Molecular theory of liquid-crystal ordering in rod-coil diblock copolymers

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Molecular-statistical theory of rod-coil diblock copolymers is proposed using the general density functional approach which enables one to consider the cases of both weak and strong segregation. The free energy of the system is expressed as a functional of the phase-space densities of rod and coil monomers, which depend on the orientational and translational order parameters. Temperature-concentration phase diagrams are obtained and the profiles of all order parameters are calculated numerically by minimizing the polymer free energy. The lamellar phase is shown to possess strong orientational order which is partially induced by the phase structural anisotropy. The enhanced stability of the lamellar phase is determined by a combination of the microphase separation effects and the emergence of long-range smectic order.

I. INTRODUCTION

Block copolymers are composed of macromolecules which consist of two different blocks that repel each other. The existence of a bond between the blocks prevents macroscopic separation and results in the formation of various microphase separated phases with periodic structure, including, in particular, lamellar and hexagonal phases. Coil-coil block copolymers composed of flexible blocks attract significant attention because of their applications in nanolithography, nanopatterning, and the development of thermoplastic materials [1–3]. Rod-coil block copolymers which are composed of rigid and flexible blocks are very different from the coil-coil copolymers. They are characterized by smaller domain sizes, richer polymorphism and orientational order of rigid fragments. Thus, these copolymer systems are very interesting from the fundamental point of view because they combine the properties of liquid crystals and block copolymers. Rod-coil block copolymers provide a natural opportunity to introduce functional rodlike fragments into phase-separated polymer structures, including semiconducting polymers [4,5], polypeptides [6,7] and polysaccharides [8,9], and also polyimines and polyaramides [10,11] These novel polymer materials may find applications in polymer photovoltaics [4,12,13], LEDs [14–16], drug delivery devices [17], and high strength polymer composites [10,11]. Rod-coil block copolymers also outperform other soft matter materials in the area of extra strong fibres [18,19].

A consistent molecular-statistical theory of rod-coil block copolymers should account both for the microphase separation between blocks and for the anisotropic interaction between rigid fragments which may lead to the orientational order. The first analytical theory of rod-coil block copolymers has been developed by Semenov and Vasilenko using a simple lattice model and assuming the perfect orientational order of rigid molecular fragments [20]. In this theory, only a transition

from the nematic to the lamellar phase has been considered. A more detailed description of the phase behavior of rod-coil copolymers has been undertaken using the Landau-de Gennes expansion of the free energy in terms of one-particle density and the orientational order parameters [21,22].

The coefficients of the free-energy expansion have been first calculated using Flory-Higgins theory [21] and then by employing the monomer-monomer correlation functions of the single copolymer chain [22] evaluated following the approach proposed by Leibler [23]. Such an approach enables one to describe several different phases but it is generally valid in the case of weak segregation because the one-particle density contains only one Fourier harmonic and the translational order parameter is the amplitude of this density wave. The existing theory also does not describe some liquid-crystal properties of rod-coil block copolymers including, in particular, the induced orientational order in the lamellar phase.

The self-consistent field theory has also been generalized to the case of rod-coil block copolymers [24–27] although the theory experiences significant computational challenges in description of the orientational degrees of freedom and anisotropic interactions between rigid fragments. As a result, simple lattice models are employed [26,27], or a 2D version of the theory is used [25], or the orientational order of rigid rods is assumed to be perfect [24], or the anisotropic interactions between rods are completely neglected [26,27] which does not allow one to describe liquid-crystal phases. One notes also that in the framework of a lattice theory only a few cross sections of the phase diagram have been calculated and the profiles of the orientational and translational order parameters have not been obtained. A molecular theory of liquid-crystal order in polymer systems has been discussed in Ref. [28].

In the alternative approach, a fluid of rod-coil diblock copolymers is modeled by worm-like chains using the self-consistent field theory and simulations [29–31]. In this theory, both coil and rod blocks are described within the same

formalism, but the rod block is characterized by a larger persistence length. The most advanced theory has been presented recently by Tang *et al.* [31], where a rich variety of different phases has been described including those of lamellar, hexagonal, gyroid, and other morphologies. Moreover, in the framework of this approach it has been possible to describe the orientational ordering of rigid chains at the interfacial area between rod and coil domains even without taking into consideration any orientational interactions. In contrast, in the paper by Wilson *et al.* [32], an athermal system of polymer tethered nanorods has been considered using Molecular Dynamics simulations and a statistical theory. In computer simulations, a polymer macromolecule has been modeled by a spherocylinder with a flexible bead chain attached at one end while in the statistical theory the flexible chain has been represented by a sphere of the corresponding radius. Dissipative particle dynamic simulations of rod-coil block copolymers and coil or rod homopolymers have also been undertaken in Ref. [33]. Finally, nematic-isotropic phase transition in athermal solutions of rod-coil diblock copolymers has been studied in detail using scaled particle theory and Monte Carlo simulations [34].

In this paper, we develop a molecular-statistical theory of rod-coil diblock copolymers using the general density functional approach which is successfully used in the theory of liquid crystals [35] and inhomogeneous fluids [36]. In this approach, the free energy is expressed as a functional of the equilibrium monomer densities which are obtained by minimization of the functional. The free energy also depends on the direct correlation functions which are expressed in terms of the pair correlation functions between monomers of a single copolymer chain via the Ornstein-Zernike equation. One notes that this theory is approximately valid in the case of both weak and strong segregation as the density contains contributions from all Fourier harmonics and does not have a cosine shape. The theory enables one to calculate numerically phase diagrams and the profiles of the order parameters in an efficient way and to study the effects of the molecular model parameters on the stability of different phases.

The paper is arranged as follows. In Sec. II the expansion of the free energy of coil-coil block copolymers, proposed by Leibler, is briefly discussed. In Sec. III the general density functional approach is considered and applied to coil-coil diblock copolymers to demonstrte a relationship with the theory of Leibler *et al.* The density functional approach is then generalized in Sec. IV to the case of liquid-crystal rod-coil diblock copolymers taking into consideration the orientational degrees of freedom of the rod segments. In Sec. V, the free energy of the rod-coil system is expressed in terms of the orientational and translational order parameters and in Sec. VI the corresponding density-density correlation functions between monomers are discussed. The numerical results including phase diagrams and order parameter profiles are presented in Sec. VII and Sec. VIII contains our conclusions.

II. LANDAU-DE GENNES EXPANSION OF THE FREE ENERGY OF DIBLOCK COPOLYMERS

One of the most successful and well-known approaches in the molecular-statistical theory of diblock copolymers,

based on the consistent free-energy expansion in terms of the translational order parameters, has been proposed in the classical paper by Leibler [23]. This approach has later been used by other authors (see, for example, Refs. [37–39]) and generalized to the case of rod-coil diblock copolymers [22]. As shown in Ref. [23] the free energy of the phase separated coil-coil diblock copolymer can be expanded in powers of the density order parameter ψ as

$$F = V^{-1} \sum_{\mathbf{q}} \Gamma_2(q)\psi(\mathbf{q})\psi(-\mathbf{q})$$
$$+ V^{-3} \sum_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3} \Gamma_3(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\psi(\mathbf{q}_1)\psi(\mathbf{q}_2)\psi(\mathbf{q}_3) + ...,$$

(1)

where the order parameter is expressed in terms of the equilibrium density

$$\psi(\mathbf{r}) = \langle (1-f)\rho_A^m(\mathbf{r}) + f\rho_B^m(\mathbf{r}) \rangle. \tag{2}$$

Here $\rho_A^m(\mathbf{r})$ and $\rho_B^m(\mathbf{r})$ are the reduced microscopic fluctuating densities of the monomers A and B in the diblock copolymer, the angular brackets $\langle ... \rangle$ denote the thermal average, and f is the average molar fraction of the monomers A in the whole sample. Assuming the incompressibility of the diblock copolymer fluid $\langle \rho_A^m(\mathbf{r}) \rangle + \langle \rho_B^m(\mathbf{r}) \rangle = 1$ [23], one obtains that $\psi(\mathbf{r}) = \langle \delta\rho_A(\mathbf{r}) \rangle = \langle \rho_A(\mathbf{r}) - f \rangle$, i.e., ψ describes the average deviation of the distribution of the monomers with respect to its average value.

The coefficients of the expansion Eq. (1) can be expressed in terms of density-density correlation functions between monomers connected in Gaussian polymer chains, composed of monomers A and B and connected together within one macromolecule of a diblock copolymer, and the Flory-Higgins parameter χ which describes the effective repulsion between monomers A and B [23]. In particular, the coefficient in the quadratic term, which determines the spinodal line, can be written in the form

$$\Gamma_2(q) = S(q)/W(q) - 2\chi, \tag{3}$$

where $S(q) = S(q)_{AA} + 2S(q)_{AB} + S(q)_{BB}$ and $W(q) = S(q)_{AA}S(q)_{BB} - S^2(q)_{AB}$.

Here $S(q)_{ij}, (i, j = A, B)$ are the monomer-monomer correlation functions of the disordered phase of ideal noninteracting copolymer chains. The functions S_{AA} and S_{BB} describe the correlations between monomers of the same kind which are connected within a copolymer macromolecule while the function S_{AB} describes the correlations between monomers A and B located in the different parts of the same copolymer macromolecule connected together. These functions are approximately expressed as [23,37]

$$S_{AA} = Nh_1(f, x), \quad S_{BB} = Nh_1(1 - f, x),$$
$$S_{AB} = \tfrac{1}{2}N[h_1(1, x) - h_1(f, x) - h_1(1 - f, x)], \tag{4}$$

where

$$h_1(f, x) = \frac{2}{x^2}[fx + \exp(-fx) - 1], \tag{5}$$

and where $x = q^2Na^2/6$, N is the total number of all monomers in a macromolecule and a is the monomer radius.

In the limit $q \to 0$ the function $S(q)$ in the quadratic term of the free-energy expansion behaves asymptotically as [37]

$$\Gamma_2(q) \sim \frac{3}{q^2 N^2 f^2 (1-f)^2}. \tag{6}$$

Here the q^{-2} dependence of $\Gamma_2(q)$ for small values of q reflects the connectivity of A and B blocks in a copolymer macromolecule. The divergence of $\Gamma_2(q)$ stems from the fact that any two monomers in the A and B coils of the same macromolecule are always connected and hence the separation between them cannot exceed the size of the block [39].

An important advantage of Leibler's approach is related to the rigorous and general expansion of the free energy where approximations are only used in the evaluation of the corresponding correlation functions of the reference state determining the expansion coefficients. At the same time, the truncated free energy can only be used in the case of weak segregation when the system is close to the transition into the disordered phase. In particular, the order parameter $\psi(\mathbf{r})$, and hence the average number density, is approximated by a single harmonic which is not realistic at relatively strong segregation. In the next Section we consider an alternative approach, based on the general density functional theory, which is not restricted to the case of weak segregation and which reduces to Leibler's theory in the limiting case of small order parameters.

III. DENSITY FUNCTIONAL THEORY OF DIBLOCK COPOLYMERS

A molecular-statistical theory of phase separated coil-coil diblock copolymers can be developed in a general way using the density functional theory of inhomogeneous fluids (see, for example, Refs. [36,40]).

In this approach, the free energy F of the inhomogeneous fluid is a functional of the equilibrium one-particle density of monomers $\rho(\mathbf{r})$. The density is normalised by the total number of monomers N, i.e., $\int \rho(\mathbf{r})d\mathbf{r} = N$. The general structure of the free-energy functional $F[\rho(\mathbf{r})]$ is not known, but its functional derivatives are related to the direct correlation functions of the system. Then the free energy of separated inhomogeneous phase of a diblock copolymer can be obtained by performing a functional Taylor expansion of the free energy around its value in the disordered reference phase. A simplified version of the density functional approach has been previously used in the theory of coil-coil block copolymers [39,41].

As discussed in the previous section, coil-coil diblock copolymers are characterized by the two monomer densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ for A and B monomers, respectively. The free energy of a phase separated block copolymer phase can then be approximately expressed as

$$\beta F = \beta F_I + \int \rho_A(\mathbf{r})[\ln \rho_A(\mathbf{r}) - 1]d\mathbf{r}$$

$$+ \int \rho_B(\mathbf{r})[\ln \rho_B(\mathbf{r}) - 1]d\mathbf{r}$$

$$- \frac{1}{2} \sum_{\nu,\eta=A,B} \int C_{\nu,\eta}(\mathbf{r}_1, \mathbf{r}_2)\delta\rho_\nu(\mathbf{r}_1)\delta\rho_\eta(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2, \tag{7}$$

where F_I is the free energy of the disordered reference phase, $C_{AA}(\mathbf{r}_1, \mathbf{r}_2)$, $C_{BB}(\mathbf{r}_1, \mathbf{r}_2)$, and $C_{AB}(\mathbf{r}_1, \mathbf{r}_2)$ are the direct correlation functions between A monomers, B monomers and A and B monomers, respectively, which are calculated in the disordered reference phase, and $\delta\rho_\nu = \rho_\nu - \rho_{0\nu}$ is the difference between the equilibrium density of monomers $\nu = A, B$ in the inhomogeneous phase and the corresponding density in the disordered phase. Here we have neglected the terms which contain higher order correlation functions.

In principle, the direct correlation functions depend on all interaction potentials between monomers of both kinds. At the same time, it makes sense to distinguish between strong interactions of monomers within one chain, which determine the connectivity of monomers, and weaker interactions of monomers in different macromolecules. In the existing molecular theory of coil-coil block copolymers (see, for example, Refs. [21–24,31]) the interactions between monomers in different macromolecules are taken into account in the so-called random phase approximation, and for simplicity only repulsion between monomers of different kinds is considered. This corresponds to the following approximation for the direct correlation functions in Eq. (7):

$$C_{\nu,\eta}(r_{12}) \approx C^0_{\nu,\eta}(r_{12}) - (1 - \delta_{\nu,\eta})\chi(r_{12}), \tag{8}$$

where $C^0_{\nu,\eta}(r_{12})$ are the direct correlation functions between monomers within a copolymer macromolecule in the disordered phase of noninteracting copolymer chains. Here the function $\chi(r_{12})$ describes the effective isotropic repulsion between the monomers of different kinds and is related to the Flory-Higgins parameter χ [21–23]. Thus, the free energy of the coil-coil diblock copolymer can now be approximately expressed as

$$\beta F = \beta F_I + \int \rho_A(\mathbf{r})[\ln \rho_A(\mathbf{r}) - 1]d\mathbf{r}$$

$$+ \int \rho_B(\mathbf{r})[\ln \rho_B(\mathbf{r}) - 1]d\mathbf{r}$$

$$- \frac{1}{2} \sum_{\nu,\eta=A,B} \int C^0_{\nu,\eta}(r_{12})\delta\rho_\nu(\mathbf{r}_1)\delta\rho_\eta(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

$$+ \int \chi(r_{12})\delta\rho_A(\mathbf{r}_1)\delta\rho_B(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2. \tag{9}$$

The one-particle densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ can be determined by minimization of the free-energy functional F which results in self-consistent integral equations for the densities. Nontrivial periodic solutions of these equations will then correspond to various separated phases. In practice, these solutions can be found if some approximate expressions for the direct correlation functions between monomers in the disordered reference system of noninteracting copolymer macromolecules are derived. Using the same model of ideal Gaussian chains as in the previous section, it is possible to express the direct correlation functions $C_{\nu,\eta}(q)$ in terms of the density-density correlation functions $S_{\nu,\mu}(q)$ between monomers in a copolymer chain which have been calculated by Leibler and other authors and which are presented in the previous section.

The correlation functions $S_{\nu,\mu}$, $(\nu, \mu = A, B)$ which determine the quadratic term in the free-energy expansion

considered in the previous section can generally be expressed as [23]

$$S_{\nu,\mu}(r_{12}) = \langle \delta \rho_\nu(\mathbf{r}_1) \delta \rho_\mu(\mathbf{r}_2) \rangle, \tag{10}$$

where the averaging is performed in the disordered state of the copolymer fluid of noninteracting copolymer chains. After some algebra the corresponding density-density correlation functions $S_{\nu,\mu}(q)$ can be rigorously expressed in terms of the corresponding direct correlation functions $C^0_{\nu,\mu}(q)$ using general formulas of statistical mechanics. We illustrate this below using a simple example of one-component isotropic flexible polymer fluid.

First, the density-density correlation function of the disordered fluid is directly related to the full pair correlation function of the fluid $g_2(r_{12})$ (see, for example, Eq. (2.4) in Ref. [40]):

$$S(r_{12}) = \langle \delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2) \rangle = \rho_0 \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_0^2 g_2(r_{12}). \tag{11}$$

This equation can be rewritten in the Fourier space as

$$S(q) = \rho_0 + \rho_0^2 g_2(q). \tag{12}$$

Second, the full pair correlation function of the disordered fluid $g_2(r_{12})$ is related to the direct correlation function $C_2(r_{12})$ by the Ornstein-Zernike equation:

$$g_2(r_{12}) = C_2(r_{12}) + \rho_0 \int C_2(r_{13}) g_2(r_{32}) d\mathbf{r}_3, \tag{13}$$

which can also be expressed in the Fourier form:

$$g_2(q) = C_2(q) + \rho_0 C_2(q) g_2(q). \tag{14}$$

Hence, the direct correlation function is analytically expressed in terms of $g_2(q)$ using Eq. (14) as

$$C_2(q) = \frac{g_2(q)}{1 + \rho_0 g_2(q)} = \left[1 - \frac{1}{1 + \rho_0 g_2(q)} \right]. \tag{15}$$

Excluding $g_2(q)$ from Eqs. (12) and (15) one finally obtains the relationship between the direct correlation function $C_2(q)$ and the density-density correlation function $S(q)$:

$$C_2(q) = \rho_0^{-1} - S^{-1}(q). \tag{16}$$

This derivation can be generalized to a diblock copolymer system in the disordered reference state of noninteracting copolymer macromolecules. Indeed the density-density correlation functions between monomers $\nu, \mu = A, B$ in the disordered phase can be expressed by the following equations which are similar to Eq. (11):

$$S_{\nu,\gamma}(r_{12}) = \langle \delta \rho_\nu(\mathbf{r}_1) \delta \rho_\gamma(\mathbf{r}_2) \rangle$$
$$= \rho_{0\nu} \delta_{\nu,\gamma} \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_{0\nu} \rho_{0\gamma} g_{\nu,\gamma}(r_{12}). \tag{17}$$

In the Fourier space one obtains

$$S_{\nu,\gamma}(q) = \rho_{0\nu} \delta_{\nu,\gamma} + \rho_{0\nu} \rho_{0\gamma} g_{\nu,\gamma}(q). \tag{18}$$

The pair correlation functions $g_{\nu,\gamma}(r_{12})$ of the disordered phase are related to the corresponding direct correlation function $C^0_{\nu,\gamma}(r_{12})$ of the same reference state by the Ornstein-Zernike equations which are similar to Eq. (13):

$$g_{\nu,\eta}(r_{12}) = C^0_{\nu,\eta}(r_{12}) + \rho_{0\eta} \int C^0_{\nu,\gamma}(r_{13}) g_{\gamma,\eta}(r_{32}) d\mathbf{r}_3, \tag{19}$$

and which can be expressed in the Fourier space as

$$g_{\nu,\eta}(q) = C^0_{\nu,\eta}(q) + \rho_\gamma g_{\nu,\gamma}(q) C^0_{\gamma,\eta}(q). \tag{20}$$

Equation (20) can be solved in the matrix form to obtain

$$C^0_{\nu,\gamma}(q) = g_{\nu,\eta}(q) [\delta_{\gamma,\eta} + \rho_\gamma g_{\gamma,\eta}(q)]^{-1}$$
$$= \rho_\nu^{-1} \delta_{\nu,\gamma} - (\rho_\nu \delta_{\nu,\gamma} + \rho_\nu \rho_\gamma g_{\nu,\gamma})^{-1}. \tag{21}$$

Substituting the right-hand side of Eq. (18) into Eq. (21) one obtains the following final expression for the direct correlation functions $C_{\nu,\gamma}(q)$ of the reference disordered phase:

$$C^0_{\nu,\gamma}(q) = \rho_\nu^{-1} \delta_{\nu,\gamma} - S_{\nu,\gamma}(q)^{-1}, \tag{22}$$

where $S_{\nu,\gamma}(q)^{-1}$ is the inverse of the matrix $S_{\nu,\gamma}(q)$.

Thus, the direct correlation functions between monomers, which enter the general free-energy expression for coil-coil diblock copolymers Eq. (9), obtained using the density functional approach, have been explicitly expressed in terms of the density-density correlation functions of monomers in noninteracting Gaussian copolymer chains which are presented in the previous Section and which have been widely used in the theory of diblock copolymers.

Now let us consider a small deviation of the density from the average value ρ_0 in the homogeneous phase, i.e., in the system close to the spinodal line. Then the free-energy Eq. (9) should be expanded in terms of $\delta\rho(\mathbf{r})$ keeping the quadratic terms. The terms containing the monomer direct correlation functions and the repulsion parameter χ are already quadratic in $\delta\rho(\mathbf{r})$ while the entropic terms are not. Expanding the latter yields

$$\int \rho_\nu(\mathbf{r})[\ln \rho_\nu(\mathbf{r}) - 1] d\mathbf{r} \approx \rho_0^{-1} \frac{1}{2} \int [\delta \rho_\nu(\mathbf{r})]^2 d\mathbf{r}, \tag{23}$$

where $\nu = A, B$.

As a result, one obtains the following quadratic term in the free-energy expansion in the Fourier space:

$$\beta \Delta F = -\frac{1}{2} \int \left[C^{(b)}_{\nu,\eta}(q) - 2\chi(1 - \delta_{\nu,\eta}) + \delta_{\nu,\eta} \rho_\eta^{-1} \right]$$
$$\times \delta \rho_\nu(\mathbf{q}) \delta \rho_\eta(-\mathbf{q}) d\mathbf{q}. \tag{24}$$

Finally, substitution of Eq. (8) for the direct correlation functions into Eq. (24) yields

$$\beta \Delta F = \frac{1}{2} \int \left[S^{-1}_{\nu,\eta}(q) - 2\chi(1 - \delta_{\nu,\eta}) \right] \delta \rho_\nu(\mathbf{q}) \delta \rho_\eta(-\mathbf{q}) d\mathbf{q}, \tag{25}$$

where $\nu, \eta = A, B$ and $S^{-1}_{\nu,\eta}$ is the inverse of the matrix $S_{\nu,\eta}$ composed of the correlation functions.

This equation can be further simplified by applying the incompressibility condition $\delta \rho_A = -\delta \rho_B$ which results in

$$\beta \Delta F = \frac{1}{2} \int \left[\Gamma^0_2(q) - 2\chi \right] \delta \rho(\mathbf{q}) \delta \rho(-\mathbf{q}) d\mathbf{q} + \text{const}, \tag{26}$$

where

$$\Gamma^0_2(q) = [S^{-1}(q)]_{AA} + [S^{-1}(q)]_{BB} - 2[S^{-1}(q)]_{AB}$$
$$= S(q)/W(q), \tag{27}$$

where $S(q) = S(q)_{AA} + 2S(q)_{AB} + S(q)_{BB}$ and $W(q) = S(q)_{AA} S(q)_{BB} - S^2(q)_{AB}$ is the determinant of the matrix $S_{\nu,\eta}$.

Comparing Eq. (3) for the coefficient in the quadratic term of the free-energy expansion Eq. (1) derived by Leibler and others with the corresponding coefficient in the free energy Eq. (26) derived in this section and taking into account that $\Gamma_2^0(q) - 2\chi$ in Eq. (26) is exactly equal to $\Gamma_2(q)$ in Eq. (3) one concludes that in the quadratic approximation (i.e., close to the spinodal line) the density functional theory of coil-coil diblock copolymers yields exactly the same expression for the free energy as the theory of Leibler, provided that the same expressions for the density-density correlation functions between monomers in the reference system of noninteracting copolymer chains are employed. The expression for the vertex in the coefficient of the quadratic term in the free-energy expansion appears to be exactly the same. As discussed in Sec. II, the q^{-2} dependence of this vertex for small q accounts for the connectivity of monomers in A and B blocks in a copolymer macromolecule which is thus taken into account in both approaches.

IV. DENSITY FUNCTIONAL THEORY OF ROD-COIL DIBLOCK COPOLYMERS

In the case of rod-coil diblock copolymers, the number density of rod monomers in the phase space $\rho_r(\mathbf{r}, \mathbf{a})$ depends both on the position of the monomer and the orientation of the rod $\mathbf{a}$, which is the same for all rod monomers within a given polymer molecule as they all are rigidly bound to form a straight rod [22]. In the present theory (similarly to previous approaches), only correlations between segments of the same macromolecule are taken into account because they are determined by the connectivity of the monomers within a coil chain or a rod. The interaction between monomers in different macromolecules is taken into account in the random phase approximation similarly to the previous approaches. These interactions include the repulsion between rod and coil monomers determined by the parameter χ and the orientational interaction between rods approximated by the Maier-Saupe potential $JP_2(\mathbf{a}_1 \cdot \mathbf{a})$. Here we assume that the repulsion between rod and coil monomers is determined by steric effects and hence the corresponding contribution to the free energy is proportional to temperature. At the same time, the Maier-Saupe anisotropic potential is mainly determined by the dispersion attraction interactions between rigid fragments which are known to play the predominant role in thermotropic liquid crystals [35]. The free energy of the rod-coil diblock copolymer is still described by the general Eq. (7), where the direct correlation functions between monomers depend on the orientation of the rod $\mathbf{a}$ and can be approximately expressed in the random phase approximation as

$$C_{\nu,\eta}(r_{12}, \mathbf{a}_1, \mathbf{a}_2) \approx C_{\nu,\eta}^0(r_{12}, \mathbf{a}_1, \mathbf{a}_2) - (1 - \delta_{\nu,\eta})\chi_{\nu,\eta}(r_{12}) + \beta J P_2(\mathbf{a}_1 \cdot \mathbf{a}_2), \quad (28)$$

where $C_{\nu,\eta}^0(r_{12}, \mathbf{a}_1, \mathbf{a}_2)$ are the direct correlation functions between monomers in the system of noninteracting copolymer macromolecules. These monomer correlation functions are determined by the monomer connectivity inside a macromolecule. Substituting these expressions into the general Eq. (7) one obtains the following approximate expression

for the free energy of a phase separated rod-coil diblock copolymer system:

$$
\begin{aligned}
\beta F_N = \beta F_I &+ \int \rho_\nu(\mathbf{r}, \mathbf{a})[\ln \rho_\nu(\mathbf{r}, \mathbf{a}) - 1]d\mathbf{r}d\mathbf{a} \\
&+ \int \chi_{rc}(r_{12})\delta\rho_r(\mathbf{r}_1, \mathbf{a}_1)\delta\rho_c(\mathbf{r}_2, \mathbf{a}_2)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{a}_1 d\mathbf{a}_2 \\
&- \frac{1}{2}\int C_{\nu,\eta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a})\delta\rho_\nu(\mathbf{r}_1, \mathbf{a})\delta\rho_\eta(\mathbf{r}_2, \mathbf{a})d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{a} \\
&- \frac{1}{2}\beta \int J(r_{12})P_2(\mathbf{a}_1 \cdot \mathbf{a}_2)\delta\rho_r(\mathbf{r}_1, \mathbf{a}_1)\delta\rho_r(\mathbf{r}_2, \mathbf{a}_2) \\
&\times d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{a}_1 d\mathbf{a}_2.
\end{aligned}
\quad (29)
$$

The first term in Eq. (29) is the free energy of the disordered phase on noninteracting copolymer chains. The second term in the free energy is the orientational and translational entropy of the system of monomers which vanishes in the disordered phase. Note that this is a standard expression for the entropy in the theory of block copolymers (see, for example, Refs. [39,41]). The third term in Eq. (29) describes the energy of repulsion between rod and coil monomers in different chains, where $\chi_{rc}(r_{12})$ is the corresponding interaction potential between rod and coil monomers, and the last term describes the energy of orientational interaction between rod monomers in different macromolecules, where $J(\mathbf{r}_{12})P_2(\mathbf{a}_1 \cdot \mathbf{a}_2)$ is the corresponding orientational interaction potential of Maier-Saupe type. Note that here $\chi > 0$ and $J > 0$. Finally, the fourth term in Eq. (29) is also of the entropic origin and presents a contribution from the correlations between rod and coil monomers connected within a copolymer chain. This contribution depends on the direct correlation functions $C_{cc}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a})$, $C_{rr}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a})$ and $C_{rc}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a})$ which describe correlations between coil monomers, rod monomers and coil and rod monomers, respectively, within one copolymer chain. These direct correlation functions are calculated in the reference disordered phase of noninteracting copolymer macromolecules and hence they exclusively account for the connectivity between monomers in the copolymer chain. Hereafter we drop the superscript 0 for simplicity.

In the disordered reference homogeneous phase, the direct correlation functions $C_{\nu,\eta}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{a})$ satisfy the same general Ornstein-Zernike equation as in the case of diblock copolymers. At the same time, all correlation functions now depend on the rod orientation $\mathbf{a}$. Thus, the direct correlation functions are expressed by the same Eq. (22) as

$$C_{\nu,\gamma}(\mathbf{q}, \mathbf{a}) = \rho_\nu^{-1}\delta_{\nu,\gamma} - G_{\nu,\gamma}(\mathbf{q}, \mathbf{a})^{-1}, \quad (30)$$

where the functions $G_{\nu,\gamma}(\mathbf{q}, \mathbf{a})$ are the corresponding density-density correlation functions between monomers in the rod-coil disordered phase of noninteractiong copolymer chains, $\nu, \gamma = r, c$. The expressions for these correlation functions, averaged over all orientations of the rod segment, have been obtained in [22]. However, one can also readily obtain the corresponding expressions before averaging using general equations derived in Ref. [22].

It should be noted that in the theory of Reenders and ten Brinke [22], the connectivity between the flexible chain and the rod within a copolymer macromolecule is accounted for by the corresponding monomer density-density correlation func-

tions which are presented below in Section VI. In this paper, we use the same correlation functions between monomers in the disordered system of noninteracting copolymer macromolecules derived in [22] and hence the present theory accounts for the rod-coil connectivity in the same general way.

Minimization of the free energy yields the equations for the phase-space densities of rod and coil monomers in separated phases:

$$
\rho_c(\mathbf{r}_1, \mathbf{a}) = Z_c^{-1} \exp\left[\int C_{cc}(\mathbf{r}_{12}, \mathbf{a}) \delta\rho_c(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a} \right.
$$
$$
\left. - \int [\chi_{rc}(\mathbf{r}_{12}) - C_{rc}(\mathbf{r}_{12}, \mathbf{a})] \delta\rho_r(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a} \right],
$$
$$(31)$$

$$
\rho_r(\mathbf{r}_1, \mathbf{a}) = Z_r^{-1} \exp\left[\int C_{rr}(\mathbf{r}_{12}, \mathbf{a}) \delta\rho_r(\mathbf{r}_2, \mathbf{a})) d\mathbf{r}_2 d\mathbf{a} \right.
$$
$$
- \int [\chi_{rc}(\mathbf{r}_{12}) - C_{rc}(\mathbf{r}_{12}, \mathbf{a})] \delta\rho_c(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2
$$
$$
\left. + \beta \int J(\mathbf{r}_{12}) P_2(\mathbf{a} \cdot \mathbf{a}_2) \delta\rho_r(\mathbf{r}_2, \mathbf{a}_2) d\mathbf{r}_2 d\mathbf{a}_2 \right], (32)
$$

where Z_c and Z_r are the normalization factors.

One notes that the equilibrium phase-space densities of the monomers are normalised by the total number N_ν of the particles of type ν, i.e., $\int \rho_\nu(\mathbf{r}, \mathbf{a}) d\mathbf{r} d\mathbf{a} = N_\nu$. The equilibrium phase-space density is proportional to the one-particle distribution function $f_{1\nu}(\mathbf{r}, \mathbf{a})$: $\rho_\nu(\mathbf{r}, \mathbf{a}) = N_\nu f_{1\nu}(\mathbf{r}, \mathbf{a})$ as $\int f_{1\nu}(\mathbf{r}, \mathbf{a}) d\mathbf{r} d\mathbf{a} = 1$.

V. MODEL FREE ENERGY OF THE ROD-COIL DIBLOCK COPOLYMER

The equations for the phase-space densities of monomers and rigid rods derived above contain mean-field potentials:

$$
U_{MF}^{(1)}(\mathbf{r}_1) = \int C_{\nu,\eta}(\mathbf{r}_{12}, \mathbf{a}) \delta\rho_\eta(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a}, \quad (33)
$$

$$
U_{MF}^{(2)}(\mathbf{r}_1) = \int \chi(\mathbf{r}_{12}) \delta\rho_\eta(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a}, \quad (34)
$$

$$
U_{MF}^{(3)}(\mathbf{r}_1, \mathbf{a}) = \beta \int J(\mathbf{r}_{12}) P_2(\mathbf{a} \cdot \mathbf{a}_2) \delta\rho_r(\mathbf{r}_2, \mathbf{a}_2) d\mathbf{r}_2 d\mathbf{a}_2, \quad (35)
$$

where the direct correlation functions and/or pair interaction potentials are averaged over the position of the second particle.

The mean-field potentials possess the same translational symmetry as the corresponding phase of the block copolymer. In particular, in the lamellar phase the mean-field potentials are periodic with the period of the macroscopic lamellar structure and hence they can be expanded in Fourier series. Such an approach has been used in the molecular theory of smectic liquid crystals [42]. A mean-field potential can be written in the following general form:

$$
U_{MF}(\mathbf{r}_1) = \int V(r_{12}) \delta\rho_\nu(\mathbf{r}_2) d\mathbf{r}_2, \quad (36)
$$

where the function $V(r_{12}, \mathbf{a})$ represents $C_{\nu,\eta}(\mathbf{r}_{12}, \mathbf{a})$, $\chi(\mathbf{r}_{12})$ or $J(\mathbf{r}_{12}) P_2(\mathbf{a} \cdot \mathbf{a}_2)$. In the simplest case, the periodic part of the mean-field potential can be approximated by the first term in the Fourier expansion:

$$
\int V(r_{12}) \delta\rho_\nu(\mathbf{r}_2) d\mathbf{r}_2 = \rho_0 f_\nu \cos(\mathbf{q} \cdot \mathbf{r}_1) V(q) \psi_\nu, \quad (37)
$$

where $V(q) = \int V(r) \cos(\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}$, $\rho_\nu = N_\nu/V = \rho_0 f_\nu$ and $\psi_\nu = \langle \cos(\mathbf{q} \cdot \mathbf{r}) \rangle = \int \cos(\mathbf{q} \cdot \mathbf{r}) \delta\rho_\nu(\mathbf{r}) d\mathbf{r}$ is the translational order parameter similar to the one used in the theory of smectic liquid crystals. Then, in particular, the periodic part of the potential (34) can be approximated as:

$$
\int \chi_{rc}(\mathbf{r}_{12}) \delta\rho_\eta(\mathbf{r}_2, \mathbf{a}) d\mathbf{r}_2 d\mathbf{a} \approx \cos(\mathbf{q} \cdot \mathbf{r}_1) \rho_0 f_\eta \chi(q) \langle \cos(\mathbf{q} \cdot \mathbf{r}) \rangle
$$
$$
= \cos(q z_1) \rho_0 f_\eta \chi(q) \psi_\eta, \quad (38)
$$

where $\chi(q) \approx \chi(0) = \chi = \text{const}$ as the function $\chi(r)$ is very short-range compared with the period of the structure.

The nematic part Eq. (35) of the mean-field potential can be approximated in a similar way as

$$
\int J(\mathbf{r}_{12}) P_2(\mathbf{a} \cdot \mathbf{a}_2) \delta\rho_r(\mathbf{r}_2, \mathbf{a}_2) d\mathbf{r}_2 d\mathbf{a}_2
$$
$$
\approx \rho_0 f_r S J_0 P_2(\mathbf{a} \cdot \mathbf{n}) + \cos q z \, P_2(\mathbf{a} \cdot \mathbf{n}) \rho_0 f_r J_2 \sigma, \quad (39)
$$

where $S = \langle P_2(\mathbf{a} \cdot \mathbf{n}) \rangle$ is the orientational nematic order parameter and $\sigma = \langle \cos q z \, P_2(\mathbf{a} \cdot \mathbf{n}) \rangle$ is the mixed orientational-translational order parameter and $J_2 \approx \text{const}$.

One notes that the phase-space densities of coil and rod monomers are nonlinear functions of the order parameters and contain all higher order Fourier harmonics as well as multiple wave vectors. Similarly to the theory of smectic liquid crystals, the order parameters here are not assumed to be small and thus the theory can also be used to describe the case of relatively strong segregation.

The direct correlation functions in Eq. (33) are rather complex functions of the orientation of rigid rod fragments. In the first approximation, it is possible to use the following interpolation expressions which allow writing the corresponding mean-field potentials in terms of the principal order parameters:

$$
C_{rc}(\mathbf{q}, \mathbf{a}) \approx C_{rc}^0(q) + C_{rc}^{(2)}(q) P_2(\mathbf{a} \cdot \mathbf{k}), \quad (40)
$$

where $\mathbf{k} = \mathbf{q}/q$ and

$$
C_{rc}^0(q) = \int C_{rc}(\mathbf{q}, \mathbf{a}) d\mathbf{a}, \quad (41)
$$

Here the function $C_{rc}^{(2)}(q)$ is determined by the condition that this approximation is exact when $\mathbf{a} = \mathbf{k}$:

$$
C_{rc}(\mathbf{q}, \mathbf{a} = \mathbf{k}) = C_{rc}^0(q) + C_{rc}^{(2)}(q). \quad (42)
$$

In a similar way, the direct correlation function between rod monomers can be approximated as

$$
C_{rr}(\mathbf{q}, \mathbf{a}_1, \mathbf{a}_2) \approx C_{rr}^0(q) + \tfrac{1}{2} C_{rr}^{(2)}(q) P_2(\mathbf{a}_1 \cdot \mathbf{k})
$$
$$
+ \tfrac{1}{2} C_{rr}^{(2)}(q) P_2(\mathbf{a}_2 \cdot \mathbf{k}), \quad (43)
$$

where we have taken into account that the correlation function is symmetric, and the function $C_{rr}^{(2)}(q)$ is determined by an equation similar to Eq. (42). After substituting into the free energy these correlation functions together with the mean-field potentials, one should set $\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}$ as the rod segments are always parallel.

Finally, the phase-space monomer densities in the lamellar phase can be written in the form:

$$\rho_c(z, \mathbf{a}) = Z_c^{-1} \exp\left[\cos(qz)\rho_0\left(f_c C_{cc}^0(q)\psi_c + f_r C_{rc}^0(q)\psi_r\right.\right.$$
$$\left.\left. + f_r C_{rc}^{(2)}(q)\sigma - f_r \chi \psi_r\right)\right], \tag{44}$$

$$\rho_r(z, \mathbf{a}) = Z_r^{-1} \exp\left[\cos(qz)\rho_0\right.$$
$$\times \left(f_r C_{rr}^0(q)\psi_r + f_c C_{rc}^0(q)\psi_c - f_c \chi \psi_c\right)$$
$$+ \tfrac{1}{2}\cos(qz)P_2(\mathbf{a}\cdot\mathbf{k})\rho_0\left(f_r C_{rr}^{(2)}(q)\psi_r + 2f_c C_{rc}^{(2)}(q)\psi_c\right.$$
$$\left. + 2f_r\beta J_2\sigma\right) + \tfrac{1}{2}\cos(qz)\rho_0 f_r C_{rr}^{(2)}(q)\sigma$$
$$\left. + \rho_0 f_r \beta J_0 S P_2(\mathbf{a}\cdot\mathbf{k})\right]. \tag{45}$$

Here one should use the relationship $f_c\psi_c = -f_r\psi_r$ which follows from the incompressibility condition in the first approximation.

Substituting Eqs. (44) and (45) into Eq. (29) one obtains the free-energy density of the lamellar phase as

$$\beta F/V = \tfrac{1}{2}\rho_0^2\sigma\left[f_r^2 C_{rr}^{(2)}(q)\psi_r + 2f_c f_r C_{rc}^{(2)}(q)\psi_c\right]$$
$$+ \tfrac{1}{2}\beta\rho_0^2 S^2 f_r^2 J_0 + \tfrac{1}{2}\beta\rho_0^2 f_r^2 J_2\sigma^2$$
$$+ \tfrac{1}{2}\rho_0^2 f_r^2 C_{rr}^0(q)\psi_r^2 + \tfrac{1}{2}\rho_0^2 f_c^2 C_{cc}^0(q)\psi_c^2$$
$$+ \rho_0^2 f_r f_c C_{rc}^0(q)\psi_r\psi_c - \rho_0^2 f_r f_c \chi \psi_c\psi_r$$
$$- \rho_0 f_r \ln Z_r - \rho_0 f_c \ln Z_c, \tag{46}$$

where V is the polymer volume and

$$Z_c = \int dz \exp\left[\rho_0\cos(qz)\left(f_c C_{cc}^0(q)\psi_c\right.\right.$$
$$\left.\left. + f_r C_{rc}^{(2)}(q)\sigma + f_r C_{rc}^0(q)\psi_r - f_r\chi\psi_r\right)\right], \tag{47}$$

$$Z_r = \int dz d\mathbf{a} \exp\left[\rho_0\cos(qz)\left(f_r C_{rr}^0(q)\psi_r\right.\right.$$
$$+ f_c C_{rc}^0(q)\psi_c - f_c\chi\psi_c) + \rho_0\cos(qz)P_2(\mathbf{a}\cdot\mathbf{k})$$
$$\times\left(\frac{1}{2}f_r C_{rr}^{(2)}(q)\psi_r + f_c C_{rc}^{(2)}(q)\psi_c + \beta f_r J_2\sigma\right)$$
$$\left. + \frac{1}{2}\cos(qz)\rho_0 f_r C_{rr}^{(2)}(q)\sigma + \rho_0 f_r\beta J_0 S P_2(\mathbf{a}\cdot\mathbf{k})\right], \tag{48}$$

where $\mathbf{k}$ is along z and $J_0 > 0$, $\chi > 0$.

VI. CORRELATION FUNCTIONS FOR ROD-COIL BLOCK COPOLYMERS

For a molecule schematically presented in Fig. 1, the direct correlation functions are given by the general Eq. (22) derived above. In particular, it yields the following explicit expressions:

$$C_{rr}^0(\mathbf{q}, \mathbf{a}) = \frac{1}{\rho_0 f_r} - \frac{G_{cc}^0}{\text{Det}^0}, \tag{49}$$

$$C_{cc}^0(\mathbf{q}, \mathbf{a}) = \frac{1}{\rho_0 f_c} - \frac{G_{rr}^0}{\text{Det}^0}, \tag{50}$$

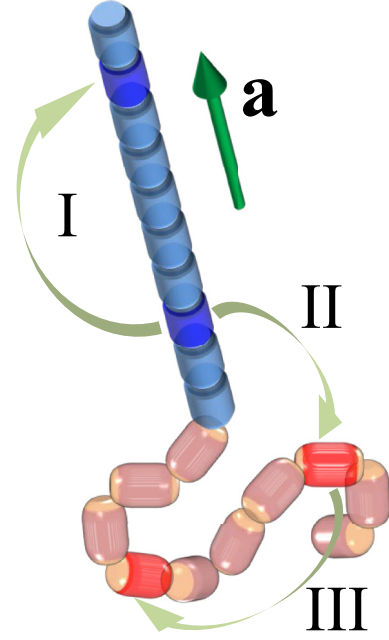$$C_{rc}^0(\mathbf{q}, \mathbf{a}) = \frac{G_{rc}^0}{\text{Det}^0}, \tag{51}$$

FIG. 1. Schematic of a rod-coil polymer molecule with rigid and flexible parts consisting of 10 fragments each. The rod axis $\mathbf{a}$ is shown by the green arrow. The explicitly accounted intra-molecular rod-rod (I), rod-coil (II), and coil-coil (III) correlations are indicated by the bent arrows.

where

$$\text{Det}^0 = G_{rr}^0 G_{cc}^0 - (G_{rc}^0)^2, \tag{52}$$

where

$$G_{rr}^0(q) = \int G_{rr}(\mathbf{q}, \mathbf{a})d\mathbf{a}, \tag{53}$$

$$G_{cc}^0(q) = \int G_{cc}(\mathbf{q}, \mathbf{a})d\mathbf{a}, \tag{54}$$

$$G_{rc}^0(q) = \int G_{rc}(\mathbf{q}, \mathbf{a})d\mathbf{a}. \tag{55}$$

The density correlation function between coil monomers in the disordered system of noninteracting copolymer chains has been calculated by several authors starting from Leibler [23,37,39]. It can be expressed as

$$G_{cc}(q) = \rho_0 N \frac{2}{x^2}[f_c x + \exp(-f_c x) - 1], \tag{56}$$

where N is the total number of monomers in the polymer molecule, f_c is the fraction of coil monomers and $x = q^2 N a^2/6 = q^2 R^2$.

The rod-coil and rod-rod monomer correlation functions $G_{rc}(\mathbf{q}, \mathbf{a})$ and $G_{rr}(\mathbf{q}, \mathbf{a})$ in the same reference disordered phase, which depend on the orientation of the rod segment of a copolymer macromolecule, can be calculated using the general expressions derived in Ref. [22] and can be expressed as

$$G_{rc}(\mathbf{q}, \mathbf{a}) = \rho_0 N f_r f_c K_R^{(1)}(y) K_c^{(1)}(x), \tag{57}$$

where

$$K_c^{(1)}(x) = \frac{1}{x}[1 - \exp(-x)], \tag{58}$$

and

$$K_R^{(1)}(y) = \text{Re} \frac{1}{N f_r} \int_0^{N f_r} \exp[i(\mathbf{q} \cdot \mathbf{a})s]ds = \frac{\sin(y)}{y}, \tag{59}$$

where $y = N f_r q^*(\mathbf{k} \cdot \mathbf{a})$ and where $q^* = qa$.

The desnity-density correlation function between rod monomers in the disordered system of noninteracting copolymer chain can be expressed as

$$G_{rr}(\mathbf{q}, \mathbf{a}) = \rho_0 \frac{1}{N} \int_0^{N f_r} \int_0^{N f_r} \exp[i(s - s')q^*(\mathbf{q} \cdot \mathbf{a})]dsds'$$

$$= 2\rho_0 N f_r^2 \frac{(1 - \cos y)}{y^2}. \tag{60}$$

Finally, the functions $C_{\nu\eta}^2(\mathbf{q})$ can be written in the form

$$C_{rr}^{(2)}(q) = C_{rr}^1(\mathbf{q}) - C_{rr}^0(q), \tag{61}$$

$$C_{cc}^{(2)}(q) = C_{cc}^1(\mathbf{q}) - C_{cc}^0(q), \tag{62}$$

$$C_{rc}^{(2)}(q) = C_{rc}^1(\mathbf{q}) - C_{rc}^0(q), \tag{63}$$

where the functions $C_{\nu\eta}^1(\mathbf{q})$ are obtained by setting $(\mathbf{a} \cdot \mathbf{k}) = 1$ in the equations for the functions $C_{\nu\eta}^{(2)}(\mathbf{q})$, and hence

$$C_{rr}^1(\mathbf{q}) = \frac{1}{\rho_0 f_r} - \frac{G_{cc}^1}{\text{Det}^1} \tag{64}$$

$$C_{cc}^1(\mathbf{q}) = \frac{1}{\rho_0 f_c} - \frac{G_{rr}^1}{\text{Det}^1} \tag{65}$$

$$C_{rc}^1(\mathbf{q}) = \frac{G_{rc}^1}{\text{Det}^1}, \tag{66}$$

where

$$\text{Det}^1 = G_{rr}^1 G_{cc}^1 - (G_{rc}^1)^2. \tag{67}$$

Here the functions $G_{rr}^1, G_{cc}^1, G_{rc}^1$ are given by Eqs. (41)–(45) with $y = y^* = N f_r q^*$.

VII. PHASE DIAGRAMS AND ORDER PARAMETER PROFILES

Phase diagrams and the profiles of the orientational and translational order parameters of rod-coil diblock copolymers can be calculated numerically by minimization of the free-energy Eq. (46). A typical temperature-concentration phase diagram is presented in Fig. 2. One notes that the same sequence of phases (i.e., isotropic-nematic-lamellar) is often observed experimentally in rod-coil diblock copolymers [4]. The same sequence is also present in the phase diagrams obtained by means of computer simulations [32,33] and self-consistent field theory [3].

At sufficiently large fraction of flexible chains (approximately above $f_c = 0.8$. both theoretically and experimentally) only the isotropic phase is stable. At lower fraction f_c, the system undergoes a transition from the isotropic phase into the nematic phase and then into the separated lamellar phase with
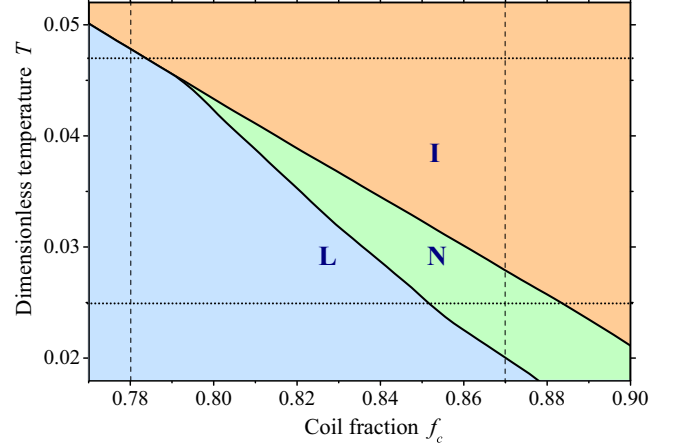

FIG. 2. Phase diagram of the rod-coil block copolymer in terms of the coil fraction f_c and dimensionless temperature $T = (\beta J_0)^{-1}$ for $\chi = 3, N = 10$ and $J_2 = J_0/3$. Three present phases are: isotropic (I), nematic (N), and lamellar (L).

the decreasing temperature or the decreasing f_c. The isotropic-nematic transition temperature $T_{\text{NI}}(f_c)$ is a decreasing function of the coil fraction f_c as it is indeed observed experimentally [43]. In this study, we ignore the possible hexagonal phase and some other complex phases because we are mainly interested in liquid-crystal-like phases and in a competition between the orientational ordering and microphase separation.

Order parameter profiles calculated as functions of the coil fraction f_c are presented in Fig. 3 for two different horizontal cross sections of the phase diagram shown in Fig. 2 at temperatures $T = 0.047$ and $T = 0.025$. The temperature
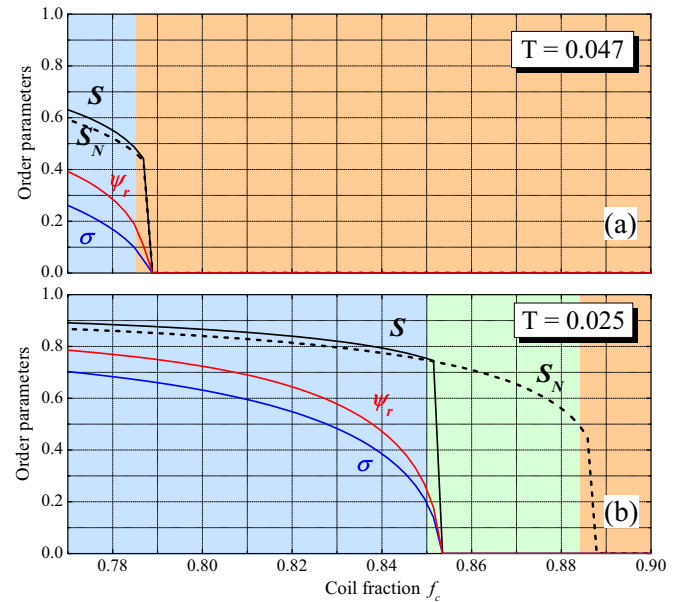

FIG. 3. Order parameters (indicated on the lines) as functions of the coil fraction f_c for two representative sections of the phase diagram in Fig. 2 at two dimensionless temperatures $T = 0.047$ (a) and $T = 0.025$ (b). The order parameters in the lamellar phase are shown by solid lines, the order parameter S_N of the homogeneous nematic phase is shown by dashed lines.
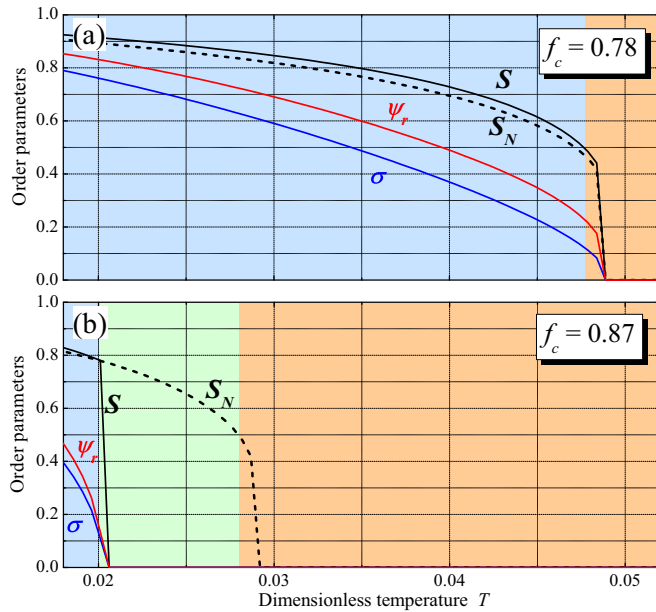
FIG. 4. Order parameters (indicated on the lines) as functions of the dimensionless temperature T for two representative sections of the phase diagram in Fig. 2 at the coil fraction values temperatures $f_c = 0.78$ (a) and $f_c = 0.87$ (b). The order parameters in the lamellar phase are shown by solid lines, the order parameter S_N of the homogeneous nematic phase is shown by dashed lines.

FIG. 5. Phase diagram of the rod-coil block copolymer in terms of the coil fraction f_c and dimensionless temperature $T = (\beta J_0)^{-1}$ for $\chi = 3$ and $J_2 = J_0$. Two present phases are isotropic (I) and lamellar (L).

variation of the same order parameters is presented in Fig. 4 for two vertical cross sections of the phase diagram which correspond to $f_c = 0.78$ and $f_c = 0.87$.

In the general case, there exist three different order parameters which specify the ordering of rigid fragments in the lamellar phase. The first parameter is the translational order parameters $\psi = \langle \cos qz \rangle$ which characterizes the positional ordering of rigid fragments in the phase separated state. One notes that exactly the same order parameter describes the smectic order in conventional smectic liquid crystals, because the lamellar phase is characterized by the same symmetry group as the smectic A phase. The second-order parameter $\sigma = \langle \cos qz \, P_2(\mathbf{a} \cdot \mathbf{k}) \rangle$ describes the simultaneous orientational and translational order of rigid fragments, and, finally, the purely orientational ordering of the rigid fragments along the axis of the lamellar phase is specified by the nematic order parameter $S = \langle P_2(\mathbf{a} \cdot \mathbf{k}) \rangle$. The temperature variation of the order parameters ψ, σ and S across the nematic and the nematic-lamellar phase is presented in Fig. 3 One notes that all order parameters experience significant jumps at the nematic-lamellar phase transition point and hence the nematic-lamellar transition is strongly first order. In contrast to the nematic-isotropic phase transition, which is always first order by symmetry, the nematic-lamellar transition may be second order similarly to the nematic-smectic A transition in liquid crystals. Apparently, in the case of rod-coil block copolymers strong microphase separation effects drive the transition towards the first order. The dependence of all three order parameters on the coil fraction f_c, presented in Fig. 4, is qualitatively similar to the corresponding temperature variation, and in this cross section the nematic-lamellar transition is also strongly first order.
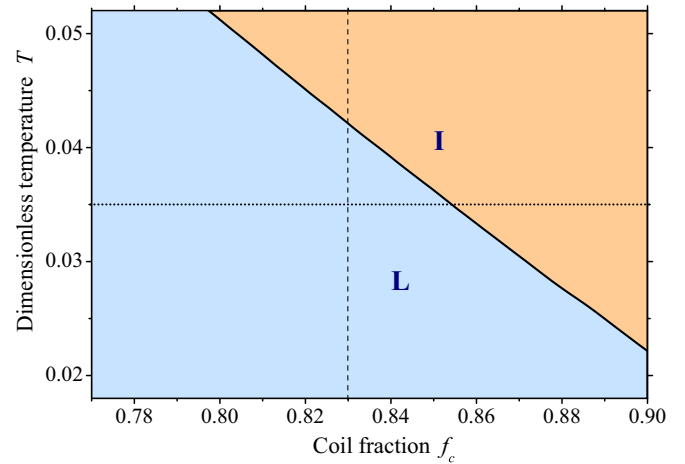
One can readily see that the orientational order parameter S and the mixed orientational-translational order parameter σ are rather large while the purely translational order parameter ψ is relatively small. This enables one to assume that the transition into the lamellar phase is driven by a condensation of the corresponding orientational-density wave characterized by the parameter σ and strongly supported by the high degree of the orientational order specified by the parameter S. In the general case the mixed order parameter σ specifies the correlation between the orientational and the translational order. When such a correlation is weak the orientational and translational degrees of freedom can approximately be decoupled and the parameter σ can be decomposed as $\sigma \approx S\psi$. In this case, the order parameter σ should be substantially smaller than both S and ψ. On the contrary, in the lamellar phase σ stays rather close to ψ, indicating that the orientational and positional orders are correlated.

It should be noted that the orientational ordering of rigid fragments in the lamellar phase of rod-coil copolymers has not been considered in the existing theory of block copolymers [21,22,25,26] and the mixed orientational-translational order parameter σ has not been employed in the theory of mesogenic polymers so far. At the same time, the parameter σ seems to be very important in the molecular theory of phase separated phases exhibited by rod-coil block copolymers because it is linearly related to the translational order parameter ψ. Taking into consideration that in the framework of this model the parameter σ remains close ψ, one may assume that the nematic-lamellar transition in rod-coil block copolymers is driven by a condensation of the orientational-density wave which simultaneously breaks the rotational and translational symmetries.

Such a behavior is not necessarily related to the existence of the high temperature nematic phase on the phase diagram presented in Fig. 2. Indeed, a phase diagram of a diblock copolymer with a larger parameter J_2 does not contain the nematic phase, as can be seen in Fig. 5, while the corresponding profiles of the order parameters are shown in Fig. 6. One can
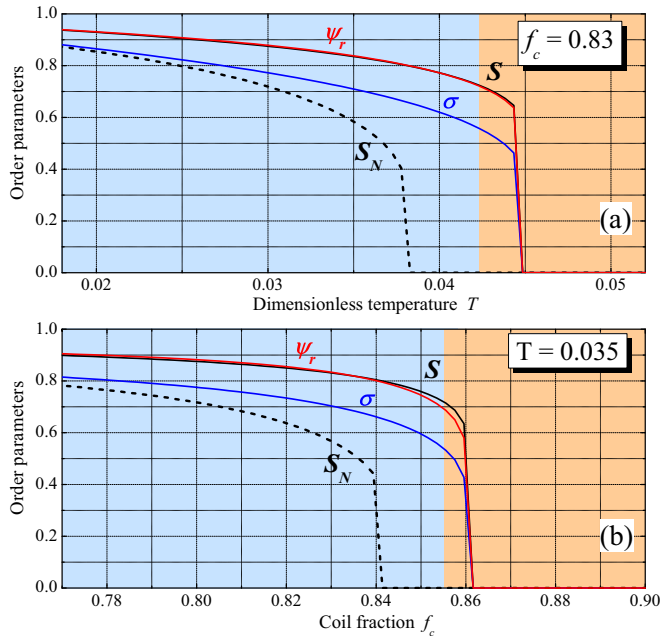
FIG. 6. Order parameters (indicated on the lines) as functions of the dimensionless temperature T (a) and the coil fraction f_c (b) for two representative sections of the phase diagram shown by the vertical dashed ($f_c = 0.83$) and horizontal dotted ($T = 0.035$) lines in Fig. 5 correspondingly. The order parameters in the lamellar phase are shown by solid lines, the order parameter S_N of the homogeneous nematic phase is shown by dashed lines. The background colours correspond to those of the stable phases indicated in Fig. 5.

readily see that the orientational order σ in the lamellar phase stays also rather close to the translational order parameter ψ here. Moreover, the parameter S in the lamellar phase is always larger than the orientational order parameter S_N in the virtual nematic phase which is globally unstable in this case.

VIII. DISCUSSION

In this paper, we have generalized the density functional approach, which is frequently used in the molecular theory of liquid crystals, to the case of rod-coil diblock copolymers. The free energy of the lamellar and the nematic phases has been expressed as a functional of the phase-space densities of rod and coil monomers which also depend on the orientation of the rods. The phase-space densities of the monomers, which are proportional to the corresponding one-particle distribution functions, are determined by minimization of the free-energy functional which results in the self-consistent equations for the densities. This also enables one to obtain self-consistent equations for translational and orientational order parameters of the rods.

The free energy is finally expressed in terms of the repulsion constant between rod and coil monomers, the orientational Maier-Saupe interaction potential between rods and the direct pair correlation functions between monomers in the copolymer chain which are calculated in the reference disordered phase of noninteracting copolymer macromolecules. The direct monomer-monomer correlation functions of the disordered reference phase have been expressed in terms of

the corresponding density-density pair correlation functions between monomers using the Ornstein-Zernike equation. Finally, the theory employs the density-density monomer correlation functions obtained by Leibler and others [23,37,39] for Gaussian flexible copolymer chains and by Reeders and ten Brinke for rod-coil copolymer chains [22], respectively. Phase diagrams and a number of orientational and translational order parameter profiles have been calculated numerically.

One notes that the present theory is not limited to the case of weak segregation. Indeed, the order parameters are not assumed to be small and the one-particle densities appear to be nonlinear functions of the order parameters and are formally valid for any values of the Flory-Higgins parameter χ. As a result, the present theory enables one to describe the case of relatively strong segregation. Indeed, in Leibler's theory, for example, the monomer density in the lamellar phase is described by a single Fourier harmonic which is valid only in the vicinity of the transition into the disordered phase. In contrast, in the present theory, the density is an exponential function of the harmonic wave and hence it contains contributions from all higher order Fourier harmonics. The theory can then be used also far from the phase transition point, when the density distribution is significantly different from a simple cosine profile. At the same time, the higher order parameters are approximately expressed in terms of the three principal order parameters of the lamellar phase $\psi = \langle \cos qz \rangle$, $S = \langle P_2(\mathbf{a} \cdot \mathbf{k}) \rangle$ and $\sigma = \langle \cos qz \, P_2(\mathbf{a} \cdot \mathbf{k}) \rangle$ which describe the positional, the orientational, and the simultaneous orientational and positional ordering of rigid molecular fragments. Thus, the present theory cannot be used in the limiting case of perfect segregation because in this case the corresponding approximation is not valid.

It should be noted that the mixed orientational-translational order parameter σ is widely used in the molecular theory of smectic liquid crystals (see, for example, Refs. [35,42,44]), but it has not been employed so far in the theory of mesogenic copolymers. At the same time the definition of the translational order parameter ψ is more general than the one used in the phenomenological theory of block copolymers [22,23]. In the present approach the order parameter ψ is defined as the thermal average $\langle \cos qz \rangle$ which is similar to the definition of the smectic order parameter in the theory of liquid crystals or in the theory of crystallization. However, in the phenomenological theory of block copolymers the translational order parameter is proportional to the amplitude of the density wave in the microphase separated state which coincides with the definition of ψ in the case of weak segregation when the densities are approximately represented by the first Fourier harmonics.

Two phase diagrams have been presented for different values of the strength J_2 of mixed orientational-translational interaction between rod monomers in different macromolecules, one of them containing both the nematic and the lamellar phase. All three order parameters have been calculated numerically as functions of temperature and composition of the block copolymer for several cross sections of the phase diagrams. In all cases all order parameters S, ψ, and σ are significantly large, which indicates that both the nematic-lamellar and the isotropic-lamellar phase transitions are driven by the condensation of the orientation-density wave with a simulta-

neous orientational and translational ordering of rigid fragments. The high values of the nematic order parameter in the lamellar phase indicate that the orientational order is partially induced by the structural anisotropy of the lamellar phase even in the case when the nematic phase is globally unstable.

Thus, the orientational ordering of rigid molecular fragments plays a very important role in the lamellar phase of rod-coil diblock copolymers, and the pronounced stability of the lamellar phase in such systems is determined both by the microphase separation effects and by the long-range smectic liquid-crystal ordering. In general, rod-coil block copolymers appear to be very interesting highly ordered soft matter systems which combine the properties of coil-coil block copolymers, which do not possess any orientational order, and conventional smectic liquid crystals where normally the order is not determined by phase separation effects. In this paper we have ignored the hexagonal phase and more complicated phases because we are mainly interested in the competition between liquid-crystal order and microphase separation. One notes that the same sequence of phases (i.e., isotropic-nematic-lamellar) has also been found in computer simulations [32,33] and described by the self-consistent field theory [3]. From the experimental point of view, the lamellar phase seems to be the most stable ordered phase although some experimental diagrams also contain the hexagonal phase as well as phases with more complicated morphology. In contrast, a broad hexagonal phase and a very rich variety of other phases has been observed in rod-coil block copolymers in which the rigid block is composed of a flexible main chain with rigid mesogenic side groups [45,46].

In the present theory the free energy of a copolymer chain in a self-consistent mean-field is calculated approximately using only pair direct correlation functions between monomers in a copolymer chain. In contrast, in the self-consistent field theory (SCFT) [24–27] the free energy of a single chain in a mean-field is calculated by numerically evaluating the path integral along the chain which is, in principle, much more accurate. The interaction between different chains is still taken into account using random phase approximation similar to the present theory and the theory of Leibler and others. The SCF theory has been very successful in the description of coil-coil block copolymers, but even in this case it is difficult to simulate large three-dimensional polymer systems as the computational cost increases dramatically with the increasing chain length. The computational challenges become even more serous in the case of rod-coil block copolymers as one has to take into consideration also the orientational degrees of freedom and anisotropic interactions between rigid rods. So far the SCFT has been applied to rod-coil block copolymers using simplified models including simple lattice models [26,27], two-dimensional models [25], or the models without anisotropic interaction between rods or with their perfect orientational order [24,26,27]. In all cases, the orientational order of rods has not been described in any detail.

Another version of the SCF theory, in which the evaluation of the path integral along the chain is replaced by solving the Edwards equations [29–31], appears to be more suitable for the qualitative description of rod-coil block copolymers because it has been possible to describe the variety of different phases and the orientational ordering of rigid chains. In this approach, however, both the flexible chain and the rigid rod are modeled using the same formalism of ideal Gaussian chains where the rod like chain is characterized by a larger persistence length.

An advanced liquid state theory (the so-called PRISM theory) has also been applied to coil-coil block copolymers [47,48]. The PRISM theory also employs direct correlation functions between monomers and the generalized Orstein-Zernike equation containing both interchain and intrachain correlation functions. In the first approximation, the intrachain correlations are treated using the model of ideal Gaussian chains similar to the present theory and the theory of Leibler. At the same time, the more general Ornstein-Zernike-like equation together with the Percus-Yevich closure enables one to evaluate the intechain radial correlation function which is a significant step forward compared with the random phase approximation. So far the PRISM theory has been successfully applied to the system of flexible chains composed of spherical monomers and, as far as we know, it has not been used for describing the rod-coil block copolymers. In principle, the main equations of the PRISM theory can be generalized to the case of copolymers with orientational degrees of freedom but the resulting coupled integral equations are expected to be very complex and difficult to solve. However, some ideas of the PRISM theory can in principle be used to develop a more advanced density functional theory of rod-coil block copolymers.

The main limitation of the present theory is related to the fact that only phases with one dimensional periodicity can be described by the equations presented above. The hexagonal phase and more complicated phases can be described analogously using the density functional formalism by expressing the mean-field potentials in a more general form (consistent with the symmetry of the corresponding phase) and by taking into account additional order parameters. This is more challenging from the computational point of view and will be implemented in our future papers.

[1] R. A. Segalman, Mater. Sci. Eng. R **48**, 191 (2005).

[2] C. Harrison, J. A. Dagata, and D. H. Adamson, *Developments in Block Copolymer Science and Technology* (John Wiley & Sons, New York, 2004), pp. 295–323.

[3] B. D. Olsen and R. A. Segalman, Mater. Sci. Eng., R **62**, 37 (2008).

[4] R. A. Segalman, B. McCulloch, S. Kirmayer, and J. J. Urban, Macromolecules **42**, 9205 (2009).

[5] K. Sivula, Z. T. Ball, N. Watanabe, and J. M. J. Fréchet, Adv. Mater. **18**, 206 (2006).

[6] J. C. M. van Hest, Polym. Rev. **47**, 63 (2007).

[7] H.-A. Klok, J. Polym. Sci., Part A: Polym. Chem. **43**, 1 (2004).

[8] K. Loos and A. H. E. Müller, Biomacromolecules **3**, 368 (2002).

[9] D. M. Haddleton and K. Ohno, Biomacromolecules **1**, 152 (2000).

[10] H. M. König, T. Gorelik, U. Kolb, and A. F. M. Kilbinger, J. Am. Chem. Soc. **129**, 704 (2007).

[11] Y. Pae and F. W. Harris, J. Polym. Sci. Part A: Polym. Chem. **38**, 4247 (2000).

[12] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).

[13] Y. Tao, B. McCulloch, S. Kim, and R. A. Segalman, Soft Matter **5**, 4219 (2009).

[14] C. L. Chochos, J. K. Kallitsis, and V. G. Gregoriou, J. Phys. Chem. B **109**, 8755 (2005).

[15] S. Becker, C. Ego, A. C. Grimsdale, E. J. List, D. Marsitzky, A. Pogantsch, S. Setayesh, G. Leising, and K. Müllen, Synth. Met. **125**, 73 (2001).

[16] Y. Tao, B. Ma, and R. A. Segalman, Macromolecules **41**, 7152 (2008).

[17] E. G. Bellomo, M. D. Wyrsta, L. Pakstis, D. J. Pochan, and T. J. Deming, Nat. Mater. **3**, 244 (2004).

[18] A.-V. Ruzette and L. Leibler, Nat. Mater. **4**, 19 (2005).

[19] G. Rabani, H. Luftmann, and A. Kraft, Polymer **47**, 4251 (2006).

[20] A. N. Semenov and S. V. Vasilenko, Sov. Phys. JETP **63**, 70 (1986).

[21] R. Hołyst and M. Schick, J. Chem. Phys. **96**, 730 (1992).

[22] M. Reenders and G. ten Brinke, Macromolecules **35**, 3266 (2002).

[23] L. Leibler, Macromolecules **13**, 1602 (1980).

[24] M. W. Matsen and C. Barrett, J. Chem. Phys. **109**, 4108 (1998).

[25] V. Pryamitsyn and V. Ganesan, J. Chem. Phys. **120**, 5824 (2004).

[26] M. Müller and M. Schick, Macromolecules **29**, 8900 (1996).

[27] J.-Z. Chen, C.-X. Zhang, Z.-Y. Sun, Y.-S. Zheng, and L.-J. An, J. Chem. Phys. **124**, 104907 (2006).

[28] R. Hołyst and P. Oswald, Macromol. Theory Simul. **10**, 1 (2001).

[29] D. Düchs and D. E. Sullivan, J. Phys.: Condens. Matter **14**, 12189 (2002).

[30] R. C. Hidalgo, D. E. Sullivan, and J. Z. Y. Chen, J. Phys.: Condens. Matter **19**, 376107 (2007).

[31] J. Tang, Y. Jiang, X. Zhang, D. Yan, and J. Z. Y. Chen, Macromolecules **48**, 9060 (2015).

[32] M. R. Wilson, A. B. Thomas, M. Dennison, and A. J. Masters, Soft Matter **5**, 363 (2009).

[33] H. Wu, L. He, X. Wang, Y. Wang, and Z. Jiang, Soft Matter **10**, 6278 (2014).

[34] T. Jiang and J. Wu, J. Chem. Phys. **127**, 034902 (2007).

[35] M. A. Osipov, *Handbook of Liquid Crystals* (Wiley-VCH Verlag GmbH, Berlin, 2008), pp. 40–71.

[36] R. Evans, *Fundamentals of Inhomogeneous Fluids* (Decker, New York, 1992).

[37] T. Ohta and K. Kawasaki, Macromolecules **19**, 2621 (1986).

[38] T. Ohta and K. Kawasaki, Macromolecules **23**, 2413 (1990).

[39] T. Uneyama and M. Doi, Macromolecules **38**, 196 (2005).

[40] Y. Singh, Phys. Rev. A **30**, 583 (1984).

[41] Y. Bohbot-Raviv and Z.-G. Wang, Phys. Rev. Lett. **85**, 3428 (2000).

[42] M. V. Gorkunov, M. A. Osipov, N. Kapernaum, D. Nonnenmacher, and F. Giesselmann, Phys. Rev. E **84**, 051704 (2011).

[43] B. D. Olsen and R. A. Segalman, Macromolecules **40**, 6922 (2007).

[44] W. L. McMillan, Phys. Rev. A **4**, 1238 (1971).

[45] L.-Y. Shi, Y. Zhou, X.-H. Fan, and Z. Shen, Macromolecules **46**, 5308 (2013).

[46] H. Pan, J. Ping, M. Zhang, A. Xiao, X. Lyu, Z. Shen, and X. Fan, Macromol. Chem. Phys. **219**, 1700593 (2018).

[47] E. F. David and K. S. Schweizer, J. Chem. Phys. **100**, 7767 (1994).

[48] K. S. Schweizer and J. G. Curro, *Advances in Polymer Science* (Springer, Berlin, 1987), pp. 319–377.