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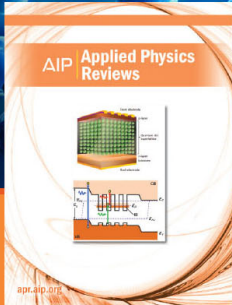
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A surface interaction model for self-assembly of block copolymers under soft confinement

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The surface interaction between substrates and block copolymers is one of the most important factors that control the alignment of self-assembled domains under thin film confinement. Most previous studies simply modeled substrates modified by grafting polymers as a hard wall with a specified surface energy, leading to an incomplete understanding of the role of grafted polymers. In this study, we propose a general model of surface interactions where the role of grafted polymers is decomposed into two independent contributions: the surface preference and the surface softness. Based on this model, we perform a numerical analysis of the stability competition between perpendicular and parallel lamellae of symmetric diblock copolymers on substrates modified by homopolymers using self-consistent field theory. The effects of the surface preference and the surface softness on the alignment of lamellar domains are carefully examined. A phase diagram of the alignment in the plane of the surface preference parameter and the surface softness parameter is constructed, which reveals a considerable parameter window for preparing stable perpendicular lamellae even on highly preferential substrates. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4968599>]

I. INTRODUCTION

Over the last few decades, the microelectronic industry achieved remarkable advancement due to the increasing ability to manufacture high-resolution patterns on the substrates of electronic materials. However, photolithography, the traditional methodology is quite expensive to produce features down to 20 nm.¹ In recent years, block copolymers emerge as a promising alternative² because of the richness of self-assembled morphologies^{3–5} and the characteristic domain size of these structures which typically falls into the interesting sub-40 nm region. In particular, lamellar structures, despite its simplicity, have attracted great attention for their ability to produce desired patterns such as isolated lines, periodic lines, and T-junctions.^{6,7} Directed self-assembly (DSA) of block copolymers in thin films is currently the main tool for the implementation of block copolymer lithography.

By confining diblock copolymers (dBCPs) in thin films, self-assembled lamellae may appear with their surface normal either parallel or perpendicular to the normal of the substrate surface. Perpendicular lamellae ($L_{\perp}$) are more useful in most applications while unfortunately parallel lamellae ($L_{\parallel}$) usually prevail as revealed by early experiments.^{8–11} Therefore much effort has been devoted to understanding the orientation of the lamellar structure in thin films.^{12–17} It has been found that film thickness and surface properties are two most important factors to determine the orientation of lamellae.^{18,19} When the film thickness is commensurate to the period of lamellae in the bulk, the parallel orientation is more favorable. Thus a

naive idea for obtaining $L_{\perp}$ would be to make the film thickness incommensurate to the bulk period which frustrates $L_{\parallel}$. However, in practice this idea often fails because most of the common substrates exhibit an energetic preference for one of the components of dBCP. And it has already been shown that for bare substrates the energetic preference can compensate the frustration effect of incommensurate film thickness, which makes $L_{\parallel}$ more preferable again.^{20–23}

To eliminate the influence of the surface preference of substrates, previous efforts have been focusing on devising neutral surfaces through modifying substrate surfaces. A popular and effective way to do so is grafting polymers onto substrates. Mansky *et al.*^{12,24} first demonstrated the surface-control ability of grafting PS-*r*-PMMA copolymers by tuning its compositions and a neutral surface regime has been identified where $L_{\perp}$ can be effectively prepared. Later on there have been numerous experimental attempts to control domain orientation on either homogeneous or chemically patterned substrates.^{14,17,22,23,25–34} In these studies, the design of neutral surfaces is mainly guided by the surface energy. The role of grafted polymers is often simply considered as modifying the surface energy of the underlying solid substrate. However, it is found that this understanding is incomplete^{35,36} and a fundamental understanding of the role of grafted polymers is in demand.³⁷

Early theoretical and numerical studies modeled both bare substrates and polymer-grafted substrates as hard walls.^{18–21,38–41} The strong-segregation theory (SST) analysis,^{18–20} which models substrates as hard walls with zero thickness (the hard-wall model), predicts that $L_{\parallel}$ and $L_{\perp}$ are equally stable on neutral surfaces when the film thickness is commensurate to the lamellar period in the bulk. Such prediction is inconsistent with the experimental observations.^{42,43} The self-consistent field theory (SCFT) studies,^{20,40} which adopt

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the “masking” technique to model the wall-dBCP interfaces (the mask model), reveal that there is actually an energy gap between $L_{\perp}$ and $L_{\parallel}$ on neutral surfaces. Obviously, the extra stability of $L_{\perp}$ is introduced by the mask. A following work by Meng and Wang⁴⁰ clarified that the mask brings two extra effects, namely, the “surface-induced compatibilization” and “surface-induced entropy loss,” where the former is mainly responsible for the stabilization of $L_{\perp}$. However, the mask is chosen merely based on numerical considerations, which renders its predictions being only qualitative.

More recently, Trombly *et al.*^{35,36} demonstrated that the stabilization of $L_{\perp}$ is even pronounced by explicitly representing the grafted random copolymers in their SCFT calculations. This work shows that both the hard-wall model and the mask model oversimplify the surface interactions between grafted polymers and dBCPs. To fully capture the role of grafted polymers, it is important to consider them explicitly. In particular, it is found that unlike the mask which is fixed, the grafted polymers are able to rearrange its density distribution in response to the self-assembly of dBCP. This additional freedom of grafted polymers introduces extra softness to the confining wall. Albert and Epps⁴⁴ used “soft confinement” to refer to the confining wall formed by air (corresponding to the “free surface”). It is natural to generalize this term to all confining walls that act as a soft potential in contrast to the “hard confinement” coined by Meng and Wang.⁴⁰ Previous studies on the soft confinement though very limited only considered the case of constant surface softness.^{35,36,45} Moreover, there is no attempt to identify a parameter to characterize the degree of surface softness.

In this study, we propose a general model of surface interactions for the soft confinement system where both the surface preference and the surface softness are considered explicitly. In this way, we can tune the surface preference and the surface softness separately. To demonstrate the feasibility of our model, we explore the stability competition between $L_{\parallel}$ and $L_{\perp}$ of dBCP on substrates modified by homopolymers which are explicitly described in SCFT calculations. The role of grafted homopolymers is then systematically examined by varying either the surface preference or the surface softness. In addition, a phase diagram of the alignment of self-assembled domains as a function of both parameters can be constructed accordingly, which clearly reveals the effects of the surface softness on the alignment.

II. NUMERICAL METHODS

We model the self-assembly of symmetric dBCP under soft confinement by a numerical SCFT method with an explicit representation of the grafted homopolymers. Both grafted polymer chain and the dBCP chain consist of N monomers with identical volume $v_0 = \rho_0^{-1}$ and length b . All spatial quantities are rescaled by the non-perturbed radius of gyration $R_g = b\sqrt{N/6}$. In all SCFT calculations, the Flory-Huggins interaction parameters of dBCP ($\chi_{AB}N$) and the grafting density ($\sigma N/\rho_0$) are fixed at 20 and 1, respectively.

The modified diffusion equations in SCFT are solved by a highly efficient fourth-order exponential time differencing Runge-Kutta method (ETDRK4).⁴⁶ In the normal direction

of substrates (z direction) Chebyshev collocation is used to resolve the interface near the wall, while Fourier spectral collocation is used along the lateral direction (x direction). This particular choice of the discrete grid retains the spectral accuracy of pseudospectral SCFT calculations involving non-periodic boundary conditions that are introduced by confinement. The accuracy of computed free energies is 10^{-6} or better with at most 128 grid points along the z direction and the spacing of grid points along the x direction fixed at 0.125. In comparison, a conventional approach which adopts Fourier spectral collocation for both x and z directions requires at least 2048 grid points along the z direction to reduce the error of the calculated free energies to 10^{-5} . Further details of formulation and implementation can be found in the [supplementary material](#).

III. RESULTS AND DISCUSSION

A. Model of surface interactions

For substrates grafted by homopolymers, the interactions between substrates and dBCP are characterized by two Flory-Huggins interaction parameters: $\chi_{AC}N$ and $\chi_{BC}N$. Here the underlying substrates are assumed to be neutral to the grafted homopolymers and the dBCPs. It is common to define a surface preference parameter as the difference of interactions,

$$\delta \equiv \frac{1}{2}|\chi_{AC}N - \chi_{BC}N|. \quad (1)$$

The remaining degree of freedom can be naturally assigned to the surface softness parameter, which is defined as the total interactions between substrates and dBCPs,

$$\gamma \equiv \frac{1}{2}(\chi_{AC}N + \chi_{BC}N). \quad (2)$$

The role of grafted homopolymers can now be described by δ and γ .

In Secs. III B–III D we will discuss these two parameters on the alignment of self-assembled domains in detail. It should be pointed out that the definition of the surface softness parameter does not take into account the grafting density and the chain length of the grafted homopolymers since these factors are independent variables which should be considered separately. In this study, we focus on the effect of the surface softness and keep both the grafting density and the chain length of the homopolymer fixed. It is also worth noting that this model of surface interactions can be generalized to the 3D confinement where the confining wall consists of solvents or air^{47,48} by simply replacing the interaction parameters between grafted polymers and dBCPs with those between solvents and dBCPs.

B. Surface softness of the confining wall

The influence of the softness of the confining wall can be investigated by setting $\delta = 0$ which isolates the effect of the surface preference. In this situation, the confining wall is effectively neutral to dBCP because the grafted polymers identically repel A and B monomers of dBCP. The calculated morphologies of $L_{\parallel}$ and $L_{\perp}$ are quite similar to those

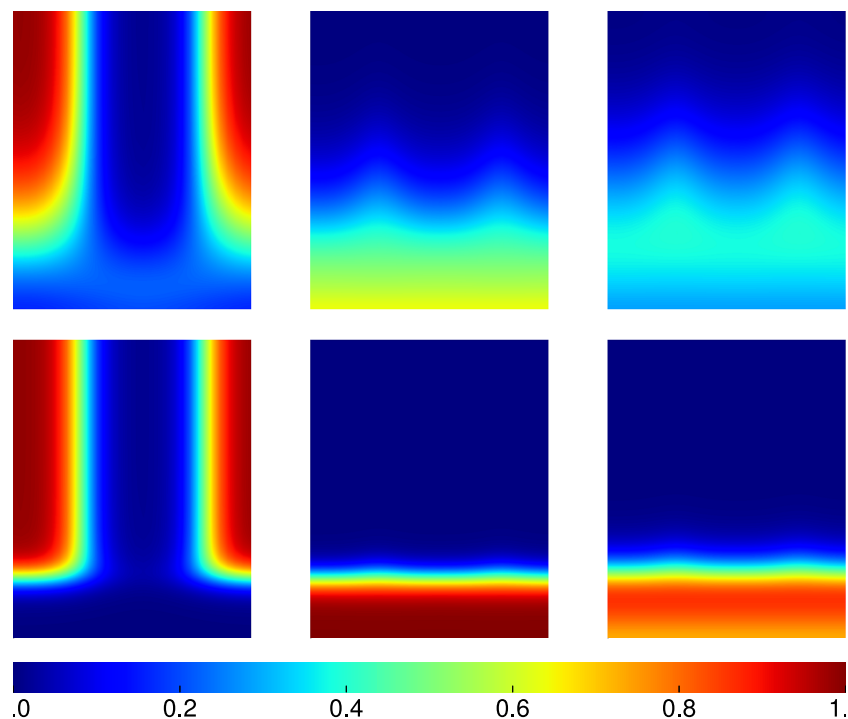


FIG. 1. Morphologies of perpendicular lamellae on the substrates modified by homopolymers with $\delta = 0$ and $\gamma = 0$ (top row), $\gamma = 20$ (bottom row). The columns from left to right are the density distributions of A component of the dBCP, the grafted homopolymers, and its chain ends, respectively.

reported by Trombly and co-workers^{35,36} but quite different from those under hard confinement calculated by SCFT using the “masking” technique.²⁰ Figure 1 gives two examples of the $L_{\perp}$ morphology for different surface softness. The morphological differences between soft confinement and hard confinement mainly exhibit near the confining wall. The differences are illustrated more clearly in Figure 2 by plotting the density distributions of the homopolymer-grafted layers. The density of grafted homopolymers contacting $L_{\parallel}$ phase under soft confinement (middle image in the inset of Figure 2) is homogeneous along the lateral dimension. At first look, it seems the same as that under hard confinement which is also homogeneous along the lateral dimension (right image in the inset of Figure 2). However, they are quite different as

revealed by plotting density profiles of the brush layers along the normal direction. The density of the grafted homopolymers decreases more slowly whenever brush chains touch the interfaces of A-rich and B-rich domains which indicates the enrichment of C monomers at the interfaces. It suggests that the aggregation of C monomers at A-B interfaces will lower the free energy of the system. For the same reason, in $L_{\perp}$ case the density of grafted homopolymers develops inhomogeneity along the lateral dimension (left image in the inset of Figure 2, also see the top row of Figure 1) due to the direct contact of the homopolymer-grafted layer with A-B interfaces. Obviously, it is more easier for $L_{\perp}$ system to enrich C monomers at A-B interfaces than $L_{\parallel}$ system because C chains have to protrude either A-rich or B-rich domains to arrive A-B interfaces in $L_{\parallel}$ system. Below we try to understand the significance of this difference acting on the stability competition between $L_{\parallel}$ and $L_{\perp}$.

One may notice that the “mask” in our hard confinement shown in Figure 2 is much wider than that of the previous hard confinement as defined by mathematical functions. Indeed, we have devised a new hard confinement model whose masks are the density distributions of the grafted homopolymers calculated from the same system as the soft confinement by setting $\chi_{AB}N = 0$ but keeping γ and δ unchanged. In this way the ambiguity of the choice of the mask is removed. Furthermore, it allows us to break the softness of the confinement into two contributions: the “immersion effect” and the “rearrangement effect.” The immersion effect describes the ability of grafted homopolymer chains to penetrate into dBCP domains thus control the width of interfaces between the homopolymer-grafted layer and dBCP domains. This effect is essentially the same as the influence of interfacial interactions upon the interfaces between A-rich and B-rich domains in the self-assembly of dBCP. Thus it can be fully characterized by the surface energies between C homopolymers and A/B homopolymers.

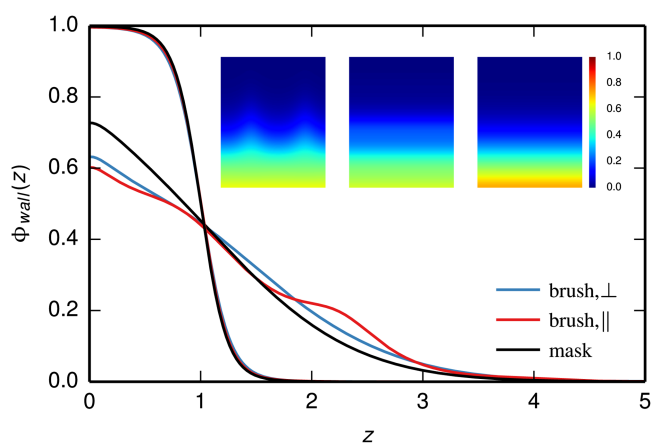


FIG. 2. Density distributions of the neutral confining wall ($\delta = 0$) along the normal of substrates. The lateral density distributions have been averaged out. The lower set of three curves is for $\gamma = 0$ while the upper set is for $\gamma = 20$. The blue, red, and black curves represent the density distributions in $L_{\perp}$, $L_{\parallel}$, and the new hard confinement model as defined in the text, respectively. The three morphologies in the inset from left to right correspond to the blue, red, and black curves in the lower set, respectively.

Within the specially designed hard confinement model, only immersion effect is retained so that we can study it separately. As shown in Figure 2, by increasing γ from 0 to 20, the density distribution of the grafted homopolymers becomes sharper. Therefore, our hard confinement model at large γ mimics the conventional hard confinement model where the confining wall is modeled by a mask which is usually quite sharp. Furthermore, we expect that it will eventually approach SST where the confining wall is modeled by a hard wall with zero thickness in the limit of $\gamma \rightarrow \infty$. Consequently, the softness of the confinement can be tuned continuously by increasing γ from 0 to ∞ : the larger the γ , the harder the confinement. In this sense, the conventional hard confinement can be viewed as a confinement model whose softness is not infinite like the bare hard wall in SST but can be associated with a finite γ determined by the width and shape of its mask. Thus our new hard confinement model provides a coherent understanding of the role of the mask.

A similar model to the above hard confinement model has been studied by Perera *et al.*⁴⁹ However, in their study the grafted polymers are implicitly modeled by a mask just like the conventional mask model. The degree of interpenetration between grafted polymers and self-assembled domains is controlled by the width of the mask. They found that the interpenetration of grafted polymers into the self-assembled domains is responsible for the deformation of domains near substrates as observed in their experiments. In their model, the rearrangement effect is ignored and the immersion effect is only studied in a qualitative way because the width of the mask is chosen arbitrarily.

As compared to the new hard confinement model, soft confinement introduces an additional effect, the rearrangement effect, that enables the grafted homopolymers rearrange its density distribution in accordance with the self-assembly of dBCP. This additional effect is responsible for the difference of morphologies between $L_{\parallel}$ and $L_{\perp}$ as mentioned above. And it further smoothes the density profile of the homopolymer-grafted layer as can be seen in Figure 2 by comparing density profiles between the soft confinement and hard confinement. For the strong repulsion between the grafted homopolymers and dBCP (e.g., $\gamma = 20$), the difference of density profiles between $L_{\parallel}$ and $L_{\perp}$ is insignificant indicating that the rearrangement effect is negligible in this situation. However, as we soften the confinement by decreasing γ , the rearrangement effect becomes more and more important. For example, the density profiles significantly deviate each other between $L_{\parallel}$ and $L_{\perp}$ at $\gamma = 0$. This rearrangement effect modifies the stability competition between $L_{\parallel}$ and $L_{\perp}$ in a very subtle manner.

The stability of $L_{\parallel}$ and $L_{\perp}$ is usually quantified by the difference of the free energy per unit area between $L_{\parallel}$ and $L_{\perp}$: $\Delta F = (F_{\parallel} - F_{\perp}) d / CVk_B T$ (d should be replaced by an effective film thickness $\bar{\phi}_{ABd}$ for hard confinement) where $C = \rho_0 R_g^3 / N$ is a dimensionless density of dBCP under confinement.^{20,39,50} A positive ΔF indicates that $L_{\perp}$ is more stable, and vice versa. In general, ΔF is an oscillatory curve as a function of film thickness. A typical plot of this curve is given in the [supplementary material](#). The minima of the $\Delta F \sim d$ curve occur whenever the film thickness is commensurate to the lamellar

period in the bulk. Remarkably, all these minimum values, $\Delta F_c = \Delta F(d_c)$ with d_c being the commensurate film thickness, are equal. Thus it serves as an excellent measure of stability of $L_{\parallel}$ and $L_{\perp}$ without considering the effect of film thickness. To study the influence of the softness of the confining wall on the stability of $L_{\parallel}$ and $L_{\perp}$, we plot ΔF_c as a function of γ in Figure 3(a). We notice that ΔF_c is always positive, which reproduces the well-known result that $L_{\perp}$ is more stable than $L_{\parallel}$ even on neutral polymer-grafted surfaces. A more interesting observation is that both curves of soft confinement and new hard confinement are nonmonotonic. The stability of $L_{\perp}$ is maximized at some optimum softness. Moreover, the additional rearrangement effect in soft confinement shifts the maximum of the $\Delta F_c \sim \gamma$ curve to a larger γ . This shift has a remarkable consequence that it allows harder confinement to produce stable $L_{\perp}$.

To understand the dependence of the stability of $L_{\perp}$ on the softness of the confining wall and the existence of an optimum softness which maximizes the stability of $L_{\perp}$, it is helpful to analyze the free energy contributions under the new hard confinement which excludes the rearrangement effect. Using the same partition scheme in the work of Matsen and Gardiner,⁵¹ we split the free energy into the energetic and entropic contributions. The entropic contributions are further decomposed into translational and configurational parts. Explicit expressions of these free energy contributions are provided in the [supplementary material](#). The differences of these free energy contributions between $L_{\parallel}$ and $L_{\perp}$ as functions of γ

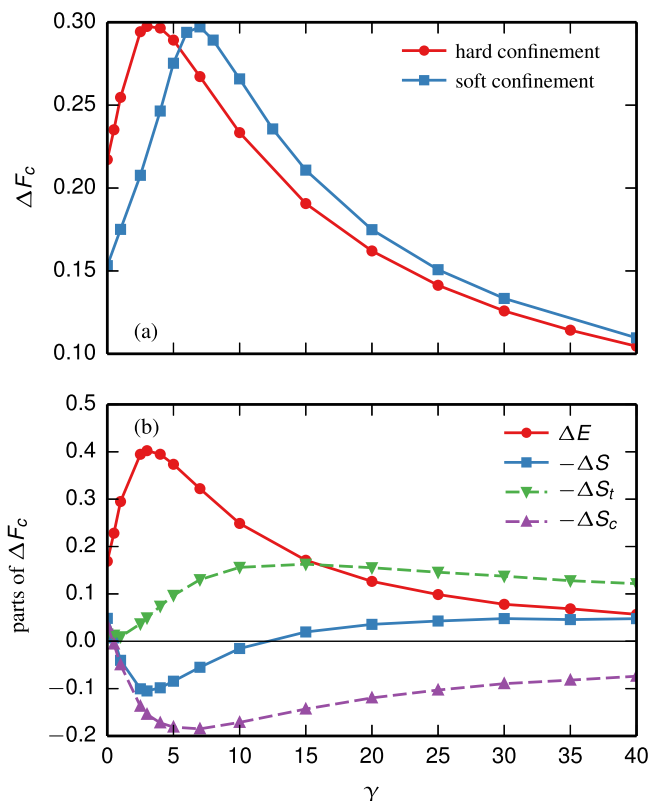


FIG. 3. (a) The difference of free energy between $L_{\parallel}$ and $L_{\perp}$ at commensurate film thickness (ΔF_c) as a function of γ on the neutral confining wall ($\delta = 0$). (b) Energetic and entropic contributions of ΔF_c in (a). The contributions from the translational entropy ($-\Delta S_t$) and from the configurational entropy ($-\Delta S_c$) adds up to the total entropic contribution ($-\Delta S$).

are presented in Figure 3(b). The difference of the enthalpy, $\Delta E = E^{\parallel}d_c - E^{\perp}d_c$, is always positive indicates that the energetic effect favors $L_{\perp}$. This effect is already termed as “surface-induced compatibilization” by Meng and Wang,⁴⁰ i.e., the decrease of the density of dBCP in the A-B interfacial region due to the immersion of grafted homopolymers reduces the repulsion between A and B monomers. As A-B interfaces contribute most of the A-B repulsion, the morphology with more A-B interfaces contacting with the confining wall is favorable, which is $L_{\perp}$ in our case. In the limit of SST ($\gamma \rightarrow \infty$), surface-induced compatibilization vanishes because C monomers can no longer penetrate into A-B interfaces. Thus there is no difference of enthalpy between $L_{\parallel}$ and $L_{\perp}$, i.e., $\Delta E = 0$. For large and moderate γ , the surface-induced compatibilization mainly presents in $L_{\perp}$ because the relative narrow distribution of the grafting layer cannot reach the A-B interface in $L_{\parallel}$. In this regime, as γ decreases, the immersion of grafted homopolymer chains into A-B interfaces becomes easier, which enlarges ΔE . The decrease of ΔE at very small γ is due to the fact that the density distribution of the grafted polymers becomes so wide that grafted polymer chains can eventually protrude the entire A or B-rich domain to interact with A-B interfaces of $L_{\parallel}$. Meanwhile, an additional A-B interface emerges in the vicinity of the confining wall in the regime of small γ (shown in the [supplementary material](#)). These new features emerging only at small γ introduce the surface-induced compatibilization into $L_{\parallel}$, which compensates its effect in $L_{\perp}$. This effect enhances more rapidly in $L_{\parallel}$ as γ decreases, leading to the decrease of ΔE .

The translational entropy is characterized by the density distribution of joint monomers which joins A and B blocks of dBCP. It also favors $L_{\perp}$ as can be seen in Figure 3. For bulk lamellae, joint monomers are mostly distributed at A-B interfaces. The distribution of joint monomers in $L_{\parallel}$ is hardly altered by the confining wall because A-B interfaces of $L_{\parallel}$ are far from the wall. But in $L_{\perp}$ things are quite different: part of joint monomers within A-B interfaces gains freedom to migrate to the interfaces of grafted polymers and A/B domains due to the immersion of grafted polymers into A-B interfaces. This redistribution of joint monomers increases the translational entropy. Hence the difference of the free energy contribution from the translational entropy defined by $-\Delta S_t = -S_t^{\parallel}d_c + S_t^{\perp}d_c$ is positive. Since the redistribution of joint monomers is closely related to the surface-induced compatibilization, $-\Delta S_t$ exhibits a similar dependence on γ . On the other hand, the configurational entropy which prefers the enrichment of chain ends of dBCP favors $L_{\parallel}$ because it has larger interfaces of C and A/B domains than those of $L_{\perp}$. The overall entropic contribution favors $L_{\perp}$ in large and moderate γ regimes and favors $L_{\parallel}$ at small γ , attributing to the fact that the translational entropy dominates at large γ while the configurational entropy dominates at small γ . In total, however, we observe that the entropic contribution plays a minor role in determining the overall behavior of ΔF_c because the curve of ΔE already resembles that of ΔF_c .

C. Surface preference of the confining wall

In our system, the surface preference of the confining wall arises whenever grafted homopolymers interact with A and B

blocks of dBCP differently. A natural measure of this difference is δ as previously defined. The influence of δ on the stability of $L_{\parallel}$ and $L_{\perp}$ can be studied by fixing γ . One should note that the domain of δ is restricted by γ as $0 \leq \delta \leq \gamma$. In Figure 4 we plot ΔF_c as a function of δ at $\gamma = 10$. We observe a continuous transition from $L_{\parallel}$ to $L_{\perp}$ at $\delta = 2.15$ as δ decreases.

To demonstrate that the homopolymer-grafted confinement is a general model for soft confinement, we show how to map the copolymer-grafted confinement developed by Trombly *et al.*^{35,36} to our model. In their work, the surface preference is controlled by varying the volume fraction of A monomers in grafted copolymers (f_A) and the Flory parameter ($\chi_{AB}N$) is fixed at 20. When f_A is equal to 1, the grafted copolymer reduces to A homopolymer which is identical to our model with $\gamma = 10$ and $\delta = 10$. Another limit $f_A = 0.5$ creates effectively neutral surfaces which should correspond to our model with $\delta = 0$. If we further assume that the softness of the confining wall is invariant with f_A and the relation between f_A and δ is linear, we can establish a mapping: $\gamma = \chi_{AB}N/2$ and $\delta = \chi_{AB}N[f_A - 0.5]$. To verify this mapping, data points reported by Trombly *et al.*^{35,36} are replotted in Figure 4. Those data points associated with $\lambda = 0$ almost coincide with the solid curve computed from our model. Here λ is a parameter that quantifies the “blockiness” of the random copolymer. The limit $\lambda = 0$ describes an ideal random copolymer which minimizes the “chemical templating effect.”^{35,36} The deviation of data points with $\lambda = 0.9$ evidently can be attributed to the chemical templating effect.

D. Phase diagram of $L_{\parallel}$ and $L_{\perp}$

Phase diagrams of $L_{\parallel}$ and $L_{\perp}$ in the plane of $\delta \sim \bar{\phi}_{AB}d/D_b$ are presented in Figure 5, where D_b is the lamellar period in the bulk. The phase diagram computed by SST corresponds to the case of $\gamma \rightarrow \infty$ which is a well known result.^{20,21} As we introduce softness into the confinement, the phase boundary is entirely pushed to higher δ . Two important consequences are worth noting: (i) a considerable window of stable $L_{\perp}$ develops

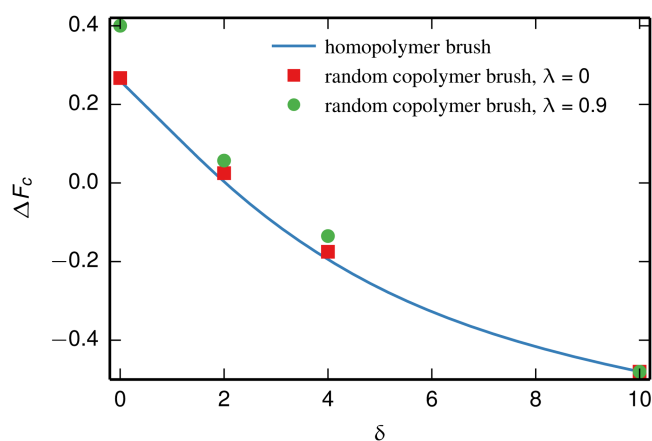


FIG. 4. The free energy difference at commensurate film thickness as a function of surface preference. The solid line corresponds to our homopolymer-grafted system, while symbols represent data reported in Refs. 35 and 36. The δ values of the symbols are mapped from the references by using the relation $\delta = \chi_{AB}N[f_A - 0.5]$. The λ parameter characterizes the randomness of the grafted copolymers. $\lambda = 0$ corresponds to a perfect random copolymer while $\lambda = 0.9$ corresponds to a random copolymer with the long sequence of A or B components.

for all film thicknesses ($0 \leq \delta \leq 2.15$); (ii) a film thickness window for stable $L_{\perp}$ exists for highly selective confining walls (e.g., $0.64 < \bar{\phi}_{ABd}/D_b < 0.76$ for $\delta = 10$). Note that the composition of grafted homopolymers is the same as that of one block of dBCPs when $\delta = 10$ and $\chi_{AB}N = 20$. Therefore our model suggests that it is possible to use homopolymers instead of more popular choice of random copolymers in some region of the film thickness to prepare $L_{\perp}$. In fact, Guo and co-workers⁵² have demonstrated experimentally that PS instead of PS-r-PMMA can be used to modify substrates to prepare perpendicular lamellae of PS-b-PMMA. They found that the film thickness window for perpendicular orientation is 0.58–0.95 which is reasonably close to our calculated window. The difference can be attributed to the fact that the chain length of the grafted homopolymer, the grafting density, and $\chi_{AB}N$ are not exactly matched between our simulations and their experiments.

More interestingly, the combination effect of γ and δ can be investigated by drawing phase diagrams in the plane of these two parameters as shown in Figure 6(a). For each film thickness, $L_{\parallel}$ and $L_{\perp}$ are separated by a smooth phase boundary whose starting point locates at the diagonal line $\delta = \gamma$, corresponding to the strongest surface preference that is allowed for producing stable $L_{\perp}$, while the other end goes to infinity. When the effective film thickness is commensurate to the lamellar period in the bulk ($\bar{\phi}_{ABd}/D_b = 1$), the phase boundary is a monotonic curve. Although decreasing slowly, it is expected that it will eventually go to 0 in the limit of $\gamma \rightarrow \infty$, i.e., SST. However, for a finite γ , i.e., under soft confinement, there is a considerable δ window to stabilize $L_{\perp}$ over $L_{\parallel}$. This has an important implication that in experiments it is not necessary to devise perfect neutral surfaces in order to produce stable $L_{\perp}$ even when the film thickness happens to be commensurate to D_b . In addition, softening the confining wall, such as choosing a homopolymer that weakly interacts with dBCP, will help widen the δ window for $L_{\perp}$.

When the film thickness strongly deviates the commensurate value, e.g., $\bar{\phi}_{ABd}/D_b = 0.75$ in Figure 6(a), the stable region for $L_{\perp}$ enlarges significantly because $L_{\parallel}$ is further frustrated under such strong confinement. We observe two notable differences from the commensurate case. One is the phase

boundary at large γ increases instead of decrease, which potentially allows $L_{\perp}$ to appear at arbitrary large δ . In other words, the effort to devise neutral or weakly preferential surfaces is not necessary in such an incommensurate situation. The other notable difference is that the phase boundary is nonmonotonic and it creates a reentry behavior of $L_{\perp}$. As can be seen in Figure 6(a), when $14.32 < \gamma < 18.58$, by increasing δ from 0 to γ , $L_{\perp}$ is first stable followed by $L_{\parallel}$ and then becomes stable again. This reentry of $L_{\perp}$ may account for many counterintuitive behaviors of the self-assembly of dBCP under soft confinement in this weak surface preference regime.²³

Interestingly, when the film thickness slightly deviates the commensurate value, e.g., $\bar{\phi}_{ABd}/D_b = 0.9$ in Figure 6(a), the phase boundary changes a little near the diagonal line but it changes significantly away from the line in comparison with the phase boundary for $\bar{\phi}_{ABd}/D_b = 1$. The two phase boundaries even intersect at about $\gamma = 6$. To illustrate this nontrivial phenomenon, we plot a phase diagram of $L_{\parallel}$ and $L_{\perp}$ in the plane of $1 - \bar{\phi}_{ABd}/D_b$ and δ as shown in Figure 6(b). In this diagram we have set $\delta = \gamma$ such that it tracks the phase transition along the diagonal line in Figure 6(a). It can be seen that the phase boundary changes slowly as the film

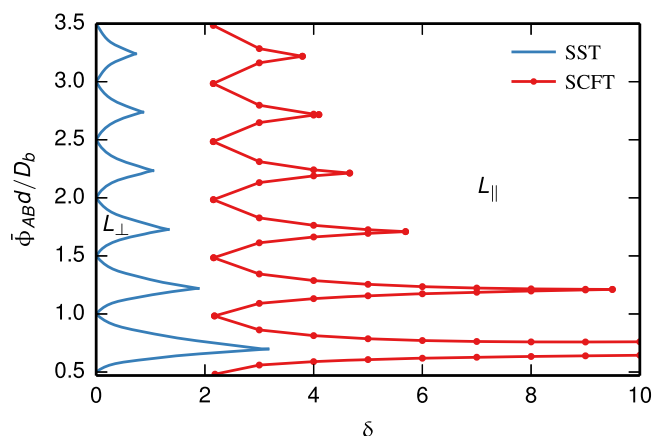


FIG. 5. Phase diagrams of $L_{\parallel}$ and $L_{\perp}$ in the plane of $\bar{\phi}_{ABd}/D_b$ and δ . The phase boundary computed by SST corresponds to the case of a pure hard wall ($\gamma \rightarrow \infty$), while that computed by SCFT is for the case of a soft wall ($\gamma = 10$).

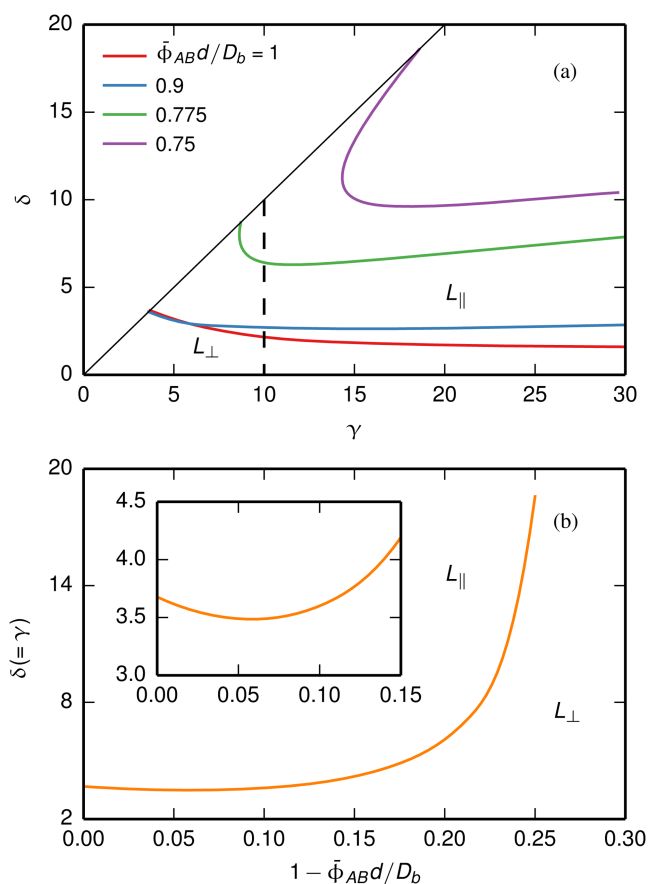


FIG. 6. (a) Phase diagram in the plane of δ and γ computed by SCFT. Note that several phase diagrams with different effective film thicknesses have been superimposed in the same $\delta \sim \gamma$ plane. For each phase boundary, the regions above and below it correspond to $L_{\parallel}$ and $L_{\perp}$ phase regions, respectively. The dashed line represents the phase diagram of the random-copolymer-grafted model.³⁵ The thin solid line ($\delta = \gamma$) is the upper bound for all phase diagrams enforcing the restriction $\delta \leq \gamma$. (b) Phase diagram in the plane of $\bar{\phi}_{ABd}/D_b$ and δ where we set $\gamma = \delta$ which corresponds to the thin solid line in (a). The inset magnifies the region around the minimum of the phase boundary.

thickness deviates from its commensurate value in the range of $0.85 \leq \phi_{AB}d/D_b \leq 1$, which means the starting points of phase boundaries for these film thicknesses in Figure 6(a) are close to each other. Moreover, the inset of Figure 6(b) clearly shows that a minimum is present in the phase boundary at 0.0585 (film thickness is 0.9415). Around this minimum, the phase transition value of δ for the incommensurate film thickness is smaller than that for the commensurate thickness. Correspondingly, the starting point of the phase boundary for the incommensurate film thickness in Figure 6(a) will be below that for the commensurate film thickness. This will eventually lead to the intersection between the phase boundaries of these two film thicknesses. We can understand this intriguing phenomenon by noticing that in this range of the film thickness, the corresponding value of δ as well as γ never exceeds 5. For such small γ as discussed in Sec. III B, the modified substrate is so soft that the grafted homopolymers can penetrate into the interfaces of A-rich and B-rich domains of $L_{||}$. Consequently this interpenetration weakens the incompatible interactions between A and B components in the A-B interfaces. This effect then compensates the frustration of $L_{||}$ arising from the deviation of the film thickness from the commensurate value. Such a delicate balance between the effects of the interpenetration and the frustration leads to almost a flat phase boundary in Figure 6(b) for those weakly incommensurate film thicknesses.

For the copolymer-grafted confinement model in the work of Trombly *et al.*,^{35,36} the phase diagram degenerates into a vertical line shown as a dashed line in Figure 6(a) since in this system γ is fixed at $\chi_{AB}N/2$. In this respect, the homopolymer-grafted confinement is superior to the specific copolymer-grafted confinement because it has a larger parameter space to tune in order to stabilize $L_{\perp}$. However, we are aware of that the parameter space of the copolymer-grafted confinement model can be expanded by removing the restriction on using identical components in both grafted copolymers and dBCPs. The introduction of the γ parameter enables us to understand the role of grafted polymers whose composition is dissimilar to that of dBCPs. Allowing the composition being different is sometimes important for experimental studies. For example, Keen *et al.*⁵³ reported a study of controlling the alignment of a high- χ material (PS-*b*-PDLA) on substrates modified by PS-*r*-PMMA. In their case, it is impossible to generate random copolymers from styrene and lactide, which forces them to use PS-*r*-PMMA instead of PS-*r*-PDLA as grafted polymers.

IV. CONCLUSIONS

In summary, the stability competition between $L_{||}$ and $L_{\perp}$ under soft confinement has been demonstrated using SCFT calculations. The soft confinement using homopolymer-grafted confining walls allows us to divide the surface interaction into two independent contributions: the surface softness (γ) and the surface preference (δ). With this separation, we elucidate the connection among bare hard wall confinement (SST), hard confinement modeled by the “masking” technique, and soft confinement. Soft confinement reduces to the mask hard confinement at large γ (ignoring the negligible

rearrangement effect) and to the SST hard confinement in the limit of $\gamma \rightarrow \infty$. It is also possible to map the soft confinement model using ideal random copolymer-grafted substrates onto our model by establishing a linear relation between f_A and δ , both controlling the surface preference in its corresponding model. Hence we believe that this separation of surface interactions into two independent parts is universal as long as no internal phase separation occurs across the confining wall itself.

Based on this model of surface interactions, we show that the homopolymer-grafted confinement is indeed a versatile platform for creating stable $L_{\perp}$ that should be seriously considered in experiments and industrial applications. By varying the surface softness and the surface preference of the confining wall, we identify a reasonable window of $L_{\perp}$ in the phase diagram of the alignment of self-assembled domains even when the confining wall is highly selective to one of blocks of the dBCP. It thus brings more options in devising substrates that favor $L_{\perp}$ by tweaking other properties of substrates that are hopefully easier to control such as the composition, length, and/or grafting density of grafted homopolymers.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the formulation and implementation of numerical SCFT method, the formulation of SST, the difference of the free energy as a function of the film thickness, and the distribution of joint monomers of parallel lamellae.

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¹R. R. Dammel, *J. Photopolym. Sci. Technol.* **24**, 33 (2011).

²*Directed Self-assembly of Block Copolymers for Nano-manufacturing*, edited by R. Gronheid and P. Nealey (Elsevier, Cambridge, 2015).

³F. S. Bates, M. A. Hillmyer, T. P. Lodge, C. M. Bates, K. T. Delaney, and G. H. Fredrickson, *Science* **336**, 434 (2012).

⁴M. W. Matsen, *Macromolecules* **45**, 2161 (2012).

⁵Y. Gao, H. Deng, W. Li, F. Qiu, and A. C. Shi, *Phys. Rev. Lett.* **116**, 068304 (2016).

⁶D. J. Herr, *J. Mater. Res.* **26**, 122 (2011).

⁷H. C. Kim, S. M. Park, and W. D. Hinsberg, *Chem. Rev.* **110**, 146 (2010).

⁸T. P. Russell, G. Coulon, V. R. Deline, and D. C. Miller, *Macromolecules* **22**, 4600 (1989).

⁹P. Lambooy, T. P. Russell, G. J. Kellogg, A. M. Mayes, P. D. Gallagher, and S. K. Satija, *Phys. Rev. Lett.* **72**, 2899 (1994).

¹⁰N. Koneripalli, N. Singh, R. Levicky, F. S. Bates, P. D. Gallagher, and S. K. Satija, *Macromolecules* **28**, 2897 (1995).

¹¹M. J. Fasolka, P. Banerjee, A. M. Mayes, G. Pickett, and A. C. Balazs, *Macromolecules* **33**, 5702 (2000).

¹²P. Mansky, *Science* **275**, 1458 (1997).

¹³Q. Wang, P. F. Nealey, and J. J. de Pablo, *Macromolecules* **34**, 3458 (2001).

¹⁴D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, and T. P. Russell, *Science* **308**, 236 (2005).

¹⁵C. M. Bates, J. R. Strahan, L. J. Santos, B. K. Mueller, B. O. Bamgbade, J. A. Lee, J. M. Katzenstein, C. J. Ellison, and C. G. Willson, *Langmuir* **27**, 2000 (2011).

¹⁶S. Kim, D. O. Shin, D.-G. Choi, J.-R. Jeong, J. H. Mun, Y.-B. Yang, J. U. Kim, S. O. Kim, and J.-H. Jeong, *Small* **8**, 1563 (2012).

- ¹⁷C. C. Liu, A. Ramírez-Hernández, E. Han, G. S. W. Craig, Y. Tada, H. Yoshida, H. Kang, S. Ji, P. Gopalan, J. J. de Pablo, and P. F. Nealey, *Macromolecules* **46**, 1415 (2013).
- ¹⁸M. S. Turner, *Phys. Rev. Lett.* **69**, 1788 (1992).
- ¹⁹D. G. Walton, G. J. Kellogg, A. M. Mayes, P. Lambooy, and T. P. Russell, *Macromolecules* **27**, 6225 (1994).
- ²⁰M. W. Matsen, *J. Chem. Phys.* **106**, 7781 (1997).
- ²¹T. Geisinger, M. Müller, and K. Binder, *J. Chem. Phys.* **111**, 5241 (1999).
- ²²E. Han, K. O. Stuenkel, Y. H. La, P. Nealey, and P. Gopalan, *Macromolecules* **41**, 9090 (2008).
- ²³W. J. Durand, M. C. Carlson, M. J. Maher, G. Blachut, L. J. Santos, S. Tein, V. Ganesan, C. J. Ellison, and C. G. Willson, *Macromolecules* **49**, 308 (2015).
- ²⁴P. Mansky, T. Russell, C. Hawker, J. Mays, D. Cook, and S. Satija, *Phys. Rev. Lett.* **79**, 237 (1997).
- ²⁵E. W. Edwards, M. F. Montague, H. H. Solak, C. J. Hawker, and P. F. Nealey, *Adv. Mater.* **16**, 1315 (2004).
- ²⁶I. In, Y.-H. La, S.-M. Park, P. F. Nealey, and P. Gopalan, *Langmuir* **22**, 7855 (2006).
- ²⁷K. O. Stuenkel, I. In, E. Han, J. A. Streifer, R. J. Hamers, P. F. Nealey, and P. Gopalan, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **25**, 1958 (2007).
- ²⁸I. Bita, J. K. W. Yang, Y. S. Jung, C. A. Ross, E. L. Thomas, and K. K. Berggren, *Science* **321**, 939 (2008).
- ²⁹R. Ruiz, H. M. Kang, F. A. Detcheverry, E. Dobisz, D. S. Kercher, T. R. Albrecht, J. J. de Pablo, and P. F. Nealey, *Science* **321**, 936 (2008).
- ³⁰G. Liu, S. Ji, K. O. Stuenkel, G. S. W. Craig, P. F. Nealey, and F. J. Himpsel, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **27**, 3038 (2009).
- ³¹S. Ji, C.-C. Liu, G. Liu, and P. F. Nealey, *ACS Nano* **4**, 599 (2010).
- ³²C. C. Liu, E. Han, M. S. Onses, C. J. Thode, S. Ji, P. Gopalan, and P. F. Nealey, *Macromolecules* **44**, 1876 (2011).
- ³³C. J. Thode, P. L. Cook, Y. Jiang, M. Serdar Onses, S. Ji, F. J. Himpsel, and P. F. Nealey, *Nanotechnology* **24**, 155602 (2013).
- ³⁴D. W. Janes, C. J. Thode, C. G. Willson, P. F. Nealey, and C. J. Ellison, *Macromolecules* **46**, 4510 (2013).
- ³⁵D. M. Trombly, V. Pryamitsyn, and V. Ganesan, *Phys. Rev. Lett.* **107**, 148304 (2011).
- ³⁶D. M. Trombly, V. Pryamitsyn, and V. Ganesan, *Macromolecules* **44**, 9867 (2011).
- ³⁷G. E. Stein, N. Mahadevapuram, and I. Mitra, *J. Polym. Sci., Part B: Polym. Phys.* **53**, 96 (2015).
- ³⁸K. R. Shull, *Macromolecules* **25**, 2122 (1992).
- ³⁹G. T. Pickett and A. C. Balazs, *Macromolecules* **30**, 3097 (1997).
- ⁴⁰D. Meng and Q. Wang, *J. Chem. Phys.* **126**, 234902 (2007).
- ⁴¹V. V. Ginzburg, J. D. Weinhold, P. D. Hustad, and P. Trefonas III, *J. Photopolym. Sci. Technol.* **26**, 817 (2013).
- ⁴²P. Mansky, T. P. Russell, C. J. Hawker, M. Pitsikalis, and J. Mays, *Macromolecules* **30**, 6810 (1997).
- ⁴³E. Huang, P. Mansky, T. P. Russell, C. Harrison, P. M. Chaikin, R. A. Register, C. J. Hawker, and J. Mays, *Macromolecules* **33**, 80 (2000).
- ⁴⁴J. N. L. Albert and T. H. Epps, *Mater. Today* **13**, 24 (2010).
- ⁴⁵G. Pandav, W. J. Durand, C. J. Ellison, C. G. Willson, and V. Ganesan, *Soft Matter* **11**, 9107 (2015).
- ⁴⁶Y. X. Liu and H. D. Zhang, *J. Chem. Phys.* **140**, 224101 (2014).
- ⁴⁷H. Yabu, T. Higuchi, and H. Jinnai, *Soft Matter* **10**, 2919 (2014).
- ⁴⁸T. Higuchi, M. Pinna, A. V. Zvelindovsky, H. Jinnai, and H. Yabu, *J. Polym. Sci., Part B: Polym. Phys.* **54**, 1702 (2016).
- ⁴⁹G. M. Perera, C. Wang, M. Doxastakis, R. J. Kline, W.-I. Wu, A. W. Bosse, and G. E. Stein, *ACS Macro Lett.* **1**, 1244 (2012).
- ⁵⁰X. Man, J. Tang, P. Zhou, D. Yan, and D. Andelman, *Macromolecules* **48**, 7689 (2015).
- ⁵¹M. W. Matsen and J. M. Gardiner, *J. Chem. Phys.* **115**, 2794 (2001).
- ⁵²R. Guo, E. Kim, J. Gong, S. Choi, S. Ham, and D. Y. Ryu, *Soft Matter* **7**, 6920 (2011).
- ⁵³I. Keen, A. Yu, H.-H. Cheng, K. S. Jack, T. M. Nicholson, A. K. Whittaker, and I. Blakey, *Langmuir* **28**, 15876 (2012).