Lamellar Phases in Nonuniform Electric Fields: Breaking the In-Plane Rotation Symmetry and the Role of Dielectric Constant Mismatch

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ABSTRACT: We consider orientational transitions of lamellar phases under the influence of a spatially nonuniform electric field. The transition between parallel and perpendicular lamellar stackings with respect to the substrate is investigated as a function of the system parameters. The dielectrophoretic energy and the energy penalty for having dielectric interfaces perpendicular to the field’s direction are identified as linear and quadratic terms in a free energy expansion in the dielectric constant mismatch. We find that if the dielectric constant mismatch $\Delta \varepsilon$ is smaller than some critical value $\Delta \varepsilon_c$, parallel lamellar stacking will be realized, no matter how large the voltage difference between electrodes is. At $\Delta \varepsilon > \Delta \varepsilon_c$, perpendicular stacking will appear if the voltage is high enough. Nonuniform fields remove the in-plane degeneracy present in the more common uniform fields. We therefore calculate the energy of grains of different orientations. The torque acting on the grains leads to the preference of only one orientation. The results have direct implications to block copolymer orientation and to surface patterning on the nanometer scale.

Introduction

In recent years we have seen a large effort directed toward finding ways to control the phase behavior and orientation of self-assembled structures.1,2 Confinement between two solid surfaces,3–13 shear flow,14 or the use of external electric fields15–27 have proved very useful. The use of electric fields is especially appealing, as the field strength scales favorably with the system size. Spatially uniform electric fields, however, pose a long-lasting problem since the orientation of the assembled phases is not unique—the symmetry of the field means that all grain rotations in the plane are energetically equivalent.

Spatially varying fields remove this degeneracy and thus can be quite useful in alignment of various mesophases. The early experiments of Russell et al.28 have employed nonuniform fields, but ever since then all research have been on uniform fields. It seems that now, when such spatially uniform fields have been well understood and exploited possibly to their full potential, it is time to come back to spatially varying fields. In this article we focus on the most simple periodic structure—the lamellar phase, which is found under the influence of an electric field emanating from a “razor-blade” electrode design (see Figure 1). The lamellae are made up of two different materials, A and B, e.g., diblock copolymers. In this example, the two polymers A and B have different dielectric constants, $\varepsilon_A$ and $\varepsilon_B$. In the following we assume ion-free polymers; alternatively, for ion-containing polymers, application of a quasi-static field in the frequency $\sim 1$ kHz renders the ions immobile but leaves the electrostatic equations unchanged.15 In spatially uniform electric fields, the lowest-order contribution to the system electrostatic free energy is quadratic in the permittivity difference of the two constituents, $\Delta \varepsilon \equiv \varepsilon_A - \varepsilon_B$. As is explained in detail below, an inhomogeneity of the field gives rise to a dielectrophoretic force which is manifested in a linear term in $\Delta \varepsilon$, and this has significance to the orientation selection and to phase-transitions.29

Figure 1. Schematic illustration of the system. (a) Two thin “razor-blade” electrodes are laid down on the substrate. The voltage difference between them is $V$. (b) Parallel stacking $L_p$ lamellae lie parallel to the field lines. (c) If the voltage is sufficiently high, electric field can overcome interfacial interactions and prefer a perpendicular stacking $L_o$ (lamellae are parallel to the field lines). (d) A defect—an unfavorable perpendicular morphology where lamellae are perpendicular to the field lines. In subsequent calculations we took the distance between electrodes to be $1 \mu$m, and the lamellar period is 100 nm unless otherwise indicated.

At this point it should also be pointed out that nonuniform electric fields are in general neither interfacial nor purely bulk ones. In the razor-blade geometry, the field is high close to the electrodes’ edge. However, sufficiently far from the electrodes the field behaves like $E(r) = V/r^2$, where $r$ is the distance from the middle of the gap. Thus, the integrated electrostatic contribution to the energy scales like $1/r$. This energy indeed decays, but very slowly, and it has an important contribution even very far from the electrodes.

We assume that the lamellae are rigid enough so that the electric field does not bend them. In the example of block copolymers, this corresponds to the so-called strong-segregation

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regime, where $\chi N \gg 1$. Let us verify the validity of this assumption. The elastic bending energy per unit volume is written as $F_{el} = \frac{1}{2} K R^2$, where $K$ is the bending modulus and $R$ is the local bending radius (inverse curvature). For strongly stretched lamellae, $K = D \gamma_{AB}$, where $D$ is the lamellar period ($D \sim 100$ nm) and $\gamma_{AB} \sim 10$ mN/m is the A/B interfacial tension. On the other hand, the electrostatic energy per unit volume is $F_{es} = \frac{1}{2} \varepsilon E^2$, where $\varepsilon$ is the dielectric constant and $E$ the local field, which cannot exceed $\sim 100$ V/µm because of dielectric breakdown. Let us take this maximum value, in this case $F_{es} = 10^7$ J/m$^3$. Therefore, $F_{el} = F_{es}$ if the lamellae are bent with a radius of curvature of 0.1 µm. The same estimate relates to the stresses (forces) of course. Electric fields cannot bend lamellae to a radius smaller than $\sim 0.1$ µm. In the razor-blade system, at larger distances from the electrodes the field is weaker, and therefore the lamellae should stay flat as well. Since the fields we consider are typically much weaker, we do not expect bent lamellae in this electrode arrangement. The above reasoning does not hold for weakly segregated lamellae: These lamellae have a much weaker modulus $K$, and therefore significant bending can occur.

A lamellar stack can therefore have the basic configurations: parallel or perpendicular to the substrate (Figure 1b,c), denoted as $L_\|\|$ and $L_\perp$, respectively. Note that in the parallel stacking the first layer at the substrate is half as thick as the others. A third state exists which we denote the perpendicular defect. Here the lamellae normals are not parallel to the electrodes’ edges. Figure 1d represents the highest energy of such defects. Weakly segregated systems exhibit lower energy defects, e.g., T-junction or grain boundary. In some experiments with weakly segregated block copolymers on preferential surfaces, few lamellar layers are adsorbed preferentially on the substrate (mixed morphology) due to the long-range effect of surface ordering.17,30 As is mentioned above, this system is out of the scope of the current work, and it will be dealt with in a subsequent publication.

A peculiar feature of nonuniform fields is that the $L_\|\|$ state can be favored over the $L_\perp$ one even in the absence of specific interfacial interactions with the substrate. In order to understand this, consider first the distribution of electric field squared for two semiinfinite planar electrodes in the $x$–$z$ plane, with a gap of 1 µm between them. This distribution is shown in Figure 2 for a medium with spatially uniform dielectric constant $\varepsilon$. Clearly $E^2$ is very high close to the surface and, in particular, close to the electrodes’ edge at $x = \pm 0.5$ µm. The field is small far from the substrate, and therefore interfacial instabilities are not expected;31 this is true even more so since above the electrodes’ edges the field at $y \to \infty$ is actually parallel to the substrate and also to the polymer/air interface. Let us now assume without loss of generality that $\varepsilon_A > \varepsilon_B$. As is well-known in the field of dielectrophoretic forces,32 a material with large value of $\varepsilon$ is drawn to regions with high fields, whereas small-$\varepsilon$ material is repelled. Since the electric field is largest near the electrodes’ edges, an $L_\|\|$ state can form with the A material touching the substrate. However, the work of Amundson et al. has shown that there is also a free energy penalty for having dielectric interfaces perpendicular to the field’s direction, and this penalty is absent in the $L_\perp$ state. Clearly, the orientation selection depends on the magnitude of $\varepsilon_A - \varepsilon_B$.

The electrostatic energy of the system is given by an integral over all space

$$F_{es} = -\frac{1}{2} \varepsilon(r) E^2(r) \, d^3 r$$

(1)

The dielectric constant $\varepsilon(r)$ is a spatially varying quantity. In this study it is a periodic function. In the $L_\|\|$ state, for example, it is given by

$$\varepsilon(r) = \begin{cases} 
\bar{\varepsilon} + \frac{1}{2} \Delta \varepsilon & \text{if } nd < y < nd + \frac{1}{2} d, 
\bar{\varepsilon} - \frac{1}{2} \Delta \varepsilon & \text{if } nd + \frac{1}{2} < y < (n + 1) d
\end{cases}$$

(2)

where $\bar{\varepsilon} = \frac{1}{2}(\varepsilon_A + \varepsilon_B)$ is the average dielectric constant, and the period is $d$. The above equation simply represents a square wave in the $y$-direction, where $\varepsilon$ alternates between $\varepsilon_A$ and $\varepsilon_B$. The dielectric constant can be defined similarly for the other stackings.

Theory and Results

Figure 3 shows $F_{es}$ for the $L_\|\|$ and $L_\perp$ stackings at a fixed value of $\bar{\varepsilon} = 6$ and varying values of the dielectric constant mismatch. The electrostatic energy is calculated numerically for a system with electrode gap of 1 µm. $F_{es}(\Delta \varepsilon)$ (dashed horizontal line) is constant for the $L_\perp$ case because the electric field between

![Figure 2](image1.png)  
**Figure 2.** Plot of $E^2(x,y)$ in the $x$–$y$ plane, for the case where the dielectric constant $\varepsilon$ is uniform, and the electrodes are at $x > 0.5$ µm ($V = \frac{1}{2} L_\|$ and $V = \frac{1}{2} L_\perp$). The largest field is at the electrodes’ edge, $x = \pm 0.5$ µm. $E^2$ is scaled by $10^{10}$ and given in $(V/\mu m)^2$.

![Figure 3](image2.png)  
**Figure 3.** Numerically calculated electrostatic energy $F_{es}$ (eq 1) of parallel $L_\|$ (solid line) and perpendicular $L_\perp$ (horizontal dash-dotted line) stackings as a function of the permittivity difference: $\Delta \varepsilon \equiv \varepsilon_A - \varepsilon_B$. $F_{es}$ is normalized by its value when $\Delta \varepsilon = 0$, $F_{es}$ of perpendicular lamellae is constant, while that of parallel ones decreases before it increases (see inset). The critical value of $\Delta \varepsilon$ is $\Delta \varepsilon_c \approx 1$. When $\Delta \varepsilon < \Delta \varepsilon_c$, $L_\|$ is preferred over $L_\perp$. If $\Delta \varepsilon > \Delta \varepsilon_c$, $L_\perp$ is preferred. We took the average dielectric constant to be $\bar{\varepsilon} = 6$, the lamellar period is 100 nm, and the electrode gap is 1 µm. The dashed line is a similar plot of $F_{es}$ for $L_\|$ lamellae, with the same parameters; only the electrode gap is 2 µm.
the electrodes is independent of \( \Delta \varepsilon \) and \( \tilde{\varepsilon} \). On the other hand, in the \( L_\parallel \) case (solid line), \( F_{es}(\Delta \varepsilon) \) decreases first before it increases. The decrease is due to the dielectrophoretic term, linear in \( \Delta \varepsilon \), while the increase is due to the penalty associated with dielectric interfaces perpendicular to the field lines, scaling like \( (\Delta \varepsilon)^2 \).

Let us make a short but very general mathematical digression which will clarify the last point. Denote \( E_0(\mathbf{r}) \) the electric field which corresponds to a system of uniform dielectric constant and a given electrode design (not necessarily the one in Figure 1). \( E_0 \) is derived from a potential \( \psi_0(\mathbf{r}) \) satisfying the proper boundary conditions on the electrodes: \( \nabla_0 \psi \equiv -V/\psi_0 \). Suppose now that the dielectric constant changes from its average value by an amount \( \varepsilon(r) - \varepsilon(r) \). This change in permittivity leads to a change in field: \( E(\mathbf{r}) = E_0(\mathbf{r}) + \varepsilon(r)E \). We may now write the integrand of eq 1 in the following way:

\[
f_{es} = -\frac{1}{2} f \varepsilon^2 - \frac{1}{2} \varepsilon E_0^2 - \frac{1}{2} \{ \varepsilon(r) E_0^2 + 2\varepsilon \varepsilon E_1^2 \} - \frac{1}{2} \varepsilon E_1^2 \tag{3}\]

The first term on the right is the electrostatic energy of the system with uniform average \( \varepsilon \), while the other three terms are the deviations from it. The second and third terms (square brackets) are the dielectrophoretic and “dielectric interfaces” terms, scaling like \( \varepsilon_1 \) and \( \varepsilon_1^2 \), respectively. Finally, the last term scales like \( \varepsilon_1^3 \) and is small if \( \varepsilon_1 \ll \varepsilon \). For the case where this last term is dealt with, the interested reader is referred to ref 20.

On the basis of this expansion and denoting \( E_1 = -\nabla \psi_1 \), one can easily show that \( \psi_1 \) obeys the following equation

\[
\nabla^2 \psi_1 = \frac{1}{\varepsilon} \nabla \varepsilon_1 \cdot E_0 \tag{4}\]

with the boundary conditions that \( \psi_1 = 0 \) on all conductors. Clearly \( \psi_1 \) can be written as \( \psi_1 = \psi_1(\mathbf{r}, \varepsilon, \varepsilon, \text{geometry}, V) \), where geometry refers to the electrode geometry and \( V \) to the electrode potential difference (in the case of just two electrodes). We now write \( \varepsilon_1 \) in a form that puts emphasis on dimensions: \( \varepsilon_1(\mathbf{r}) = \Delta \varepsilon(r) \). Thus, \( \varepsilon(r) \) is a dimensionless function containing the spatial variation of \( \varepsilon_1 \) and whose spatial average vanishes: \( \langle \varepsilon(r) \rangle = 0 \). For the square-wave example of eq 2, \( \varepsilon = \pm \varepsilon_0 / 2 \). It then directly follows that

\[
\psi_1 = \frac{\Delta \varepsilon(r)}{\varepsilon} \psi_0(\mathbf{r}; \varepsilon, \text{geometry}, V) \tag{5}\]

where \( \psi_1 \) obeys the equations

\[
\nabla^2 \psi_1 = \nabla \varepsilon \cdot E_0 \tag{6}\]

and \( \psi = 0 \) on all electrodes. Since \( \psi_1 \) is a universal potential independent of \( \Delta \varepsilon \), \( \psi_1 \) is linear in \( \varepsilon \varepsilon_0 \) (and in fact it is linear in \( V \) as well). Similarly, we find \( E_1 = (\Delta \varepsilon) \tilde{E}_0(\mathbf{r}; \varepsilon, \text{geometry}, V) \), with \( \tilde{E}_0 \) independent of \( \Delta \varepsilon \). We now rewrite eq 3 as follows:

\[
F_{es} = \Delta \varepsilon I_1 + \frac{(\Delta \varepsilon)^2}{\varepsilon} I_2 + \text{const} \tag{7}\]

\[
I_1 = -\frac{1}{2} \int [c(r) E_0^2 + 2 E_0 \tilde{E}_1] \, d^3 r \tag{7a}\]

\[
I_2 = -\frac{1}{2} \int [2 c(r) E_0 \tilde{E}_1 + \tilde{E}_1^2] \, d^3 r \tag{7b}\]

\[
\Delta F = I_1 \Delta \varepsilon + I_2 \frac{(\Delta \varepsilon)^2}{\varepsilon} + \frac{1}{2} \text{const} \gamma_{\text{AS}} - \text{const} \gamma_{\text{BS}} \tag{9}\]

where \( \text{const} \) is the substrate area. The prevailing state is \( L_0 \) if \( \Delta F \) is negative and \( L_\perp \) otherwise. On the basis of this free energy

![Figure 4. Electrostatic energy \( F_{es} \) of perpendicular-defect structure (Figure 1d) as a function of \( \Delta \varepsilon \). \( F_{es} \) is normalized by its value when \( \Delta \varepsilon = 0 \) and is always increasing. Other parameters as in Figure 3.](image)
while the system experiences torque which tends to align the stacking, preferring lamellar thickness and the surface separation can be neglected. Here we have assumed that the film is homogeneous and that the edges are perpendicular to the field’s direction. We have shown that a simple electrode realization which gives rise to nonuniform electric fields can bring about orientational transitions between several lamellar stackings. Specifically, for $\Delta \epsilon < \Delta \epsilon_c$, parallel lamellae are preferred over perpendicular ones even at very high fields. When $\Delta \epsilon > \Delta \epsilon_c$, there is an interplay between electrostatic forces and interfacial interactions. The “razorblade” electrode design suggested here can find numerous applications in nanotechnology: the large torque is expected to remove the degeneracy between the $L_\perp$ states by orienting the lamellae perpendicular to the substrate and the electrodes’ edges. More complex morphologies are expected to occur for block copolymers in the intermediate and weak segregations, where the lamellar bending and grain boundary energies are smaller, and these systems should be systematically explored in this and more advanced electrode arrangements.

**Conclusions**

Lamellar phases under the influence of a spatially nonuniform electric field are considered. The role of the dielectric constant mismatch $\Delta \epsilon$ is highlighted: the linear term in the free energy expansion is due to a dielectrophoretic force, while the quadratic term includes the free energy penalty for having dielectric interfaces perpendicular to the field’s direction. We have shown that a simple electrode realization which gives rise to nonuniform fields can bring about orientational transitions between several lamellar stackings. Specifically, for $\Delta \epsilon < \Delta \epsilon_c$, parallel lamellae are preferred over perpendicular ones even at very high voltages. When $\Delta \epsilon > \Delta \epsilon_c$, there is an interplay between electrostatic forces and interfacial interactions. The “razorblade” electrode design suggested here can find numerous applications in nanotechnology: the large torque is expected to remove the degeneracy between the $L_\perp$ states by orienting the lamellae perpendicular to the substrate and the electrodes’ edges. More complex morphologies are expected to occur for block copolymers in the intermediate and weak segregations, where the lamellar bending and grain boundary energies are smaller, and these systems should be systematically explored in this and more advanced electrode arrangements.

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**References and Notes**


