Free-Energy Functionals for Semiflexible Polymer-Solutions and Blends

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Free Energy Functionals for Semiflexible Polymer Solutions and Blends

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Received November 30, 1992; Revised Manuscript Received February 9, 1993

ABSTRACT: We present free energy functionals that describe the phase behavior of polymers of arbitrary flexibility in solution and in binary blends. The functionals were calculated from a microscopic model of wormlike chains and depend only on a small set of parameters, most of which can be measured from the pure components. These parameters are the Flory χ parameter, which measures the strength of isotropic interactions, the Maier–Saupe parameter, which measures the strength of anisotropic interactions, and the pure-component bending rigidities and molecular weights. The free energy expressions provide the basis for bulk and interfacial thermodynamic analysis of liquid crystalline and conjugated polymer solutions and blends.

I. Introduction

Two decades ago, the discovery that extremely high strength fibers could be spun from stiff polymers in solution provided the impetus for further research in the field of liquid crystalline polymers.[1] Since then, a great deal of attention has focused on the equilibrium and transport properties of liquid crystalline polymer solutions and melts. Many liquid crystalline polymers are stiff due to the presence of rigid mesogenic groups along their backbones. In addition, conjugated polymers are also known to be quite stiff due to electronic delocalization. Indeed, a modern technique for processing conjugated polymers exploits their propensity to form liquid crystalline phases in solution.[2]

In spite of the significant commercial interest in liquid crystalline and conjugated polymer solutions and melts, our understanding of their phase behaviors and dynamics is still quite limited, particularly in the areas of interfacial phenomena and blend thermodynamics. For example, the role of backbone flexibility in establishing interfacial tensions and polymer–polymer miscibility has only recently garnered attention.[3,4] As interest in polymeric composites (consisting of blends of stiff and flexible macromolecules) grows, these issues will likely become even more important.

The present paper is the first in a series of publications that will address the bulk and interfacial thermodynamics of polymeric composites. Of key interest is the dependence of quantities, such as interfacial tension, that can be correlated with strength, adhesion, and toughness, on microscopic parameters such as persistence lengths. These microscopic parameters can be tailored at the time of synthesis; thus, our structure–property relations will permit a systematic approach to the modification of materials properties. In this first paper, we develop a theoretical framework for achieving these goals. We construct Landau expansions for the free energies of semiflexible polymer solutions and blends. These free energy expressions are the basis for subsequent calculations of phase diagrams, interfacial properties, and dynamics and are intended to apply to polymer solutions and composites that contain macromolecules of arbitrary, but prescribed, flexibilities. Our free energy expressions should be equally valid for conjugated, main-chain liquid crystalline or flexible (conventional) linear polymers.

Our approach is to calculate a free energy functional that depends on two order parameters, namely the concentration and orientational density of polymer segments. Ordinarily, the phase behavior of flexible polymers[5] is described in terms of a single order parameter, the concentration. However, due to the fact that individual monomers may have a rigid, anisotropic character, a description of stiff polymers must include the orientational density as a second order parameter. To describe both the isotropic–nematic transition and ordinary phase separation, we expand to arbitrary order in concentration and up to fourth order in orientation density, by combining a density functional theory with a Landau–de Gennes theory for the orientational order parameter. A similar approach was adopted by Khokhlov and Semenov,[6,7] Brochard, Jouffroy, and Levinson,[8] Doi and Kuzuu,[9] ten Bosch, Pinton, Maissa, and Sixou,[10] and by Gupta and Edwards.[11] Khokhlov and Semenov[6] derived free energy expressions for solutions and melts of arbitrary rigidity but did not consider blends. In addition, their expressions do not include nonlocal terms. Brochard and co-workers[8] neglected the persistence-length dependence of the coefficients of terms coupling orientation and concentration; thus their work is more applicable to side-chain than to main-chain liquid crystalline polymers. ten Bosch and co-workers,[9] on the other hand, formulated the free energy as a functional of concentration and orientation for persistent chains. Their free energy is left in the form of integrals over pair potentials. The advantage of our work is that we have explicitly computed the coefficients of the terms in the free energy expansion, so they are *not unknown parameters*. We have obtained them as precise functions of the chain lengths, persistence lengths, and interactions, by evaluating correlation functions in the concentration and orientation for wormlike chains with bending rigidity. In calculating our free energy functional, we have included nonlocal terms in both the concentration and the orientational density. These "square-gradient" terms will allow us to investigate the interfacial structure between two phases in phase-separated polymer composites.[12] Gupta and Edwards have recently formulated a similar mean field theory for wormlike chains. The difference between their work and ours is that we consider chains that are locally inextensible, while they allow local extensibility. Their approximation yields coefficients for the terms involving the orientational order parameter that differ from ours by factors on the order of unity. They considered polymer solutions and melts but have not

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examined blends. In addition, they have not calculated square-gradient terms, which might be significantly different in their theory because of local extensibility.

Carton and Leibler[13] were the first to calculate the coefficients of a Landau expansion in concentration and orientation from a microscopic model of polymers. They studied the conformations of Gaussian chains near polymer–solvent or polymer–polymer interfaces. Fredrickson and Leibler[14] have investigated the bulk phase behavior of random liquid crystalline copolymers within the same framework. In addition, Holyst and Schick[10] have studied blends of Gaussian chains with completely rigid rods and binary blends of rigid rods within a Landau expansion in concentration and orientation. In our case, we use a microscopic model of wormlike chains[15] rather than Gaussian chains to calculate the expansion coefficients. There are two advantages to using wormlike chains. First, we can continuously tune the persistence length from the flexible limit to the rod limit. Second, Gaussian chains are unphysical in that the orientation of each segment is completely uncorrelated with that of neighboring segments. Within mean field theory, this property causes the square-gradient terms of the orientational density in the free energy functional to vanish. In other words, the Frank constants for Gaussian chains are identically zero. By using wormlike chains, we have obtained estimates for the Frank constants for solutions and blends of polymers of arbitrary flexibility.

To calculate the free energy functional of a polymer blend, we begin by computing the free energy functional of a single polymer species in solution. In section II, we describe the solution calculation. This calculation is divided into two parts; in the first, we derive the Landau–Ginzburg free energy for the polymer solution as an expansion in both order parameters. We then generalize this result by deriving a density functional theory that holds for arbitrary concentrations, where we expand in the orientational density only. The resulting free energy functional can be applied to the limit of strong segregation of blend components but cannot be used deep in the nematic phase. In section III, we generalize the free energy of a polymer solution to the free energy of a binary polymer blend. Section IV contains a discussion of our results.

II. Free Energy of a Semiflexible Polymer Solution

We begin with a solution of semiflexible polymers of volume fraction c. For simplicity, we assume that the chains consist of rigid cylindrical segments of fixed length a_0, diameter $d_0 \equiv a_0\sqrt{4/\pi}$ and volume $v_0 = a_0^3$. Each chain contains N segments. The flexibility of the polymer is characterized by a dimensionless elastic constant κ; the persistence length is κa_0.

In calculating the mean field free energy functional, we retain two interaction parameters. The isotropic interaction between segments is characterized by the conventional Flory parameter χ, which favors demixing of polymer from solvent. We also include a quadrupolar interaction characterized by a Maier–Saupe parameter w that favors mutual alignment of segments. This interaction could arise from anisotropic interactions or from steric excluded volume interactions.[16]

We now introduce two microscopic order parameters. The first describes the deviation of the local volume fraction of polymer $\hat{\phi}(\vec{r})$ from the average global volume fraction c:

$$\hat{\varphi}(\vec{r}) = \hat{\phi}(\vec{r}) - c \qquad (2.1)$$

where

$$\hat{\phi}(\vec{r}) = a_0^3 \sum_n \int_0^N ds\, \delta(\vec{r} - \vec{r}_n(s)) \qquad (2.2)$$

The second order parameter is the standard local nematic tensor order parameter

$$\hat{S}^{ij}(\vec{r}) = a_0^3 \sum_n \int_0^N ds\, \left[u_n^i(s) u_n^j(s) - \frac{1}{3}\delta^{ij} \right] \delta(\vec{r} - \vec{r}_n(s)) \qquad (2.3)$$

where the solution is assumed to be isotropic on average. The index n runs over chains and the index s runs over segments in a given chain. We define $\vec{r}_n(s)$ as the position vector and $u_n^i(s)$ as the ith component of the tangent vector of segment s on chain n. The length of the tangent vector is constrained to be unity for all segments. The order parameters are defined such that the thermal average of $\hat{\varphi}$ vanishes in the homogeneous single-phase region, and the thermal average of $\hat{S}^{ij}$ vanishes in the isotropic phase.[17]

The Hamiltonian for the polymer solution is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{int} \qquad (2.4)$$

where $\mathcal{H}_0$ is the wormlike chain Hamiltonian, describing the energy penalty for bending the *individual* polymers:

$$\beta\mathcal{H}_0 = \frac{1}{2}\kappa \sum_n \int_0^N ds \left(\frac{\partial \vec{u}_n}{\partial s} \right)^2 \qquad (2.5)$$

The interaction Hamiltonian is taken to be of the Edwards form in both concentration and orientation:

$$\beta\mathcal{H}_{int} = \rho_0\chi \int d\vec{r}\, \hat{\phi}(\vec{r})(1 - \hat{\phi}(\vec{r})) - \frac{1}{2}\rho_0 w \int d\vec{r}\, \hat{\vec{S}}(\vec{r}){:}\hat{\vec{S}}(\vec{r}) \qquad (2.6)$$

where $\rho_0 = 1/a_0^3$ is the segment density and χ and w characterize the strengths of isotropic and anisotropic interactions, respectively.

The Hamiltonian in eq 2.4 leads to a free energy that can be expressed as an expansion in powers of the two order parameters. Since we are primarily interested in the phase behavior in the vicinity of an isotropic–nematic or phase-separation transition, a Landau–Ginzburg expansion should be sufficient. The expansion does not accurately describe properties of the low-temperature nematic phase, however, as originally pointed out by de Gennes.[18] To calculate the free energy, we must start with the partition function

$$Z = \int \mathcal{D}\vec{r} \int \mathcal{D}\vec{u}\, e^{-\beta\mathcal{H}} \delta\left(\vec{u} - \frac{1}{a_0}\partial\vec{r}/\partial s \right) \delta(u^2 - 1) \qquad (2.7)$$

where the integrals denote functional integrals over the positions and orientations of all segments and the delta functions constrain $a_0\vec{u}_n(s) = \partial\vec{r}_n/\partial s$ and $u_n^2(s) = 1$ for all n and s. In order to separate the interaction part of the Hamiltonian, we rewrite eq 2.7 as

$$Z = \int \mathcal{D}\vec{\vec{S}} \int \mathcal{D}\phi\, e^{-\beta\mathcal{H}_{int}} \int \mathcal{D}\vec{r} \int \mathcal{D}\vec{u} \times \\ \delta(\vec{\vec{S}} - \hat{\vec{S}})\delta(\phi - \hat{\phi})e^{-\beta\mathcal{H}_0}\delta\left(\vec{u} - \frac{1}{a_0}\partial\vec{r}/\partial s \right)\delta(u^2 - 1) \qquad (2.8)$$

The functional Dirac delta functions can be written as functional integrals by introducing conjugate fields h_ϕ and $\vec{\vec{h}}_S$:

$$\delta(\phi - \hat{\phi}) = \int \mathcal{D}h_\varphi \exp[i \int d\vec{r}\, h_\phi(\phi - \hat{\phi})]$$

$$\delta(\vec{\vec{S}} - \hat{\vec{S}}) = \int \mathcal{D}h_S \exp[i \int d\vec{r} \, \vec{\vec{h}}_S : (\vec{\vec{S}} - \hat{\vec{S}})] \quad (2.9)$$

After these manipulations, the partition function assumes the form

$$Z = \int \mathcal{D}\phi \, \exp[-\rho_0 \chi \int d\vec{r} \, \phi(\vec{r})(1 - \phi(\vec{r}))] \int \mathcal{D}\vec{\vec{S}} \times$$

$$\exp\left[\frac{1}{2}\rho_0 w \int d\vec{r} \, \vec{\vec{S}} : \vec{\vec{S}}\right] \int \mathcal{D}h_\varphi \, \exp[i \int d\vec{r} \, h_\phi \phi] \int \mathcal{D}\vec{\vec{h}}_S \times$$

$$\exp[i \int d\vec{r} \, \vec{\vec{h}}_S : \vec{\vec{S}}] Z_0 \quad (2.10)$$

where Z_0, the partition function for a noninteracting system, is given by

$$Z_0 = \int \mathcal{D}\vec{r} \int \mathcal{D}\vec{u} \, \exp[-\beta \mathcal{H}_0 - i \int d\vec{r} \, (h_\phi \hat{\phi} + \vec{\vec{h}}_S : \hat{\vec{S}})] \times$$

$$\delta\left(\vec{u} - \frac{1}{a_0}\partial\vec{r}/\partial s\right)\delta(u^2 - 1)$$

$$\equiv \langle \exp[-i \int d\vec{r} \, (h_\phi \hat{\phi} + \vec{\vec{h}}_S : \hat{\vec{S}})] \rangle_0 \quad (2.11)$$

The partition function Z_0 cannot be evaluated exactly. We perform a cumulant expansion by expanding the exponential in powers of the conjugate fields h_ϕ and $\vec{\vec{h}}_S$. The integrals over h_ϕ and $\vec{\vec{h}}_S$ are then approximated using the saddle-point method. This last step is in essence a Legendre transformation that expresses the fields h_ϕ and $\vec{\vec{h}}_S$ in terms of the order parameters ϕ and $\vec{\vec{S}}$. The remainder of the calculation is similar to the calculations presented in section III of Leibler's paper[19] and those of Appendix A of Ohta and Kawasaki's paper,[20] so we will not discuss it here. We have carried the expansion to fourth order in the two order parameters. Note that the procedure involves the evaluation of single-chain correlation functions such as $\langle \phi(\vec{r})\vec{\vec{S}}(\vec{r}')\rangle_0$. An illustrative calculation of this correlation function is provided in the Appendix. Unfortunately, the correlation functions cannot be calculated exactly for the wormlike chain model; we have calculated them within a gradient expansion, which restricts our theory to slow spatial variations of the two order parameter fields.

The Landau–Ginzburg free energy is conveniently expressed as a dimensionless free energy per monomer

$$\mathcal{F}[\varphi, \vec{\vec{S}}] = \frac{\beta F[\varphi, \vec{\vec{S}}]}{\rho_0 V} \quad (2.12)$$

The free energy $\mathcal{F}$ in reciprocal space is expressed in terms of an expansion in powers of the order parameters as

$$\mathcal{F} = \frac{1}{V^2}\sum_q \mathcal{F}_2 - \frac{1}{V^3}\sum_{q_1, q_2, q_3} \mathcal{F}_3 \delta_{q_1 + q_2, q_3} +$$

$$\frac{1}{V^4}\sum_{q_1, q_2, q_3, q_4} \mathcal{F}_4 \delta_{q_1 + q_2 + q_3, q_4} + \dots \quad (2.13)$$

where

$$\mathcal{F}_2 = \frac{1}{2}(A - 2\chi + M_0 q^2)\varphi(q)\varphi(-q) - L_0 q^i q^j \varphi(q) S^{ij}(-q) +$$

$$\frac{1}{2}(B - w + L_1 q^2)\vec{\vec{S}}(q):\vec{\vec{S}}(-q) + \frac{1}{2}L_2 q^i q^j S^{ik}(q)S^{jk}(-q) \quad (2.14)$$

$$\mathcal{F}_3 = \frac{1}{3}C_0 \varphi(q_1)\varphi(q_2)\varphi(q_3) +$$

$$[C_{11}(q_1^i q_1^j + q_2^i q_2^j) + C_{12} q_1^i q_2^j]\varphi(q_1)\varphi(q_2)S^{ij}(q_3) +$$

$$C_2 \varphi(q_1)\vec{\vec{S}}(q_2):\vec{\vec{S}}(q_3) + \frac{1}{3}C_3 S^{ij}(q_1)S^{ik}(q_2)S^{jk}(q_3) \quad (2.15)$$

$$\mathcal{F}_4 = \frac{1}{4}D_0 \varphi(q_1)\varphi(q_2)\varphi(q_3)\varphi(q_4) +$$

$$\frac{3}{2}D_2 \varphi(q_1)\varphi(q_2)\vec{\vec{S}}(q_3):\vec{\vec{S}}(q_4) +$$

$$D_3 \varphi(q_1)S^{ij}(q_2)S^{ik}(q_3)S^{jk}(q_4) +$$

$$\frac{1}{4}D_4 \vec{\vec{S}}(q_1):\vec{\vec{S}}(q_2)\vec{\vec{S}}(q_3):\vec{\vec{S}}(q_4) \quad (2.16)$$

where we have included all terms up to order q^2 in $\mathcal{F}_2$, the lowest order terms in q in $\mathcal{F}_3$, and only terms of order q^0 in $\mathcal{F}_4$.

The coefficients A, B, C_i, D_i, and L_i are functions of the average volume fraction c, the persistence length κ, the chain length N, and the ratio $\lambda = N/\kappa$. The second order coefficients are

$$A = \frac{1}{cN}$$

$$B = \frac{45}{4c\kappa I_1(3\lambda)}$$

$$M_0/A = \frac{1}{9}\kappa N J_0(\lambda)a_0^2$$

$$L_0 = \frac{\kappa}{2c}\frac{J_1(\lambda)}{I_1(3\lambda)}a_0^2$$

$$L_1/B = \frac{\kappa^2}{126}\frac{J_2(3\lambda)}{I_1(3\lambda)}a_0^2$$

$$L_2/B = \frac{\kappa^2}{7}\frac{J_3(3\lambda)}{I_1(3\lambda)}a_0^2 \quad (2.17)$$

The third order coefficients are

$$C_0 = \frac{A}{2c}$$

$$C_{11} = \frac{47\kappa}{64c^2}I_1(3\lambda)J_4(\lambda)a_0^2$$

$$C_{12} = \frac{\kappa}{c^2}I_1(3\lambda)J_5(\lambda)a_0^2$$

$$C_2 = \frac{B}{2c}$$

$$C_3 = \frac{2025}{56c^2\kappa}\frac{I_2(3\lambda)}{[I_1(3\lambda)]^3} \quad (2.18)$$

Finally, the fourth order coefficients are

$$D_0 = \frac{A}{3c^2}$$

$$D_2 = \frac{B}{3c^2}$$

$$D_3 = \frac{2C_3}{3c}$$

$$D_4 = \frac{10665}{196c^3\kappa}\frac{I_3(3\lambda)}{[I_1(3\lambda)]^4} \quad (2.19)$$

All of the functions $I_i(\lambda)$ and $J_i(\lambda)$ reduce to unity in the flexible limit ($\lambda \to \infty$) and are of order unity for all $\lambda \geq$

1. They vanish as powers of λ in the rigid rod limit ($\lambda \to 0$). We find

$$I_1(x) = 1 - (1 - e^{-x})/x$$

$$I_2(x) = 2I_1(x) - (1 - e^{-x})$$

$$I_3(x) = \frac{225}{316}\frac{[I_2(x)]^2}{I_1(x)} + \frac{91}{316}I_4(x) \qquad (2.20)$$

where

$$I_4(x) = 1 - \frac{269}{130x} - \frac{50}{91}xe^{-x} + \frac{1490}{637}e^{-x} + \frac{3370}{4459x}e^{-x} + \frac{35}{26x}e^{-2x} - \frac{729}{22295x}e^{-10x/3} \qquad (2.21)$$

The functions $J_i(x)$ are given by

$$J_0(x) = 1 - \frac{3}{x} + \frac{6}{x^2}I_1(x)$$

$$J_1(x) = 1 - \frac{8}{3x} + \frac{26}{9x^2} - \frac{3}{x^2}e^{-x} + \frac{1}{9x^2}e^{-3x}$$

$$J_2(x) = 1 - \frac{5}{2x} + 2\left(1 + \frac{1}{x}\right)e^{-x} + \frac{1}{2x}e^{-2x}$$

$$J_3(x) = 1 - \frac{29}{6x} + \frac{63}{10x}e^{-x/3} - \frac{1}{3}e^{-x} - \frac{3}{2x}e^{-x} + \frac{1}{30x}e^{-2x}$$

$$J_4(x) = 1 - \frac{3}{x}I_1(x) + \frac{1}{3x}I_1(3x)$$

$$J_5(x) = 1 + \frac{3}{2x} - \frac{47}{3x^2} + \frac{262}{9x^3} - \frac{27}{2x^2}e^{-x} - \frac{117}{4x^3}e^{-x} + \frac{1}{3x^2}e^{-3x} + \frac{5}{36x^3}e^{-3x} \qquad (2.22)$$

The Landau–Ginzburg free energy appears quite complicated, but when it is separated into terms involving only φ, terms involving only $\overset{\leftrightarrow}{S}$, and coupling terms, the physical interpretation is more transparent. The terms involving φ alone constitute the usual Landau–Ginzburg expansion in φ. Thus, the parameter A is the coefficient of the φ^2 term obtained by expanding the Flory–Huggins free energy in powers of φ around c:

$$\mathscr{F}_{FH} = \frac{\phi_1}{N}\log\phi_1 + \phi_2\log\phi_2 + \chi\phi_1\phi_2 \qquad (2.23)$$

where $\phi_1 = c + \varphi$ and $\phi_2 = 1 - c - \varphi$. The terms involving $\overset{\leftrightarrow}{S}$ alone constitute a Landau–de Gennes expansion of the orientational free energy of the form

$$\mathscr{F}_{LdG} = \frac{1}{2}(B - w)\overset{\leftrightarrow}{S}:\overset{\leftrightarrow}{S} - \frac{1}{3}C_3 S^{ij}S^{ik}S^{jk} + \frac{1}{4}D_4(\overset{\leftrightarrow}{S}:\overset{\leftrightarrow}{S})^2 \qquad (2.24)$$

We can rewrite the free energy in a more physically transparent form by transforming into real space and recasting it in the following form

$$\mathscr{F} = \frac{1}{V}\int d\vec{r}\,\tilde{\mathscr{F}}[\phi,\overset{\leftrightarrow}{S}] \qquad (2.25)$$

where

$$\tilde{\mathscr{F}} = \mathscr{F}_{FH} + \mathscr{F}_{LdG} + \mathscr{F}_{grad} \qquad (2.26)$$

The first term is simply the Flory–Huggins free energy of

a polymer solution, eq 2.23, with $\phi_1 = \phi(\vec{r})$ and $\phi_2 = 1 - \phi(\vec{r})$, where $\phi(\vec{r})$ is the average *local* volume fraction of polymer. The second term is the Landau–de Gennes free energy, where the coefficients $B(\phi)$, $C_3(\phi)$, and $D_4(\phi)$ are given by eqs 2.17–2.19 with the average *global* volume fraction c replaced by the average *local* volume fraction $\phi(\vec{r})$. Finally, the gradient terms in the free energy are

$$\mathscr{F}_{grad} = \frac{1}{2}L_1(\phi)(\partial_k S^{ij})^2 + \frac{1}{2}L_2(\phi)\partial_i S^{ik}\partial_j S^{jk} - L_0(\phi)\partial_i\phi\partial_j S^{ij} + \frac{1}{2}M_0(\phi)(\nabla\phi)^2 \dots \qquad (2.27)$$

where $M_0, L_1, L_2,$ and L_0 are given by their expressions in eq 2.17 with c replaced by ϕ.

If we now expand eq 2.26 in powers of φ, where $\phi = c + \varphi$, we recover all of the coefficients in eqs 2.17–2.19. Thus, the expansion of the term $^1/_2 B(\phi)S^{ij}S^{ij}$, for example, yields

$$\frac{1}{2}B\,S^{ij}\,S^{ij} - C_2\varphi S^{ij}\,S^{ij} + \frac{3}{2}D_2\varphi^2\,S^{ij}\,S^{ij} + \dots \qquad (2.28)$$

with B, C_2, and D_2 given by eqs 2.17–2.19. In fact, we can show that the above expansion yields the correct coefficients of *all* the terms of the form $\phi^n\,S^{ij}\,S^{ij}$ of the Landau–Ginzburg free energy. For this demonstration, we employ a density functional method similar to that used by Tang and Freed.[21] In this approach, we again express the partition function Z in terms of the single-chain partition function Z_0, as in eq 2.10 where Z_0 is given by eq 2.11. In developing the Landau–Ginzburg expansion, we calculated Z_0 by expanding in powers of h_ϕ and h_S. In contrast, in the density functional approach, we expand h_ϕ and h_S in gradients around the center-of-mass $\vec{r}_0$, given by $\vec{r}_0 = (1/N)\int_0^N ds\,\vec{r}(s)$. The term $\int d\vec{r}\,h_\phi(\vec{r})\phi(\vec{r})$ in the integrand of Z_0 then becomes

$$\int d\vec{r}\,h_\phi(\vec{r})\hat{\phi}(\vec{r}) = h_\phi(\vec{r}_0)\int d\vec{r}\,\hat{\phi}(\vec{r}) + \partial_i h_\phi(\vec{r}_0)\int d\vec{r}\,\hat{\phi}(\vec{r})R_i + \frac{1}{2}\partial_i\partial_j h_\phi(\vec{r}_0)\int d\vec{r}\,\hat{\phi}(\vec{r})R_iR_j + \dots \qquad (2.29)$$

where $R = \vec{r} - \vec{r}_0$. Now recall the $\hat{\phi}$ for a single chain is defined as

$$\hat{\phi}(\vec{r}) = a_0^3\int_0^N ds\,\delta(\vec{r} - \vec{r}(s)) \qquad (2.30)$$

Thus, eq 2.29 can be simplified to

$$\rho_0\int d\vec{r}\,h_\phi(\vec{r})\hat{\phi}(\vec{r}) = h_\phi(\vec{r}_0)N + \frac{1}{2}\partial_i\partial_j h_\phi(\vec{r}_0)\int_0^N ds(\vec{r}(s) - \vec{r}_0)_i(\vec{r}(s) - \vec{r}_0)_j + \dots \qquad (2.31)$$

Similarly, we can expand $\overset{\leftrightarrow}{h}_S(\vec{r})$ around the center-of-mass and replace the integral $\int d\vec{r}\,\overset{\leftrightarrow}{h}_S(\vec{r}):\overset{\leftrightarrow}{S}(\vec{r})$ with an expansion similar to eq 2.31. We then expand the partition function in powers of $\overset{\leftrightarrow}{h}_S(\vec{r}_0)$ and the gradients of $h_\phi(\vec{r}_0)$ and $\overset{\leftrightarrow}{h}_S(\vec{r}_0)$. The rest of the calculation is a straightforward extension of Tang and Freed's calculation.[21] In the end, we exactly recover the free energy in eq 2.26. This remarkable result shows that the density functional form of the free energy in terms of ϕ and S, valid for arbitrary ϕ, can be obtained trivially from the Landau–Ginzburg expansion, valid for small φ, by replacing the global volume fraction c with the local volume fraction ϕ in the coefficients in eq 2.17–2.19.

Finally, we remark that a density functional theory can be constructed to be valid for arbitrary ϕ *and* $\overset{\leftrightarrow}{S}$ for a discrete model of freely jointed chains, by evaluating $\langle$exp$[-\rho_0 h_S(\vec{r}_0)\colon\int d\vec{r}\ \overset{\leftrightarrow}{S}(\vec{r})]\rangle_0$ exactly. (This quantity cannot be evaluated exactly for wormlike chains, so there we are forced to expand in $\overset{\leftrightarrow}{h}_S$.) In the case of freely jointed chains, the Legendre transformation cannot be carried out analytically, but it can be done numerically.

III. Free Energy of a Liquid Crystalline Polymer Blend

The free energy of a blend of two polymers is readily obtained once the free energy of a polymer solution is known. We consider a blend of two species, A and B, with bending rigidities κ_A and κ_B, molecular weights, N_A and N_B, the volume fractions ϕ_A and ϕ_B. The entropic terms are obtained by adding the entropic terms for two polymer solutions, one with volume fraction ϕ_A of species A, and the other with volume fraction ϕ_B of species B, with the solvent volume fraction set to zero. We introduce several new interaction terms; the isotropic interactions are now characterized by χ_{AA}, χ_{BB}, and χ_{AB}, and the anisotropic interactions are characterized by w_{AA}, w_{BB}, and w_{AB}. Finally, there are now four order parameters: ϕ_A, ϕ_B, $\overset{\leftrightarrow}{S}_A$, and $\overset{\leftrightarrow}{S}_B$. A theory with four order parameters is unwieldy, so we reduce the number of order parameters to two. First, we eliminate ϕ_B by assuming that the blend is incompressible, so that $\phi_B = 1 - \phi_A \equiv 1 - \phi$. Finally, we reduce the number of orientational order parameters from two to one as follows. We define sum and different order parameters as $\overset{\leftrightarrow}{S} = \overset{\leftrightarrow}{S}_A + \overset{\leftrightarrow}{S}_B$ and $\overset{\leftrightarrow}{Q} = \overset{\leftrightarrow}{S}_A - \overset{\leftrightarrow}{S}_B$. We then integrate over the difference $\overset{\leftrightarrow}{Q}$ using the saddle-point method. By integrating over $\overset{\leftrightarrow}{Q}$, we lose the ability to distinguish between phases with the same concentration $\phi_A \equiv \phi$ and the same $\overset{\leftrightarrow}{S}$, but different $\overset{\leftrightarrow}{Q}$. It is difficult to imagine a physical realization of such a situation; in most cases, the compositions of the two phases will be different or the orientational sums $\overset{\leftrightarrow}{S}$ will be different. Note that we still retain the ability to distinguish between two nematic phases, for example, where one phase is rich in species A and the other is rich in species B. Thus our two order parameter description, in terms of the volume fraction of species A, ϕ, and total orientation density, $\overset{\leftrightarrow}{S}$, will describe all phases of interest to us.

For an incompressible blend, the only combination of isotropic interaction parameters which enters the free energy is the standard $\chi = \frac{1}{2}(\chi_{AA} + \chi_{BB}) - \chi_{AB}$. The situation for the anisotropic interaction parameters is more complicated. In the results that follow, we assume that $w_{AA} = w_{BB} = w_{AB} \equiv \frac{1}{4}w$. We have calculated the free energy functional for the general case, but the expression is too lengthy to be presented here. The interested reader should contact us for the general result.

The free energy functional for a blend has exactly the same form as the free energy functional for a polymer solution in eq 2.26, where the Flory–Huggins free energy is now the Flory–Huggins blend free energy:

$$\mathcal{F}_{FH} = \frac{\phi}{N_A}\log\phi + \frac{1-\phi}{N_B}\log(1-\phi) + \chi\phi(1-\phi) \qquad (3.1)$$

The Landau–de Gennes expansion and the gradient free energy have the same forms as in eqs 2.24 and 2.27, but with different coefficients. The ratios of the chain lengths to the persistence lengths are now given by $\lambda_A = N_A/\kappa_A$ and $\lambda_B = N_B/\kappa_B$. In addition, we define new variables $\tilde{\kappa}_A = \kappa_A I_1(3\lambda_A)$ and $\tilde{\kappa}_B = \kappa_B I_1(3\lambda_B)$. The coefficients of the Landau–de Gennes expansion are

$$B(\phi) = \frac{45}{4}\frac{1}{\phi\tilde{\kappa}_A + (1-\phi)\tilde{\kappa}_B}$$

$$C_3(\phi) = \frac{2025}{56}\frac{\phi\kappa_A^2 I_2(3\lambda_A) + (1-\phi)\kappa_B^2 I_2(3\lambda_B)}{[\phi\tilde{\kappa}_A + (1-\phi)\tilde{\kappa}_B]^3}$$

$$D_4(\phi) = \frac{135}{196}\Bigg[79\frac{\phi\kappa_A^3 I_3(3\lambda_A) + (1-\phi)\kappa_B^3 I_3(3\lambda_B)}{[\phi\tilde{\kappa}_A + (1-\phi)\tilde{\kappa}_B]^4} - \frac{2025}{16}\times$$
$$\frac{\phi(1-\phi)\tilde{\kappa}_A\tilde{\kappa}_B[\kappa_A I_2(3\lambda_A)/I_1(3\lambda_A) - \kappa_B I_2(3\lambda_B)/I_1(3\lambda_B)]^2}{[\phi\tilde{\kappa}_A + (1-\phi)\tilde{\kappa}_B]^5}\Bigg]$$
$$(3.2)$$

Finally, the coefficients of the gradient terms are

$$M_0(\phi)/A =$$
$$\frac{2}{9}\left(\frac{\kappa_A J_0(\lambda_A)}{\phi} + \frac{\kappa_B J_0(\lambda_B)}{1-\phi}\right)(1/\sqrt{N_A} + 1/\sqrt{N_B})^{-2}a_0^2$$

$$L_0(\phi) =$$
$$\frac{\tilde{\kappa}_A\tilde{\kappa}_B}{2[\phi\tilde{\kappa}_A + (1-\phi)\tilde{\kappa}_B]}\left[\frac{1-\phi}{\phi}\frac{J_1(3\lambda_A)}{(I_1(3\lambda_A))^2} - \frac{\phi}{1-\phi}\frac{J_1(3\lambda_B)}{(I_1(3\lambda_B))^2}\right]a_0^2$$

$$L_1(\phi)/B(\phi) = \frac{1}{126}\left[\kappa_A^2\frac{J_2(3\lambda_A)}{I_1(3\lambda_A)} + \kappa_B^2\frac{J_2(3\lambda_B)}{I_1(3\lambda_B)}\right]a_0^2$$

$$L_2(\phi)/B(\phi) = \frac{1}{7}\left[\kappa_A^2\frac{J_3(3\lambda_A)}{I_1(3\lambda_A)} + \kappa_B^2\frac{J_3(3\lambda_B)}{I_1(3\lambda_B)}\right]a_0^2 \qquad (3.3)$$

Note that we recover the free energy functional for a polymer *solution* by setting $\kappa_B = 0$ and $N_B = 1$.

IV. Discussion of Results

A. Comparison with Previous Results. The Landau–de Gennes coefficients were calculated up to fourth order for a *pure* liquid crystalline polymer melt using the wormlike chain model by ten Bosch, Maissa, and Sixou[22] and later corrected by Rusakov and Shliomis.[23] Our more general results for the coefficients of polymer solutions and blends reduce to theirs in the pure polymer limit. If we denote the coefficients of the Landau–de Gennes expansion in eq 2.24 for the pure melt by $\bar{B}$, $\bar{C}_3$, and $\bar{D}_4$, then our results for a *solution* of wormlike chains are related to the results of Rusakov and Shliomis[23] for the *melt* by powers of the local volume fraction ϕ. Thus, we find

$$B = \bar{B}/\phi$$

$$C_3 = \bar{C}_3/\phi^2$$

$$D_4 = \bar{D}_4/\phi^3 \qquad (4.1)$$

Our expressions for the corresponding coefficients of a polymer blend are more complicated, but the coefficient $B(\phi)$ assumes a fairly transparent form. By comparing our result for $B(\phi)$ in eq 3.2 to that of Rusakov and Shliomis,[23] we find that the bending rigidity $\tilde{\kappa}$ of a liquid crystalline polymer in a melt is replaced by the volume fraction weighted average of the two rigidities in a blend; in other words, $\tilde{\kappa}$ is replaced by $\tilde{\kappa} = \phi\tilde{\kappa}_A + (1-\phi)\tilde{\kappa}_B$.

The coefficients L_1 and L_2 of the gradient terms in $\overset{\leftrightarrow}{S}$, which are directly related to the Frank elastic con-

stants in the nematic phase, were calculated for a melt of wormlike chains by Shimada, Doi, and Okano.[24] Their expressions for L_1/B and L_2/B are identical to ours for a polymer solution. For a polymer blend, our more general theory shows that the quantity $\kappa^2 J_2(3\lambda)/I_1(3\lambda)$ in $L_1(\phi)/B(\phi)$ is replaced by the sum of the corresponding quantities for the two species. Similarly, the quantity $\kappa^2 J_3(3\lambda)/I_1(3\lambda)$ in $L_2(\phi)/B(\phi)$ is replaced by the corresponding sum.

B. Scaling of Interaction Parameters. The solution and blend free energy functionals yield insight into the scaling of the interaction parameters χ and w near the phase-separation and isotropic–nematic transitions with molecular weight and bending rigidity. If we neglect for the moment the Landau–de Gennes terms in the free energy, it is well-known that the spinodal for phase separation occurs when the coefficient of the φ^2 term in the Landau–Ginzburg expansion of the Flory–Huggins free energy vanishes. For a solution, this corresponds to the condition $\chi = {}^1\!/_2 A \equiv 1/2cN$, while for a blend, this corresponds to the condition $\chi = A \equiv {}^1\!/_2(1/\sqrt{N_A} + 1/\sqrt{N_B})^2$. The coefficient A represents the loss in entropy of mixing due to phase separation; this entropic term decreases as the *chain lengths* Na_0 (solution) or $N_A a_0$ and $N_B a_0$ (blend) increase.

Similarly, the spinodal for the isotropic–nematic transition (ignoring for a moment the Flory–Huggins free energy) is located by finding the point at which the coefficient of the $(TrS)^2$ term in the Landau–de Gennes expansion vanishes. The location of the spinodal is only an approximation to the position of the isotropic–nematic transition, because the transition is first order. Thus, the isotropic–nematic transition occurs roughly when $w = B(\phi)$, where $B(\phi)$ is given by $B(\phi) = 45/4\bar{\kappa}\phi$ for a solution, and by $B(\phi) = 45/4\bar{\kappa}$ for a blend, where $\bar{\kappa} = \phi\bar{\kappa}_A + (1-\phi)\bar{\kappa}_B$. (Recall that $\bar{\kappa} = \kappa I_1(3\lambda)$, $\bar{\kappa}_A = \kappa_A I_1(3\lambda_A)$ and $\bar{\kappa}_B = \kappa_B I_1(3\lambda_B)$, where $I_1(x)$ is given by eq 2.20.) The coefficient $B(\phi)$ represents the loss in configurational entropy due to orientational order. In contrast to the entropy of mixing, which decreases as the chain lengths increase, this entropic term decreases as the *persistence lengths* κa_0, $\kappa_A a_0$, and $\kappa_B a_0$ increase. For a polymer solution, the condition $w \sim 1/\bar{\kappa}\phi$ implies that concentrated solutions of stiffer chains require weaker Maier–Saupe interactions to reach a nematic phase than dilute solutions of more flexible polymers. Similarly, for a blend, the condition $w \sim 1/\bar{\kappa}$ demonstrates that as the average rigidity increases, a weaker anisotropic interaction is required to drive the system into a nematic phase.

C. Nature of the Isotropic–Nematic Transition. Rusakov and Shliomis[23] demonstrated that for a melt of wormlike chains, the isotropic–nematic transition is always first order. They found that the jump in the order parameter S_c at the transition depends only weakly on κ and N. If we neglect the Flory–Huggins free energy and examine only the Landau–de Gennes expansion for a polymer solution or blend, we find a line of first order transitions as a function of concentration. The jump in the order parameter at the transition is given by

$$S_c = \frac{1}{3}\frac{C_3(\phi)}{D_4(\phi)} \qquad (4.2)$$

From the expressions for C_3 and D_4 in eqs 2.18 and 2.19 for a polymer solution, we see that S_c is proportional to the polymer volume fraction ϕ. Thus, the transition appears to become continuous as the polymer volume fraction vanishes. However, the entropic cost of aligning polymers also diverges since $B(\phi) \propto 1/\phi$, so the strength

of the Maier–Saupe interaction required to reach the nematic phase diverges. Note also that we have defined $\overset{\leftrightarrow}{S}$ as the orientational order per *volume*. Another reasonable order parameter, used by Olmsted and Milner,[25] is the orientational order per *monomer*, $\overset{\leftrightarrow}{\Sigma} \equiv \overset{\leftrightarrow}{S}/\phi$. If we adopt this definition, then we see that the jump in the order parameter at the isotropic–nematic transition, Σ_c, is independent of ϕ. Thus, the amount of orientational order per monomer is independent of the volume fraction, but the amount of orientational order per volume decreases as the volume fraction decreases.

When we include the Flory–Huggins free energy, the line of first order transitions opens up into a biphasic region of an isotropic, solvent-rich phase coexisting with a nematic, polymer-rich phase. Similarly, a biphasic region can occur in the blend, with an isotropic, B-rich phase coexisting with a nematic, A-rich phase.[14] (We have assumed $\kappa_A > \kappa_B$.) A detailed description of the phase behavior of liquid crystalline polymer solutions and blends based on the free energy functionals contained herein will be presented elsewhere.[26]

Finally, we can compare our results for a solution of athermal rigid rods to the Onsager result.[27] Odijk[28] has cited recent numerical analyses by Kayser and Raveché[29] and Lekkerkerker and co-workers[30] on Onsager's solution, where they find the volume fractions $\phi_i = 3.29D/L$ and $\phi_n = 4.19D/L$ that bound the biphase region, where D is the diameter and L is the length of the rods. For volume fractions below ϕ_i, the solution is isotropic, for volume fractions between ϕ_i and ϕ_n, an isotropic phase coexists with a nematic phase, and for volume fractions above ϕ_n, the solution is nematic. In our notation, the rod diameter is the segment diameter $D = d_0 = a_0\sqrt{4/\pi}$ and the rod length is $L = a_0 N$. Thus, the biphase boundaries correspond to volume fractions $\phi_i = 3.71/N$ and $\phi_n = 4.73/N$. We can use our free energy functional with $\chi = 0$ to estimate the Maier–Saupe interaction needed to produce a biphase in this range of volume fraction. Note that for rigid rods, we have $\lambda \equiv N/\kappa = 0$ and $\bar{\kappa} = 3N/2$. We adjust $w = 1.839$ to reproduce the Onsager result for the lower boundary of the biphase region $\phi_i = 3.71/N$ and find that the resulting upper boundary is $\phi_n = 4.03/N$ for $N \gtrsim 100$.[26] Thus, in the long rod limit, our result exhibits the same scaling with rod length as Onsager's for rods sufficiently long, but our theory yields a narrower biphase region. It is not surprising that the two theories obey the same scaling only for sufficiently long rods, since both involve approximations that are more accurate in that limit. Note that the result for the Maier–Saupe parameter $w = 1.839$ quoted above is an estimate of the excluded volume interaction for rods and is independent of N.

D. Frank Elastic Constants. The gradient terms in $\overset{\leftrightarrow}{S}$ in eqs 2.17 and 3.3 are related to the Frank elastic constants.[31] Since the tensor order parameter $\overset{\leftrightarrow}{S}$ is traceless and symmetric, it can be written as

$$\overset{\leftrightarrow}{S} = S\left(n_i n_j - \frac{1}{3}\delta^{ij}\right) \qquad (4.3)$$

where $\hat{n}(\vec{r})$ is the local director. If we assume that the magnitude S is fixed, then the gradient terms in $\overset{\leftrightarrow}{S}$ assume the form

$$\mathscr{F}_{grad S} = \frac{1}{2}L_1(\phi)S^2(\partial_k n_i n_j)^2 +$$

$$\frac{1}{2}L_2(\phi)S^2(\partial_i n_i n_k)(\partial_j n_j n_k) \qquad (4.4)$$

This can be rewritten in the more standard form:

$$\mathcal{F}_{\text{grad}S} = \frac{1}{2}K_1(\nabla \cdot n)^2 + \frac{1}{2}K_2[n \cdot (\nabla \times n)]^2 +$$
$$\frac{1}{2}K_3[n \times (\nabla \times n)]^2 \quad (4.5)$$

where the coefficients K_i are the splay, twist, and bend Frank elastic constants. By comparing eq 4.4 to eq 4.5, we find that the Frank constants in the nematic phase are given by

$$K_1 = K_3 = [2L_1(\phi) + L_2(\phi)]S^2$$
$$K_2 = 2L_1(\phi)S^2 \quad (4.6)$$

where $L_1(\phi)$ and $L_2(\phi)$ are given by eq 2.17 for a polymer solution, with c replaced by ϕ, and by eq 3.3 for a polymer blend. Note that these are the bare elastic constants; in the case where no solvent is present, de Gennes has pointed out that the splay modulus K_1 is renormalized due to incompressibility and diverges as the molecular weight N diverges.[32] At the isotropic–nematic transition, the Frank constants are given by eq 4.6 with $S = S_c$. Since the jump in the transition is only weakly dependent on the bending rigidity and molecular weight, the scaling of the Frank constants is dominated by the behavior of L_1 and L_2. By combining the ratios L_i/B given by eqs 2.17 and 3.3 with the expressions for B given in eqs 2.17 and 3.2, we find that the Frank constants scale linearly with the bending constant for both solutions and blends.

E. Conclusion. In summary, we have constructed free energy functionals for polymers of arbitrary flexibility either in solution or blended with other polymers. Our functionals combine a density functional theory in concentration with a Landau–de Gennes expansion in an orientational order parameter. In contrast to previous theories, we have exploited the polymeric nature of the constituent molecules to calculate all of the coefficients in the theory up to fourth order in the orientational order parameter. We have also calculated the coefficients of several square-gradient terms. As a result, there are very few free parameters in our theory. These are the Flory parameter χ and the Maier–Saupe parameter w, as well as the bending rigidities κ_A and κ_B and the molecular weights N_A and N_B. The bending rigidities and molecular weights can be determined by measurements of the pure components. The interaction parameters can be estimated by comparing phase diagrams calculated from the theory with experimental results. The phase diagrams that result from the free energy functionals derived here are quite complex and will be presented elsewhere.[26]

Appendix A: Single-Chain Correlation Functions

The calculation of the free energy in terms of the concentration and orientational order parameters involves the evaluation of single-chain correlation functions. In this appendix, we will describe the calculation of the $\langle \phi(\mathbf{q}) S^{ij}(-\mathbf{q})\rangle_0$ correlation function to lowest order in the wavevector q.

For a single chain, the microscopic order parameters are given by

$$\hat{\phi}(\vec{r}) = a_0^3 \int_0^N ds\, \delta(\vec{r} - \vec{r}(s))$$

$$S^{ij}(\vec{r}) = a_0^3 \int_0^N ds\, \left[u^i(s)u^j(s) - \frac{1}{3}\delta^{ij}\right]\delta(\vec{r} - \vec{r}(s)) \quad (A1)$$

We wish to calculate the correlation function

$$G_{\phi S}^{ij}(\vec{r} - \vec{r}') = \langle \phi(\vec{r})S^{ij}(\vec{r}')\rangle \quad (A2)$$

where the thermal average is taken over the wormlike chain Hamiltonian

$$\beta \mathcal{H}_0 = \frac{1}{2}\kappa \int_0^N ds \left(\frac{\partial \vec{u}}{\partial s}\right)^2 \quad (A3)$$

We begin by taking the Fourier transform

$$G_{\phi S}^{ij}(q) = \langle \phi(q)S^{ij}(-q)\rangle$$
$$= \int_0^N ds \int_0^N ds_0 \left\langle e^{iq(\vec{r}(s)-\vec{r}(s_0))}\left(u^i(s_0)u^j(s_0) - \frac{1}{3}\delta^{ij}\right)\right\rangle \quad (A4)$$

and expand the exponential for small q. The zeroth order term vanishes because the system is isotropic, and the linear term vanishes by virtue of translational symmetry. So the lowest order term is

$$G_{\phi S}^{ij}(q) \approx -\frac{1}{2}q^k q^l \int_0^N ds \int_0^N ds_0 \times$$
$$\langle(r^k(s) - r^k(s_0))(r^l(s) - r^l(s_0))S^{ij}(\vec{u}_0)\rangle \quad (A5)$$

where we defined

$$S^{ij}(\vec{u}_0) = u^i(s_0)u^j(s_0) - \frac{1}{3}\delta^{ij} \quad (A6)$$

and $\vec{u}_0 \equiv \vec{u}(s_0)$. Next, we note that the distance between two segments is related to the tangent vectors of the segments between them:

$$\vec{r}(s) - \vec{r}(s_0) = a_0 \int_{s_0}^s ds_1\, \vec{u}(s_1) \quad (A7)$$

The correlation function is then given by

$$G_{\phi S}^{ij}(q) \approx -\frac{1}{2}a_0^2 q^k q^l \int_0^N ds \int_0^N ds_0 \int_{s_0}^s ds_1 \int_{s_0}^s ds_2\, g^{ijkl} \quad (A8)$$

where

$$g^{ijkl} = \langle u(s_1)^k u(s_2)^l S^{ij}(\vec{u}_0)\rangle \quad (A9)$$

We first consider the case $s_0 < s_1 < s_2 < s$. Then the thermal average over the wormlike Hamiltonian can be evaluated by using Green's function provided by Saito et al.[15] Thus we are left with

$$g^{ijkl} = \frac{1}{4\pi}\sum_\ell \sum_{\ell'} \exp[-\ell(\ell + 1)(s_1 - s_0)/2\kappa] \times$$
$$\exp[-\ell'(\ell' + 1)(s_2 - s_1)/2\kappa]U^{ijkl} \quad (A10)$$

where the angular average U is given by

$$U^{ijkl} = \sum_{m,m'} U_0^{ij} U_1^k U_2^l \quad (A11)$$

where the sums over m and m' run from $-\ell$ to ℓ and $-\ell'$ to ℓ', respectively, and

$$U_0^{ij} = \int d\vec{u}_0\, S^{ij}(\vec{u}_0)Y_{\ell m}(\vec{u}_0)$$
$$U_1^k = \int d\vec{u}_1\, Y_{\ell m}^*(\vec{u}_1)Y_{\ell' m'}(\vec{u}_1)u_1^k$$
$$U_2^l = \int d\vec{u}_2\, Y_{\ell' m'}^*(\vec{u}_2)u_2^l \quad (A12)$$

These angular averages yield

$$U^{ijkl} = 2\left[\delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk} - \frac{1}{3}\delta^{ij}\delta^{kl}\right]\delta_{\ell,2}\delta_{\ell',2} \quad \text{(A13)}$$

We substitute eq A13 into eq A10, which we in turn substitute into eq A8. Note that the positions of the monomers s_0, s_1, s_2 and s must be permuted appropriately. The final result is

$$G_{\phi S}^{ij}(\mathbf{q}) \approx -\frac{2}{45}\kappa^2 N^2 J_0(\lambda)\left(q^i q^j - \frac{1}{3}q^2\delta^{ij}\right)a_0^2 \quad \text{(A14)}$$

where $J_0(\lambda)$ is given by eq 2.22.

By similar methods, we find that the $\langle S^{ij}(\mathbf{q})S^{kl}(-\mathbf{q})\rangle$ correlation function is given by

$$G_{SS}^{ijkl} = \frac{\kappa N}{15}I_1(3\lambda)\left[\delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk} - \frac{2}{3}\delta^{ij}\delta^{kl}\right] + O(q^2) \quad \text{(A15)}$$

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