Block Copolymers in Electric Fields: A Comparison of Single-Mode and Self-Consistent Field Approximations

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We compare two theoretical approaches to dielectric diblock copolymer melts in an external electric field. The first is a relatively simple analytic expansion in the relative copolymer concentration, and includes the full electrostatic contribution consistent with that expansion. It is valid close to the order-disorder transition point, the weak segregation limit. The second employs self-consistent field (SCF) theory and includes the full electrostatic contribution to the free energy at any copolymer segregation. It is more accurate but computationally more intensive. Motivated by recent experiments, we explore a section of the phase diagram in the three-dimensional parameter space of the block architecture, the interaction parameter and the external electric field. The relative stability of the lamellar, hexagonal and distorted body-centered-cubic (bcc) phases is compared within the two models. As function of an increasing electric field, the distorted bcc region in the phase diagram shrinks and disappears above a triple point, at which the lamellar, hexagonal and distorted bcc phases coexist. We examine the deformation of the bcc phase under the influence of the external field. While the elongation of the spheres is larger in the one-mode expansion than that predicted by the full SCF theory, the general features of the schemes are in satisfactory agreement. This indicates the general utility of the simple theory for exploratory calculations.

I. INTRODUCTION

Block copolymers (BCP) consist of several chemically distinct sub-chains. They are not only interesting as a model system for self-assembly, but also for their chemical versatility and affordability which have enabled their use in applications such as photonic waveguides [1], tough plastics [2], ordered arrays of nano-wires [3], etc. At a given chemical architecture and temperature, there is one thermodynamically stable meso-phase, with typical length-scales comparable to the chain size (~ 10-500 nm). However, the material is rarely perfectly ordered, but rather is composed of many randomly oriented grains of size ~ 1 μm. This has an adverse effect on nanotechnological applications.

A useful way to achieve improved long-range order is to subject the BCP sample above its glass transition to an external electric field \( E_0 \). Due to the coupling between the field and the spatially-varying dielectric constant \( \kappa(r) \), there is a preferred orientation of the grains with respect to the field [4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. It has been shown by Amundson et al. [4, 5] that the electrostatic free-energy penalty associated with dielectric interfaces which are not parallel to the electric field direction is the driving force for structures to reorient so that their interfaces are parallel to the field (\( \nabla \kappa(r) \) perpendicular to \( E_0 \)). While the free energy penalty can be eliminated by this reorientation of lamellae and cylinders, it cannot be eliminated in the body-centered-cubic (bcc) phase, but only reduced by distorting the bcc spheres. Thus, the free energy of this distorted bcc phase, whose symmetry is reduced to \( R^3m \), increases with respect to the full disordered liquid (dis), lamellar (lam) and hexagonal (hex) phases [11], a circumstance which can bring about a phase transition. The effect of the electric field on the BCP morphology has been substantially accounted for recently [14] by incorporating the electrostatic Maxwell equations in the full set of self-consistent field (SCF) equations, which permits calculation of the phase diagram at arbitrary degrees of segregation.

In this paper we compare two theoretical approaches to such a system; the aforementioned SCF study and a simple analytical approximation consisting of a Ginzburg-Landau expansion of the free-energy [15], valid only close to the order-disorder temperature (ODT). The paper is organized as follows. In Section 2 we present the free-energy model which includes the electrostatic energy of the BCP in the field. In Section 3 we calculate the way in which an initial mesophile deforms under the influence of the field, and also find the relative stability of the competing phases. A comparison is made with the results of the SCF model. Section 4 contains a brief conclusion.

II. MODEL

Although the effect we consider here is generic to any multi-block BCP melts, we will restrict the discussion in this paper to the simplest \( A/B \) diblock copolymer, where a spatial variation of the relative \( A/B \) monomer concentration yields a spatial dependence of the dielectric constant and, hence, of the response to an external electric field.

We also assume for simplicity that the A monomeric vol-
ume is equal to the B one. Then the volume fraction of the A monomers $f$, ($0 \leq f \leq 1$), is equal to its molar fraction. The order parameter $\phi (r)$ is defined as the local deviation of the A-monomer concentration $\phi_A (r)$ from its average value: $\phi (r) = \phi_A (r) - f$. From an incompressibility condition of the melt we also have at each point $r$, $\phi_B (r) = 1 - \phi_A (r)$. In the absence of any external electric fields, the bulk BCP free-energy per polymer chain, $F_p$, in units of $k_BT$, can be written as a functional of the order parameter, $\phi (r)$. One way of generating a simple analytical expansion in the order parameter relies on a Ginzburg-Landau-like free energy, which can be justified close to the order-disorder point (ODT) \cite{15, 16, 17} and is repeated here without further justifications:

$$F_b = \frac{1}{\Omega} \int \left\{ \frac{1}{2} \tau \phi^2 + \frac{1}{2} h (\nabla^2 \phi + q_0^2 \phi)^2 + \frac{\lambda}{6} \phi^3 + \frac{u}{24} \phi^4 \right\} d^3r$$

where $\Omega$ is the system volume, and

$$\tau = \frac{2N(\chi - \chi_{c})}{c^2}, \quad q_0 \sim 1/R_g = \left( \frac{1}{N} \right)^{1/2}, \quad h = \frac{3 R_g^2}{2 q_0}$$

$b$ is the Kuhn length, $R_g$ the radius of gyration, $\chi$ is the Flory parameter, $N = N_A + N_B$ the total chain polymerization index, $N\chi_c$, the spinodal value of $\chi N$ \cite{15}, $c$ is a constant of order 1, and $\lambda$ and $u$ are functions of $f$ as in refs. \cite{15, 16, 17}. The phase diagram in the $(f, \chi N)$ plane, as derived from the free-energy, eq(1) is symmetric with respect to exchange of $f$ and $1-f$. For small values of $\chi \sim 1/T$, the melt is disordered: $\phi (r) = f$ is constant. For $\chi N$ larger than the ODT value of $\approx 10.5$ and for nearly symmetric BCP composition ($f \approx \frac{1}{2}$), the lamellar phase is the most stable. As $|f - \frac{1}{2}|$ increases, the stable phases are doubly-connected gyroid, hexagonal and bcc phases \cite{15, 16, 17}.

Let us now consider a BCP slab placed in an external electric field, $E_0$. The free-energy per polymer chain, again in units of $k_BT$, is $F_{\text{tot}} = F_b + F_{\text{es}}$, where the electrostatic energy contribution $F_{\text{es}}$ is given by the integral

$$F_{\text{es}} = -\frac{1}{2} \frac{\varepsilon_0 v_p}{k_BT\Omega} \int k' (r) |\nabla \psi (r)|^2 d^3r$$

Here $\varepsilon_0$ is the vacuum permittivity, $k' (r)$ is the local dielectric constant, $v_p$ is the volume per chain, and $\psi$ is the electrostatic potential obeying the proper boundary conditions on the electrodes. The local field is $E(r) = -\nabla \psi$. We note that the variation of $F_{\text{es}}$ with respect to $\psi$ yields

$$\nabla \cdot (\varepsilon_0 k' (r) \nabla \psi) = 0$$

which is the usual Maxwell equation $\nabla \cdot D = 0$ for the displacement field $D = \varepsilon_0 k' E$. We consider a simple geometry of a BCP slab filling the gap between two parallel and flat electrodes separated by a distance $d$ and potential difference $V$. Even when a non-homogeneous dielectric material like a BCP fills the gap between the two electrodes, the spatially averaged electric field in between the electrodes ($E$) is constrained to be $E_0 = V/d$. The local field $E(r)$ differs from its average due to the nonuniformity of the dielectric constant, since $\kappa = k(\phi)$ depends on the local concentration $\phi (r)$ through a constitutive equation. In this paper we assume for simplicity a linear constitutive relation,

$$\kappa (r) = \langle \kappa \rangle + \phi (r) \Delta \kappa, \quad \Delta \kappa = \kappa_A - \kappa_B,$$

$$\langle \kappa \rangle = f \kappa_A + (1-f) \kappa_B$$

where throughout this paper we use $\kappa_A = 6.0$ and $\kappa_B = 2.5$, thus modelling an A/B diblock copolymer where the A block is polymethylmethacrylate (PMMA) and the B block is polystyrene (PS), as is used in many experiments. Other constitutive relations can be considered \cite{19}.

When a field is applied on a melt in the lamellar or hexagonal phases, it exerts torque which causes sample rotation. The torque is zero, and the energy lowest, when the lamellae or cylinders are oriented parallel to the field. In such states, as well as the disordered phase, the electrostatic energy, eq(3) of the system is equal to a reference energy, given in eq(8). The bcc array of spheres, on the other hand, always has dielectric interfaces that are not parallel to the field, and its electrostatic energy is higher than the reference value. Hence, the spheres elongate in the applied field direction, to an extent which is a balance between electrostatic and elastic forces, as calculated below.

The reference energy per polymer chain, in units of $k_BT$, is simply $-\frac{1}{2} \langle \kappa \rangle \tilde{E}_0^2$, where $\tilde{E}_0$ is the applied field measured in the natural unit $(k_BT/\varepsilon_0 v_p)^{1/2}$,

$$\tilde{E}_0 = \left( \frac{\varepsilon_0 v_p}{k_BT} \right)^{1/2} E_0$$

Let us estimate the value of the actual applied field corresponding to $\tilde{E}_0 = 1$. At $100^\circ$ C and using typical polymer volume per chain in the range $v_p \approx 50 - 250$ nm$^3$, we find $E_0 \approx 47 - 107$ V/μm. This is a relatively large field that can cause dielectric breakdown in some BCP films. Therefore, the experimentally interesting regime is usually $\tilde{E}_0 \lesssim 1$.

The free-energy $F_{\text{tot}}$ as formulated above is valid close to the ODT point (weak segregation limit), where the concentration variations are small, $\phi (r) \ll 1$, and therefore the analysis can be carried out within the so-called one-mode approximation. Motivated by recent experiments \cite{11, 13}, we concentrate on the transition from distorted spheres to cylinders or disordered melt in presence of an applied electric field. Taking $E_0$ to be in the $(1,1,1)$ direction, we write the order parameter $\phi$ as a linear superposition of six components

$$\phi = w \phi_1 + g \phi_2$$

where

$$\phi_1 = \sum_{i=1}^{3} \cos (q_i \cdot \mathbf{r}) \quad \phi_2 = \sum_{i=1}^{3} \cos (k_i \cdot \mathbf{r})$$
The $q$'s and $k$'s are wave-vectors given by

\[ q_1 = \frac{q_0}{\sqrt{2}}(-1,0,1), \quad k_1 = \frac{q_0}{\sqrt{2}}(1,0,1), \]
\[ q_2 = \frac{q_0}{\sqrt{2}}(1,-1,0), \quad k_2 = \frac{q_0}{\sqrt{2}}(1,1,0), \]
\[ q_3 = \frac{q_0}{\sqrt{2}}(0,1,-1) \quad k_3 = \frac{q_0}{\sqrt{2}}(0,1,1) \]  

(9)

and all have the same magnitude $q_0$. The three linearly dependent $q_i$ are orthogonal to the (1,1,1) direction and describe a hexagonal phase with axis along that direction. The three $k_i$ have equal and non-zero projections on the (1,1,1) axis. The six wavevectors transform into one another under the symmetry operations of the bcc phase. In the absence of an external field, each of these wavevectors would contribute equally in the order parameter expansion, so that $g$ and $w$ would be equal. These wavevectors characterize the first mode in such an expansion. Hence the name of the approximation.

The amplitudes $w(E_0)$ and $g(E_0)$ depend on the magnitude of the average external field $E_0$. Depending on the values of the two amplitudes, $g$ and $w$, we can represent the order parameter of all phases of interest in the form of eq 7:

\[ \bar{\kappa}(r) = \kappa_0 \cdot \hat{\kappa}(r) \]

where $\bar{\kappa}$ is determined by a given value of $w$ and $g$, the values of $\alpha(w,g)$ and $\beta(w,g)$ are determined by the Maxwell equation, eq 4. This is equivalent to obtaining them by varying $F_{es}$ with respect to $\alpha$ and $\beta$. The procedure yields $\alpha = 0$ and $\beta = -\sqrt{2/3}\Delta k_0 g/\langle \kappa \rangle + 1/2 \Delta \kappa w$. Thus, $F_{es}$ is given by

\[ F_{es} = \left[ \frac{(\Delta \kappa)^2}{2(\kappa)^2} + \frac{1}{2} \langle \kappa \rangle \right] \hat{E}_0^2 \]  

(15)

It is instructive to compare this result with the perturbation expression used by Amundson, Helfand and co-workers [4, 5].

\[ F_{es}^{\text{LH}} = \left[ \frac{(\Delta \kappa)^2}{2(\kappa)^2} + \frac{1}{2} \langle \kappa \rangle \right] \hat{E}_0^2, \]  

(16)

a result obtained from eq 15 in the limit $\Delta \kappa/\langle \kappa \rangle \rightarrow 0$. In particular, the result of eq 16 yields a free energy which is symmetric under the interchange of monomers A and B, while the result of eq 15 does not. Such a symmetry is not expected in general: a system of ultra-high $\kappa$ spheres (metallic limit) embedded in an insulator matrix has a different energy than the system of insulating spheres embedded in a ultra-high $\kappa$ matrix, even when the average dielectric constant is the same $\langle \kappa \rangle$.

Employing the single-mode Ansatz $\phi = w\phi_1 + g\phi_2$ in eq 11 we finally obtain for the total free-energy per polymer chain in units of $k_B T$

\[ F_{\text{tot}} = \frac{3\pi}{4}(w^2 + g^2) + \frac{\lambda}{4}w(3g^2 + w^2) + \frac{15}{64}u(g^4 + 4g^2w^2 + w^4) + \left[ \frac{(\Delta \kappa)^2}{(2(\kappa)^2 + \Delta \kappa w)} \right] \hat{E}_0^2, \]  

(17)

In the next section we minimize this energy with respect to $w$ and $g$ at a given dimensionless external field $\hat{E}_0$ and polymer architecture $f$, calculate the elongation the spheres of the bcc phase, and obtain the phase diagram.
We compare the one-mode calculation (solid line) as obtained from minimization of eq (17) with a SCF calculation (dashed line). The R3m phase in the SCF calculation has a lower free energy that the solid line (one mode), and crosses the hex energy at higher value of $\hat{E}_0$ of about 0.49, while the one-mode approximation crosses at $\hat{E}_0 \approx 0.43$ (both marked with arrows). In this figure and following ones we used $\kappa_4 = 6$ and $\kappa_6 = 2.5$, modelling a PMMA-PS copolymer.

In the figure we show how the free energy $f_n$ changes with $\hat{E}_0$ for $f = 0.3$ and $N\chi = 14.4$. At $\hat{E}_0 = 0$ the bcc is the stable phase, and its free energy increases with increasing field $\hat{E}_0$, until it equals the free energy of the hex phase at a transition field $\hat{E}_0 \approx 0.43$. At larger fields the stable structure is a hex phase of cylinders oriented along the external field $\hat{E}_0$. The solid line in figure 1 is the result obtained from the one-mode approximation given above, while the dashed line is a obtained from the SCF theory, (as in Ref [14]). It has a lower free-energy. Consequently, the transition field in the SCF framework is higher and occurs at about $\hat{E}_0 \approx 0.49$.

Figure 2 is a plot of the amplitudes $w(\hat{E}_0)$ and $g(\hat{E}_0)$, normalized by their zero-field value $w(\hat{E}_0 = 0) = g(\hat{E}_0 = 0)$. Both amplitudes start at their common value in the undistorted bcc phase. As the field increases, $w$ increases while $g$ decreases. The spheres elongate in the direction of the field as a result of competition between electrostatic and elastic forces. At the transition field, there is a sharp, discontinuous, transition in the order parameter. Above this field, $w$ attains a fixed value while $g$ drops abruptly to zero. In this state the BCP morphology is that of cylinders oriented parallel to the external field. The dashed lines correspond to the values obtained from the SCF theory. Clearly, in the one-mode approximation, the spheres' deformation and eccentricity are larger than in the SCF theory.

The above calculation can be repeated for any $(f, N\chi)$ and $\hat{E}_0$ field values and allows the construction of the full three-dimensional phase diagram in the $(f, N\chi, \hat{E}_0)$ parameter space. In figure 3 we present a cut of the phase diagram at fixed $f = 0.3$. The region of a stable R3m phase (distorted bcc) is bound by two lines of phase transitions: one between this phase and the disordered phase, and the other between it and the hex phase. These two lines meet at the triple point $(\chi, E_t)$. In figure 3, the different triple point values obtained from the two calculations are used to rescale both axes: $\chi/\chi_t$ and $\hat{E}_0/E_t$. At fields larger than $E_t$ the R3m is not stable at any value of $\chi$. The solid lines in the figure are the one-mode prediction, while the dashed lines are obtained with the SCF calculation. The values of $E_t$ are 0.49 and 0.67 for the two

![Figure 1: Normalized free-energy per polymer chain $f_n$, defined in eq (18) of the distorted bcc phase (R3m) as a function of dimensionless field $\hat{E}_0$. The system is characterized by $f = 0.3$ and $\chi N = 14.4$. We compare the one-mode calculation (solid line) as obtained from minimization of eq (17) with a SCF calculation (dashed line). The R3m phase in the SCF calculation has a lower free energy that the solid line (one mode), and crosses the hex energy at higher value of $\hat{E}_0$ of about 0.49, while the one-mode approximation crosses at $\hat{E}_0 \approx 0.43$ (both marked with arrows). In this figure and following ones we used $\kappa_4 = 6$ and $\kappa_6 = 2.5$, modelling a PMMA-PS copolymer.]

![Figure 2: The amplitudes $w$ and $g$ normalized by their common value at zero $E$-field, $g(0) = w(0)$, as a function of dimensionless external field $\hat{E}_0$. Solid line: one-mode approximation. The amplitudes have a discontinuous jump at $\hat{E}_0 \approx 0.43$, where the structure contains cylinders oriented along the field ($g = 0$). Dashed lines: the same, but taken from a multi-mode SCF calculation with a jump at higher $E$ values of $\hat{E}_0 \approx 0.49$. All parameters as in figure 1.]

III. RESULTS

As noted above, the functional form $\phi = w\phi_1 + g\phi_2$ allows us to distort smoothly a bcc array of spheres (having nonzero $w = g$) via a distorted bcc phase ($w \neq g$), and into a hexagonal array of cylinders (non-zero $w$ but with $g = 0$). The disordered phase is given by $w = g = 0$. One is thus able to obtain the full phase diagram by minimizing eq (17) with respect to the amplitudes $w$ and $g$.

Before presenting the phase diagram, let us consider a point in the $(f, N\chi)$ plane for which the stable phase at zero $E$ field has a bcc symmetry. For presentation purposes, in figure 1 we have subtracted from the free energy the reference electrostatic energy, $-\langle \kappa \rangle E_0^2/2$, common to all phases, also subtracted the total free energy of the bcc phase in zero field, $F_{\text{tot}}^{\text{bcc}}(0)$, and normalized the resulting free energy by that of the hex phase in zero field; that is we have plotted

$$f_n = \frac{F_{\text{tot}}(\hat{E}_0) + \langle \kappa \rangle E_0^2/2 - F_{\text{tot}}^{\text{bcc}}(0)}{F_{\text{hex}}^{\text{tot}}(0)} \quad (18)$$

In the figure we show how the free energy $f_n$ changes with $\hat{E}_0$ for $f = 0.3$ and $N\chi = 14.4$. At $\hat{E}_0 = 0$ the bcc is the stable phase, and its free energy increases with increasing field $\hat{E}_0$, until it equals the free energy of the hex phase at a transition field $\hat{E}_0 \approx 0.43$. At larger fields the stable structure is a hex phase of cylinders oriented along the external field $\hat{E}_0$. The solid line in figure 1 is the result obtained from the one-mode approximation given above, while the dashed line is obtained from the SCF theory, (as in Ref [14]). It has a lower free-energy. Consequently, the transition field in the SCF framework is higher and occurs at about $\hat{E}_0 \approx 0.49$.

![Figure 3: A cut of the phase diagram at fixed $f = 0.3$. The region of a stable R3m phase (distorted bcc) is bound by two lines of phase transitions: one between this phase and the disordered phase, and the other between it and the hex phase. These two lines meet at the triple point $(\chi, E_t)$. In figure 3, the different triple point values obtained from the two calculations are used to rescale both axes: $\chi/\chi_t$ and $\hat{E}_0/E_t$. At fields larger than $E_t$ the R3m is not stable at any value of $\chi$. The solid lines in the figure are the one-mode prediction, while the dashed lines are obtained with the SCF calculation. The values of $E_t$ are 0.49 and 0.67 for the two]
are interchanged (dielectric constants of the majority and minority components examined the case in which, at a fixed value of the theories, respectively. In both theories we find an increase in the value of \( \kappa_2 \) as shown in figure 2. At a threshold value of the electric field, a first-order transition to a hexagonal phase occurs and the amplitudes jump discontinuously.

As shown in figure 3, the simple, analytic, one-mode approximation also captures the essence of the phase diagram; the reduction in the phase space occupied by the distorted bcc phase as the field increases, and its eventual disappearance at a triple point.

Lastly the one-mode theory also captures the subtle interplay between structure and electrostatic response as evidenced by its prediction of a different critical field for phase transitions when the dielectric constants of the constituents are interchanged, a prediction in agreement with the more accurate theory [14].

Given its ability to capture all of the above effects, and given its extreme simplicity, such a theory could serve for useful exploratory studies in other problems concerning the effect of electric fields on block copolymers.

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