the trace of Q_{ij}. We have stressed that the order parameter Q_{ij} is not necessarily traceless as in the usual case [28] because we deal with extensible chains. The trace of Q_{ij} implies the fluctuation of the segment length of the chain. If we take Q_{ij} as

$$Q_{ij} = \lambda\delta_{ij} + Q\left(n_i n_j - \frac{1}{d}\delta_{ij}\right), \tag{75}$$

the entropic part of the bulk energy is

$$f = \frac{\phi}{2N}\left\{-\ln((1+3\lambda-Q)^2(1+3\lambda+2Q)) + 9\lambda\right\}. \tag{76}$$

Equation (76) is minimized for fixed Q at

$$\lambda = \frac{1}{6}\left\{-(1+Q)+\sqrt{(1+Q)^2+8Q^2}\right\} > 0, \qquad (77)$$

which implies that segment length (or contour length) of polymer chains becomes larger in the ordered phase. The configuration of a semiflexible polymer chain in a nematic phase has been investigated theoretically [19,29] and it has been shown that polymer chains are stretched in the nematic phase. However, most of the theoretical studies are based on the microscopic model of polymer chains of constant segment length and the neutron scattering experiment [30] shows a stronger anisotropy than expected theoretically. The elongation of the contour length may explain this stronger anisotropy, although quantitative comparison is difficult because the free energy cannot be evaluated rigorously for chains of arbitrary rigidity.

4 Interfacial properties

In this section we discuss the properties of the interfaces between polymer-rich and polymer-poor regions. Since the form of the free energy obtained before is quite complicated, we restrict ourselves to some typical cases and show the results obtained numerically.

We consider a binary polymer blend and assume that only polymers of one species (denoted by A below) possess orientational order. The free energy for this system in terms of the order parameters $\phi = \phi_A$ and $Q_{ij} = Q_{Aij}$ can be written as

$$\begin{aligned} v_0\,\beta F = \int d\mathbf{r}\,\Big\{ & \frac{\phi}{N}\ln\phi + \frac{1-\phi}{N'}\ln(1-\phi) + \chi\phi(1-\phi) \\ & - \frac{\phi}{2N}\mathrm{Tr}\{\log(\mathbf{1}+dQ_{ij}) - dQ_{ii}\} - \frac{1}{2}w\phi^2\tilde{Q}_{ij}\tilde{Q}_{ij} \\ & + \frac{1}{2}\left(\frac{C_0}{\phi}+\frac{C_0'}{1-\phi}\right)(\partial_i\phi)^2 \\ & + L_0\left(\partial_i\phi\partial_j Q_{ij} + \frac{1}{2\phi}Q_{ij}\partial_i\phi\partial_j\phi\right) \\ & + \frac{1}{2}L_1\phi(\partial_k Q_{ij})^2 + \frac{1}{2}L_2\phi\left(\partial_i Q_{ij}\partial_k Q_{kj} + \partial_k Q_{ij}\partial_i Q_{jk}\right)\Big\}. \end{aligned} \qquad (78)$$

with $C_0 = Nb^2/12d, L_0 = Nb^2/12, L_1 = dNb^2/24$ and $L_2 = dNb^2/12$, where rigid rod limit is taken. In the numerical calculation shown below, we set $N' = N$ and $C_0' = C_0$ for simplicity.

We take the z-axis perpendicular to the plane interface (x-y plane) and assume that $\phi(\mathbf{r})$ and $Q_{ij}(\mathbf{r})$ depend only on z and that Q_{ij} is traceless. We also assume that the principal axis of Q_{ij} lies on the x-z plane throughout the system (which can be realized by a rotation around the z-axis) and set $Q_{xy} = Q_{yz} = 0$. We find a solution which minimizes the free energy (78) by numerically solving

$$\frac{\delta F}{\delta\phi(z)} = \mu, \qquad (79)$$

$$\frac{\delta F}{\delta Q_{ij}(z)} = \nu(z)\delta_{ij}, \qquad (80)$$

under the boundary conditions $\lim_{z\to\pm\infty} d\phi(z)/dz = \lim_{z\to\pm\infty} dQ_{ij}(z)/dz = 0$, $\lim_{z\to-\infty}\phi(z) = \phi_1$ and $\lim_{z\to\infty}\phi(z) = \phi_2$ with $\phi_1 < \phi_2$. The Lagrange multipliers μ and $\nu(z)$ are associated with the conservation of ϕ and the tracelessness of Q_{ij}, respectively.

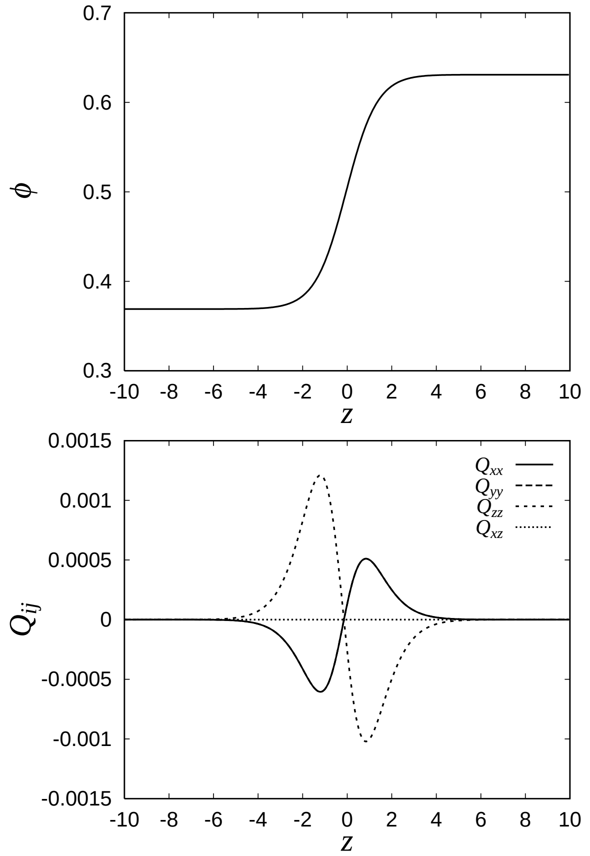


Fig. 2. Order parameter profiles for an isotropic-isotropic interface with $\chi N = 2.05$ and $wN = 0$. Note that $Q_{xx} = Q_{yy}$ throughout the system. Length z is measured in unit of Nb.

First we consider an interface between an isotropic A-poor region and an isotropic A-rich region. We show in Figure 2 the order parameter profiles obtained numerically by setting $\chi N = 2.05$ and $wN = 0$. We find that on the A-poor side ($z < 0$), $Q_{zz} > 0$ and $Q_{xx}, Q_{yy} < 0$, while $Q_{zz} < 0$ and $Q_{xx}, Q_{yy} > 0$ on the A-rich side ($z > 0$). We also find that $Q_{xz} = 0$ throughout the system. This result indicates that polymer chains of species A are oriented perpendicular on the A-poor side and parallel on the A-rich side. A similar behavior has been found in a lattice model [20] and for flexible polymers [21]. We also note that the rotational symmetry around the z-axis is not broken for this system.

Next we seek a solution for an interface between an isotropic A-poor region and a nematic A-rich region. We set $\chi N = 2.7$ and $wN = 4.8$ and the order parameter profiles are shown in Figure 3. We find a region on the A-poor side where polymer chains are oriented perpendicular to

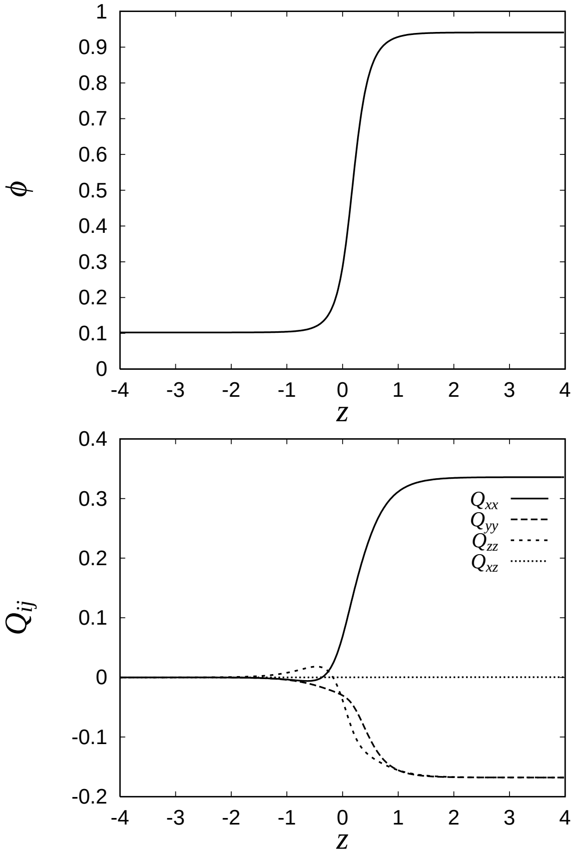


Fig. 3. Order parameter profiles for an isotropic-nematic interface with $\chi N = 2.7$ and $wN = 4.8$.

the interface ($Q_{zz} > 0$) as in the previous case, although the magnitude of the orientational order is small. There exists a transient biaxial region at the interface ($z \approx 0$) and in a nematic region, the orientational order parallel to the interface can be observed. Notice that the orientational order parallel to the interface is attributed to the coupling terms proportional to L_0 in equation (78), because they lower the free energy of the interface when $Q_{zz} < 0$ and Q_{zz} decreases with the increase of ϕ.

5 Conclusion

We have calculated the free energy of an inhomogeneous system composed of semiflexible polymers. Our calculations are based on the microscopic model of wormlike chains without the constraint of constant segment length and the free energy can be given in a gradient expansion and an expansion with respect to $Q_{ij} = S_{ij}/\phi$, orientational order per segment. The expansion coefficients can be evaluated for arbitrary stiffness (ϵ_K in Eq. (4)) of the chain and the bulk entropic part of the free energy can be rigorously calculated for the rigid rod limit. From the bulk free energy for the rigid rod limit, we have calculated the nematic-isotropic transition point and found that the contour length of the polymer chain is larger in a nematic phase than in an isotropic phase. Previous theoretical works have paid little attention to the fluctuation of contour length and it may explain the discrepancy between theories and experiments for the configuration of polymer chains in a nematic phase.

We have also investigated the properties of interfaces between two coexisting phases by numerically finding order parameter profiles for the interfaces which minimize the free energy. We have found for isotropic-isotropic and isotropic-nematic interfaces that polymer chains on the polymer-poor side tend to orient perpendicular to the interface, while on the polymer-rich side orientational order parallel to the interface is preferred.

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Appendix A: Two point correlation functions

In this Appendix we derive the explicit form for the two point correlation functions $c_1(s_1, s_2)$, $c_2(s_1, s_2)$ and $c_3(s_1, s_2)$ defined by equations (26, 46, 47).

Here we introduce the Fourier transform of $\mathbf{R}(s)$ [24]

$$\mathbf{R}(s) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dq \mathbf{R}_q e^{iqs}. \tag{A.1}$$

The summation over q is replaced by an integral, which corresponds to supposing an infinite chain. This treatment greatly simplifies the calculation because we can neglect the inhomogeneity due to the end of the chain [23], although it may play an important role in actual polymers [27].

The single chain Hamiltonian is defined in equation (4) and can be written using $\mathbf{R}_q$ as

$$\beta\mathcal{H}_0\{\mathbf{R}_q\} = \frac{1}{2} \int_{-\infty}^{\infty} dq \left(\frac{d}{lb} q^2 + \epsilon b q^4 \right) \mathbf{R}_q \mathbf{R}_{-q}. \tag{A.2}$$

Hereafter we omit the subscript K. From equation (A.2) we get

$$\langle \mathbf{R}_{qi} \mathbf{R}_{-qj} \rangle_0 = \frac{1}{\frac{d}{lb} q^2 + \epsilon b q^4} \delta_{ij}. \tag{A.3}$$

We obtain from equations (26, A.1, A.3)

$$\begin{aligned} c_1(s_1, s_2) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dq \frac{e^{iq(s_1 - s_2)}}{\frac{d}{lb} + \epsilon b q^2} \\ &= \frac{1}{2} \sqrt{\frac{l}{d\epsilon}} \exp\left\{ -\sqrt{\frac{d}{l\epsilon}} \frac{|s_1 - s_2|}{b} \right\}. \end{aligned} \tag{A.4}$$

We can derive equation (6) using equation (A.4) and noticing that $\langle \dot{\mathbf{R}}(s)^2 \rangle_0 = d c_1(s, s)$. Using (6) we can write equation (A.4) as

$$c_1(s_1, s_2) = \frac{1}{d} \exp\left\{ -\frac{d}{2\epsilon} \frac{|s_1 - s_2|}{b} \right\}. \tag{A.5}$$

$$\begin{aligned}c_2(s_1,s_2) &= \frac{1}{2\pi Nb}\int_{-\infty}^{\infty} dq \frac{1}{\frac{d^2}{4\epsilon b}q^2+\epsilon b q^4} e^{-iqs_2}(-iqNbe^{iqs_1}-1+e^{iqNb})\\ &= \frac{4\epsilon}{d^2N}\left(s_2-\frac{Nb}{2}\right)+\frac{2\epsilon b}{d^2}\frac{s_1-s_2}{|s_1-s_2|}\left(1-\exp\left(-\frac{d}{2\epsilon b}|s_1-s_2|\right)\right)\\ &\quad+\frac{8\epsilon^2 b}{d^3N}\exp\left(-\frac{dN}{4\epsilon}\right)\sinh\left(-\frac{d}{2\epsilon b}\left(s_2-\frac{Nb}{2}\right)\right). \end{aligned}\tag{A.7}$$

$$\begin{aligned}c_3(s_1,s_2) &= \frac{1}{2\pi Nb}\int_{-\infty}^{\infty} dq \frac{1}{\frac{d^2}{4\epsilon b}q^2+\epsilon b q^4}\left(e^{iqs_1}+\frac{1}{iqNb}(1-e^{iqNb})\right)\\ &\quad\times\left(e^{-iqs_2}-\frac{1}{iqNb}(1-e^{-iqNb})\right)\\ &= \frac{32\epsilon^4b^2}{d^5N^2}\left(1-\exp\left(-\frac{dN}{2\epsilon}\right)\right)+\frac{16\epsilon^3b^2}{d^4N}+\frac{4\epsilon Nb^2}{3d^2}\\ &\quad-\frac{2\epsilon b}{d^2}(s_1+s_2+|s_1-s_2|)+\frac{2\epsilon}{d^2N}(s_1^2+s_2^2)-\frac{4\epsilon^2b^2}{d^3}\exp\left(-\frac{d}{2\epsilon b}|s_1-s_2|\right)\\ &\quad-\frac{16\epsilon^3b^2}{d^4N}\exp\left(-\frac{dN}{4\epsilon}\right)\left(\cosh\left(\frac{d}{2\epsilon b}\left(\frac{Nb}{2}-s_1\right)\right)\right.\\ &\quad\left.+\cosh\left(\frac{d}{2\epsilon b}\left(\frac{Nb}{2}-s_2\right)\right)\right). \end{aligned}\tag{A.8}$$

Before discussing $c_2(s_1,s_2)$ and $c_3(s_1,s_2)$, we write the center of gravity $\mathbf{R}_G$ in terms of $\mathbf{R}_q$:

$$\begin{aligned}\mathbf{R}_G &= \frac{1}{Nb}\int_0^{Nb} ds \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dq \mathbf{R}_q e^{iqs}\\ &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dq \mathbf{R}_q \frac{1}{iqNb}(e^{iqNb}-1).\end{aligned}\tag{A.6}$$

Using (6, 46, 47, A.1, A.3, A.6) we can write $c_2(s_1,s_2)$ $c_3(s_1,s_2)$ as

See equations (A.7, A.8) above.

Appendix B: Explicit form of the coefficients in $\mathbf{f}_K^{(2)}$

Here we give the explicit form of the coefficients in equation (59). Throughout this appendix we omit the subscripts K. We present only the final results, which are given by

$$C_{00} = \frac{Nb^2}{12d}E_1, \tag{B.1}$$

$$C_{01} = \frac{Nb^2}{12D_2}E_1, \tag{B.2}$$

$$C_{02} = \frac{dNb^2}{6D_2^3}(D_2E_3-D_3E_2), \tag{B.3}$$

$$L_1 = \frac{dNb^2}{24D_2^2}F_1, \tag{B.4}$$

$$L_{21} = \frac{dNb^2}{12D_2^2}F_2, \tag{B.5}$$

$$L_{22} = \frac{dNb^2}{12D_2^2}F_3, \tag{B.6}$$

$$L_0 = \frac{Nb^2}{12D_2}F_4, \tag{B.7}$$

$$L_{01} = \frac{dNb^2}{24D_2^2}(F_1-F_5), \tag{B.8}$$

$$L_{02} = \frac{dNb^2}{6D_2^3}(D_2F_6-D_3F_4). \tag{B.9}$$

Here D_1, D_2 and D_3 are defined in equations (30, 31, 32) and

$$E_1 = \mathcal{I}_4(dN/2\epsilon), \tag{B.10}$$

$$\begin{aligned}E_2 &= -\frac{4}{5}\mathcal{I}_5(dN/2\epsilon)-\frac{16}{5}\mathcal{I}_5(dN/\epsilon)+\mathcal{I}_4(dN/2\epsilon)\\ &\quad+4\mathcal{I}_4(dN/\epsilon),\end{aligned}\tag{B.11}$$

$$\begin{aligned}E_3 &= \frac{2}{5}\mathcal{I}_6(dN/2\epsilon)+\frac{88}{15}\mathcal{I}_6(dN/\epsilon)-\frac{4}{5}\mathcal{I}_5(dN/2\epsilon)\\ &\quad-\frac{64}{5}\mathcal{I}_5(dN/\epsilon)+\frac{1}{2}\mathcal{I}_4(dN/2\epsilon)\mathcal{I}_2(dN/\epsilon)\\ &\quad+\frac{1}{2}\mathcal{I}_4(dN/2\epsilon)+6\mathcal{I}_4(dN/\epsilon)+\frac{4}{3}\mathcal{I}_3(dN/\epsilon),\end{aligned}\tag{B.12}$$

$$F_1 = 9\mathcal{I}_4(3dN/2\epsilon) - 8\mathcal{I}_3(dN/\epsilon), \tag{B.13}$$

$$F_2 = -\frac{3}{10}\mathcal{I}_5(dN/2\epsilon) - \frac{24}{5}\mathcal{I}_5(dN/\epsilon) + \frac{81}{10}\mathcal{I}_5(3dN/2\epsilon) + 2\mathcal{I}_4(dN/2\epsilon) - 4\mathcal{I}_4(dN/\epsilon), \tag{B.14}$$

$$F_3 = \frac{3}{10}\mathcal{I}_5(dN/2\epsilon) + \frac{24}{5}\mathcal{I}_5(dN/\epsilon) - \frac{81}{10}\mathcal{I}_5(3dN/2\epsilon) - \mathcal{I}_4(dN/2\epsilon) - 4\mathcal{I}_4(dN/\epsilon) + 9\mathcal{I}_4(3dN/2\epsilon), \tag{B.15}$$

$$F_4 = 2\mathcal{I}_4(dN/\epsilon) - \mathcal{I}_4(dN/2\epsilon), \tag{B.16}$$

$$F_5 = \frac{8}{15}\mathcal{I}_5(dN/2\epsilon) - \frac{8}{15}\mathcal{I}_5(dN/\epsilon) + 2\mathcal{I}_4(dN/2\epsilon)\mathcal{I}_2(dN/\epsilon) - \frac{8}{3}\mathcal{I}_3(dN/2\epsilon)\mathcal{I}_2(dN/\epsilon) - \frac{2}{3}\mathcal{I}_4(dN/2\epsilon) - \frac{4}{3}\mathcal{I}_4(dN/\epsilon) + 9\mathcal{I}_4(3dN/2\epsilon) - \frac{16}{3}\mathcal{I}_3(dN/\epsilon), \tag{B.17}$$

$$F_6 = \frac{13}{20}\mathcal{I}_5(dN/2\epsilon) - \frac{16}{15}\mathcal{I}_5(dN/\epsilon) + \frac{81}{20}\mathcal{I}_5(3dN/2\epsilon) - \frac{1}{2}\mathcal{I}_4(dN/2\epsilon), \tag{B.18}$$

where $\mathcal{I}_n$ is defined in equation (33).

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