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Theory of Anisotropic Fluctuations in Ordered Block Copolymer Phases

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ABSTRACT: A general theoretical framework for the study of anisotropic composition fluctuations about an ordered block copolymer phase is developed. The approach is based on the idea that, in order to study the effects of fluctuations around an ordered broken symmetry phase, the theory must be formulated as a self-consistent expansion around the mean-field solution of this ordered state. A random phase approximation treatment of the theory leads to anisotropic correlation functions for the system. It is shown that the calculation of the polymer correlation functions in an ordered phase is equivalent to the calculation of the energy bands and eigenfunctions for an electron in a periodic potential. This general method is applied to the lamellar phase of block copolymers. The calculated anisotropic scattering intensity captures the main features observed experimentally, including the secondary peaks due to fluctuations with hexagonal symmetry. The origin of the anisotropic fluctuations can be traced to the formation of "energy" bands, similar to electronic states in solids.

I. Introduction

Block copolymers are fascinating materials with unique structural and mechanical properties.[1,2] Due to their amphiphilic nature, AB diblock copolymers self-assemble into a variety of ordered microphases.[1−3] At high temperatures, A and B blocks mix homogeneously to form a disordered phase. As the temperature is decreased (or the Flory−Huggins χ parameter is increased), the blocks undergo a spatial segregation. However, a macroscopic phase separation cannot occur because the AB blocks are chemically connected at the junctions. The phase separation is, therefore, necessarily on a mesoscopic scale, forming A- and B-rich domains separated by internal interfaces. The competition between the spontaneous curvature of the internal interfaces and the entropic stretching (or packing) of the A and B blocks dictates the symmetry of the equilibrium phases. The symmetry of the ordered phases is controlled by the degree of segregation and the chemical composition of the copolymers. The segregation of the blocks is quantified by the product χZ, where $Z = Z_A + Z_B$ is the degree of polymerization of the copolymers, and Z_A and Z_B are the degrees of polymerization of the A and B blocks, respectively. The chemical composition of the copolymers is quantified by the ratio $f = Z_A/Z$. A decrease in χZ drives the melt from an ordered phase to the disordered phase. Changes in f affect the shape and packing symmetry of the ordered structure. Besides the well-known lamellar, cylindrical, and spherical phases,[1,3,4] more complicated structures such as the bicontinuous cubic phase and the hexagonally modulated and perforated layered phases have been recently identified.[3,5,6]

Theoretically, the study of diblock copolymer melts has been based on a simplified, standard model, in which the diblock copolymer chains are assumed to be flexible chains obeying Gaussian statistics.[7] The polymer conformations are specified by the position of the monomer, $\mathbf{R}(t)$. Each monomer is further assumed to

have a statistical length b_α. The hard-core repulsive interactions between the molecules are accounted for by an incompressibility constraint where the average monomer concentration is required to be uniform. The remaining interactions are modeled by a local enthalpy term $\chi \phi_A(\mathbf{r}) \phi_B(\mathbf{r})$, where $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are the volume fractions of the A and B monomers at position $\mathbf{r}$. This simple model captures the three most important features of the system: chain conformation entropy, incompressibility, and immiscibility between unlike monomers. The thermodynamics of a diblock copolymer melt can, therefore, be described by the partition function of the model. The partition function may be cast in several equivalent forms. On particularly simple and convenient formulation is to write the partition function of the melt as a functional integral over the monomer concentrations $\phi_\alpha(\mathbf{r})$ and two auxiliary fields $\omega_\alpha(\mathbf{r})$ ($\alpha =$ A, B).[8,9] The functional integral is carried out with the incompressibility constraint and with an integrand of the form $\exp\{-F(\{\phi\}, \{\omega\})\}$. The free energy functional is the sum of three terms: an enthalpic contribution, an entropic contribution, and a coupling term,

$$F = \int d\mathbf{r} \left[\chi \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - \sum_\alpha \omega_\alpha(\mathbf{r}) \phi_\alpha(\mathbf{r}) \right] - \frac{V}{Z} \ln Q_c(\{\omega_\alpha\}) \quad (1)$$

where V is the volume of the system, and Q_c is the partition function of a single diblock copolymer chain in the external fields $\omega_\alpha(\mathbf{r})$.[9] It is important to note that $Q_c(\{\omega\})$ is a functional of $\omega_\alpha(\mathbf{r})$. Specifically, the single-chain partition function Q_c is determined by

$$Q_c = \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_A(\mathbf{r}_1, Z_A | \mathbf{r}_2) Q_B(\mathbf{r}_2, Z_B | \mathbf{r}_3) \quad (2)$$

where the propagators $Q_\alpha(\mathbf{r}, t | \mathbf{r}')$ are

$$Q_\alpha(\mathbf{r},\ t|\mathbf{r}') =$$

$$\int_{\mathbf{R}(0)=\mathbf{r}'}^{\mathbf{R}(t)=\mathbf{r}} \mathscr{D}\mathbf{R}(t)\ \exp\left[-\int_0^{Z_\alpha} dt\left(\frac{3}{2b_\alpha^2}\left(\frac{d\mathbf{R}(t)}{dt}\right)^2 + \omega_\alpha[\mathbf{R}(t)]\right)\right] \tag{3}$$

Physically $Q_\alpha(\mathbf{r},\ t|\mathbf{r}')$ is the probability distribution of monomer t at $\mathbf{r}$, given that monomer 0 is at $\mathbf{r}'$, in the presence of an external field $\omega_\alpha(\mathbf{r})$. From the expression for the free energy functional, it is obvious that there are two kinds of inhomogeneities in the system. The first is the inhomogeneity in the polymer concentrations, $\phi_\alpha(\mathbf{r})$, which leads to an enthalpic contribution to the free energy. The second is the inhomogeneity in the field $\omega_\alpha(\mathbf{r})$, which leads to non-Gaussian polymer conformations. These two kinds of inhomogeneities are coupled. In principle, the partition function of a diblock copolymer melt could be obtained by evaluating the functional integral, and the thermodynamics of the system would be determined. In practice, this is intractable at present, and a variety of approximation methods have been developed to study the phase behavior of the system.

The simplest method for estimating the functional integral is to use the saddle-point approximation, which amounts to replacing the functional integral by the maximum of the integrand. Physically, this approximation is equivalent to the mean-field approximation, which ignores the composition fluctuations of the system. The mean-field theory of block copolymers is, in its most general form, a self-consistent field theory (SCFT). Because of the complexity of the theory even within the mean-field approximation, numerous additional approximations have been developed to solve the mean-field equations for diblock copolymer melts. The approximation methods can be roughly classified into the strong segregation theory[10-12] and the weak segregation theory.[13,14] The strong segregation theory introduced by Semenov[10] makes the further approximation of ignoring chain conformation fluctuations, thus restricting the theory to the infinite χZ limit. The weak segregation theory introduced by Leibler,[13] on the other hand, is developed as a Landau expansion of the full SCFT based on the random phase approximation (RPA) around the high-temperature, homogeneous phase; thus the theory is restricted to the weak segregation regime ($\chi Z \sim 10$). A density functional theory in the form of a truncated density expansion based on the RPA has also been developed by several authors.[15-19] These density functional theories give qualitatively correct results, but they are quantitatively inaccurate. Other approaches, which involve neither *a priori* assumptions about the shape of the equilibrium density profiles nor a truncated free energy, correspond to solving the mean-field equations numerically.[20-24] Earlier numerical methods[20-22] involved further approximations for solving the equations for the propagators. However, there is no further approximation involved when the mean-field equations are cast in terms of the basis functions with the full symmetry of the ordered phases.[23] With the development of this plane wave expansion method by Matsen and Schick,[23] the mean-field theory of diblock copolymers can be solved exactly for weak and intermediate segregation regimes. The mean-field phase diagram of the standard model for diblock copolymer melts has been calculated and it captures most of the features observed experimentally.[24]

II. Nature of Anisotropic Fluctuations in Ordered Phases

Comparing with the mean-field results, very little has been done on the effects of fluctuations on the phase behavior of block copolymers. The composition fluctuations are ignored in the mean-field approximation, and a proper treatment of the fluctuations leads to non-mean-field results. The first work in the block copolymer literature to treat composition fluctuations is by Fredrickson and Helfand,[25] who extended the Brasovskii theory[26] to diblock copolymers. In this work, the Landau free energy functional of Leibler[13] was reduced to a form considered by Brasovskii,[26] and a saddle-point approximation (the self-consistent Hartree approximation) was made for the fluctuations. However, this theory is confined to the weak segregation region due to the use of the Landau free energy functional. This work was extended by Mayes and Olvera de la Cruz[27] to include the leading wave vector dependence of the vertex functions but keeping the saddle-point approximation and remaining in the weak-segregation limit. More recently, Muthukumar[28] studied composition fluctuation effects on the diblock copolymer phase diagram by incorporating composition fluctuations into a density functional theory. However, the chain conformations are treated approximately due to the truncated form of the free energy functional.

In this paper, we develop a theory for the anisotropic fluctuations in the ordered phases of diblock copolymers by a self-consistent expansion around the *exact* mean-field solution of the system. The lowest correction to the mean-field approximation is in the form of Gaussian fluctuations around the mean-field solution. The application of a generalized RPA for the system yields the density–density correlation functions. The RPA has proven to be a valuable tool in understanding polymer systems. Essentially the RPA is a self-consistent expansion around the mean-field state. The RPA can give the stability, and the magnitude of Gaussian fluctuations in an equilibrium state. For example, with the RPA one can predict the scattering function and phase boundary of homopolymer[29] and copolymer melts.[13] However, the usual formulation of the RPA assumes a spatially uniform mean-field state,[29,13] whereby the fluctuations are assumed to be isotropic. If the translational symmetry is broken, this assumption is no longer valid. Instead, the RPA must be reformulated as an expansion around the broken-symmetry mean-field state. It is obvious that the correct mean-field solution is crucial for the validity of the RPA, otherwise one cannot distinguish between approximations to the zeroth-order solution and contributions arising from composition fluctuations. The essential result of this approach is the RPA density–density correlation function $C^{\text{RPA}}(\mathbf{r},\mathbf{r}')$, characterizing the anisotropic composition fluctuations. The availability of the RPA correlation function enables several important applications:[30] (1) The experimentally observed scattering intensity, which is the Fourier transform of $C^{\text{RPA}}(\mathbf{r},\mathbf{r}')$. Our method accounts for the anisotropic nature of the fluctuations, and the calculated scattering function captures the main features found experimentally.[6] (2) The mean-field solution is linearly unstable if any eigenvalue of $[C^{\text{RPA}}]^{-1}$ is negative. The boundary where an eigenvalue first becomes zero is the limit of metastability of a particular phase, i.e., the spinodal line for that phase. The least stable mode at this point dominates the fluctuations. (3) The elastic moduli of the

ordered phase can be extracted from the behavior of the scattering function near the Bragg peaks. Significant corrections to the limiting strong stretching theory result are found for the experimentally relevant parameters. (4) The effect of fluctuations on the phase diagram can be computed by calculating the Gaussian fluctuation contribution to the free energy, as demonstrated by Muthukumar[28] using the approximate free energy functional.

The calculation of the polymer correlation functions in an ordered phase involves the eigenvalues and eigenfunctions of the chain Hamiltonian

$$\mathcal{H}_\alpha = -\frac{b_\alpha^2}{6}\nabla^2 + \omega_\alpha^{(0)}(\mathbf{r}) \qquad (4)$$

where $\omega_\alpha^{(0)}(\mathbf{r})$ are the self-consistent mean fields of the ordered phase. Because the chain Hamiltonian has the same form as the Hamiltonian of electrons in periodic potentials, the eigenvalue problem for the diblock copolymers corresponds to the quantum mechanical problem of electrons in periodic potentials. In particular, the eigenvalues correspond to the energy bands in solid-state physics.

As a first step in this study, we have applied the generalized RPA to the diblock copolymer lamellar phase and communicated the main results in a short publication.[30] The results are that the anisotropic nature of the fluctuations is revealed in the scattering functions, which can be obtained via small-angle neutron scattering. For the lamellar phase, Hamley et al.[6] have observed the following from shear-oriented samples: (1) At low temperature, the scattering pattern shows meridional Bragg peaks at a wave vector k_0 with higher order reflections at $2k_0$ and $3k_0$, indicative of very small layer undulations. (2) At higher temperatures, four weak peaks corresponding to the layer undulations are observed, which shows an approximate hexagonal order. The periodicity of the in-plane undulations is about 10% larger than the interlayer spacing. Our calculated scattering functions for the lamellae capture all these features.[30] In this paper, we give a detailed exposition of the theoretical framework and illustrate the physics by studying a simple weak segregated lamellar phase. We will leave the study of fluctuation effects on diblock copolymer phase behavior for the future.

In order to understand the origin and nature of the anisotropic fluctuations in an ordered phase, we apply the theory to the weakly segregated lamellar phase. Close to the order−disorder transition, the mean-field symmetric diblock copolymer densities can be approximated by sinusoidal profiles. The resulting eigenvalue problem has the form of the Mathieu equation. Perturbation calculations reveal that there are two sources of anisotropy: (1) The change in the eigenvalues leads to a renormalization of the polymer radius of gyration along the direction perpendicular to the lamellas, and (2) the appearance of the gap in the eigenvalue spectrum at the Bragg points leads to the strong resonance peaks.

The organization of this paper is as follows: Section III describes the model system, the derivation of the free energy functional, the generalized RPA for diblock copolymers, and methods for calculating the polymer correlation functions in an ordered phase. Section IV applies the theory to the simplest broken symmetry phase, the weakly segregated lamellar phase. Section

V includes discussions and conclusions. Some mathematical details are included in the Appendix.

III. Theoretical Framework

A. The Model and Functional Integral Formulation. We assume that the polymer chains are described by the many-chain Edwards Hamiltonian.[31] The degrees of polymerization of the chains are Z_A, Z_B, with $Z = Z_A + Z_B$ being the total degree of polymerization of the diblock copolymers. We assume that there are N_c diblock copolymer chains contained in a finite volume V. We associate each block α (= A, B) with a Kuhn statistical length b_α and a bulk monomer density $\rho_{0\alpha}$. Let $\mathbf{R}_\alpha^i(t)$ denote the position of monomer t at block α of chain i. Let $\mathbf{r}$ denote a spatial position. The density profile of the polymers is characterized by the volume fraction of block α at position $\mathbf{r}$, which can be expressed in terms of the chain conformation,

$$\hat{\phi}_\alpha(\mathbf{r}) = \hat{\phi}_\alpha(\mathbf{r},\{\mathbf{R}_\alpha^i(t)\}) = \frac{1}{\rho_{0\alpha}}\sum_{i=1}^{N_c}\int_0^{Z_\alpha}\mathrm{d}t\delta(\mathbf{r} - \mathbf{R}_\alpha^i(t)) \quad (5)$$

where the chevron denotes that $\hat{\phi}_\alpha(\mathbf{r})$ is a functional of the chain conformations $\mathbf{R}_\alpha^i(t)$.

The partition function of the diblock copolymer melt can be written in terms of a functional integral over all the chain conformations

$$Z = \frac{z_c^{N_c}}{N_c!}\int \mathcal{D}\mathbf{R}(\tau) P_0(\{\mathbf{R}(\tau)\})\prod_{\{\mathbf{r}\}}\delta[1 - \sum_\alpha\hat{\phi}_\alpha(\mathbf{r})] \times \\ \exp[-W\{\hat{\phi}\})] \quad (6)$$

where z_c is the partition function of a copolymer chain due to the kinetic energy, and $W(\{\hat{\phi}\}) \equiv V(\{\hat{\phi}\})/k_B T$ is the intermolecular potential. The integral is over all space curves $\mathbf{R}_\alpha^i(t)$. The probability density functional $P_0(\{\mathbf{R}(t)\})$ is assumed to be of the form

$$P_0(\{\mathbf{R}(t)\}) = \prod_{i=1}^{N_c}\{\delta[\mathbf{R}_A^i(Z_A) - \\ \mathbf{R}_B^i(Z_B)]p_0(\{\mathbf{R}_A^i(t)\})p_0(\{\mathbf{R}_B^i(t)\})\} \quad (7)$$

where the δ function ensures that the copolymer chains are connected at one end, and the single-chain probability distribution $p_0(\{\mathbf{R}_\alpha^i(t)\})$ has the standard Wiener form

$$p_0(\{\mathbf{R}_\alpha^i(t)\}) \propto \exp\left[-\frac{3}{2b_\alpha^2}\int_0^{Z_\alpha}\mathrm{d}t\left(\frac{\mathrm{d}\mathbf{R}_\alpha^i(t)}{\mathrm{d}t}\right)^2\right] \quad (8)$$

We have also introduced, in eq 6, a δ function, $\delta[1 - \sum_\alpha\hat{\phi}_\alpha(\mathbf{r})]$, to ensure the incompressibility constraint for the system. The interaction potential $W(\{\hat{\phi}\})$ is assumed to have the two-body Flory−Huggins form

$$W(\{\hat{\phi}\}) = \chi\int \mathrm{d}\mathbf{r}\hat{\phi}_A(\mathbf{r})\hat{\phi}_B(\mathbf{r}) \quad (9)$$

For simplicity, we will assume that all the reference densities are the same and set to unity, $\rho_{0\alpha} = \rho_0 = 1$. We also assume that both blocks have the same Kuhn length $b_\alpha = b$.

We now introduce the monomer concentrations $\phi_\alpha(\mathbf{r})$ and two auxiliary fields $\omega_\alpha(\mathbf{r})$ (α = A, B) following Helfand[8] and Hong and Noolandi.[9] The partition func-

tion of a diblock copolymer melt in a volume V can be written as a functional integral over the volume fractions $\phi_\alpha(\mathbf{r})$ and fields $\omega_\alpha(\mathbf{r})$,

$$Z = \int \prod_\alpha \{ \mathcal{D}\phi_\alpha \mathcal{D}\omega_\alpha \} \prod_{\{\mathbf{r}\}} \delta[1 - \sum_\alpha \phi_\alpha(\mathbf{r})] \times$$
$$\exp[-F(\{\phi\}, \{\omega\})] \quad (10)$$

where the δ functions are introduced to ensure incompressibility $\sum_\alpha \phi_\alpha(\mathbf{r}) = 1$. The free energy functional $F(\{\phi\}, \{\omega\})$ has the form

$$F = \int d\mathbf{r} [\chi \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - \sum_\alpha \omega_\alpha(\mathbf{r}) \phi_\alpha(\mathbf{r})] - \frac{V}{Z} \ln Q_c \quad (11)$$

where Q_c is the partition function of a single diblock copolymer chain in the external fields, $\omega_\alpha(\mathbf{r})$.[8,9] The chain conformation contribution to the partition function is contained in the single-chain partition function Q_c, which is related to the propagators of the diblock copolymer chains, defined by

$$Q_\alpha(\mathbf{r}, t|\mathbf{r}') =$$
$$\int_{\mathbf{R}(0)=\mathbf{r}'}^{\mathbf{R}(t)=\mathbf{r}} \mathcal{D}\mathbf{R}(t) \exp\left[-\int_0^{Z_\alpha} dt \left(\frac{3}{2b_\alpha^2} \left(\frac{d\mathbf{R}(t)}{dt} \right)^2 + \omega_\alpha[\mathbf{R}(t)] \right) \right]$$
$$(12)$$

which is the probability distribution of monomer t at $\mathbf{r}$, given that monomer 0 is at $\mathbf{r}'$, in the presence of an external field $\omega_\alpha(\mathbf{r})$. It is easy to show that these propagators satisfy the modified diffusion equations[8]

$$\frac{\partial}{\partial t} Q_\alpha(\mathbf{r}, t|\mathbf{r}') = \frac{b_\alpha^2}{6} \nabla^2 Q_\alpha(\mathbf{r}, t|\mathbf{r}') - \omega_\alpha(\mathbf{r}) Q_\alpha(\mathbf{r}, t|\mathbf{r}') \quad (13)$$

with the initial conditions $Q_\alpha(\mathbf{r}, 0|\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. In terms of these propagators, we have

$$Q_c = \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_A(\mathbf{r}_1, Z_A|\mathbf{r}_2) Q_B(\mathbf{r}_2, Z_B|\mathbf{r}_3) \quad (14)$$

Note that since the propagators depend on the fields $\omega_\alpha(\mathbf{r})$, the single-chain partition function Q_c is a functional of $\omega_\alpha(\mathbf{r})$. In order to treat the imcompressibility and the monomer conservation constraints, we introduce two sets of Lagrangian multipliers[9] and write the partition function in the form

$$Z = \int \prod_\alpha \{ \mathcal{D}\phi_\alpha \mathcal{D}\omega_\alpha d\lambda_\alpha \} \mathcal{D}\eta \exp[-\Omega(\{\phi\}, \{\omega\},$$
$$\{\eta\}, \lambda_\alpha)] \quad (15)$$

where the grand potential Ω is given by

$$\Omega = \int d\mathbf{r} [\chi \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - \sum_\alpha \omega_\alpha(\mathbf{r}) \phi_\alpha(\mathbf{r})] - \frac{V}{Z} \ln Q_c -$$
$$\int d\mathbf{r} [\eta(\mathbf{r})(1 - \sum_\alpha \phi_\alpha(\mathbf{r})) + \sum_\alpha \lambda_\alpha(\bar{\phi}_\alpha - \phi_\alpha(\mathbf{r}))] \quad (16)$$

where $\bar{\phi}_\alpha = Z_\alpha/Z$ is the average volume fraction of block α.

The thermodynamics of a diblock copolymer melt would be completely determined if the partition function of the system could be evaluated. The exact evaluation of the functional integral is, however, a formidable task. There are essentially two sets of difficulties involved

here. The first is the calculation of the single-chain partition function Q_c to express it explicitly in terms of the fields $\omega_\alpha(\mathbf{r})$, so that the chain conformation contributions to the free energy functional are obtained in terms of $\omega_\alpha(\mathbf{r})$. The second is the evaluation of the functional integrals over the polymer concentrations $\phi_\alpha(\mathbf{r})$ and the field $\omega_\alpha(\mathbf{r})$. The simplest method by which to evaluate the functional integral is the saddle-point approximation, which replaces the integral by the maximum of integrand and yields the mean-field equations. In what follows, we will take the mean-field solution as the zeroth order solution and express the free energy functional as an expansion around the mean-field solution. We then truncate the expansion at the lowest nontrivial order. The functional integral is Gaussian at this order and can be evaluated.

As mentioned above, because the single-chain partition function Q_c depends on the fields $\omega_\alpha(\mathbf{r})$ in an implicit form, it is useful to write Q_c explicitly in term of $\omega_\alpha(\mathbf{r})$. This can be achieved by writing $\omega_\alpha(\mathbf{r})$ in the form

$$\omega_\alpha(\mathbf{r}) = \omega_\alpha^{(0)}(\mathbf{r}) + \delta\omega_\alpha(\mathbf{r}) \quad (17)$$

where $\omega_\alpha^{(0)}(\mathbf{r})$ are known functions which will be determined later as the mean-field solutions of the system. The propagator can then be cast in the form

$$Q_\alpha(\mathbf{r}, t|\mathbf{r}') = Q^{(0)}(\mathbf{r}, t|\mathbf{r}') + \delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') \quad (18)$$

where the zeroth order propagators are the solutions of

$$\frac{\partial}{\partial t} Q_\alpha^{(0)}(\mathbf{r}, t|\mathbf{r}') = \frac{b_\alpha^2}{6} \nabla^2 Q_\alpha^{(0)}(\mathbf{r}, t|\mathbf{r}') - \omega_\alpha^{(0)}(\mathbf{r}) Q_\alpha^{(0)}(\mathbf{r}, t|\mathbf{r}')$$
$$(19)$$

with the initial conditions $Q_\alpha^{(0)}(\mathbf{r}, 0|\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. The fluctuation part $\delta Q_\alpha(\mathbf{r}, t|\mathbf{r}')$ of the propagators is a solution of

$$\frac{\partial}{\partial t} \delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') = \frac{b_\alpha^2}{6} \nabla^2 \delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') -$$
$$\omega_\alpha^{(0)}(\mathbf{r}) \delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') - \delta\omega_\alpha(\mathbf{r}) Q_\alpha^{(0)}(\mathbf{r}, t|\mathbf{r}') -$$
$$\delta\omega_\alpha(\mathbf{r}) \delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') \quad (20)$$

with the initial conditions $\delta Q_\alpha(\mathbf{r}, 0|\mathbf{r}') = 0$. In order to obtain a formal solution for $\delta Q_\alpha(\mathbf{r}, t|\mathbf{r}')$, it is convenient to define Green functions in the zeroth-order fields $\omega_\alpha^{(0)}(\mathbf{r})$

$$\left\{ \frac{\partial}{\partial t} - \frac{b_\alpha^2}{6} \nabla^2 + \omega_\alpha^{(0)}(\mathbf{r}) \right\} G_\alpha(\mathbf{r}, t|\mathbf{r}', t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}')$$
$$(21)$$

It is easy to see that the Green functions defined this way are related to the propagators in the field $\omega_\alpha^{(0)}(\mathbf{r})$

$$G_\alpha(\mathbf{r}, t|\mathbf{r}', t') = \theta(t - t') Q_\alpha^{(0)}(\mathbf{r}, t - t'|\mathbf{r}') \quad (22)$$

where $\theta(t)$ is the step function. In terms of the Green functions, the formal solution of $\delta Q_\alpha(\mathbf{r}, t|\mathbf{r}')$ can be obtained:

$$\delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') =$$
$$- \int d\mathbf{r}_1 \int dt_1 G_\alpha(\mathbf{r}, t|\mathbf{r}_1, t_1) G_\alpha(\mathbf{r}_1, t_1|\mathbf{r}', 0)\delta\omega_\alpha(\mathbf{r}_1) -$$
$$\int d\mathbf{r}_1 \int dt_1 G_\alpha(\mathbf{r}, t|\mathbf{r}_1, t_1)\delta Q_\alpha(\mathbf{r}_1, t_1|\mathbf{r}')\delta\omega_\alpha(\mathbf{r}_1) \quad (23)$$

The formal solution allows us to obtain the solution for δQ_α by iteration

$$\delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') = \delta Q_\alpha^{(1)}(\mathbf{r}, t|\mathbf{r}') + \delta Q_\alpha^{(2)}(\mathbf{r}, t|\mathbf{r}') + ... \quad (24)$$

where the nth-order solution is

$$\delta Q_\alpha^{(n)}(\mathbf{r}, t|\mathbf{r}') = (-)^n \int d\mathbf{r}_1...d\mathbf{r}_n \int dt_1...$$
$$dt_n G_\alpha(\mathbf{r}, t|\mathbf{r}_n, t_n) G_\alpha(\mathbf{r}_n, t_n|\mathbf{r}_{n-1}, t_{n-1})...$$
$$G_\alpha(\mathbf{r}_2, t_2|\mathbf{r}_1, t_1) G_\alpha(\mathbf{r}_1, t_1|\mathbf{r}', 0)\delta\omega_\alpha(\mathbf{r}_1)...\delta\omega_\alpha(\mathbf{r}_n) \quad (25)$$

Using the perturbation solutions of $Q_\alpha(\mathbf{r}, t|\mathbf{r}')$, the single-chain partition Q_c can be obtained as a series in the $\delta\omega_\alpha$'s. Appendix A gives details of the perturbation calculations. The single-chain partition function term in the free energy can then be cast in the form of an expansion

$$\frac{V}{Z}\ln Q_c = \frac{V}{Z}\ln Q_c^{(0)} + \sum_{n=1}^{\infty}\frac{(-1)^n}{n!} \times$$
$$\sum_{\alpha_1,...,\alpha_n}\int d\mathbf{r}_1...d\mathbf{r}_n C_{\alpha_1,...,\alpha_n}(\mathbf{r}_1,...,\mathbf{r}_n)\delta\omega_{\alpha_1}(\mathbf{r}_1)...\delta\omega_{\alpha_n}(\mathbf{r}_n)$$
$$(26)$$

where the coefficients $C_{\alpha_1,...,\alpha_n}(\mathbf{r}_1, ..., \mathbf{r}_n)$ are the nth-order cumulant correlation function for a noninteracting diblock chain in the field $\omega_\alpha^{(0)}(\mathbf{r})$. The lowest order cumulant correlation functions are given in Appendix A.

In order to proceed, we expand all the variables around the zeroth-order solution of the system,

$$\phi_\alpha(\mathbf{r}) = \phi_\alpha^{(0)}(\mathbf{r}) + \delta\phi_\alpha(\mathbf{r})$$

$$\omega_\alpha(\mathbf{r}) = \omega_\alpha^{(0)}(\mathbf{r}) + \delta\omega_\alpha(\mathbf{r})$$

$$\eta(\mathbf{r}) = \eta^{(0)}(\mathbf{r}) + \delta\eta(\mathbf{r})$$

$$\lambda_\alpha = \lambda_\alpha^{(0)} + \delta\lambda_\alpha \quad (27)$$

In terms of the zeroth-order solution and the δ variables, the grand free energy functional Ω can be expanded in the form

$$\Omega = \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + ... \quad (28)$$

where the zeroth-order term $\Omega^{(0)}$ is given by

$$\Omega^{(0)} = \int d\mathbf{r}[\chi\phi_A^{(0)}(\mathbf{r})\phi_B^{(0)}(\mathbf{r}) - \sum_\alpha \omega_\alpha^{(0)}(\mathbf{r})\phi_\alpha^{(0)}(\mathbf{r})] -$$
$$\frac{V}{Z}\ln Q_c^{(0)}$$
$$-\int d\mathbf{r}[\eta^{(0)}(\mathbf{r})(1 - \sum_\alpha\phi_\alpha^{(0)}(\mathbf{r})) + \sum_\alpha\lambda_\alpha^{(0)}(\bar{\phi}_\alpha - \phi_\alpha^{(0)}(\mathbf{r}))]$$
$$(29)$$

The first-order term has the form

$$\Omega^{(1)} = \int d\mathbf{r}\{[\chi\phi_B^{(0)}(\mathbf{r}) - \omega_A^{(0)}(\mathbf{r}) + \eta^{(0)}(\mathbf{r}) +$$
$$\lambda_A^{(0)}]\delta\phi_A(\mathbf{r}) + [\chi\phi_A^{(0)}(\mathbf{r}) - \omega_B^{(0)}(\mathbf{r}) + \eta^{(0)}(\mathbf{r}) +$$
$$\lambda_B^{(0)}]\delta\phi_B(\mathbf{r}) - \sum_\alpha[\phi_\alpha^{(0)}(\mathbf{r}) - C_\alpha(\mathbf{r})]\delta\omega_\alpha(\mathbf{r}) -$$
$$[1 - \sum_\alpha\phi_\alpha^{(0)}(\mathbf{r})]\delta\eta(\mathbf{r}) - \sum_\alpha[\bar{\phi}_\alpha - \phi_\alpha^{(0)}(\mathbf{r})]\delta\lambda_\alpha\} \quad (30)$$

and the second-order term has the form

$$\Omega^{(2)} = \int d\mathbf{r}\{\chi\delta\phi_A(\mathbf{r})\delta\phi_B(\mathbf{r}) - \sum_\alpha\delta\phi_\alpha(\mathbf{r})[\delta\omega_\alpha(\mathbf{r}) -$$
$$\delta\eta(\mathbf{r}) - \delta\lambda_\alpha]\} - \frac{1}{2}\sum_{\alpha,\beta}\int d\mathbf{r}d\mathbf{r}' C_{\alpha\beta}(\mathbf{r},\mathbf{r}')\delta\omega_\alpha(\mathbf{r})\delta\omega_\beta(\mathbf{r}')$$
$$(31)$$

The higher-order terms have the generic form

$$\Omega^{(n)} = -\frac{(-1)^n}{n!}\sum_{\alpha_1,...,\alpha_n}\int \times$$
$$d\mathbf{r}_1...d\mathbf{r}_n C_{\alpha_1,...,\alpha_n}(\mathbf{r}_1,...,\mathbf{r}_n)\delta\omega_{\alpha_1}(\mathbf{r}_1)...\delta\omega_{\alpha_n}(\mathbf{r}_n) \quad (32)$$

It should be noted that there is no explicit χ dependence in $\Omega^{(n)}$ for $n > 2$. However, there is an implicit χ dependence because the correlation functions are obtained in terms of the mean fields $\omega_\alpha^{(0)}(\mathbf{r})$.

B. Mean-Field Approximation. The mean-field approximation reduces the interacting chain system to a system of independent chains in the self-consistent fields of the other chains. Technically, this amounts to evaluating the functional integral over ω and ϕ by the saddle-function method, i.e., replacing the integral by the maximum value of the integrand.[9] This extremization yields a set of mean-field equations, with the solutions $\phi_\alpha^{(0)}(\mathbf{r})$ and $\omega_\alpha^{(0)}(\mathbf{r})$. Specifically, the mean-field solution is that for which the first-order term $\Omega^{(1)}$ vanishes. Since the δ variables are arbitrary functions, $\Omega^{(1)} = 0$ results in the mean-field equations

$$\omega_A^{(0)}(\mathbf{r}) = \chi\phi_B^{(0)}(\mathbf{r}) + \eta^{(0)}(\mathbf{r}) + \lambda_A^{(0)}$$

$$\omega_B^{(0)}(\mathbf{r}) = \chi\phi_A^{(0)}(\mathbf{r}) + \eta^{(0)}(\mathbf{r}) + \lambda_B^{(0)}$$

$$\phi_\alpha^{(0)}(\mathbf{r}) = C_\alpha^{(0)}(\mathbf{r})$$

$$1 = \sum_\alpha\phi_\alpha^{(0)}(\mathbf{r})$$

$$0 = \int d\mathbf{r}[\bar{\phi}_\alpha - \phi_\alpha^{(0)}(\mathbf{r})] \quad (33)$$

In order to obtain *exact* solutions, these equations must be solved self-consistently using numerical methods. For the more complex phases, an expansion in terms of a complete set of basis functions with the desired symmetry is required.

The mean-field free energy is then obtained by inserting the mean-field solution into the free energy expression. When we expand around the mean-field solution, the first-order contribution to the free energy vanishes, and the zeroth-order contribution to the free energy is just the mean-field free energy $F^{(0)}$

$$F^{(0)} = \int d\mathbf{r} [\chi \phi_A^{(0)}(\mathbf{r}) \phi_B^{(0)}(\mathbf{r}) - \sum_\alpha \omega_\alpha^{(0)}(\mathbf{r}) \phi_\alpha^{(0)}(\mathbf{r})] - \frac{V}{Z} \ln Q_c^{(0)} \quad (34)$$

The partition function of the melt can now be written in the form

$$Z = \exp[-F^{(0)}] \int \prod_\alpha \{ \mathcal{D}\delta\phi_\alpha \mathcal{D}\delta\omega_\alpha \, d\delta\lambda_\alpha \} \mathcal{D}\delta\eta \times \exp[-\sum_{n=2}^\infty \Omega^{(n)}] \quad (35)$$

C. Gaussian Fluctuations and the Random Phase Approximation. So far there has been no approximation made in the theory. What we have accomplished is the rewriting of the partition function in the explicit form given above. In what follows we will choose the zeroth-order solution as the mean-field solution and keep only the expansion to the lowest (second-order) order; thus we are only dealing with Gaussian fluctuations around the mean-field solution. We will also use the fact that the addition of a constant to the field $\omega_\alpha(\mathbf{r})$ is equivalent to the addition of a constant to the free energy, thus the constants $\delta\lambda_\alpha$ can be neglected in the free energy (or absorbed into $\delta\eta(\mathbf{r})$). These simplifications lead to the approximate partition function of the system

$$Z \approx \exp[-F^{(0)}] \int \prod_\alpha \{ \mathcal{D}\delta\phi_\alpha \mathcal{D}\delta\omega_\alpha \} \prod_{\{\mathbf{r}\}} \delta[\sum_\alpha \delta\phi_\alpha(\mathbf{r})] \times \exp[-\Omega^{(2)}] \quad (36)$$

where we have replaced the functional integral over $\delta\eta(\mathbf{r})$ by the explicit incompressibility condition, and the Gaussian fluctuation free energy functional $\Omega^{(2)}$ is given by

$$\Omega^{(2)} = \int d\mathbf{r} \{\chi \delta\phi_A(\mathbf{r}) \delta\phi_B(\mathbf{r}) - \sum_\alpha \delta\phi_\alpha(\mathbf{r}) \delta\omega_\alpha(\mathbf{r})\} - \frac{1}{2} \sum_{\alpha,\beta} \int d\mathbf{r} d\mathbf{r}' C_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \delta\omega_\alpha(\mathbf{r}) \delta\omega_\beta(\mathbf{r}') \quad (37)$$

In order to treat the incompressibility condition explicitly, we use the condition $\delta\phi_A(\mathbf{r}) + \delta\phi_B(\mathbf{r}) = 0$, and introduce three new variables

$$\delta\phi(\mathbf{r}) = \delta\phi_A(\mathbf{r}) - \delta\phi_B(\mathbf{r})$$

$$\delta\omega(\mathbf{r}) = \frac{1}{2}[\delta\omega_A(\mathbf{r}) - \delta\omega_B(\mathbf{r})]$$

$$\delta\zeta(\mathbf{r}) = \frac{1}{2}[\delta\omega_A(\mathbf{r}) + \delta\omega_B(\mathbf{r})] \quad (38)$$

In terms of these new variables, the partition function of the diblock copolymers has the form

$$Z \approx \exp[-F^{(0)}] \int \mathcal{D}\delta\phi \mathcal{D}\delta\omega \mathcal{D}\delta\zeta \exp[-\Omega^{(2)}] \quad (39)$$

where the Gaussian fluctuation free energy functional is given by

$$\Omega^{(2)} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \Big\{ -\frac{\chi}{2} \delta(\mathbf{r} - \mathbf{r}') \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}') - 2\delta(\mathbf{r} - \mathbf{r}') \delta\phi(\mathbf{r}) \delta\omega(\mathbf{r}') - C(\mathbf{r},\mathbf{r}') \delta\omega(\mathbf{r}) \delta\omega(\mathbf{r}') - 2\Delta(\mathbf{r},\mathbf{r}') \delta\omega(\mathbf{r}) \delta\zeta(\mathbf{r}') - \Sigma(\mathbf{r},\mathbf{r}') \delta\zeta(\mathbf{r}) \delta\zeta(\mathbf{r}') \Big\} \quad (40)$$

In the above expression for the free energy functional, we have introduced three new quantities which are combinations of the diblock copolymer correlation functions

$$C(\mathbf{r},\mathbf{r}') \equiv C_{AA}(\mathbf{r},\mathbf{r}') - C_{AB}(\mathbf{r},\mathbf{r}') - C_{BA}(\mathbf{r},\mathbf{r}') + C_{BB}(\mathbf{r},\mathbf{r}')$$

$$\Delta(\mathbf{r},\mathbf{r}') \equiv C_{AA}(\mathbf{r},\mathbf{r}') + C_{AB}(\mathbf{r},\mathbf{r}') - C_{BA}(\mathbf{r},\mathbf{r}') - C_{BB}(\mathbf{r},\mathbf{r}')$$

$$\Sigma(\mathbf{r},\mathbf{r}') \equiv C_{AA}(\mathbf{r},\mathbf{r}') + C_{AB}(\mathbf{r},\mathbf{r}') + C_{BA}(\mathbf{r},\mathbf{r}') + C_{BB}(\mathbf{r},\mathbf{r}') \quad (41)$$

To proceed, we invoke the RPA, which is technically equivalent to extremizing the free energy functional with respect to $\delta\zeta(\mathbf{r})$ and $\delta\omega(\mathbf{r})$. To eliminate the $\delta\zeta(\mathbf{r})$ variable, we use the relation $\partial\Omega^{(2)}/\partial\delta\zeta(\mathbf{r}) = 0$, which leads to

$$\int d\mathbf{r}' \{\Sigma(\mathbf{r},\mathbf{r}') \delta\zeta(\mathbf{r}') + \Delta(\mathbf{r},\mathbf{r}') \delta\omega(\mathbf{r}')\} = 0 \quad (42)$$

This relation can be used to eliminate $\delta\zeta(\mathbf{r})$ in the theory. In order to achieve this, we introduce the inverse functional operation $\Sigma^{-1}(\mathbf{r},\mathbf{r}')$ through the relation $\int d\mathbf{r}'' \Sigma^{-1}(\mathbf{r},\mathbf{r}'') \Sigma(\mathbf{r}'',\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. In terms of this inverse relation, we have

$$\delta\zeta(\mathbf{r}) = -\int d\mathbf{r}' d\mathbf{r}'' \Sigma^{-1}(\mathbf{r},\mathbf{r}') \Delta(\mathbf{r}',\mathbf{r}'') \delta\omega(\mathbf{r}'') \quad (43)$$

Inserting this relation back into $\Omega^{(2)}$, we have

$$\Omega^{(2)} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \Big\{ -\frac{\chi}{2} \delta(\mathbf{r} - \mathbf{r}') \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}') - 2\delta(\mathbf{r} - \mathbf{r}') \delta\phi(\mathbf{r}) \delta\omega(\mathbf{r}') - \delta\omega(\mathbf{r}) \delta\omega(\mathbf{r}') [C(\mathbf{r},\mathbf{r}') - \int d\mathbf{r}_1 d\mathbf{r}_2 \Delta(\mathbf{r},\mathbf{r}_1) \Sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2) \Delta(\mathbf{r}_2,\mathbf{r}')] \Big\} \quad (44)$$

It is clear from this expression that the incompressibility condition contributes to the chain correlation function. We can introduce an incompressibility corrected correlation function by

$$\tilde{C}(\mathbf{r},\mathbf{r}') = C(\mathbf{r},\mathbf{r}') - \int d\mathbf{r}_1 d\mathbf{r}_2 \Delta(\mathbf{r},\mathbf{r}_1) \Sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2) \Delta(\mathbf{r}_2,\mathbf{r}') \quad (45)$$

and write the Gaussian fluctuation free energy in the simpler form

$$\Omega^{(2)} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \Big\{ -\Big[\frac{\chi}{2} \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}') + 2\delta\phi(\mathbf{r}) \delta\omega(\mathbf{r}')\Big] \delta(\mathbf{r} - \mathbf{r}') - \tilde{C}(\mathbf{r},\mathbf{r}') \delta\omega(\mathbf{r}) \delta\omega(\mathbf{r}') \Big\} \quad (46)$$

We now use the same approximation to eliminate the field variables $\delta\omega(\mathbf{r})$. Minimizing the free energy function with respect to $\delta\omega(\mathbf{r})$ leads to the relation $\partial\Omega^{(2)}/\partial\delta\omega(\mathbf{r}) = 0$. Explicitly, we have

$$\int d\mathbf{r}' \tilde{C}(\mathbf{r},\mathbf{r}') \delta\omega(\mathbf{r}') + \delta\phi(\mathbf{r}) = 0 \quad (47)$$

Introducing the inverse operator of $\tilde{C}(\mathbf{r},\mathbf{r}')$ through $\int d\mathbf{r}'' \tilde{C}^{-1}(\mathbf{r},\mathbf{r}'') \tilde{C}(\mathbf{r}'',\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, we can write

$$\delta\omega(\mathbf{r}) = -\int d\mathbf{r}' \tilde{C}^{-1}(\mathbf{r},\mathbf{r}')\delta\phi(\mathbf{r}') \qquad (48)$$

Inserting this expression into $\Omega^{(2)}$, we get

$$\Omega^{(2)} = \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\left\{\tilde{C}^{-1}(\mathbf{r},\mathbf{r}') - \frac{\chi}{2}\delta(\mathbf{r}-\mathbf{r}')\right\}\delta\phi(\mathbf{r})\delta\phi(\mathbf{r}')$$

$$= \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'[C^{\mathrm{RPA}}]^{-1}(\mathbf{r},\mathbf{r}')\delta\phi(\mathbf{r})\delta\phi(\mathbf{r}') \qquad (49)$$

where the RPA correlation function $[C^{\mathrm{RPA}}]^{-1}(\mathbf{r},\mathbf{r}')$ is defined by

$$[C^{\mathrm{RPA}}]^{-1}(\mathbf{r},\mathbf{r}') = \left\{\tilde{C}^{-1}(\mathbf{r},\mathbf{r}') - \frac{\chi}{2}\delta(\mathbf{r}-\mathbf{r}')\right\}^{-1} \quad (50)$$

which can be written in a imple form

$$C^{\mathrm{RPA}}(\mathbf{r},\mathbf{r}') = \left\{\left[I - \frac{\chi}{2}\tilde{C}\right]^{-1}\tilde{C}\right\}(\mathbf{r},\mathbf{r}') \qquad (51)$$

where $I = \delta(\mathbf{r}-\mathbf{r}')$ is the unit operator.

The upshot of the above calculation is that the partition function of the diblock melt can be written as a Gaussian integral within the RPA. The RPA correlation function can be calculated once the *exact* mean-field solution is known. Because of the complex nature of the problem, the mean-field equations have to be solved numerically.

Technically, the RPA is simply the mean-field theory applied to an ensemble in which $\delta\phi(\mathbf{r})$ is held fixed. To the lowest order, the RPA free energy becomes

$$F = F^{(0)} + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\,[C^{\mathrm{RPA}}(\mathbf{r},\mathbf{r}')]^{-1}\delta\phi(\mathbf{r})\delta\phi(\mathbf{r}') +$$

$$\mathcal{O}(\delta\phi^3) \quad (52)$$

The RPA formalism can also be derived using the concept of response functions. Formally the equations above are identical to those for the high-temperature RPA. The essential difference is that the independent chain correlation functions $C_{\alpha,\beta}(\mathbf{r},\mathbf{r}')$ arise from the full mean-field solution and hence include the anisotropic nature of the system. If the $C_{\alpha,\beta}$ are replaced by the correlation function for Gaussian coils we recover the result of Leibler.[13]

D. Method of Solution: Reciprocal Space Formalism. The above theoretical framework was developed in real space. In order to exploit the fact that the ordered phases are broken symmetry phases, we now formulate the theory in reciprocal space. To begin with, we note that the symmetry of an ordered phase is completely specified by a space group with a set of real space lattice points $\{\mathbf{R}_n\}$ or the corresponding reciprocal space lattice points $\{\mathbf{G}\}$. The equilibrium density profiles and the mean fields are periodic functions with the periodicity of the lattice. Because the modified diffusion equation can be regarded as a Schrödinger equation with imaginary time, we can make use of analogy with quantum mechanics by defining a "Hamiltonian"

$$\mathcal{H}_\alpha = -\frac{b_\alpha^2}{6}\nabla^2 + \omega_\alpha(\mathbf{r}) \qquad (53)$$

where $\omega_\alpha(\mathbf{r})$ are the mean-field potentials. The symmetry of the ordered phase dictates that the mean fields are periodic functions, $\omega_\alpha(\mathbf{r}) = \omega_\alpha(\mathbf{r} + \mathbf{R}_n)$. According to Bloch's theorem,[32] the eigenvalues $\epsilon_n^\alpha(\mathbf{k})$ of the

Hamiltonian $\mathcal{H}_\alpha$ have a band structure, which can be labeled by n and a wave vector $\mathbf{k}$, where $\mathbf{k}$ is restricted to the first Brillouin zone. The corresponding eigenfunctions have the form of a modulated plane wave

$$\psi_{n\mathbf{k}}^\alpha(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}^\alpha(\mathbf{r}) \qquad (54)$$

where the $u_{n\mathbf{k}}^\alpha(\mathbf{r})$ are periodic functions, which are solutions of the Schrödinger equation

$$\left[-\frac{b_\alpha^2}{6}(i\mathbf{k}+\nabla)^2 + \omega_\alpha(\mathbf{r})\right]u_{n\mathbf{k}}^\alpha(\mathbf{r}) = \epsilon_n^\alpha(\mathbf{k})u_{n\mathbf{k}}^\alpha(\mathbf{r}) \quad (55)$$

Because the Hamiltonian is Hermitian, the eigenfunctions are orthogonal and form a complete basis set

$$\frac{1}{V}\sum_{n\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}u_{n\mathbf{k}}^\alpha(\mathbf{r})u_{n\mathbf{k}}^{\alpha*}(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

$$\frac{1}{V}\int d\mathbf{r}\,e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}u_{n\mathbf{k}}^\alpha(\mathbf{r})u_{n'\mathbf{k}'}^{\alpha*}(\mathbf{r}) = \delta_{n,n'}\delta(\mathbf{k}-\mathbf{k}') \quad (56)$$

Because the eigenfunctions form a complete set, we can use them as basis functions to formulate the theory. This will allow us to take advantage of the symmetry of the ordered phases. In particular, the mean-field propagators $Q_\alpha(\mathbf{r}, t|\mathbf{r}')$ can be written in the simple form

$$Q_\alpha(\mathbf{r}, t|\mathbf{r}') = \sum_{n\mathbf{k}}e^{-\epsilon_n^\alpha(\mathbf{k})t}\psi_{n\mathbf{k}}^\alpha(\mathbf{r})\psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r}') \qquad (57)$$

The RPA correlation function can, therefore, be expressed in terms of the eigenfunctions and eigenvalues of the Hamiltonian. Moreover, the above result shows that the single-chain propagators $Q_\alpha(\mathbf{r}, t|\mathbf{r}')$ are diagonal if we use the eigenfunctions $\psi_{n\mathbf{k}}^\alpha(\mathbf{r})$ as our basis functions, i.e.,

$$Q_{n\mathbf{k},n'\mathbf{k}'}^\alpha(t) \equiv \int d\mathbf{r}\int d\mathbf{r}'\psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r})Q_\alpha(\mathbf{r}, t|\mathbf{r}')\psi_{n'\mathbf{k}'}^\alpha(\mathbf{r}')$$

$$= e^{-\epsilon_n^\alpha(\mathbf{k})t}\delta_{n,n'}\delta(\mathbf{k}-\mathbf{k}') \qquad (58)$$

With these basis functions, the cumulant correlation functions can be cast in the form

$$C_\alpha(\mathbf{r}) = \sqrt{V}\sum_{n\mathbf{k}}C_{n\mathbf{k}}^\alpha\psi_{n\mathbf{k}}^\alpha(\mathbf{r})$$

$$C_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \sum_{n\mathbf{k}}\sum_{n'\mathbf{k}'}C_{n\mathbf{k},n'\mathbf{k}'}^{\alpha\beta}\psi_{n\mathbf{k}}^\alpha(\mathbf{r})\psi_{n'\mathbf{k}'}^{\beta*}(\mathbf{r}') \qquad (59)$$

Using the eigenfunctions of the chain Hamiltonians $\mathcal{H}_\alpha$ as the basis functions, it can be shown (see Appendix B) that the cumulant correlation functions are diagonal in the lattice wave vector $\mathbf{k}$ space

$$C_{n\mathbf{k}}^\alpha = C_n^\alpha\delta_{\mathbf{k},\mathbf{0}}$$

$$C_{n\mathbf{k},n'\mathbf{k}'}^{\alpha\beta} = C_{n,n'}^{\alpha\beta}(\mathbf{k})\delta_{\mathbf{k},\mathbf{k}'} \qquad (60)$$

The details of calculating the $n\mathbf{k}$ space correlation functions C_n^α and $C_{n,n'}^{\alpha\beta}(\mathbf{k})$ are given in Appendix B. The one- and two-point correlation functions in real space are then given by

$$C_\alpha(\mathbf{r}) = \sum_n C_n^\alpha u_{n\mathbf{0}}^\alpha(\mathbf{r})$$

$$C_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \sum_{n,n'} \frac{1}{V} \sum_{\mathbf{k}} C_{n,n'}^{\alpha\beta}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} u_{n\mathbf{k}}^\alpha(\mathbf{r}) u_{n\mathbf{k}}^{\beta*}(\mathbf{r}') \quad (61)$$

E. Special Case: Expansion around the High-Temperature Solution.
The simplest case is the homogeneous phase at high temperatures; the RPA correlation function in this case has been obtained by Leibler.[13] For the homogeneous phase, the mean fields are constants, which can be taken as zero. The chain Hamiltonian becomes the free-particle Hamiltonian. The eigenfunctions and eigenvalues of the Hamiltonian in this case are $u_{n\mathbf{k}}^\alpha(\mathbf{r}) = 1$ and $\epsilon^\alpha(\mathbf{k}) = b_\alpha^2 k^2/6$. There is only one energy band for the homogeneous phase, so that the band index n becomes redundant. The Fourier components of the Bloch functions become $u_{n\mathbf{k}}^\alpha(\mathbf{G}) = \delta_{\mathbf{G},\mathbf{0}}$. The reduced integrals needed in the correlation functions reduce to (see Appendix B)

$$q_n^\alpha = \Gamma_{n,n'}^{\alpha\beta}(\mathbf{k}) = \Psi_{n_1,n_2,n_3}^\alpha(\mathbf{k}) = 1 \quad (62)$$

We also have $Q_c = 1$ for the homogeneous phase. With these expressions, the single-chain correlation functions can be easily obtained, $C_n^\alpha = Z_\alpha/Z = \bar\phi_\alpha$. In real space, we have $C^\alpha(\mathbf{r}) = \bar\phi_\alpha$, as expected for a homogeneous phase. The two-point correlation functions are

$$C^{AA}(k) = \frac{Z_A^2}{Z} \frac{2[(R_A k)^2 - 1 + e^{-(R_A k)^2}]}{(R_A k)^4}$$

$$C^{AB}(k) = C^{BA}(k) = \frac{Z_A Z_B}{Z} \frac{1 - e^{-(R_A k)^2}}{(R_A k)^2} \frac{1 - e^{-(R_B k)2}}{(R_B k)^2}$$

$$C^{BB}(k) = \frac{Z_B^2}{Z} \frac{2[(R_B k)^2 - 1 + e^{-(R_B k)^2}]}{(R_B k)^4} \quad (63)$$

Here we have introduced the radii of gyration for the two blocks $R_\alpha = b^2 Z_\alpha/6$ and used the explicit form of the function $g(x) = [1 - \exp(-x)]/x$. These correlation functions for the homogeneous phase have been obtained earlier.[13] The RPA correlation function in k space is

$$C^{RPA}(k) = \frac{\tilde{C}(k)}{1 - \chi\tilde{C}(k)/2} \quad (64)$$

where the incompressibility-corrected noninteracting correlation function $\tilde{C}(k)$ is

$$\tilde{C}(k) = C(k) - \Delta(k)(\Sigma(k))^{-1}\Delta(k) \quad (65)$$

and the quantities $C(k)$, $\Delta(k)$, and $\Sigma(k)$ are combinations of $C^{\alpha\beta}(k)$

$$C(k) = C^{AA}(k) + C^{BB}(k) - 2C^{AB}(k)$$

$$\Delta(k) = C^{AA}(k) - C^{BB}(k)$$

$$\Sigma(k) = C^{AA}(k) + C^{BB}(k) + 2C^{AB}(k) \quad (66)$$

The RPA correlation function obtained above is identical to earlier work.[13] For a block copolymer, the incompressibility correction gives $\tilde{C}(k) \to 0$ as $k \to 0$.

IV. Effects of Anisotropic Fluctuations for Lamellar Phase

A. Lamellar Phase.
We now apply the theory to the lamellar phase. For fixed χ, Z, f, and lamellar periodicity L, we first solve the mean-field equations. The free energy density is then minimized as a function of L to obtain the equilibrium periodicity for the set of χ, f, and Z. The detailed numerical studies of the lamellar phases have been published elsewhere[30] and will not be repeated here. In what follows we will formulate the theory in the planar geometry appropriate for the lamellar phase. We then apply the theory to a weakly segregated lamellar phase of a symmetric $f = \frac{1}{2}$ diblock copolymer melt.

For the lamellar phase, the system is described by a planar geometry. In particular, the mean-field solution is homogeneous in the $x - y$ direction and periodic in the z direction. The mean-field potentials $\omega_\alpha(\mathbf{r})$ become periodic functions along the direction perpendicular to the layers, i.e.,

$$\omega_\alpha(\mathbf{r}) = \omega_\alpha(z) = \omega_\alpha(z + mL) \quad (67)$$

where m is an integer and L is the periodicity of the layers. The polymer chain Hamiltonian may be separated into the parallel and perpendicular parts

$$H_\alpha = H_\alpha(\mathbf{x}) + H_\alpha(z) \quad (68)$$

where we have written the spatial vector in the form $\mathbf{r} = (\mathbf{x}, z)$. The parallel and perpendicular Hamiltonians are

$$H_\alpha(\mathbf{x}) = -\frac{b_\alpha^2}{6}\frac{\partial^2}{\partial \mathbf{x}^2}$$

$$H_\alpha(z) = -\frac{b_\alpha^2}{6}\frac{\partial^2}{\partial z^2} + \omega_\alpha(z) \quad (69)$$

where $H_\alpha(\mathbf{x})$ corresponds to a two-dimensional Hamiltonian for a free particle, and $H_\alpha(z)$ is the Hamiltonian in the z direction, which has the same periodic properties as the mean-field potential $\omega_\alpha(z)$. The eigenfunctions of the system can be separated into an $\mathbf{x}$-dependent part and a z-dependent part

$$\psi_{n\mathbf{k}}^\alpha(\mathbf{r}) = \psi_{\mathbf{q}}^\alpha(\mathbf{x})\psi_{nk_z}^\alpha(z) \quad (70)$$

where we have written the wave vector in the form $\mathbf{k} = (\mathbf{q}, k_z)$. The corresponding eigenvalues have the form

$$\epsilon_n^\alpha(\mathbf{k}) = \epsilon^\alpha(\mathbf{q}) + \epsilon_n^\alpha(k_z) \quad (71)$$

The equations determining the eigenvalues and eigenfunctions are

$$H_\alpha(\mathbf{x})\psi_{\mathbf{q}}^\alpha(\mathbf{x}) = \epsilon^\alpha(\mathbf{q})\psi_{\mathbf{q}}^\alpha(\mathbf{x})$$

$$H_\alpha(z)\psi_{nk_z}^\alpha(z) = \epsilon_{nk_z}^\alpha\psi_{nk_z}^\alpha(z) \quad (72)$$

The $\mathbf{x}$-dependent eigenfunctions and eigenvalues are easily found

$$\psi_{\mathbf{q}}^{\alpha}(\mathbf{x}) = \frac{1}{\sqrt{A_0}} e^{i\mathbf{q}\cdot\mathbf{x}}$$

$$\epsilon^{\alpha}(\mathbf{q}) = \frac{b_{\alpha}^2 q^2}{6} \tag{73}$$

where A_0 is the area of the system in the $x - y$ direction. The eigenvalue problem for the z-dependent part is nontrivial in that it corresponds to a particle moving in a periodic potential. According to Bloch's theorem, the eigenvalues of a particle moving in a periodic potential form energy bands, which can be labeled by a band index n and a wave vector k_z which is restricted to the first Brillouin zone ($-\pi/L < k_z \le \pi/L$). The corresponding eigenfunctions are of the form

$$\psi_{nk_z}^{\alpha}(z) = \frac{1}{\sqrt{L_0}} e^{ik_z z} u_{nk_z}(z) \tag{74}$$

where we have defined the length of the system in the z direction as L_0. Therefore, the total volume of the system is $V = A_0 L_0$, and the number of unit cells in the z direction is L_0/L. $u_{nk_z}(z)$ is a periodic function with period L and obeys

$$\left[-\frac{b_{\alpha}^2}{6}\left(ik_z + \frac{\partial}{\partial z}\right)^2 + \omega_{\alpha}(z) \right] u_{nk_z}(z) = \epsilon_{nk_z}^{\alpha} u_{nk_z}(z) \tag{75}$$

The eigenfunctions of $H_{\alpha}(z)$ form a complete basis set and are orthogonal with the normalization

$$\sum_{nk_z} \psi_{nk_z}^{\alpha}(z)\psi_{nk_z}^{\alpha*}(z') = \delta(z - z')$$

$$\int dz\, \psi_{nk_z}^{\alpha}(z)\psi_{n'k_z'}^{\alpha*}(z) = \delta(k_z - k_z')\delta_{n,n'} \tag{76}$$

where the notation $\sum_{nk_z}$ indicates a summation over n and an integral over k_z.

The fact that the **x**-dependent wave functions are plane waves leads to simple expressions for the coefficients required in the correlation functions (see Appendix B)

$$q_n^{\alpha} = \frac{1}{L} \int_0^L dz\, u_{n0}^{\alpha}(z)$$

$$\Gamma_{n,n'}^{\alpha\beta}(k_z) = \frac{1}{L} \int_0^L dz\, u_{nk_z}^{\alpha*}(z) u_{n'k_z}^{\beta}(z)$$

$$\Psi_{n_1,n_2,n_3}^{\alpha}(k_z) = \frac{1}{L} \int_0^L dz\, u_{n_1 k_z}^{\alpha*}(z) u_{n_2 0}^{\alpha*}(z) u_{n_3 k_z}^{\alpha}(z) \tag{77}$$

The expressions for the cumulant correlation functions and, therefore, the RPA correlation functions can be obtained in terms of these coefficients. In practice, the mean-field equations of the system have to be solved numerically. The resulting mean fields can then be used to calculate the eigenvalues (energy bands) and the eigenfunctions for the A and B blocks. These energy bands and Bloch functions can be used to compute the variety of correlation functions, and eventually the RPA correlation function. The scattering function, the fluctuating modes, etc., of the ordered phases can then be obtained. This program has been implemented for the lamellar phase and the results have been published.[30] In what follows we will apply the theory to the weakly

segregated lamellas by assuming that the mean-field solution contains only one mode.

B. Weakly Segregated Lamellas. In order to illustrate the origin of the anisotropic fluctuations, we consider a weakly segregated symmetric diblock melt so that $Z_A = Z_B = Z/2$. Close to the order−disorder point, $\chi Z \approx 10.5$, the polymer concentrations can be approximated by

$$\phi_A(z) = \frac{1}{2} + \phi \cos\frac{2\pi z}{L}$$

$$\phi_B(z) = \frac{1}{2} - \phi \cos\frac{2\pi z}{L} \tag{78}$$

where $\phi \ll 1$ is the amplitude and L is the period of the lamellar structure. Both ϕ and L are determined from the mean-field equations. This simple form of the polymer concentrations produces a set of self-consistent mean fields of the form

$$\omega_{\alpha}(z) = \omega_{\alpha} \cos\frac{2\pi z}{L} \tag{79}$$

where the amplitudes of the mean fields are obtained from the mean-field equations

$$\omega_A = -\chi\phi$$

$$\omega_B = \chi\phi \tag{80}$$

It should be noted that the Lagrangian factor $\eta(z)$ ensuring the incompressibility condition has been omitted. It can be shown that $\eta(z)$ has the form $\eta \cos(4\pi z/L)$, and the amplitude η is much smaller than ϕ, so that it can be neglected in the mean fields.

With the simple form for the potentials $\omega_{\alpha}(z)$, the Schrödinger equation determining the eigenvalues and eigenfunctions has the form

$$-\frac{b_{\alpha}^2}{6}\frac{d^2\psi^{\alpha}(z)}{dz^2} + \omega_{\alpha}\cos\frac{2\pi z}{L}\psi^{\alpha}(z) = \epsilon^{\alpha}\psi^{\alpha}(z) \tag{81}$$

This equation corresponds to the Mathieu differential equation[34]

$$\frac{d^2\psi}{d\tilde{z}^2} + (a - 2q\cos 2\tilde{z})\psi = 0 \tag{82}$$

where the new variables are defined by

$$\tilde{z} = \pi z/L$$

$$a = 4\frac{\epsilon^{\alpha} Z_{\alpha}}{(2\pi R_{\alpha}/L)^2}$$

$$q = 2\frac{\omega_{\alpha} Z_{\alpha}}{(2\pi R_{\alpha}/L)^2} \tag{83}$$

and $R_{\alpha} = b_{\alpha}^2 Z_{\alpha}/6$ are the radii of gyration for the α blocks. According to Floquet, the Mathieu equation has solutions of the form[34]

$$\psi(\tilde{z}) = u(\tilde{z})e^{\mu\tilde{z}} + u(-\tilde{z})e^{-\mu\tilde{z}} \tag{84}$$

where $u(\tilde{z}) = u(\tilde{z} + l\pi)$ and l an integer. According to the values of parameters a and q, there are two types of solutions: undamped waves modulated by $u(\tilde{z})$ (Bloch
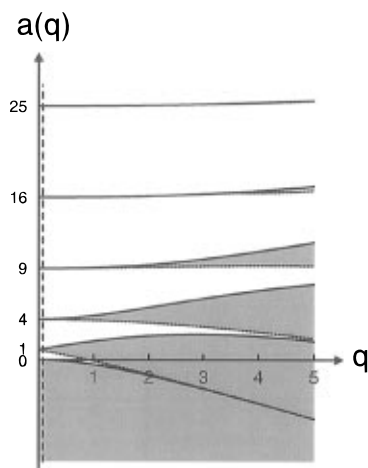
Figure 1. Stability diagram for solutions of the Mathieu equation.[34] The solid and dotted lines represent the characteristic curves $a_n(q)$ and $b_n(q)$, which divide the $a-q$ plane into regions of stability and instability (shaded area). At $q = 0$, all values of $a(q) > 0$ are allowed. For the cases of small q (dashed line), a gap occurs and the $a(q)$ spectrum splits into bands.

waves) for $\mu = ik$ and damped waves for complex μ. Only the case of the undamped modulated waves is physically interesting. The regions of existence of the modulated waves form bands in the $a-q$ plane (see Figure 1). For $q = 0$ (homogeneous phase), undamped waves exist for all energy values $a > 0$. This case corresponds to the energy spectrum of free particles $\epsilon^\alpha = b_\alpha^2 k_z^2/6$, and the resulting correlation functions are isotropic. For nonzero q (periodic potentials), only finite regions of a are possible for undamped waves (Figure 1). This corresponds to the existence of energy bands, and the free particle spectrum $\epsilon^\alpha = b_\alpha^2 k_z^2/6$ has to be modified to include the band structure. The appearance of energy bands is an extremely important phenomenon in solid-state physics in that it forms the basis for distinguishing metals, semiconductors, and insulators. In the case of diblock copolymers, the formation of energy bands is associated with the broken symmetry in the system and corresponds to the deviation of the spectrum from the free-particle isotropic behavior. This naturally leads to anisotropy in the correlation functions, reflecting the fact that the fluctuations are inherently anisotropic for a broken symmetry phase.

1. Mean-Field Theory. The mean-field solution of the weakly segregated symmetric lamellar phase can be found by using the fact that all the mean-field equations involve only the $k_z = 0$ solutions of the system. The Bloch functions $\psi_{nk_z}^\alpha(z)$ at $k_z = 0$ reduce to periodic functions $u_{n0}^\alpha(z)$. Because of the symmetry of the lamellar phase, the solutions $u_{n0}(z)$ are even functions with period L. Since the eigenfunctions are related to the Mathieu functions, the mean-field solution of the problem requires Mathieu functions which are even functions of period π. According to the theory of Mathieu functions,[34] these eigenfunctions are denoted by $\mathrm{ce}_{2n}(\check{z},q)$ with the corresponding eigenvalues $a_{2n}(q)$. The parameter q is proportional to the amplitude ϕ, so that $q \ll 1$ for weak segregated lamellae. For small values of q, the eigenvalues $a_{2n}(q)$ can be obtained as expansions of q.[34] The first few eigenvalues are

$$a_0(q) = -\frac{1}{2}q^2 + \frac{7}{128}q^4 + \dots$$

$$a_2(q) = 4 + \frac{5}{12}q^2 - \frac{763}{13824}q^4 + \dots$$

$$a_4(q) = 16 + \frac{1}{30}q^2 + \frac{433}{864000}q^4 + \dots \tag{85}$$

The corresponding eigenfunctions have the form

$$\mathrm{ce}_{2n}(\check{z},q) = \sum_{m=0}^{\infty} A_{2m}^{2n}(q) \cos(2m\check{z}) \tag{86}$$

where the coefficients $A_{2m}^{2n}(q)$ can be obtained as expansions in terms of q.[34] The normalization of these functions is chosen so that

$$\frac{1}{\pi} \int_0^{2\pi} \mathrm{ce}_{2n}(\check{z},q)\,\mathrm{ce}_{2n'}(\check{z},q) = \delta_{n,n'} \tag{87}$$

The eigenfunctions and eigenvalues for the A and B blocks are then given in terms of the Mathieu functions

$$u_{n0}^\alpha(z) = \sqrt{2}\,\mathrm{ce}_{2n}\!\left(\frac{\pi z}{L},q^\alpha\right)$$

$$\epsilon_n^\alpha(0)Z_\alpha = \frac{X}{4}a_{2n}(q^\alpha) \tag{88}$$

where the parameter X is defined by

$$X = \left(\frac{2\pi R_\alpha}{L}\right)^2 = \frac{b^2}{6}\left(\frac{2\pi}{L}\right)^2\frac{Z}{2} \tag{89}$$

The parameters q^α are

$$q^A = -\frac{\chi Z\phi}{X}$$

$$q^B = \frac{\chi Z\phi}{X} \tag{90}$$

Here we have used the relation for symmetric diblocks $R_A = R_B = b^2 Z/12$. With the availability of the Mathieu functions, the one-, two-, and three-point integrals q_m^α, $\Gamma_{n,n'}^{\alpha\beta}(0)$, and $\Psi_{n,n',n''}^\alpha(0)$ can be evaluated. The results can then be used to calculate the single-chain partition function Q and the one-body correlation functions C_n^α. After some lengthy computations, we obtain for the single-chain partition function

$$Q = 1 + \frac{1}{2}(\chi Z\phi)^2 g_2(X) + \dots \tag{91}$$

where the function $g_2(X)$ is defined by

$$g_2(X) = \frac{2X - 3 + 4e^{-X} - e^{-2X}}{4X^2} \tag{92}$$

It should be noted that the independent-chain homogeneous-phase RPA correlation function is given by $C(k) = 2Zg_2[(kR)^2/2]$. The one-point correlation functions C_n^α can then be used to calculate the polymer concentrations, and straightforward calculations yield

$$\phi_A(z) = \frac{1}{2} + [g_2(X)(\chi Z\phi) - g_4(X)(\chi Z\phi)^3]\cos\frac{2\pi z}{L} + \dots$$

$$\phi_B(z) = \frac{1}{2} - [g_2(X)(\chi Z\phi) - g_4(X)(\chi Z\phi)^3]\cos\frac{2\pi z}{L} + \dots \tag{93}$$

where the function $g_4(X)$ is

$$g_4(X) = \frac{1}{4608X^4}(504X - 1647 + 2112Xe^{-X} +$$
$$880e^{-X} - 1056Xe^{-2X} + 1776e^{-2X} - 1152e^{-3X} +$$
$$128e^{-4X} + 16e^{-5X} - e^{-8X}) \quad (94)$$

In order to determine the equilibrium period L of the system, we need to calculate the free energy density and then to minimize the free energy density with respect to L or, equivalently, to X. Inserting the mean-field solution of $\phi_\alpha(z)$, $\omega_\alpha(z)$, and Q into the mean-field free energy, we obtain to lowest order

$$\Delta f = \frac{1}{L}\int_0^L dz\Big\{\chi\Big(\phi_A(z) - \frac{1}{2}\Big)\Big(\phi_B(z) - \frac{1}{2}\Big) - \omega_A(z)\phi_A(z) -$$
$$\omega_B(z)\phi_B(z)\Big\} - \frac{1}{Z}\ln Q$$

$$\approx \frac{1}{2}\chi\phi^2\{1 - \chi Z g_2(X)\} + \dots \quad (95)$$

The minimization of the free energy density at the lowest order is therefore equivalent to the maximum of the function $g_2(X)$. The maximum of $g_2(X)$ occurs at $X^* = 1.892\ 485$ with $g_2(X^*) = 0.0952\ 847$. The equilibrium period is then given by $L^* = 3.2296R_g = 1.3185Z^{1/2}b$, where $R_g = (b^2Z/6)^{1/2}$ is the radius of gyration of the polymer chains. The polymer concentrations are now given by

$$\phi_A(z) = \frac{1}{2} + \phi \cos\frac{2\pi z}{L}$$
$$2 + [g_2(X^*)(\chi Z\phi) - g_4(X^*)(\chi Z\phi)^3]\cos\frac{2\pi z}{L} + \dots$$

$$\phi_B(z) = \frac{1}{2} - \phi \cos\frac{2\pi z}{L}$$
$$2 - [g_2(X^*)(\chi Z\phi) - g_4(X^*)(\chi Z\phi)^3]\cos\frac{2\pi z}{L} + \dots$$
$$(96)$$

where the coefficients are $g_2(X^*) = 0.095\ 284\ 66$, $g_4(X^*) = 0.000\ 555\ 31$. Self-consistency of the mean-field equations requires that

$$\phi = g_2(X^*)(\chi Z\phi) - g_4(X^*)(\chi Z\phi)^3 + \dots$$
$$(\chi Z)_c\phi - g_4(X^*)(\chi Z\phi)^3 \quad (97)$$

where the critical value of χZ is given by $(\chi Z)_c = 1/g_2(X^*) = 10.495$. The solution of this mean-field equation for ϕ can be easily found by plotting the left-hand side ($f_1(\phi) = \phi$) and the right-hand side ($f_2(\phi) = \chi Z/(\chi Z)_c\phi - g_4(X^*)(\chi Z\phi)^3$) of the mean-field equation as functions of ϕ (Figure 2). The existence of a nonzero solution for ϕ depends on the initial slope $\chi Z/(\chi Z)_c$ of the function $f_2(\phi)$. The mean-field equation for the amplitude ϕ has solution $\phi = 0$ if $\chi Z < (\chi Z)_c = 10.495$, and for $\chi Z > (\chi Z)_c = 10.495$, the stable solution for ϕ is

$$\phi = \frac{1}{\sqrt{g_4(X^*)(\chi Z)^3}}\Big(\frac{\chi Z}{(\chi Z)_c} - 1\Big)^{1/2} \quad (98)$$

Note that the exponent $^1/_2$ is typical for mean-field theories. This lowest-order mean-field solution derived above could be obtained more conveniently using the Landau free energy functional of Leibler.[13] It should
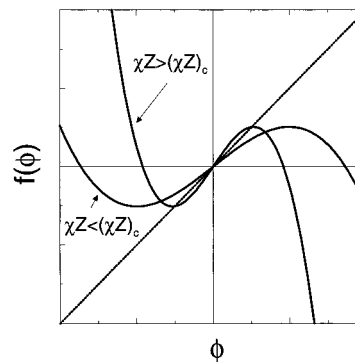

Figure 2. Solution of the mean-field equation for the amplitute ϕ. The dotted line is $f_1(\phi) = \phi$, and the solid lines are $f_2(\phi) = g_2(X^*)\chi Z\phi - g_4(X^*)(\chi Z\phi)^3$.

be emphasized that the above mean-field solution is obtained to the lowest order of ϕ, and there is no χ dependence in the equilibrium period L at this order of approximation. However, the inclusion of higher-order terms will introduce a χ dependence into L, as demonstrated by Olvera de la Cruz[14,35] using the Landau free energy functional of Leibler, and by many numerical solutions of the mean-field theory.[24]

2. The Nature of the Anisotropic Fluctuations. Because the Mathieu functions are described in the literature, we can in principle use them as the eigenfunctions and proceed to calculate the correlation functions. However, *explicit* forms for the eigenvalues and the Mathieu functions for $k_z \neq 0$ are not available. Furthermore, because we are dealing with a weak potential ($\omega_\alpha \ll 1$), it is not necessary to use the general solution for arbitrary values of ω_α. Instead, we use a perturbation scheme developed by Brillouin[33] to calculate the energy bands for the weakly segregated potential. We first write the potential $\omega_\alpha(z)$ in terms of a Fourier series

$$\omega_\alpha(z) = V_\alpha[e^{i(2\pi z/L)} + e^{-i(2\pi z/L)}] \quad (99)$$

where $V_\alpha = \omega_\alpha/2$, $\omega_A = -\chi\phi$, and $\omega_B = \chi\phi$. As mentioned earlier, the eigenfunctions for a periodic potential have the Bloch form

$$\psi_{k_z}^\alpha(z) = \frac{1}{\sqrt{L_0}}e^{ik_z z}u_{k_z}^\alpha(z) \quad (100)$$

The periodic modulation factor $u_{k_z}^\alpha(z)$ can be expanded in a Fourier series

$$u_{k_z}^\alpha(z) = \sum_{n=-\infty}^{+\infty} c_n^\alpha(k_z)e^{i(2n\pi z/L)}$$
$$k_z + \sum_{\substack{n=-\infty\\n\neq0}}^{+\infty} c_n^\alpha(k_z)e^{i(2n\pi z/L)} \quad (101)$$

Hence the eigenfunctions for the z direction have the form

$$\psi_{k_z}^\alpha(z) = \frac{1}{\sqrt{L_0}}c_0^\alpha(k_z)e^{ik_z z} + \frac{1}{\sqrt{L_0}}\sum_{\substack{n=-\infty\\n\neq0}}^{+\infty} c_n^\alpha(k_z)e^{i(k_z+(2n\pi/L))z}$$
$$(102)$$

The first term of this equation corresponds to the

solution for the homogeneous phase, the second term accounts for the position-dependent amplitude of the mean fields and can be taken as a perturbation term. The energy spectrum (eigenvalues) $\epsilon^\alpha(k_z)$ is obtained by substituting the solution into the Schrödinger equation. Manipulation of the equation leads to the equations determining the coefficients

$$[\epsilon^\alpha(k_z) - (\tilde{k}_z + n)^2]c_n^\alpha(k_z) - \nu_\alpha[c_{n-1}^\alpha(k_z) + c_{n+1}^\alpha(k_z)] = 0 \tag{103}$$

where the new variables are defined by $k_0 = 2\pi/L$, $\tilde{k}_z = k_z/k_0$, $\epsilon^\alpha(k_z) = (b^2 k_0^2/6)\tilde{\epsilon}^\alpha(k_z)$, $V^\alpha = (b^2 k_0^2/6)\nu^\alpha$. For the coefficients $c_n^\alpha(k_z)$ of the Bloch function, we have

$$c_n^\alpha(k_z) = \frac{\nu_\alpha[c_{n-1}^\alpha(k_z) + c_{n+1}^\alpha(k_z)]}{\tilde{\epsilon}^\alpha(k_z) - (\tilde{k}_z + n)^2} \tag{104}$$

Because the periodic potential is weak, we can make a perturbation substitution in the denominator, $\tilde{\epsilon}^\alpha(k_z) \approx \tilde{\epsilon}_0^\alpha(k_z) = \tilde{k}_z^2$, and discuss the behavior of $c_n^\alpha(k_z)$. According to the value of k_z, we must distinguish two cases. For the first case where $\tilde{k}_z^2 \neq (\tilde{k}_z + n)^2$, the denominator is nonzero. In the weak-potential approximation, the coefficient ν_α is small as well as the coefficients $c_n^\alpha(k_z)$ of the Bloch function, with the exception of $c_0^\alpha(k_z)$. In this case we have

$$c_1^\alpha(k_z) \approx -\frac{\nu_\alpha c_0^\alpha(k_z)}{2\tilde{k}_z + 1}$$

$$c_{-1}^\alpha(k_z) \approx \frac{\nu_\alpha c_0^\alpha(k_z)}{2\tilde{k}_z - 1} \tag{105}$$

The eigenfunctions have the form

$$u_{k_z}^\alpha(z) \approx c_0^\alpha(k_z)\left[1 - \frac{\nu_\alpha}{2\tilde{k}_z + 1}e^{ik_0 z} + \frac{\nu_\alpha}{2\tilde{k}_z - 1}e^{-ik_0 z}\right] \tag{106}$$

where the coefficients $c_0^\alpha(k_z)$ are determined by the normalization condition

$$c_0^\alpha(k_z) \approx 1 - \frac{4\tilde{k}_z^2 + 1}{(4\tilde{k}_z^2 - 1)^2}\nu_\alpha^2 \tag{107}$$

The corresponding eigenvalues are

$$\tilde{\epsilon}^\alpha(k_z) \approx \tilde{k}_z^2 + 2\nu_\alpha^2/(4\tilde{k}_z^2 - 1) \tag{108}$$

For small values of $k_z \sim 0$, the eigenvalues become $\tilde{\epsilon}^\alpha(k_z) \approx (1 - 8\nu_\alpha^2)\tilde{k}_z^2 - 2\nu_\alpha^2$. From this expression it is clear that the effect of a nonzero potential ω_α for small k_z is to renormalize the Kuhn length along the z direction into an effective $b_z < b$,

$$b_z^2 = b^2(1 - 8\nu_\alpha^2) \tag{109}$$

The total eigenvalues are now of the form $b^2 q^2/6 + b_z^2 k_z^2/6$, which is clearly anisotropic. Because $b_z < b$, the anisotropy introduced through $\epsilon^\alpha(\mathbf{q}, k_z) = b^2 q^2/6 + b_z^2 k_z^2/6$ breaks the circular symmetry of the scattering function in the $q - k_z$ plane so that the scattering ring becomes elongated in the k_z direction. It should also be noted that the effective Kuhn length introduced

above is closely related to the effective electron mass introduced in solid-state physics.[32]

It is clear from these expressions that the perturbation results given above break down when $\tilde{k}_z \to \tilde{k}_c = \pm^1/_2$, which leads us to consider the second case where k_z approaches the critical values $k_c = \pm\pi/L$. Here some of the denominators in the perturbation expressions become zero and the corresponding $c_n^\alpha(k_z)$ assumes high values. From the behavior of the coefficients $c_0^\alpha(k_z)$ and $c_n^\alpha(k_z)$ in the neighborhood of the critical values k_c, we can draw conclusions about the energy spectrum $\epsilon^\alpha(k_z)$ curve near k_c. From the equations for the coefficients, we have near $\tilde{k}_z = \pm^1/_2$

$$c_n^\alpha(k_z) = \frac{\nu_\alpha c_0^\alpha(k_z)}{\epsilon^\alpha(k_z) - (\tilde{k}_z + n)^2}$$

$$c_0^\alpha(k_z) = \frac{\nu_\alpha c_n^\alpha(k_z)}{\epsilon^\alpha(k_z) - \tilde{k}_z^2} \tag{110}$$

where $n = \pm 1$. Independent of the value of k_z, the coefficient $c_0^\alpha(k_z)$ is in principle very large because the denominator always tends to zero. Also, because $\omega_n^\alpha = 0$ for $|n| \neq 1$, $c_n^\alpha(k_z)$ are vanishingly small for $n \neq \pm 1$. We therefore conclude that all the other coefficients can be neglected for $k_z = \pm\pi/L$, except the coefficients $c_0^\alpha(k_z)$ and $c_{\mp 1}^\alpha(k_z)$. Because the eigenvalues and eigenfunctions have the symmetry that $\epsilon^\alpha(-k_z) = \epsilon^\alpha(k_z)$, $c_n^\alpha(-k_z) = c_{-n}^{\alpha*}(k_z)$,[32] we only need to consider the cases where $k_z \geq 0$. Considering the two modes $n = 0$ and $n = -1$ only, the coefficients obey the equations

$$c_{-1}^\alpha(k_z)[\delta\epsilon^\alpha(k_z) + 2\delta] = c_0^\alpha(k_z)\nu_\alpha$$

$$c_0^\alpha(k_z)\delta\epsilon_{k_z}^\alpha = c_{-1}^\alpha(k_z)\nu_\alpha \tag{111}$$

where we have written the eigenvalues in the form $\tilde{\epsilon}^\alpha(k_z) = \tilde{k}_z^2 + \delta\epsilon^\alpha(k_z)$, and the wave vector in the form $\tilde{k}_z = ^1/_2 + \delta$. These homogeneous and linear equations for $c_0^\alpha(k_z)$ and $c_{-1}^\alpha(k_z)$ have a nontrivial solution if the determinant of the coefficients vanishes, leading to the eigenvalues

$$\delta\epsilon^\alpha(k_z) = -\delta \pm \sqrt{\delta^2 + \nu_\alpha^2} \tag{112}$$

According to this result, the spectrum of the eigenvalues $\epsilon^\alpha(k_z)$ near $k_z = k_0/2 = \pi/L$ has two different values

$$\epsilon_\pm^\alpha\left(\frac{k_0}{2}\right) = \frac{b^2}{6}\left(\frac{k_0}{2}\right)^2 \pm |V_\alpha| \tag{113}$$

That is, the eigenvalue spectrum becomes discontinuous at $k_z = \pi/L$, and an "energy" gap, $\Delta\epsilon^\alpha(\pi/L) = 2|V^\alpha| = |\omega_\alpha|$, appears. There are only two gaps at $k_z = \pm\pi/L$ observed in our system since the only nonzero Fourier components in the potential $\omega_\alpha(z)$ are for $n = \pm 1$. This above argument applies to every $|n| \neq 0$. Energy gaps, however, need not appear for every n. If the nth coefficient $\omega_n^\alpha = 0$, the $\epsilon^\alpha(k_z)$ curve will become continuous at the points $k_z = \pm n\pi/L$. For the special case of a weakly segregated lamellar phase, we have $\omega_n^\alpha = 0$ for all $|n| > 1$. Therefore the eigenvalue spectrum of the system has gaps only at $k_z = \pm\pi/L$, as shown in Figure 3. Generically, the $\epsilon^\alpha(k_z)$ function is single-valued and parabolic, as in the case of the homogeneous
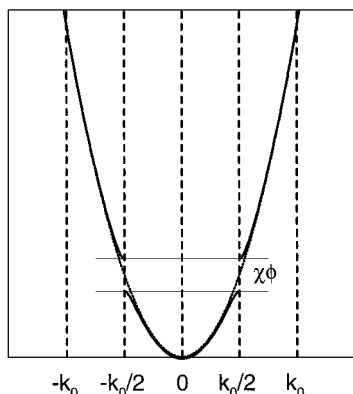
Figure 3. Eigenvalue spectrum for the weak potential eq 82. The dotted curve is the parabolic spectrum for the homogeneous phase. The solid curves represent the band structure when $\omega_\alpha = \chi\phi \neq 0$.

phase, except for the critical points $k_z = \pm\pi/L$ where the $\epsilon^\alpha(k_z)$ curve has discontinuities and the energy splits into two values (Figure 3, thick solid line). It should be noted that we have used an extended zone scheme in our description of the eigenvalues.[32] In this representation the nth energy band is attributed to the nth Brillouin zone. Because of the periodicity of the wavenumber, the $\epsilon^\alpha(k_z)$ curve has a periodicity of $2\pi/L$. When we restrict ourselves to the reduced wavenumber k_z, we can assign all the energy bands to the first Brillouin zone. This makes the $\epsilon^\alpha(k_z)$ relation multivalued and the energy bands must be labeled by a corresponding band number n; therefore, $\epsilon^\alpha(k_z) = \epsilon_n^\alpha(k_z)$. In what follows we will use the extended zone scheme so that the band index n is not necessary. The eigenvalues are discontinuous at $k_z = k_0/2 = \pi/L$ (see Figure 3),

$$\epsilon^\alpha(k_z) = \frac{b^2 k_0^2}{6}\left[\frac{1}{4} + \delta^2 - \sqrt{\delta^2 + v_\alpha^2}\right] \ \text{if} \ \ k_z \leq \frac{\pi}{L}$$

$$\epsilon^\alpha(k_z) = \frac{b^2 k_0^2}{6}\left[\frac{1}{4} + \delta^2 + \sqrt{\delta^2 + v_\alpha^2}\right] \ \text{if} \ \ k_z > \frac{\pi}{L} \quad (114)$$

The coefficients $c_n^\alpha(k_z)$ are obtained by inserting the eigenvalues into their corresponding equations and by the normalization requirement

$$c_0^\alpha(k_z) = \frac{v_\alpha}{\sqrt{v_\alpha^2 + [\delta\epsilon^\alpha(k_z)]^2}}$$

$$c_{-1}^\alpha(k_z) = \frac{\delta\epsilon^\alpha(k_z)}{\sqrt{v_\alpha^2 + [\delta\epsilon^\alpha(k_z)]^2}} \quad (115)$$

Because the eigenvalues $\delta\epsilon^\alpha(k_z) = -\delta \mp (\delta^2 + v_\alpha^2)^{1/2}$ are derived under the assumption that only the $n = 0$ and $n = -1$ modes are important, they are valid only when $k_z \sim \pi/L$, i.e., $\delta \sim 0$. For small values of δ, the eigenvalues have the form

$$\delta\epsilon^\alpha(k_z) \approx -\delta \mp |v_\alpha| \mp \frac{\delta^2}{2|v_\alpha|} + ... \quad (116)$$

The coefficients c_0^α and c_{-1}^α are

$$c_0^\alpha \approx \frac{1}{\sqrt{2}}\frac{v_\alpha}{|v_\alpha|}\left(1 \mp \frac{\delta}{2|v_\alpha|} - \frac{\delta^2}{8v_\alpha^2}\right) + ...$$

$$c_{-1}^\alpha \approx \mp\frac{1}{\sqrt{2}}\left(1 \pm \frac{\delta}{2|v_\alpha|} - \frac{\delta^2}{8v_\alpha^2}\right) + ... \quad (117)$$

The eigenfunctions of the system are then given by

$$u_{k_z}^\alpha(z) \approx \frac{1}{\sqrt{2}}\left[\frac{v_\alpha}{|v_\alpha|}\left(1 \mp \frac{\delta}{2|v_\alpha|} - \frac{\delta^2}{8v_\alpha^2}\right) \mp \right.$$
$$\left. \left(1 \pm \frac{\delta}{2|v_\alpha|} - \frac{\delta^2}{8v_\alpha^2}\right)e^{-ik_0 z}\right] \quad (118)$$

The results obtained from our perturbation calculations show that there exist critical k_z points at $\pm\pi/L$ (the Bragg points). The eigenvalues and eigenfunctions of the chain Hamiltonian have a qualitatively different behavior when k_z is close to the Bragg points. In particular, when k_z is away from $\pm\pi/L$, the corrections to the eigenfunctions and eigenvalues due to the weak periodic potential $\omega_\alpha(z)$ are of the order $O(\omega_\alpha^2)$. On the other hand, when $k_z \sim \pm\pi/L$, the corrections to the eigenfunctions and eigenvalues due to the weak periodic potential $\omega_\alpha(z)$ are of the order $O(\omega_\alpha)$. We can therefore conclude that, to the lowest order of the perturbation, the eigenfunctions of the system are well approximated by the homogeneous eigenfunctions except when k_z is close to the Bragg point $\pm\pi/L$. The eigenvalue spectrum of the diblocks in a weakly segregated lamellar phase is well approximated by the homogeneous parabolic relation except near the Bragg points $k = \pm\pi/L$, where the spectrum splits to form gaps of magnitude $|\omega_\alpha\} = \chi\phi$, i.e., the width of the gap is determined by the mean-field amplitude ϕ (Figure 3).

In summary, the behavior of the eigenvalues and eigenfunctions is, to the lowest order of the potential, controlled by the variable $\delta = k_z/k_0 - 1/2$. For large values of $|\delta|$, e.g., $|\delta| \geq |v_\alpha|$, the eigenfunctions and eigenvalues are well described by the relations for the homogeneous phase

$$\epsilon^\alpha(k_z) \approx \frac{b^2 k_z^2}{6} + O(\omega_\alpha^2)$$

$$u_{k_z}^\alpha(z) \approx 1 + O(\omega_\alpha) \quad (119)$$

For small values of $|\delta|$, $|\delta| < |v_\alpha|$, the eigenvalue spectrum becomes discontinuous,

$$\epsilon^\alpha(k_z) = \frac{b^2 k_0^2}{6}\left[\frac{1}{4} - |v_\alpha| - \left(\frac{1}{2|v_\alpha|} - 1\right)\delta^2\right] \ \text{if} \ \ k_z \leq \frac{\pi}{L}$$

$$\epsilon^\alpha(k_z) = \frac{b^2 k_0^2}{6}\left[\frac{1}{4} + |v_\alpha| + \left(\frac{1}{2|v_\alpha|} + 1\right)\delta^2\right] \ \text{if} \ \ k_z > \frac{\pi}{L}$$
$$(120)$$

Because the variable δ is proportional to $k_z - \pi/L$, the eigenvalue spectrum near the Bragg point is again parabolic. The corresponding eigenfunctions are

$$u_{k_z}^\alpha(z) = \frac{1}{\sqrt{2}}\left[\frac{v_\alpha}{|v_\alpha|}\left(1 - \frac{\delta}{2|v_\alpha|} - \frac{\delta^2}{8v_\alpha^2}\right) - \right.$$
$$\left. \left(1 + \frac{\delta}{2|v_\alpha|} - \frac{\delta^2}{8v_\alpha^2}\right)e^{-ik_0 z}\right] \ \ \delta \leq 0$$

$$u_{k_z}^\alpha(z) = \frac{1}{\sqrt{2}}\left[\frac{\nu_\alpha}{|\nu_\alpha|}\left(1 + \frac{\delta}{2|\nu_\alpha|} - \frac{\delta^2}{8\nu_\alpha^2}\right) + \left(1 - \frac{\delta}{2|\nu_\alpha|} - \frac{\delta^2}{8\nu_\alpha^2}\right)e^{-ik_0 z}\right] \quad \delta > 0 \quad (121)$$

These eigenfunctions correspond to standing waves in the system. Therefore, the appearance of the energy gap corresponds to the formation of standing waves in the system. Because the energy gap appears at nonzero Fourier components of the potential $\omega_\alpha(\mathbf{r})$, which corresponds to the appearance of an ordered structure, there is an intrinsic relationship between the symmetry breaking in the system and the gaps in the eigenvalues.

With the availability of the eigenvalues and eigenfunctions, it is straightforward to compute the block copolymer correlation functions and RPA density–density correlation functions according to the procedure given above. For the weakly segregated lamellae within the one-mode approximation, we see that there are two sources contributing to the anisotropic correlation functions. The first is the renormalization of the Kuhn length arising from the correction to the eigenvalues; the second is the strong resonant scattering at $k_z = \pm k_0/2$, leading to the appearance of gaps in the eigenvalue spectrum. The scattering function changes from isotropic ringlike behavior to anisotropic behavior with two strong peaks at the Bragg points $k = \pm\pi/L$. Furthermore, the coupling between the $x - y$ modes and the z mode through the non-Gaussian correlation functions leads to additional scattering peaks corresponding to the fluctuating layers. The lamellar phase RPA scattering functions are given in ref 30.

V. Conclusions and Discussions

A general theoretical framework for the study of anisotropic fluctuations in ordered block copolymer systems has been developed. The theory is based on a systematic expansion around the broken-symmetry ordered mean-field solution. The truncation of the theory at the Gaussian fluctuation level and the application of the random phase approximation result in a density–density correlation function $C_{n,n'}^{\text{RPA}}(\mathbf{k})$, which contains information about the *anisotropic* composition fluctuations in the system and can be measured by scattering experiments. Methods of calculating the polymer correlation functions in an inhomogeneous phase are developed. It has been shown that the important quantities controlling the fluctuations are the spectra of the eigenvalues of the chain Hamiltonian $\mathcal{H}_\alpha$ and the corresponding eigenfunctions. The eigenvalues and eigenfunctions correspond to the energy bands and wave functions for an electron in a periodic potential $\omega_\alpha(\mathbf{r})$. The calculation of the RPA correlation functions for block copolymers is therefore equivalent to band structure calculations in solid-state physics, and many methods developed for the band structure calculations can be used for the polymer problem. The calculated correlation function can be used to study the stability and the elastic properties of the ordered phases, as has been demonstrated for the lamellar phase.[30] The calculated scattering functions correspond to all the essential features of experimental measurements.

In order to illustrate the mean features of the anisotropic fluctuations, a weakly ordered lamellar phase was studied in detail using perturbation theory. The most important feature emerging from the theory is the appearance of a band structure in the eigenvalues of

the problem. The appearance of gaps in the energy band is related to the broken symmetry of the system. For the lamellar phases, the first gap appears at $k_z = k_0/2$, resulting in the most unstable fluctuation modes at $k_z = k_0/2$.[30] Although the perturbation theory was presented for the lamellar phase, the generic conclusion from the theory applies to any ordered phase.[32] In particular, when the wave vector $\mathbf{k}$ lies on a Bragg plane defined by $\mathbf{k}^2 = (\mathbf{k} - \mathbf{G})^2$, the eigenvalue of the chain Hamiltonian has the form $\epsilon^0(\mathbf{k}) \pm |V_\mathbf{G}|$, resulting in a gap of order $2|V_\mathbf{G}|$ if the Fourier component of the potential at $\mathbf{G}$ is not zero ($V_\mathbf{G} \neq 0$).

It is appropriate to compare the theory developed in this paper and the Brasovskii–Fredrickson–Helfand (BFH) theory.[25,26] We start with the exact expansion of the free energy functional in terms of fluctuations (eqs 28–32). The Gaussian fluctuation theory developed in our paper is obtained by neglecting the higher-order terms $\Omega^{(n)}$ ($n > 2$) but treating the Gaussian fluctuations exactly. The BFH theory is developed using several approximations: (1) the $\omega_\alpha(\mathbf{r})$ field variables are eliminated using the RPA,[13] resulting in a Landau free energy functional; (2) the Landau free energy functional is reduced to the Brasovskii form;[25] and (3) the fluctuations are treated using a self-consistent Hartree approximation,[26] resulting in a renormalized Landau free energy functional. The renormalization Landau free energy is then treated using the mean-field approximation. For the symmetric diblock copolymer ($f = 1/2$), mean-field theory predicts a continuous order–disorder transition.[13] The inclusion of the fluctuations within the BFH theory results in a weakly first-order phase transition in this case. On the other hand, the Gaussian fluctuation approximation cannot be used at the critical point. The use of the Landau free energy functional restricts the validity of the BFH theory to the weak segregation regime, while our Gaussian fluctuation theory applies to the whole phase space except the critical point. Therefore, the two theories complement each other.

The general theoretical framework developed in our paper provides a promising technique for the study of the physical properties of ordered microphases of block copolymer melts, as demonstrated for the lamellar phase.[30] The calculated RPA correlation functions for the ordered phases characterize the anisotropic fluctuations. The origin and nature of the anisotropic fluctuations can be attributed to the formation of a band structure for the eigenvalues of the correlation functions. The gaps in the spectrum lead to unstable modes, which are observed as scattering peaks in scattering experiments. Future applications of the theory will include calculations of the RPA correlation functions for the complex block copolymer phases, and the effects of fluctuations on the first-order phase boundaries of the system.

Appendix A: Expansion of Q_c

In this appendix we outline the derivation of the single-chain partition function Q_c as an expansion in terms of the variables $\delta\omega_\alpha(\mathbf{r})$. The formal solution of the propagators allows us to obtain the solution for δQ_α

by iteration

$$\delta Q_\alpha(\mathbf{r}, t|\mathbf{r}') = \delta Q_\alpha^{(1)}(\mathbf{r}, t|\mathbf{r}') + \delta Q_\alpha^{(2)}(\mathbf{r}, t|\mathbf{r}') + \ldots \quad (A1)$$

where the nth-order solution is

$$\delta Q_\alpha^{(n)}(\mathbf{r}, t|\mathbf{r}') = (-)^n \int d\mathbf{r}_1 \ldots d\mathbf{r}_n \int dt_1 \ldots$$
$$dt_n G_\alpha(\mathbf{r}, t|\mathbf{r}_n, t_4n) G_\alpha(\mathbf{r}_n, t_n|\mathbf{r}_{n-1}, t_{n-1}) \ldots$$
$$G_\alpha(\mathbf{r}_2, t_2|\mathbf{r}_1, t_1) G_\alpha(\mathbf{r}_1, t_1|\mathbf{r}', 0)\delta\omega_\alpha(\mathbf{r}_1) \ldots \delta\omega_\alpha(\mathbf{r}_n) \quad (A2)$$

Therefore the perturbation solution of the propagators has the form

$$Q_\alpha(\mathbf{r}, t|\mathbf{r}') = Q_\alpha^{(0)}(\mathbf{r}, t|\mathbf{r}') + \sum_{n=1}^\infty (-)^n \int d\mathbf{r}_1 \ldots d\mathbf{r}_n \times$$

$$\int dt_1 \ldots dt_n G_\alpha(\mathbf{r}, t|\mathbf{r}_n, t_n) G_\alpha(\mathbf{r}_n, t_n|\mathbf{r}_{n-1}, t_{n-1}) \ldots$$
$$G_\alpha(\mathbf{r}_2, t_2|\mathbf{r}_1, t_1) G_\alpha(\mathbf{r}_1, t_1|\mathbf{r}', 0)\delta\omega_\alpha(\mathbf{r}_1) \ldots \delta\omega_\alpha(\mathbf{r}_n) \quad (A3)$$

Using the perturbation solution of $Q_\alpha(\mathbf{r}, t|\mathbf{r}')$, the single chain partition Q_c can be obtained as a series in the $\delta\omega_\alpha$. The expansion of Q_c can be written in a more symmetric form by introducing the symmetrized n-point correlation functions $C_{\alpha_1,\ldots,\alpha_n}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ in the fields $\omega_\alpha^{(0)}(\mathbf{r})$,

$$Q_c = Q_c^{(0)} + Q_c^{(1)} + Q_c^{(2)} + \ldots$$
$$0 + \frac{1}{V}\sum_{n=1}^\infty \sum_{\alpha_1,\ldots\alpha_n} \frac{(-)^n}{n!} \int d\mathbf{r}_1 \ldots d\mathbf{r}_n C_{\alpha_1,\ldots,\alpha_n}^{(n)} \times$$
$$(\mathbf{r}\ldots,\mathbf{r}_n)\delta\omega_{\alpha_1}(\mathbf{r}_1) \ldots \delta\omega_{\alpha_n}(\mathbf{r}_n) \quad (A4)$$

where the $C_{\alpha_1,\ldots,\alpha_n}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ are the appropriate combinations of the single-chain correlation functions G_α, and the summation over α_n is for $\alpha_n = $ A, B. These correlation functions can be written in terms of the zeroth order propagators $Q_\alpha(\mathbf{r}, t|\mathbf{r}')$ using the relation

$$G_\alpha(\mathbf{r}, t|\mathbf{r}', t') = \theta(t - t')Q_\alpha(\mathbf{r}, t - t'|\mathbf{r}') \quad (A5)$$

Note that we have neglected the superscript in $Q^{(0)}(\mathbf{r}, t|\mathbf{r}')$ to simplify the notation, and in what follows $Q(\mathbf{r}, t|\mathbf{r}')$ represent the zeroth order propagator. We will also drop the superscript 0 in the cumulant correlation functions, with the understanding that these correlation functions are determined in the mean fields. The chain conformation contribution to the free energy functional can be obtained by using the relation

$$\ln \frac{Q_c}{Q_c^{(0)}} \approx \frac{Q_c^{(1)}}{Q_c^{(0)}} + \frac{Q_c^{(2)}}{Q_c^{(0)}} - \frac{1}{2}\left(\frac{Q_c^{(1)}}{Q_c^{(0)}}\right)^2 + \ldots \quad (A6)$$

The single-chain partition function term has the free energy in the form of an expansion

$$\frac{V}{Z}\ln Q_c = \frac{V}{Z}\ln Q_c^{(0)} - \frac{1}{Q_c^{(0)}Z}\sum_\alpha \int d\mathbf{r} C_\alpha^{(1)}(\mathbf{r})\delta\omega_\alpha(\mathbf{r}) +$$
$$\frac{1}{2Q_c^{(0)}Z}\sum_{\alpha,\beta} \int d\mathbf{r}d\mathbf{r}'\left\{C_{\alpha\beta}^{(2)}(\mathbf{r}, \mathbf{r}') - \right.$$
$$\left. \frac{1}{Q_c^{(0)}V}C_\alpha^{(1)}(\mathbf{r})C_\beta^{(1)}(\mathbf{r}')\right\}\delta\omega_\alpha(\mathbf{r})\delta\omega_\beta(\mathbf{r}') + \ldots =$$
$$\frac{V}{Z}\ln Q_c^{(0)} + \sum_{n=1}^\infty \frac{(-1)^n}{n!} \sum_{\alpha_1,\ldots,\alpha_n} \int d\mathbf{r}_1 \ldots d\mathbf{r}_n \times$$
$$C_{\alpha_1,\ldots,\alpha_n}(\mathbf{r}_1, \ldots, \mathbf{r}_n)\delta\omega_{\alpha_1}(\mathbf{r}_1) \ldots \delta\omega_{\alpha_n}(\mathbf{r}_n) \quad (A7)$$

where the coefficients $C_{\alpha_1,\ldots,\alpha_n}(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ are given in terms of the single-chain correlation functions $C_{\alpha_1,\ldots,\alpha_n}^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$. Physically the $C_{\alpha_1,\ldots,\alpha_n}(\mathbf{r}\ldots, \mathbf{r}_n)$ is the nth order cumulant correlation function for a noninteracting diblock chain in the field $\omega_\alpha^{(0)}(\mathbf{r})$. The lowest-order cumulant correlation functions are

$$C_A(\mathbf{r}) = \frac{1}{Q_cZ}\int_0^{Z_A} dt \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_A(\mathbf{r}_1, t|\mathbf{r}) \times$$
$$Q_A(\mathbf{r}, Z_A - t|\mathbf{r}_2)Q_B(\mathbf{r}_2, Z_B|\mathbf{r}_3)$$

$$C_B(\mathbf{r}) = \frac{1}{Q_cZ}\int_0^{Z_B} dt \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_B(\mathbf{r}_1, t|\mathbf{r}) \times$$
$$Q_B(\mathbf{r}, Z_B - t|\mathbf{r}_2)Q_A(\mathbf{r}_2, Z_A|\mathbf{r}_3) \quad (A8)$$

$$C_{AA}(\mathbf{r}, \mathbf{r}') = \frac{1}{Q_cZ}\int_0^{Z_A} dt \int_0^t dt' \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \times$$
$$[Q_A(\mathbf{r}_1, Z_A - t|\mathbf{r})Q_A(\mathbf{r}, t - t'|\mathbf{r}')Q_A(\mathbf{r}', t'|\mathbf{r}_2) \times$$
$$Q_B(\mathbf{r}_2, Z_B|\mathbf{r}_3) + Q_B(\mathbf{r}_1, Z_B|\mathbf{r}_2)Q_A(\mathbf{r}_2, Z_A - t|\mathbf{r}) \times$$
$$Q_A(\mathbf{r}, t - t'|\mathbf{r}')Q_A(\mathbf{r}', t'|\mathbf{r}_3)]$$

$$C_{AB}(\mathbf{r},\mathbf{r}') =$$
$$\frac{1}{Q_cZ}\int_0^{Z_A} dt \int_0^{Z_B} dt' \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_A(\mathbf{r}_1, Z_A -$$
$$t|\mathbf{r})Q_A(\mathbf{r}, t|\mathbf{r}_2)Q_B(\mathbf{r}_2, t'|\mathbf{r}')Q_B(\mathbf{r}', Z_B - t'|\mathbf{r}_3)$$

$$C_{BA}(\mathbf{r}, \mathbf{r}') =$$
$$\frac{1}{Q_cZ}\int_0^{Z_A} dt \int_0^{Z_B} dt' \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_B(\mathbf{r}_1, Z_B -$$
$$t|\mathbf{r})Q_B(\mathbf{r}, t|\mathbf{r}_2)Q_A(\mathbf{r}_2, t'|\mathbf{r}')Q_A(\mathbf{r}', Z_A - t'|\mathbf{r}_3)$$

$$C_{BB}(\mathbf{r}, \mathbf{r}') =$$
$$\frac{1}{Q_cZ}\int_0^{Z_B} dt \int_0^t dt' \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 [Q_B(\mathbf{r}_1, Z_B -$$
$$t|\mathbf{r})Q_B(\mathbf{r}, t - t'|\mathbf{r}')Q_B(\mathbf{r}', t'|\mathbf{r}_2)Q_A(\mathbf{r}_2, Z_A|\mathbf{r}_3) +$$
$$Q_A(\mathbf{r}_1, Z_A|\mathbf{r}_2)Q_B(\mathbf{r}_2, Z_B - t|\mathbf{r}) \times$$
$$Q_B(\mathbf{r}, t - t'|\mathbf{r}')Q_B(\mathbf{r}', t'|\mathbf{r}_3)] \quad (A9)$$

where we have used the fact that, in the thermodynamic limit, the second term in $C_{\alpha\beta}$ (which is proportional to $1/V$) can be ignored. The single-chain mean-field partition function Q_c is given by

$$Q_c = \frac{1}{V}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 Q_A(\mathbf{r}_1, Z_A|\mathbf{r}_2)Q_B(\mathbf{r}_2, Z_B|\mathbf{r}_3) \quad (A10)$$

It should be noted that these two-point correlation

functions have the symmetries $C_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = C_{\beta\alpha}(\mathbf{r}', \mathbf{r})$, i.e., the matrix $C_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ is real and symmetric.

Appendix B: Reciprocal Space Formulation

Here we give a detailed exposition of the correlation functions in terms of the eigenfunction and eigenvalues of the chain Hamiltonian $\mathcal{H}_\alpha$. Using the eigenfunctions of $\mathcal{H}_\alpha$ as the basis functions, the one- and two-point cumulant correlation functions can be cast in the form

$$C_{n\mathbf{k}}^\alpha = \frac{1}{\sqrt{V}} \int d\mathbf{r}\, \psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r}) C_\alpha(\mathbf{r}) \tag{B1}$$

$$C_{n\mathbf{k},n'\mathbf{k}'}^{\alpha\beta} = \int d\mathbf{r} \int d\mathbf{r}'\, \psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r}) C_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \psi_{n'\mathbf{k}'}^{\beta}(\mathbf{r}') \tag{B2}$$

It will be useful to define one-, two-, and three-point integrals

$$q_{n\mathbf{k}}^\alpha \equiv \frac{1}{\sqrt{V}} \int d\mathbf{r}\, \psi_{n\mathbf{k}}^\alpha(\mathbf{r})$$

$$\Gamma_{n\mathbf{k},n'\mathbf{k}'}^{\alpha\beta} \equiv \int d\mathbf{r}\, \psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r}) \psi_{n'\mathbf{k}'}^{\beta}(\mathbf{r})$$

$$\Psi_{n\mathbf{k},n'\mathbf{k}',n''\mathbf{k}''}^\alpha \equiv \sqrt{V} \int d\mathbf{r}\, \psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r}) \psi_{n'\mathbf{k}'}^{\alpha*}(\mathbf{r}) \psi_{n''\mathbf{k}''}^{\alpha}(\mathbf{r}) \tag{B3}$$

The factors involving $V^{1/2}$ in the above expressions are introduced for convenience. As has been stated in the main text, the mean-field propagators can be written in terms of the eigenfunctions. Inserting the expressions for $Q_\alpha(\mathbf{r}, t|\mathbf{r}')$ into the correlation functions, we can perform the integrals over the t variables and obtain simple expressions for the correlation functions in the reciprocal space. In terms of the eigenfunctions, the one-body correlation functions can then be written as

$$C_{n\mathbf{k}}^A = \frac{Z_A}{Q_c Z} \sum_{n_1 \mathbf{k}_1} \sum_{n_2 \mathbf{k}_2} \sum_{n_3 \mathbf{k}_3} g[\epsilon_{n_1}^A(\mathbf{k}_1) Z_A - \epsilon_{n_2}^A(\mathbf{k}_2) Z_A] \times$$
$$e^{-\epsilon_{n_2}^A(\mathbf{k}_2) Z_A - \epsilon_{n_3}^B(\mathbf{k}_3) Z_B} q_{n_1 \mathbf{k}_1}^A \Psi_{n\mathbf{k},n_1\mathbf{k}_1,n_2\mathbf{k}_2}^A \Gamma_{n_2\mathbf{k}_2,n_3\mathbf{k}_3}^{AB} q_{n_3,\mathbf{k}_3}^{B*}$$

$$C_{n\mathbf{k}}^B = \frac{Z_B}{Q_c Z} \sum_{n_1 \mathbf{k}_1} \sum_{n_2 \mathbf{k}_2} \sum_{n_3 \mathbf{k}_3} g[\epsilon_{n_1}^B(\mathbf{k}_1) Z_B - \epsilon_{n_2}^B(\mathbf{k}_2) Z_B] \times$$
$$e^{-\epsilon_{n_2}^B(\mathbf{k}_2) Z_B - \epsilon_{n_3}^A(\mathbf{k}_3) Z_A} q_{n_1 \mathbf{k}_1}^B \Psi_{n\mathbf{k},n_1\mathbf{k}_1,n_2\mathbf{k}_2}^B \Gamma_{n_2\mathbf{k}_2,n_3\mathbf{k}_3}^{BA} q_{n_3\mathbf{k}_3}^{A*} \tag{B4}$$

where the function $g(x)$ is defined by

$$g(x) \equiv \frac{1 - e^{-x}}{x} \tag{B5}$$

The expressions for the two-body correlation functions are

$$C_{n\mathbf{k},n'\mathbf{k}'}^{AA} = \frac{Z_A^2}{Q_c Z} \sum_{n_1 \mathbf{k}_1} \sum_{n_2 \mathbf{k}_2} \sum_{n_3 \mathbf{k}_3} \sum_{n_4 \mathbf{k}_4} \times$$
$$\frac{g[\epsilon_{n_2}^A(\mathbf{k}_2) Z_A - \epsilon_{n_1}^A(\mathbf{k}_1) Z_A] - g[\epsilon_{n_3}^A(\mathbf{k}_3) Z_A - \epsilon_{n_1}^A(\mathbf{k}_1) Z_A]}{\epsilon_{n_3}^A(\mathbf{k}_3) Z_A - \epsilon_{n_2}^A(\mathbf{k}_2) Z_A} \times$$
$$e^{-\epsilon_{n_1}^A(\mathbf{k}_1) Z_A - \epsilon_{n_4}^B(\mathbf{k}_4) Z_B} \times$$
$$[q_{n_1\mathbf{k}_1}^A \Psi_{n\mathbf{k},n_1\mathbf{k}_1,n_2\mathbf{k}_2}^A \Psi_{n'\mathbf{k}',n_3\mathbf{k}_3,n_2\mathbf{k}_2}^{A*} \Gamma_{n_3\mathbf{k}_3,n_4\mathbf{k}_4}^{AB} q_{n_4\mathbf{k}_4}^{B*} +$$
$$q_{n_1\mathbf{k}_1}^{A*} \Psi_{n\mathbf{k},n_3\mathbf{k}_3,n_2\mathbf{k}_2}^A \Psi_{n'\mathbf{k}',n_1\mathbf{k}_1,n_2\mathbf{k}_2}^{A*} \Gamma_{n_3\mathbf{k}_3,n_4\mathbf{k}_4}^{AB*} q_{n_4\mathbf{k}_4}^{B}]$$

$$C_{n\mathbf{k},n'\mathbf{k}'}^{AB} = \frac{Z_A Z_B}{Q_c Z} \sum_{n_1 \mathbf{k}_1} \sum_{n_2 \mathbf{k}_2} \sum_{n_3 \mathbf{k}_3} \sum_{n_4 \mathbf{k}_4} g[\epsilon_{n_2}^A(\mathbf{k}_2) Z_A -$$
$$\epsilon_{n_1}^A(\mathbf{k}_1) Z_A] g[\epsilon_{n_3}^B(\mathbf{k}_3) Z_B - \epsilon_{n_4}^B(\mathbf{k}_4) Z_B] e^{-\epsilon_{n_1}^A(\mathbf{k}_1) Z_A - \epsilon_{n_4}^B(\mathbf{k}_4) Z_B} \times$$
$$q_{n_1\mathbf{k}_1}^A \Psi_{n\mathbf{k},n_1\mathbf{k}_1,n_2\mathbf{k}_2}^A \Gamma_{n_2\mathbf{k}_2,n_3\mathbf{k}_3}^{AB} \Psi_{n'\mathbf{k}',n_4\mathbf{k}_4,n_3\mathbf{k}_3}^{B*} q_{n_4\mathbf{k}_4}^{B*}$$

$$C_{n\mathbf{k},n'\mathbf{k}'}^{BA} = \frac{Z_A Z_B}{Q_c Z} \sum_{n_1 \mathbf{k}_1} \sum_{n_2 \mathbf{k}_2} \sum_{n_3 \mathbf{k}_3} \sum_{n_4 \mathbf{k}_4} g[\epsilon_{n_2}^B(\mathbf{k}_2) Z_B -$$
$$\epsilon_{n_1}^B(\mathbf{k}_1) Z_B] g[\epsilon_{n_3}^A(\mathbf{k}_3) Z_A - \epsilon_{n_4}^A(\mathbf{k}_4) Z_A] e^{-\epsilon_{n_4}^A(\mathbf{k}_4) Z_A - \epsilon_{n_1}^B(\mathbf{k}_1) Z_B} \times$$
$$q_{n_1\mathbf{k}_1}^B \Psi_{n\mathbf{k},n_1\mathbf{k}_1,n_2\mathbf{k}_2}^B \Gamma_{n_2\mathbf{k}_2,n_3\mathbf{k}_3}^{BA} \Psi_{n'\mathbf{k}',n_4\mathbf{k}_4,n_3\mathbf{k}_3}^{A*} q_{n_4\mathbf{k}_4}^{A*}$$

$$C_{n\mathbf{k},n'\mathbf{k}'}^{BB} = \frac{Z_B^2}{Q_c Z} \sum_{n_1 \mathbf{k}_1} \sum_{n_2 \mathbf{k}_2} \sum_{n_3 \mathbf{k}_3} \sum_{n_4 \mathbf{k}_4}$$
$$\frac{g[\epsilon_{n_2}^B(\mathbf{k}_2) Z_B - \epsilon_{n_1}^B(\mathbf{k}_1) Z_B] - g[\epsilon_{n_3}^B(\mathbf{k}_3) Z_B - \epsilon_{n_1}^B(\mathbf{k}_1) Z_B]}{\epsilon_{n_3}^B(\mathbf{k}_3) Z_B - \epsilon_{n_2}^B(\mathbf{k}_2) Z_B} \times$$
$$e^{-\epsilon_{n_1}^B(\mathbf{k}_1) Z_B - \epsilon_{n_4}^A(\mathbf{k}_4) Z_A} \times$$
$$[q_{n_1\mathbf{k}_1}^B \Psi_{n\mathbf{k},n_1\mathbf{k}_1,n_2\mathbf{k}_2}^B \Psi_{n'\mathbf{k}',n_3\mathbf{k}_3,n_2\mathbf{k}_2}^{B*} \Gamma_{n_3\mathbf{k}_3,n_4\mathbf{k}_4}^{BA} q_{n_4\mathbf{k}_4}^{A*} +$$
$$q_{n_1\mathbf{k}_1}^{B*} \Psi_{n\mathbf{k},n_3\mathbf{k}_3,n_2\mathbf{k}_2}^B \Psi_{n'\mathbf{k}',n_1\mathbf{k}_1,n_2\mathbf{k}_2}^{B*} \Gamma_{n_3\mathbf{k}_3,n_4\mathbf{k}_4}^{BA*} q_{n_4\mathbf{k}_4}^{A}] \tag{B6}$$

The mean-field single-chain partition function Q_c can also be cast in terms of these integrals

$$Q_c = \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\, Q_A(\mathbf{r}_1, Z_A | \mathbf{r}_2) Q_B(\mathbf{r}_2, Z_B | \mathbf{r}_3)$$
$$\sum_{\substack{n_1 \mathbf{k}_1 \\ n_2 \mathbf{k}_2}} e^{-\epsilon_{n_1}^A(\mathbf{k}_1) Z_A - \epsilon_{n_2}^B(\mathbf{k}_2) Z_B} q_{n_1\mathbf{k}_1}^A \Gamma_{n_1\mathbf{k}_1,n_2\mathbf{k}_2}^{AB} q_{n_2\mathbf{k}_2}^{B*} \tag{B7}$$

We now consider the most general case, in which the only restriction is that the mean fields $\omega_\alpha(\mathbf{r})$ are periodic functions. As we have mentioned before, the eigenfunctions for the chain Hamiltonian are Bloch functions of the form

$$\psi_{n\mathbf{k}}^\alpha(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}^\alpha(\mathbf{r}) \tag{B8}$$

where $u_{n\mathbf{k}}^\alpha(\mathbf{r})$ are periodic functions, and the factor $1/(V)^{1/2}$ is introduced for convenience. In order to proceed, we expand the periodic function $u_{n\mathbf{k}}^\alpha(\mathbf{r})$ using the reciprocal lattice vectors of the system

$$u_{n\mathbf{k}}^\alpha(\mathbf{r}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}^\alpha(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{B9}$$

where $\{\mathbf{G}\}$ are the reciprocal lattice points of the ordered phase under consideration. Because the mean fields $\omega_\alpha(\mathbf{r})$ can be expanded in the form

$$\omega_\alpha(\mathbf{r}) = \sum_{\mathbf{G}} \omega^\alpha(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{B10}$$

the Schrödinger equation becomes

$$\left[\frac{b^2}{6}(\mathbf{k} + \mathbf{G})^2 - \epsilon_{n\mathbf{k}}^\alpha\right] u_{n\mathbf{k}}^\alpha(\mathbf{G}) + \sum_{\mathbf{G}'} \omega^\alpha(\mathbf{G} - \mathbf{G}') u_{n\mathbf{k}}^\alpha(\mathbf{G}') = 0 \tag{B11}$$

This result for different reciprocal lattice vectors $\mathbf{G}$ generates an infinite number of equations. The condition of having a nonzero solution is that the determinant

of the system vanishes

$$\det\left|\left[\frac{b^2}{6}(\mathbf{k} + \mathbf{G})^2 - \epsilon_{n\mathbf{k}}^\alpha\right]\delta_{\mathbf{G},\mathbf{G}'} + \omega^\alpha(\mathbf{G} - \mathbf{G}')\right| = 0 \quad (B12)$$

The order of this determinant is infinite. In practice, we can only deal with a finite determinant; e.g., if we take 200 plane waves, we will have a determinant of order 200, and the solution of the eigenvalue equation gives 200 eigenvalues $\epsilon_{n\mathbf{k}}^\alpha$ ($n = 1, 2, ..., 200$). The energy bands are obtained by changing the values of the $\mathbf{k}$'s in the Schrödinger equation.

The required integrals can now be cast using the Bloch functions. In particular, we have

$$q_{n\mathbf{k}}^\alpha \equiv \frac{1}{\sqrt{V}} \int d\mathbf{r}\,\psi_{n\mathbf{k}}^\alpha(\mathbf{r})$$

$$= \sum_{\mathbf{G}} u_{n\mathbf{k}}^\alpha(\mathbf{G})\frac{1}{V}\int d\mathbf{r}\,e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$= \sum_{\mathbf{G}} u_{n\mathbf{k}}^\alpha(\mathbf{G})\delta_{\mathbf{k}+\mathbf{G},\mathbf{0}} \quad (B13)$$

Since $\mathbf{k}$ is restricted in the first Brillouin zone, the condition $\mathbf{k} = \mathbf{G}$ leads to $\mathbf{k} = \mathbf{G} = \mathbf{0}$. Therefore we have for the one-point integrals

$$q_{n\mathbf{k}}^\alpha = u_{n\mathbf{k}}^\alpha(\mathbf{0})\delta_{\mathbf{k},\mathbf{0}}$$

$$= q_n^\alpha\delta_{\mathbf{k},\mathbf{0}} \quad (B14)$$

where the reduced one-point integrals q_n^α are given by

$$q_n^\alpha = u_{n\mathbf{0}}^\alpha(\mathbf{0}) \quad (B15)$$

Let us now consider the two-point integrals. Using the Bloch functions and integrating out the $\mathbf{r}$ variable, we have

$$\Gamma_{n\mathbf{k},n'\mathbf{k}'}^{\alpha\beta} \equiv \int d\mathbf{r}\,\psi_{n\mathbf{k}}^{\alpha*}(\mathbf{r})\psi_{n'\mathbf{k}'}^{\beta}(\mathbf{r})$$

$$= \sum_{\mathbf{G}}\sum_{\mathbf{K}} u_{n\mathbf{k}}^{\alpha*}(\mathbf{G})u_{n'\mathbf{k}'}^{\beta}(\mathbf{G}+\mathbf{K})\delta_{\mathbf{k}-\mathbf{k}',\mathbf{K}} \quad (B16)$$

The delta function in the above expression $\delta_{\mathbf{k}-\mathbf{k}',\mathbf{K}}$ requires that $\mathbf{k} - \mathbf{k}'$ equals a reciprocal lattice vector $\mathbf{K}$. Since both $\mathbf{k}$ and $\mathbf{k}'$ are restricted in the first Brillouin zone, this condition puts a severe restriction on the values of $\mathbf{K}$. We note that $\mathbf{K} = \mathbf{0}$ is always allowed, which leads to $\delta_{\mathbf{k}-\mathbf{k}',\mathbf{K}} = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\mathbf{K},\mathbf{0}}$. It is possible to prove that $\mathbf{K} = \mathbf{0}$ is the only solution for the requirement $\mathbf{k} - \mathbf{k}' = \mathbf{K}$: (a) It is obvious that the only possible $\mathbf{K}$'s are the nearest and (possibly) the next-nearest neighbors to the lattice point $\mathbf{K} = \mathbf{0}$; (b) the possible $\mathbf{k}$ and $\mathbf{k}'$ values are confined by the two perpendicular planes bisecting $\mathbf{K}$ and $-\mathbf{K}$; (c) for any vector $\mathbf{k}'$ within the first Brillouin zone, the vector $\mathbf{k}' + \mathbf{K}$ is always outside the first Brillouin zone, except that $\mathbf{k}'$ is on the plane bisecting $-\mathbf{K}$; (d) when $\mathbf{k}'$ is on the plane bisecting $-\mathbf{K}$, the sum $\mathbf{k}' + \mathbf{K}$ is at the corresponding point on the plane bisecting $\mathbf{K}$. However, these two points are degenerate and only one of them can be included in the spectrum for a given band. Therefore it is not possible to have nonzero $\mathbf{K}$ so that $\mathbf{k} - \mathbf{k}' = \mathbf{K}$, and the two-point integrals are diagonal in the $\mathbf{k}$ space

$$\Gamma_{n\mathbf{k},n'\mathbf{k}'}^{\alpha\beta} = \sum_{\mathbf{G}} u_{n\mathbf{k}}^{\alpha*}(\mathbf{G})\,u_{n'\mathbf{k}}^{\beta}(\mathbf{G})\delta_{\mathbf{k},\mathbf{k}'}$$

$$= \Gamma_{n,n'}^{\alpha\beta}(\mathbf{k})\delta_{\mathbf{k},\mathbf{k}'} \quad (B17)$$

where the reduced two-point integrals $\Gamma_{n,n'}^{\alpha\beta}(\mathbf{k})$ are given by

$$\Gamma_{n,n'}^{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{G}} u_{n\mathbf{k}}^{\alpha*}(\mathbf{G})\,u_{n'\mathbf{k}}^{\beta}(\mathbf{G}) \quad (B18)$$

For the three-point integrals, the integral over the spatial variables leads to

$$\Psi_{n_1\mathbf{k}_1,n_2\mathbf{k}_2,n_3\mathbf{k}_3}^\alpha \equiv \sqrt{V}\int d\mathbf{r}\,\psi_{n_1\mathbf{k}_1}^{\alpha*}(\mathbf{r})\psi_{n_2\mathbf{k}_2}^{\alpha*}(\mathbf{r})\psi_{n_3\mathbf{k}_3}^{\alpha}(\mathbf{r})$$

$$= \sum_{\mathbf{G}_1}\sum_{\mathbf{G}_2}\sum_{\mathbf{G}_3} u_{n_1\mathbf{k}_1}^{\alpha*}(\mathbf{G}_1)u_{n_2\mathbf{k}_2}^{\alpha*}(\mathbf{G}_2)u_{n_3\mathbf{k}_3}^{\alpha}$$

$$(\mathbf{G}_3)\delta_{\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3+\mathbf{G}_1+\mathbf{G}_2-\mathbf{G}_3,\mathbf{0}} \quad (B19)$$

Again, the delta function $\delta_{\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3+\mathbf{G}_1+\mathbf{G}_2-\mathbf{G}_3,\mathbf{0}}$ requires that $\mathbf{k} + \mathbf{k}_2 - \mathbf{k}_3 = \mathbf{K}$ is a reciprocal lattice vector, which puts severe restrictions on the possible values of $\mathbf{K}$. A detailed consideration is needed to obtain the possible values of $\mathbf{K}$. There is, however, a simplification in that, for all the three-body integrals needed in the first- and second-order cumulant correlation functions, one of the $\mathbf{k}$'s is always zero. Therefore, the three-body restriction reduces to the two-body restriction, $\mathbf{k}_1 - \mathbf{k}_2 = \mathbf{K}$. The fact that there is always one $\mathbf{k} = \mathbf{0}$ in Ψ can be seen easily from the expressions for the correlation functions by noting that the one-body and two-body integrals have the generic form given above. These expressions ensure that the needed three-point integrals have at least one $\mathbf{k} = \mathbf{0}$. Using the expressions for the Ψ's, we have

$$\Psi_{n_1\mathbf{k}_1,n_2\mathbf{0},n_3\mathbf{k}_3}^\alpha = \sum_{\mathbf{G}_1}\sum_{\mathbf{G}_2}\sum_{\mathbf{G}_3} u_{n_1\mathbf{k}_1}^{\alpha*}(\mathbf{G}_1)u_{n_2\mathbf{0}}^{\alpha*}(\mathbf{G}_2)u_{n_\mathbf{k}_3}^{\alpha}$$

$$(\mathbf{G}_3)\delta_{\mathbf{k}_1-\mathbf{k}_3+\mathbf{G}_1+\mathbf{G}_2-\mathbf{G}_3,\mathbf{0}}$$

$$= \sum_{\mathbf{G}_1}\sum_{\mathbf{G}_2} u_{n_1\mathbf{k}_1}^{\alpha*}(\mathbf{G}_1)u_{n_2\mathbf{0}}^{\alpha*}(\mathbf{G}_2)u_{n_3\mathbf{K}_1}^{\alpha}$$

$$(\mathbf{G}_1+\mathbf{G}_2)\delta_{\mathbf{k}_1,\mathbf{k}_3}$$

$$= \Psi_{n,n_2,n_3}^\alpha(\mathbf{k}_1)\delta_{\mathbf{k}_1,\mathbf{k}_3} \quad (B20)$$

where the reduced three-point integrals $\Psi_{n_1,n_2,n_3}^\alpha(\mathbf{k})$ are given by

$$\Psi_{n_1,n_2,n_3}^\alpha(\mathbf{k}) = \sum_{\mathbf{G}_1}\sum_{\mathbf{G}_2} u_{n_1\mathbf{k}}^{\alpha*}(\mathbf{G}_1)u_{n_2\mathbf{0}}^{\alpha*}(\mathbf{G}_2)u_{n_3\mathbf{k}}^{\alpha}(\mathbf{G}_1+\mathbf{G}_2)$$

$$(B21)$$

We can now use these reduced three-body integrals to eliminate the sums over $\mathbf{k}$'s in the correlation functions. After some simple manipulations, we obtain the expressions for the cumulant correlation functions and the single-chain partition function. For the one-point correlation functions we have

$$C_n^A = \frac{Z_A}{Q_c Z}\sum_{n_1,n_2,n_3} g[\epsilon_{n_1}^A(\mathbf{0})Z_A -$$

$$\epsilon_{n_2}^A(\mathbf{0})Z_A]e^{-\epsilon_{n_2}^A(\mathbf{0})Z_A-\epsilon_{n_3}^B(\mathbf{0})Z_B}q_{n_1}^A\Psi_{n,n_1,n_2}^A(\mathbf{0})\Gamma_{n_2,n_3}^{AB}(\mathbf{0})q_{n_3}^{B*}$$

$$C_n^B = \frac{Z_B}{Q_c Z} \sum_{n_1,n_2,n_3} g[\epsilon_{n_1}^B(\mathbf{0})Z_B -$$

$$e_{n_2}^B(\mathbf{0})Z_B] e^{-\epsilon_{n_2}^B(\mathbf{0})Z_B - \epsilon_{n_3}^A(\mathbf{0})Z_A} q_{n_1}^B \Psi_{n,n_1,n_2}^B(\mathbf{0}) \Gamma_{n_2,n_3}^{BA}(\mathbf{0}) q_{n_3}^{A*} \quad \text{(B22)}$$

For the two-point correlation functions we have

$$C_{n,n'}^{AA}(\mathbf{k}) = \frac{Z_A^2}{Q_c Z} \sum_{n_1,n_2,n_3,n_4} \times$$

$$\frac{g[\epsilon_{n_2}^A(\mathbf{k})Z_A - \epsilon_{n_1}^A(\mathbf{0})Z_A] - g[\epsilon_{n_3}^A(\mathbf{0})Z_A - \epsilon_{n_1}^A(\mathbf{0})Z_A]}{\epsilon_{n_3}^A(\mathbf{0})Z_A - \epsilon_{n_2}^A(\mathbf{k})Z_A} \times$$

$$e^{-\epsilon_{n_3}^A(\mathbf{0})Z_A - \epsilon_{n_4}^B(\mathbf{0})Z_B} [q_{n_1}^A \Psi_{n,n_1,n_2}^A(\mathbf{k}) \Psi_{n',n_3,n_2}^{A*}(\mathbf{k}) \Gamma_{n_3,n_4}^{AB}(\mathbf{0}) q_{n_4}^{B*} +$$

$$q_{n_1}^{A*} \Psi_{n,n_3,n_2}^A(\mathbf{k}) \Psi_{n',n_1,n_2}^{A*}(\mathbf{k}) \Gamma_{n_3,n_4}^{AB*}(\mathbf{0}) q_{n_4}^B]$$

$$C_{n,n'}^{AB}(\mathbf{k}) = \frac{Z_A Z_B}{Q_c Z} \sum_{n_1,n_2,n_3,n_4} g[\epsilon_{n_2}^A(\mathbf{k})Z_A - \epsilon_{n_1}^A(\mathbf{0})Z_A] \times$$

$$g[\epsilon_{n_3}^B(\mathbf{k})Z_B - \epsilon_{n_4}^B(\mathbf{0})Z_B] e^{-\epsilon_{n_1}^A(\mathbf{0})Z_A - \epsilon_{n_4}^B(\mathbf{0})Z_B} \times$$

$$q_{n_1}^A \Psi_{n,n_1,n_2}^A(\mathbf{k}) \Gamma_{n_2,n_3}^{AB}(\mathbf{k}) \Psi_{n',n_4,n_3}^{B*}(\mathbf{k}) q_{n_4}^{B*}$$

$$C_{n,n'}^{BA}(\mathbf{k}) = \frac{Z_A Z_B}{Q_c Z} \sum_{n_1,n_2,n_3,n_4} g[\epsilon_{n_2}^B(\mathbf{k})Z_B - \epsilon_{n_1}^B(\mathbf{0})Z_B] \times$$

$$g[\epsilon_{n_3}^A(\mathbf{k})Z_A - \epsilon_{n_4}^A(\mathbf{0})Z_A] e^{-\epsilon_{n_4}^A(\mathbf{0})Z_A - \epsilon_{n_1}^B(\mathbf{0})Z_B} \times$$

$$q_{n_1}^B \Psi_{n,n_1,n_2}^B(\mathbf{k}) \Gamma_{n_2,n_3}^{BA}(\mathbf{k}) \Psi_{n',n_4,n_3}^{A*}(\mathbf{k}) q_{n_4}^{A*}$$

$$C_{n,n'}^{BB}(\mathbf{k}) = \frac{Z_B^2}{Q_c Z} \sum_{n_1,n_2,n_3,n_4} \times$$

$$\frac{g[\epsilon_{n_2}^B(\mathbf{k})Z_B - \epsilon_{n_1}^B(\mathbf{0})Z_B] - g[\epsilon_{n_3}^B(\mathbf{0})Z_B - \epsilon_{n_1}^B(\mathbf{0})Z_B]}{\epsilon_{n_3}^B(\mathbf{0})Z_B - \epsilon_{n_2}^B(\mathbf{k})Z_B} \times$$

$$e^{-\epsilon_{n_1}^B(\mathbf{0})Z_B - \epsilon_{n_4}^A(\mathbf{0})Z_A} [q_{n_1}^B \Psi_{n,n_1,n_2}^B(\mathbf{k}) \Psi_{n',n_3,n_2}^{B*}(\mathbf{k}) \Gamma_{n_3,n_4}^{BA}(\mathbf{0}) q_{n_4}^{A*} +$$

$$q_{n_1}^{B*} \Psi_{n,n_3,n_2}^B(\mathbf{k}) \Psi_{n',n_1,n_2}^{B*}(\mathbf{k}) \Gamma_{n_3,n_4}^{BA*}(\mathbf{0}) q_{n_4}^A] \quad \text{(B23)}$$

For the single-chain mean-field partition function Q_c, we obtain

$$Q_c = \sum_{n_1,n_2} e^{-\epsilon_{n_1}^A(\mathbf{0})Z_A - \epsilon_{n_2}^B(\mathbf{0})Z_B} q_{n_1}^A \Gamma_{n_1,n_2}^{AB}(\mathbf{0}) q_{n_2}^{B*} \quad \text{(B24)}$$

In all these expressions, the required quantities are the reduced one-, two-, and three-point integrals of the eigenfunctions

$$q_n^\alpha = \frac{1}{V_c} \int_c d\mathbf{r} \; u_{n\mathbf{0}}^\alpha(\mathbf{r})$$

$$\Gamma_{n,n'}^{\alpha\beta}(\mathbf{k}) = \frac{1}{V_c} \int_c d\mathbf{r} \; u_{n\mathbf{k}}^{\alpha*}(\mathbf{r}) u_{n'\mathbf{k}}^\beta(\mathbf{r})$$

$$\Psi_{n_1,n_2,n_3}^\alpha(\mathbf{k}) = \frac{1}{V_c} \int_c d\mathbf{r} \; u_{n_1\mathbf{k}}^{\alpha*}(\mathbf{r}) u_{n_2\mathbf{0}}^{\alpha*}(\mathbf{r}) u_{n_3\mathbf{k}}^\alpha(\mathbf{r}) \quad \text{(B25)}$$

where $u_{n\mathbf{k}}^\alpha(\mathbf{r})$ are the periodic parts of the Bloch functions, V_c is the volume of the unit cell, and the integrals are over one unit cell.

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