

Fluctuation Effects in the Theory of Microphase Separation of Diblock Copolymers in the Presence of an Electric Field

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ABSTRACT: We generalize the Fredrickson–Helfand theory of the microphase separation in symmetric diblock copolymer melts by taking into account the influence of a time-independent homogeneous electric field on the composition fluctuations within the self-consistent Hartree approximation. We predict that electric fields suppress composition fluctuations, and consequently weaken the first-order transition. In the presence of an electric field the critical temperature of the order–disorder transition is shifted toward its mean-field value. The collective structure factor in the disordered phase becomes anisotropic in the presence of the electric field. Fluctuational modulations of the order parameter along the field direction are strongest suppressed. The latter is in accordance with the parallel orientation of the lamellae in the ordered state.

I. Introduction

The effect of electric fields on the behavior of dielectric block copolymer melts in bulk and in thin films has found increasing interest in recent years^{1–14} (and references therein) due to the possibility to create uniform alignment in macroscopic microphase separated samples. This is of special relevance for applications using self-assembled block copolymer structures for patterning and templating of nanostructures.¹⁵ The driving force for electric field induced alignment is the orientation-dependent polarization in a material composed of domains with anisotropic shape. The reason for the orientation in electric fields has a very simple explanation in samples where the inhomogeneities appear only at interfaces of cylinders or lamellae, as it is roughly the case in the strong segregation limit. The polarization of the sample in this case induces surface charges at the interfaces depending on the relative orientation of the interfaces with respect to the field. The system is lowering its free energy, if the interfaces orient parallel to the field. If the composition of a block copolymer sample and consequently also the local dielectric constant varies gradually, the polarization charges appear in the whole system. However, interfaces parallel to the field possess the lowest electric energy also in this case.

The effects of electric fields on the behavior of diblock copolymer melts have been studied in⁴ by taking into account the electric part to the free energy (quadratic in the strength of the electric field and the order parameter) in addition to the thermodynamic potential including composition fluctuations in the absence of the field. The influence of an electric field on the composition fluctuations has not been considered yet. However, the general relation between the derivatives of the thermodynamic potential and the correlation function of the order parameter, given by eq 6, requires the inclusion of the electric field into the correlation function of the Brazovskii self-consistent Hartree approach, too. The angular dependence of the structure factor without taking into account the fluctuation effects was derived previously for polymer solutions in,¹ and for copolymer melts in.⁶ Intuitively it seems obvious that fluctuations become anisotropic in an electric field, and moreover fluctuations of modes with wave vectors parallel to

the electric field are suppressed. The effects of an electric field on composition fluctuations are directly accessible in scattering experiments, and were studied for polymer solutions in¹ and for asymmetric diblock copolymers in.¹⁰ In this paper, we present the results of the generalization of the Fredrickson–Helfand theory¹⁶ by taking into account the effects of the electric field on the composition fluctuations in symmetric diblock copolymer melts.

The paper is organized as follows. Section IIA reviews the collective description of the diblock copolymer melt. Section IIB describes the coupling of the block copolymer melt to external time-independent electric fields. Section IIC gives an introduction to the Brazovskii–Fredrickson–Helfand treatment of composition fluctuations in the presence of time-independent electric fields. Section III contains our results.

II. Theory

A. A Brief Review of the Collective Description. In a diblock copolymer (AB), a chain of N_A subunits of type A is at one end covalently bonded to a chain of N_B subunits of type B. A net repulsive A–B interaction energy $E \propto \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$ between the monomers leads to microphase separation. Thus, at an order–disorder transition concentration waves are formed spontaneously, having a wavelength of the same order as the radius of gyration of the coils. The type of the long range order that forms depends on the composition of the copolymers $f = N_A/N$ with $N = N_A + N_B$. Here we treat only the symmetric composition with $f = 1/2$ for which the lamellar mesophase is formed. As an order parameter we consider the deviation of the density of A-polymers from its mean value, $\delta\Phi_A(r) = \rho_A(r) - f\rho_m$, where $\rho_A(r)$ is the monomer density of the A monomers and ρ_m is the average monomer density of the melt. Since the system is assumed to be incompressible, the condition $\delta\Phi_A(r) + \delta\Phi_B(r) = 0$ should be fulfilled. The expansion of the effective Landau Hamiltonian in powers of the fluctuating order parameter $\delta\Phi(r) \equiv \delta\Phi_A(r)$ was derived by Leibler¹⁷ using the random phase approximation (RPA). Following to Fredrickson and Helfand¹⁶ let us introduce instead of $\delta\Phi(r)$ the dimensionless order parameter $\psi(r) = \delta\Phi_A(r)/\rho_m$. The effective Hamiltonian in terms of $\psi(r)$ is given in units of $k_B T$ for

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symmetric composition by¹⁶

$$H(\psi) = \frac{1}{2} \int_q \psi(-q) \gamma_2(q) \psi(q) + \frac{1}{4!} \int_{q_1} \int_{q_2} \int_{q_3} \gamma_4(q_1, q_2, q_3, -q_1 - q_2 - q_3) \times \psi(q_1) \psi(q_2) \psi(q_3) \psi(-q_1 - q_2 - q_3) \quad (1)$$

where the wave vector q is the Fourier conjugate to $x \equiv \rho_m^{1/3} r$, and the shortcut $\int_q \equiv \int (d^3q)/(2\pi)^3$ is introduced. Furthermore, q_r is the Fourier conjugate to r and is defined via $q = q_r \rho_m^{-1/3}$. The quantity $\gamma_2(q)$ in eq 1 is defined as

$$\gamma_2(q) = (F(y) - 2\chi N)/N$$

with

$$F(y) = \frac{g_D(y, 1)}{g_D(y, f) g_D(y, 1 - f) - \frac{1}{4} [g_D(y, 1) - g_D(y, f) - g_D(y, 1 - f)]^2}$$

and

$$g_D(y, f) = \frac{2}{y^2} (fy + e^{-fy} - 1)$$

Here $g_D(y, f)$ is the Debye function and $y = q_r^2 R_g^2 = q^2 \rho_m^{2/3} R_g^2 = q^2 N/6$, where $R_g = b \sqrt{N}/6$ is the unperturbed radius of gyration of the copolymer chain. We assume that both blocks have equal statistical segment lengths denoted by b and furthermore $b = \rho_m^{-1/3}$. The collective structure factor of the copolymer melt $S_c(q) = \langle \delta \Phi_A(q_r) \delta \Phi_A(-q_r) \rangle$ is related to $\gamma_2(q)$ by

$$S_c(q) = \gamma_2^{-1}(q)$$

The scattering function of a Gaussian polymer chain $S(q_r) = (2/N) \sum_{i < j} \langle \exp(-iq_r r_{ij}) \rangle$ can be expressed by the Debye function $g_D(x, 1)$ via the relation $S(q) = N g_D(x, 1)$. The vertex function $\gamma_4(q_1, q_2, q_3, -q_1 - q_2 - q_3)$ is expressed in the random phase approximation through the correlation functions of one and two Gaussian copolymer chains.¹⁷ The vertex function as well as the quantity $F(y)$ in $\gamma_2(q)$ are independent of temperature. The collective structure factor $S_c(q)$ has a pronounced peak at the wave vector q^* , obeying the condition $y^* = (q_r^* R_g)^2 = 3.7852$ for $f = 1/2$, i.e. y^* is independent of both temperature and molecular weight. As it is well-known,¹⁶ the composition fluctuations, which are described according to Brazovskii¹⁹ within the self-consistent Hartree approach, change the type of the phase transition to the ordered state from second order to fluctuation-induced weak first-order. In this theory^{19,16} the inverse of the collective structure factor is approximated near to the peak by

$$\begin{aligned} N\gamma_2(q) &= F(y^*) - 2\chi N + \frac{1}{2} \frac{\partial^2 F}{\partial y^{*2}} (y - y^*)^2 + \dots \\ &= 2(\chi N)_s - 2\chi N + \frac{1}{2} \frac{\partial^2 F}{\partial y^{*2}} 4y^* \frac{N}{6} (q - q^*)^2 + \dots \\ &\simeq Nc^2 (\tilde{\tau} + (q - q^*)^2) \end{aligned} \quad (2)$$

According to¹⁶ the notations

$$(2\chi N)_s = F(y^*) = 20.990$$

$$c = \sqrt{y^* \partial^2 F / \partial y^{*2} / 3} = 1.1019$$

$$\tilde{\tau} = \frac{2(\chi N)_s - 2\chi N}{Nc^2} \quad (3)$$

are introduced. Redefining the order parameter by $\psi = c^{-1} \phi$ and inserting eq 2 into eq 1, the effective Hamiltonian can be written as

$$H(\phi) = \frac{1}{2} \int_q \phi(-q) (\tilde{\tau} + (q - q^*)^2) \phi(q) + \frac{\tilde{\lambda}}{4!} \int_{q_1} \int_{q_2} \int_{q_3} \phi(q_1) \phi(q_2) \phi(q_3) \phi(-q_1 - q_2 - q_3) \quad (4)$$

where $\tilde{\lambda} = \gamma_4(q^*, q^*, q^*, -q^* - q^* - q^*)/c^4$. Following¹⁶ the vertex γ_4 is approximated by its value at q^* . The quantity $\tilde{\tau}$ plays the role of the reduced temperature in the Landau theory of phase transitions. Note that the scattering function is obtained from eq 2 as

$$S_c^{-1}(q) = \tilde{\tau} + (q - q^*)^2 \quad (5)$$

In order to study the composition fluctuations in symmetric diblock copolymer melts based on the effective Hamiltonian (4), it is convenient to introduce an auxiliary field $h(x)$, which is coupled linearly to the order parameter. Thus, the term $\int d^3r h(x) \phi(x)$ should be added to eq 4. Consequently the average value of the order parameter can be written as $\bar{\phi}(x) = -\delta \mathcal{F}(h)/\delta h(x)|_{h=0}$, where $\mathcal{F}(h)$ is the free energy related to the partition function $Z(h)$ by $\mathcal{F}(h) = -k_B T \ln Z(h)$. The Legendre transformation, $\delta(\mathcal{F} + \int d^3r h(x) \bar{\phi}(x)) \equiv \delta \Gamma(\bar{\phi}) = \int d^3r h(x) \delta \bar{\phi}(x)$ introduces the thermodynamic potential $\Gamma(\bar{\phi})$, which is a functional of the average value of the order parameter $\phi(x)$. In terms of the Gibbs potential $\Gamma(\bar{\phi})$ the spontaneous value of the order parameter is determined by the equation $0 = \delta \Gamma(\bar{\phi})/\delta \bar{\phi}(x)$. The potential $\Gamma(\bar{\phi})$ is the generating functional of the one-particle irreducible Greens's function, and can be represented as a series by using Feynman diagrams.²¹ The second derivative of the Gibbs potential with respect to the order parameter yields the inverse correlation function

$$\frac{\delta^2 \Gamma(\bar{\phi})}{\delta \bar{\phi}(x_1) \delta \bar{\phi}(x_2)} = S^{-1}(x_1, x_2, \bar{\phi}) \quad (6)$$

The correlation functions of composition fluctuations in the disordered and ordered phase are defined by

$$S(x_1, x_2) = \langle \phi(x_1) \phi(x_2) \rangle, \quad S(x_1, x_2, \bar{\phi}) = \langle \Delta \phi(x_1) \Delta \phi(x_2) \rangle$$

respectively, where the abbreviation $\Delta \phi(x) = \phi(x) - \bar{\phi}(x)$ is introduced. Equation 6 is the pendent of the well-known relation

$$\frac{\delta^2 \mathcal{A}(h)}{\delta h(x_1) \delta h(x_2)}|_{h=0} = S(x_1, x_2) \quad (7)$$

which represents the relation between the thermodynamic quantities and the correlation function of the composition $\phi(x)$. For $\bar{\phi} = 0$, eq 6 is obtained from eq 7 using the Legendre transform. In the case of a constant auxiliary field the variational derivatives on the left-hand side of eq 7 should be replaced by the partial ones, while the integration over x_1 and x_2 is carried out on the right-hand side. Then the derivative $-\partial \mathcal{A}/\partial h$ is the mean value of the order parameter $\bar{\phi}(x)$ multiplied by the volume

of the system. The second derivative of the free energy, $\partial^2 \mathcal{F} / \partial h^2$, is related to the susceptibility, which in accordance to eq 7 is equal to the integral of the correlation function.

The order parameter for a symmetric diblock copolymer melt can be approximated in the vicinity of the critical temperature of the microphase separation by

$$\bar{\phi}(x) = 2A \cos(q^*nx) \quad (8)$$

where n is a unit vector in the direction of the wave vector perpendicular to the lamellae and A is an amplitude. The Brazovskii self-consistent Hartree approach, which takes into account the fluctuation effects on the microphase separation, is based on the following expression of the derivative of the Gibbs potential with respect to the amplitude A of the order parameter

$$\frac{1}{A} \frac{\partial \Gamma(A)/V}{\partial A} = 2 \left(\tilde{\tau} + \frac{\tilde{\lambda}}{2} \int_q S_0(q, A) + \frac{\tilde{\lambda}}{2} A^2 \right) \quad (9)$$

The second term in eq 9 includes the propagator

$$S_0(q, A) = 1/(\tilde{\tau} + (q - q^*)^2 + \tilde{\lambda}A^2) \quad (10)$$

and represents the first-order correction to the thermodynamic potential owing to the self-energy. The first two terms in the brackets on the right-hand side of eq 9 are summarized to an effective reduced temperature denoted by $\tilde{\tau}_r$. The equation for $\tilde{\tau}_r$ becomes self-consistent by replacing $\tilde{\tau}$ in eq 10 for $S_0(q, A)$ by $\tilde{\tau}_r$. Then we get

$$\tilde{\tau}_r = \tilde{\tau} + \frac{\tilde{\lambda}}{2} \int_q S(q, A) \quad (11)$$

where $S^{-1}(q, A) = \tilde{\tau}_r + (q - q^*)^2 + \tilde{\lambda}A^2$ is the inverse of the effective propagator.

B. Contribution of the Electric Field to the Effective Hamiltonian. In this subsection we discuss the coupling of the diblock copolymer melt to an external time-independent electric field. The system we consider is a linear dielectric and is free of external charges. The field satisfies the Maxwell equation

$$\text{div}(\epsilon(r)E(r)) = 0$$

where the inhomogeneities of the dielectric constant $\epsilon(r)$ are caused by the inhomogeneities of the order parameter. According to ref 3, we adopt the expansion of the dielectric constant in powers of the order parameter up to quadratic terms

$$\epsilon(r) = \epsilon_D(r) + \beta \bar{\phi}(r) + \frac{1}{2} \frac{\partial^2 \epsilon}{\partial \bar{\phi}^2} \bar{\phi}(r)^2 \quad (12)$$

In the case of zero-order parameter $\bar{\phi}(r) = 0$ the dielectric constant is assumed to be homogeneous, i.e., $\epsilon_D(r) = \epsilon_D$. The above Maxwell equation can be rewritten as integral equation as follows

$$E(r) = E_0 + \frac{1}{4\pi} \nabla \int d^3r_1 G_0(r - r_1) (E(r_1) \nabla) \ln \epsilon(r_1) \quad (13)$$

where $G_0(r) = 1/r$ is the Green's function of the Poisson equation. The integral eq 13 is convenient to derive iterative solutions for the electric field, and to take into account the dependencies of $\epsilon(r)$ on the order parameter. The second term in eq 13 takes into account the polarization due to the inhomogeneities of the order parameter. The substitution $E(r_1) = E_0$ on the right-hand side of eq 13 gives the first-order correction to the external electric field as

$$\begin{aligned} E(r) &= E_0 + E_1(r) + \dots \\ &= E_0 + \frac{1}{4\pi} \frac{\beta}{\epsilon_D} \nabla \int d^3r_1 G_0(r - r_1) (E_0 \nabla) \bar{\phi}(r_1) + \dots \end{aligned} \quad (14)$$

The higher-order terms $E_i(r)$ ($i = 2, 3, \dots$) in the last equation are linear in the external field, too.

In taking into account the electric energy in thermodynamic potentials one should distinguish between the thermodynamic potentials with respect to the charges or the potential.¹⁸ These thermodynamic potentials are connected with each other by a Legendre transformation. Here, in calculating the effects of fluctuations we interpret in fact the Landau free energy as an Hamiltonian, which weights the fluctuations by the Boltzmann factor $\exp(-H)$. Therefore, the contribution of the electric field to the effective Hamiltonian corresponds to the energy of the electric field, and is given in Gaussian units by

$$k_B T \Gamma_{\text{el}} = \frac{1}{8\pi} \int d^3r \epsilon(r) E^2(r)$$

where $\epsilon(r)$ and $E(r)$ are given by eqs 12 and 14.

In the following we consider only the polarization part of Γ_{el} . The quadratic part of the latter in powers of the order parameter is given by

$$\begin{aligned} k_B T \Gamma_{\text{el}} &= \frac{1}{8\pi} \int d^3r \frac{1}{2} \frac{\partial^2 \epsilon}{\partial \bar{\phi}^2} \bar{\phi}(r)^2 E_0^2 + \\ &\quad \frac{1}{8\pi} \int d^3r \epsilon_D \frac{1}{4\pi} \nabla^m \int d^3r_1 G_0(r - r_1) E_0^m \frac{\beta}{\epsilon_D} \nabla^n \bar{\phi}(r_1) \times \\ &\quad \frac{1}{4\pi} \nabla^m \int d^3r_2 G_0(r - r_2) E_0^k \frac{\beta}{\epsilon_D} \nabla^k \bar{\phi}(r_2) \\ &= \frac{1}{2} \int d^3r_1 \int d^3r_2 \bar{\phi}(r_1) \tilde{\gamma}_2^{\text{el}}(r_1, r_2) \bar{\phi}(r_2) \end{aligned} \quad (15)$$

with

$$\begin{aligned} \tilde{\gamma}_2^{\text{el}}(r_1, r_2) &= \frac{1}{8\pi} \frac{\partial^2 \epsilon}{\partial \bar{\phi}^2} E_0^2 \delta(r_1 - r_2) + \frac{\beta^2}{(4\pi)^3 \epsilon_D} \int d^3r \nabla_r^m \nabla_{r_1}^n G_0 \\ &\quad (r - r_1) \nabla_r^m \nabla_{r_2}^k G_0(r - r_2) E_0^n E_0^k \end{aligned}$$

Notice the sum convention over the indices m, n, k ($= x, y, z$) in the above two equations and in eq 17. Expressing Γ_{el} by the Fourier components of the order parameter yields

$$\Gamma_{\text{el}} = \frac{1}{2} \int_q \bar{\phi}(-q) \tilde{\gamma}_2^{\text{el}}(q) \bar{\phi}(q) \quad (16)$$

whereas $\tilde{\gamma}_2^{\text{el}}(q)$ is given by

$$\tilde{\gamma}_2^{\text{el}}(q) = \frac{1}{4\pi \rho_m k_B T} \left(\frac{1}{2} \frac{\partial^2 \epsilon}{\partial \bar{\phi}^2} E_0^2 + \frac{\beta^2}{\epsilon_D} \frac{q^n q^k}{q^2} E_0^n E_0^k \right) \quad (17)$$

The electric contribution to the correlation function can be obtained using eq 6. Note that the factor $\rho_m^{-1/3}$ in eq 17 is due to the length redefinition $r = \rho_m^{-1/3}x$. Equations (15–17) are used in the subsequent section to analyze the influence of the electric field on the composition fluctuations of the order parameter. Assuming that the electric field is directed along the z -axis, and denoting the angle between the field and the wave vector q by θ , we obtain the quantity $\tilde{\gamma}_2^{\text{el}}(q)$ in eq 17 as

$$\tilde{\gamma}_2^{\text{el}}(q) = \tilde{\alpha} \cos^2 \theta + \tilde{\alpha}_2 \quad (18)$$

where the notations

$$\tilde{\alpha} = \frac{1}{4\pi\rho_m k_B T} \frac{\beta^2}{\epsilon_D} E_0^2, \quad \tilde{\alpha}_2 = \frac{1}{4\pi\rho_m k_B T} \frac{1}{2} \frac{\partial^2 \epsilon}{\partial \phi^2} E_0^2 \quad (19)$$

are used.

The thermodynamic potential given by eq 15 is quadratic in both the external electric field E_0 and the order parameter. The terms $E_i(r)$ with $i > 1$ in eq 14 are still linear in E_0 , but contain higher powers of the order parameter and its derivatives. In the vicinity of the order–disorder transition, where the order parameter is small and its inhomogeneities are weak, the higher-order contributions to Γ_{el} can be neglected.

C. Hartree Treatment of Fluctuations in the Presence of the Electric Field. The Brazovskii–Hartree approach in absence of the electric field is summarized in eqs 9 and 11. According to eq 6 the contribution of the electric field should be taken into account both to the thermodynamic potential and to the propagator. Therefore, instead of eq 9 we obtain

$$\frac{1}{A} \frac{\partial}{\partial A} (g - \tilde{\gamma}_2^{el}(q^*) A^2) = \tilde{\tau} + 2\tilde{\lambda} \int_q \frac{1}{\tilde{\tau} + \tilde{\gamma}_2^{el}(q) + (q - q^*)^2 + \tilde{\lambda} A^2} + \tilde{\lambda} A^2 \quad (20)$$

where $g = \Gamma(A)/V$ is the thermodynamic potential per volume. The term $\tilde{\gamma}_2^{el}(q^*)$ in (20) is the contribution to g associated with the lamellae in the electric field below the transition with the orientation defined by the angle between the wave vector q^* and the field strength E_0 , $q^* E_0 = q^* E_0 \cos \theta^*$. The equilibrium orientation of the lamellae is derived by minimization of the thermodynamic potential with respect to the angle θ^* , and yields $\theta^* = \pi/2$. As a consequence, the modulations of the order parameter perpendicular to the electric field possess the lowest electric energy. The term $\tilde{\gamma}_2^{el}(q^*) A^2$ in (20) disappears in the equilibrium state and will not be considered below. The isotropic part of $\tilde{\gamma}_2^{el}(q)$ in eq 19, which is associated with $\tilde{\alpha}_2$, shifts $\tilde{\tau}$ for positive $\partial^2 \epsilon / \partial \phi^2$ to higher values, i.e., shifts the critical temperature to lower values and favors mixing. The sign of this term agrees with that in ref 1, where the effect of this term was observed and studied for polymer solutions near the critical point. Since this term is isotropic and small, it will not contribute directly to alignment and will be not considered further. The demixing of the low molecular mixtures studied recently in ref 20 is due to field gradients. The fluctuations in the presence of the electric field become anisotropic due to $\tilde{\gamma}_2^{el}(q)$ in eq 20. The first two terms on the right-hand side of eq 20 define as before an effective $\tilde{\tau}$, which is denoted by $\tilde{\tau}_r$. Replacing $\tilde{\tau}$ under the integral in eq 20 by $\tilde{\tau}_r$ we obtain a self-consistent equation for $\tilde{\tau}_r$

$$\tilde{\tau}_r = \tilde{\tau} + \frac{\tilde{\lambda}}{2} \int_q \frac{1}{\tilde{\tau}_r + \tilde{\alpha} \cos^2 \theta + (q - q^*)^2 + \tilde{\lambda} A^2} \quad (21)$$

which generalizes eq 11 for $E \neq 0$. Carrying out the integration over q , we obtain

$$\begin{aligned} \frac{\tilde{\lambda}}{2} \int_q \frac{1}{\tilde{\tau}_r + \tilde{\lambda} A^2 + \tilde{\alpha} \cos^2 \theta + (q - q^*)^2} &= \frac{\tilde{\lambda} q_*^2}{4\pi\sqrt{\tilde{\alpha}}} \operatorname{arcsinh} \sqrt{\frac{\tilde{\alpha}}{\tilde{\tau}_r + \tilde{\lambda} A^2}} \\ &= \frac{d\tilde{\lambda}}{N\sqrt{\tilde{\alpha}}} \operatorname{arcsinh} \sqrt{\frac{\tilde{\alpha}}{\tilde{\tau}_r + \tilde{\lambda} A^2}} \end{aligned} \quad (22)$$

where the notation $d = 3y^*/2\pi$ with $y^* = q^{*2}N/6 = 3.7852$ is used. Equation 21 shows that the fluctuations in the presence of the electric field are suppressed due to the angular dependence of the integrand. Consequently an electric field weakens the first-order phase transition. In computing the integral in eq 22 we realize that the leading contribution comes from the peak of the structure factor at q^* . The contributions of large wave vectors, which become finite after an introduction of an appropriate cutoff at large q , are expected to renormalize the local parameters such as the χ parameter etc. Very recently these fluctuations have been considered in.²³ The self-consistent equation for $\tilde{\tau}_r$ in the presence of the electric field reads

$$\tilde{\tau}_r = \tilde{\tau} + \frac{\tilde{\lambda} d}{N\sqrt{\tilde{\alpha}}} \operatorname{arcsinh} \sqrt{\frac{\tilde{\alpha}}{\tilde{\tau}_r + \tilde{\lambda} A^2}} \quad (23)$$

The equation for $\tilde{\tau}_r$ in the Brazovskii–Fredrickson–Helfand theory is obtained from eq 23 in the limit $\alpha \rightarrow 0$ as

$$\tilde{\tau}_r = \tilde{\tau} + \frac{\tilde{\lambda} d}{N} (\tilde{\tau}_r + \tilde{\lambda} A^2)^{-1/2}$$

Because the quantities $\tilde{\tau}$ and $\tilde{\lambda}$ are of the order $O(N^{-1})$, it is convenient to replace them in favor of

$$\tau = \tilde{\tau} N, \quad \lambda = \tilde{\lambda} N \quad (24)$$

Note that the transformation from $\tilde{\tau}$ to τ implies the redefinition of the thermodynamic potential $g \rightarrow gN$. Instead of eq 23, we then obtain

$$\tau_r = \tau + \frac{\lambda d}{\sqrt{N\alpha}} \operatorname{arcsinh} \sqrt{\frac{\alpha}{\tau_r + \lambda A^2}} \quad (25)$$

where the quantity α is defined by $\alpha = \tilde{\alpha} N = (\beta^2 N / 4\pi\rho_m k_B T \epsilon_D) E_0^2$. For symmetric composition λ was computed in¹⁷ as $\lambda = 106.18$. Using the substitution $t = \tau_r + \lambda A^2$ we obtain

$$t = \tau + \frac{\lambda d}{\sqrt{N\alpha}} \operatorname{arcsinh} \sqrt{\frac{\alpha}{t} + \lambda A^2} \quad (26)$$

The derivative of the potential g with respect to the amplitude of the order parameter A is obtained from eq 20 as

$$\frac{\partial g}{\partial A} = 2\tau_r(A)A + \lambda A^3 = 2t(A)A - \lambda A^3$$

The integration gives the thermodynamic potential as

$$\begin{aligned} g = \int_0^A 2t(A)A \, dA - \frac{\lambda}{4} A^4 &= \frac{1}{2\lambda} (t^2 - t_0^2) + \\ &\quad \frac{d}{\sqrt{N}} (\sqrt{t + \alpha} - \sqrt{t_0 + \alpha}) - \frac{\lambda}{4} A^4 \end{aligned} \quad (27)$$

whereas the inverse susceptibility of the disordered phase $t_0 \equiv t(A = 0)$ satisfies the equation

$$t_0 = \tau + \frac{d\lambda}{\sqrt{N\alpha}} \operatorname{arcsinh} \sqrt{\frac{\alpha}{t_0}} \quad (28)$$

Equations 26–28 generalize the Fredrickson–Helfand treatment of the composition fluctuations in symmetric diblock copolymer melts in the presence of an external time-independent electric field.

III. Results

The position of the phase transition is determined by the conditions

$$g = 0, \quad \frac{\partial g}{\partial A} = 0 \quad (29)$$

and result in the following equation

$$\frac{1}{2}(t^2 + t_0^2) = \frac{d\lambda}{\sqrt{N}}(\sqrt{t + \alpha} - \sqrt{t_0 + \alpha}) \quad (30)$$

The perturbational solution of eqs 26, 28, and 30 to first order in powers of α yields for the transition temperature

$$\tau_t = -2.0308 (d\lambda)^{2/3} N^{-1/3} + 0.48930\alpha \quad (31)$$

By making use of eqs 3 and 24, we find

$$(\chi N)_t = (\chi N)_s + 1.0154c^2(d\lambda)^{2/3}N^{-1/3} - 0.48930\alpha \frac{c^2}{2} \quad (32)$$

The solution of eqs 26 and (30) results in the following expression for the amplitude of the order parameter at the transition

$$A_t = 1.4554 (d^2/\lambda)^{1/6} N^{-1/6} - 0.42701 (d^2\lambda^5)^{-1/6} N^{1/6} \alpha \quad (33)$$

where α is defined by $\alpha = N\beta^2/(4\pi\rho_m k_B T \epsilon_D) E_0^2$. The corrections associated with the electric field in eqs 31–33 are controlled by the dimensionless expansion parameter $\alpha N^{1/3}/(d\lambda)^{2/3}$. Inserting the values of the coefficients for $f = 1/2$ gives

$$(\chi N)_t = 10.495 + 41.018 N^{-1/3} - 0.29705\alpha \quad (34)$$

$$A_t = 0.81469 N^{-1/6} - 0.0071843 N^{1/6} \alpha \quad (35)$$

Note that for $N \rightarrow \infty$ the strength of the electric field E_0 should tend to zero in order that the dimensionless expansion parameter $\alpha N^{1/3}/(d\lambda)^{2/3}$ remains small.

Equations 34 and 35 are our main results. The terms in eqs 34 and 35 depending on α describe the effects of the electric field on fluctuations, and they were not considered in previous studies.^{3,4} This influence of the electric field on fluctuations originates from the term $\tilde{\gamma}_2^{\text{el}}(q)$ under the integral in eq 20. Equation 34 shows that the electric field shifts the parameter $(\chi N)_t$ to lower values, and correspondingly the transition temperature to higher values toward its mean-field value. The latter means also that the electric field favors demixing with respect to the free field case. According to eq 35 the electric field lowers the value of the order parameter at the transition point. In other words, the electric field weakens the fluctuations, and consequently the first-order phase transition.

We now will discuss the limits of the Brazovskii–Hartree approach in the presence of the electric field. The general conditions on the validity of the Brazovskii–Hartree approach,

which are discussed in refs 16 and 24, hold also in the presence of the electric field. Essentially, while taking into account the fluctuations the peak of the structure factor at the transition should remain sufficiently sharp, i.e., the transition should be a weak first-order transition. This requires large values of N .¹⁶ A specific approximation used in the presence of the electric field consists in adopting the expansion of the dielectric constant in powers of the order parameter to second order, which however is justified in the vicinity of the transition. The smallness of the linear term in powers of α in eqs 34 and 35 imposes a condition on E_0 : $E_0^2 \ll \lambda^{2/3} \rho_m k_B T \epsilon_D / \beta^2 N^{4/3}$. The applicability of the approach of linear dielectric requires also a limitation on the strength of the electric field.

The dependence of the propagator on α in the field theory associated with the effective Hamiltonian, which is due to the term $\tilde{\gamma}_2^{\text{el}}(q)$, enables us to make a general conclusion that fluctuations (in Brazovskii–Hartree approach and beyond) are suppressed for large α . According to this one expects that the order–disorder transition will become second order for strong fields. The numerical solution of eqs 29 yields that the mean-field behavior is recovered only in the limit $\alpha \rightarrow \infty$, which is therefore outside the applicability of linear electrodynamics. The angular dependence of γ_4 , which has not been taken into account in the present work, gives rise to corrections which are beyond the linear order of α .

The main prediction of the present work that the electric field weakens fluctuations agrees qualitatively with the behavior of diblock copolymer melts in shear flow studied in,²⁵ where the shear also suppresses the fluctuations. Because of the completely different couplings to the order parameter the calculation schemes are different in both cases.

We now will estimate the shift of the critical temperature for the diblock copolymer poly(styrene-*block*-methyl methacrylate) in an electric field. Without an electric field its transition temperature is at 182 °C for a molecular weight of 31000 g/mol.² We use the following values of the parameters:⁴ $\epsilon_{\text{PS}} = 2.5$, $\epsilon_{\text{PMMA}} = 5.9$,²⁶ $\beta = \epsilon_{\text{PMMA}} - \epsilon_{\text{PS}}$, $\epsilon_D = (\epsilon_{\text{PS}} + \epsilon_{\text{PMMA}})/2$, and $\chi = 0.012 + 17.1/T$. The estimation of the number of statistical segments N using the relation $(\chi N)_t = 10.495 + 41.018 N^{-1/3}$ for $T_t = 182$ °C yields $N \approx 331$. As described in⁴ and⁵ for this calculation a mean statistical segment length $b = 7.1$ Å was assumed, while the approximation $b = \rho_m^{-1/3}$ used here implies $b \approx 5.2$ Å.²⁷ This comparison reflects the limits of the above approximation. For a field strength $E_0 = 40$ V/μm, the shift is obtained using eq 34 as

$$\Delta T_t \approx 2.5 \text{ K}$$

The numerical value of the dimensionless expansion parameter, $\alpha N^{1/3}/(d\lambda)^{2/3}$, is computed in the case under consideration as 0.059. The experimental determination of ΔT_t would be very helpful to make more detailed fit of the theory to experimental data.

The scattering function in the disordered phase is obtained by taking into account the composition fluctuations in the presence of the electric field as

$$S_{\text{dis}}(q) \simeq \frac{1}{t_0 + \alpha \cos^2 \theta + (q - q^*)^2} \quad (36)$$

The fluctuational part of the scattering function in the ordered state is obtained as

$$S_{\text{ord}}(q) \simeq \frac{1}{t + \alpha \cos^2 \theta + (q - q^*)^2} \quad (37)$$

At the transition point the expansion of t_0 and t in powers of the field strength is derived from eqs (26, 28) as

$$t_{0,t} = 0.20079(\lambda d)^{2/3} N^{-1/3} - 0.20787\alpha + \dots \quad (38)$$

$$t_t = 1.0591(\lambda d)^{2/3} N^{-1/3} - 0.62147\alpha + \dots \quad (39)$$

The difference between $t_{0,t}$ and t_t , which is due to the finite value of the order parameter at the transition, results in the jump of the peak at the transition point. The structure factor becomes owing to the term $\alpha \cos^2 \theta$ anisotropic in the presence of the electric field. The structure factor depends on the electric field via $t_{0,t}$ (t_t) and the term $\alpha \cos^2 \theta$. The suppression of $t_{0,t}$ (t_t) in an electric field according to eqs (38, 39) results in an increase of the peak. Thus, for wave vectors perpendicular to the field direction, where the angular-dependent term is zero, the peak is more pronounced than that for $E_0 = 0$. In the opposite case for wave vectors parallel to E_0 the anisotropic term ($=\alpha \cos^2 \theta$) dominates, so that the peak is less pronounced than that for $E_0 = 0$. Composition fluctuations can be associated with fluctuational modulations of the order parameter. According to eqs 36 and 37, fluctuational modulations of the order parameter with wave vectors parallel to the field are strongest suppressed. The latter correlates with the behavior in the ordered state where the lamellae with the wave vector perpendicular to the field direction possess the lowest energy.

IV. Conclusions

We have generalized the Fredrickson–Helfand theory of microphase separation in symmetric diblock copolymer melts by taking into account the effects of the electric field on the composition fluctuations. We have shown that an electric field suppresses the fluctuations and therefore weakens the first-order phase transition. However, the mean-field behavior is recovered in the limit $\alpha \rightarrow \infty$, which is therefore outside the applicability of the linear electrodynamics. The collective structure factor in the disordered phase becomes anisotropic in the presence of the electric field. Fluctuational modulations of the order parameter along the field direction are strongest suppressed. Thus, the anisotropy of fluctuational modulations in the disordered state correlates with the parallel orientation of the lamellae in the ordered state.

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- (26) These values for ϵ refer to the liquid state ($T \approx 160$ °C), since the corresponding orientation experiments are performed in this temperature range.
- (27) The relation $\rho_m = \rho N N_A / M$, where N_A denotes the Avogadro number, M the molecular mass of the block copolymer, and $\rho \approx 1.12$ g/cm³ its mass density, results in $\rho_m \approx 7.20 \times 10^{21}$ cm⁻³.

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