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Diblock copolymer lamellae on sinusoidal and fractal surfaces

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A scaling analysis of equilibrium orientation of diblock copolymer molecules on fractal surfaces and a brief comparison with a particular experiment is presented in this paper. This work is motivated by a recent experimental finding that a diblock copolymer film of polystyrene-PMMA, when deposited on a rough substrate, can orient its lamellae from a parallel to a perpendicular configuration depending on the topographical characteristics of the substrate surface. It was found that the RMS height itself is not enough to effect the equilibrium configuration, but the fractal dimension of the surface is also important. In general, the orientation of lamellae is a function of the the power spectral density (PSD) curves of the underlying substrate surface. Assuming the diblock lamellae to behave like an Alexander-deGennes brush, we obtain the free energy expressions for this brush in both parallel and perpendicular orientations in various asymptotic regimes. Comparison of their free energy expressions predicts the equilibrium configuration. By examining the PSD curves and using our scaling results, we are able to qualitatively explain some aspects of the experimental observations regarding the equilibrium orientation of the diblock copolymer lamellae on rough surfaces. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3685223]

I. INTRODUCTION

Block copolymers possess a rich phase behavior in both bulk and confined geometries due to their ability to undergo micro-phase segregation and thereby form ordered meso-structures such as one dimensionally periodic lamellae, cylinders arranged on a two-dimensional hexagonal lattice, and spheres arranged on a three-dimensional bcc lattice. Their phase behavior has been studied extensively both theoretically and experimentally, and the free energy minimization criterion has been successfully applied to uncover the underlying physics.[1–8] These materials offer a wide range of tunable parameters for realizing microstructured fluids for various interesting applications such as nanopatterning, fuel cell membranes, solar cells, optoelectronics, strong elastomers, etc.[9–17] In confined geometries such as thin films, the properties of substrate surface also become important constraints in dictating the equilibrium behavior of the molecules in the film.[3,18–23]

Owing to their propensity to form ordered structures, block copolymers are suitable candidate materials for fabricating ordered micro/nanopatterned thin films. In a thin film, self-assembled block copolymer lamellae can be oriented parallel or perpendicular to the substrate surface. Since, for the purpose of nanopatterning, a perpendicularly oriented lamellae would be more suitable, therefore control over their orientation is highly desirable. Chemical patterning and topographical patterning of the substrate surface have been two successful techniques of generating ordered structure in the deposited block copolymer thin films where the lamellae are oriented perpendicular to the substrate.[21,22] In the former technique, the chemical nature of the substrate varies along the surface thereby modulating the surface interaction of the substrate with the block monomers, whereas in the latter, a topographical property such as the surface height is modulated. Effect of variation in height modulation, the subject of the current work, has attracted interest of both theorists and experimentalists.[24–32] On a surface with sinusoidally varying height profile with a single wavelength, large amplitude is believed to result into lamellae oriented perpendicular to the surface. This can be attributed to a smaller bending energy of the interface in the perpendicular lamellar arrangement as compared to the parallel lamellae, when surface amplitude variation is large. However, since the wavelength (or $\mathbf{k} = 2\pi/\lambda$) of the modulation of the underlying substrate is also an important parameter, therefore, in a fractal surface wherein various wavelength regimes are simultaneously present with varying strength, consideration of power spectral density of the surface which is directly related to the fractal dimension, becomes important in predicting the equilibrium orientation of the molecules on a fractal surface. It would appear intuitively that higher the RMS height of the substrate, the lamellae are always more likely to organize in perpendicular configuration in an effort to minimize the surface energy of the interface between two monomeric domains.[32] However, it has been observed experimentally by Kulkarni *et al.*[33] that a substrate with surface RMS height (30 Å) as large as the lamellar domain size (30 /AA), achieved less perpendicularly oriented lamellae than the one with smaller RMS height (5 Å). The two surfaces differed in their fractal nature.[33]

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We treat the two-dimensional fractal surface having height variation along the third dimension as an isotropic random fractal surface, which, like a Fourier series, can be considered to be a linear superposition of multiple sinusoids with varying amplitudes. However, unlike in a Fourier sum, the frequencies of the component-sinusoids of a random fractal don't increase in arithmetic progression but in geometric progression.[34–36] Therefore, before analyzing the effect of the entire spectrum, it is useful to analyze the effect of a single sinusoid with wave-vector lying in different asymptotic limits. Eventually, the effect of the fractal nature of the surfaces is estimated by considering the power spectra of their height variations, which essentially characterize the relative strengths of various component sinusoids, in our asymptotic results. In this paper, the general expressions of free energy for perpendicular and parallel lamellae films on a sinusoidally varying substrate in various regimes are derived first under some simplifying assumptions. When comparing to the experimental results in Sec. IV the fractal nature of the surface is accounted for by consideration of their power spectral density functions.

We assume that the lamellae can be treated as an Alexander-deGennes brush[37,38] with the domain interface acting as a grafting surface. The substrate surface height is assumed to have a sinusoidal variation along the spatial coordinates. We also ignore the effect of polymer-air and polymer-substrate interfacial energy. We justify ignoring these important interactions by referring to the the experiments to which we compare our analytical results. The authors in Ref. 33 were able to pre-treat the substrate surface so as to make them neutral with respect to the two monomers. The details are presented in Sec. IV. Only interfacial energy considered in this analysis is the one between the monomeric domains. Finally, we apply these results obtained for various **k**-regimes to the case of the aforementioned experimental observation on a fractal surface. Our results confirm the experimental findings that both the RMS height as well as the power spectral density (PSD) of various length scales present in the substrate surface are important in influencing the equilibrium lamellar orientation.

We consider a lamellar monolayer film on a flat substrate shown in Figure 1 as our reference configuration, which has the following reference free energy per unit area (in units of kT):

$$f_0 \approx \gamma + \frac{h_0^3}{4N^2 b^2 v}, \qquad (1)$$

where the first term on right corresponds to the surface tension of the *AB* interface, and the second term accounts for the conformational free energies of the blocks acting like brush molecules lying on both sides of the interface (henceforth referred as $f_{0,\text{stretch}}$). Here, we have assumed the diblock copolymer to be conformationally symmetric, so that N, the chain length, b, the statistical segment length, and v, the monomeric volume, are the same for two monomers A and B. h_0 is the domain size of the lamellae, which is twice the brush height. Note that this total unperturbed free energy remains the same irrespective of whether the monolayer film is realized using parallel or perpendicular configuration.

The organization of this paper is as follows. In Sec. II, we analyze the case of diblock copolymer thin films where lamellae are arranged parallel to a sinusoidally undulating surface. We derive general expressions for the cases when the interface between the monomeric domains A and B is flat and oscillating in phase with the underlying substrate. In Sec. III A, the case of lamellae oriented perpendicular to a sinusoidally varying substrate is presented. Both parallel and perpendicular orientation are treated in various asymptotic limits of experimental interest as discussed in the next paragraph. Results obtained for perpendicular and parallel lamellae are used for explaining some recent experimental observations in Sec. IV.

Various length scales of interest in the problem are h_0, the unperturbed domain spacing (also equal to twice the brush height), ϵh_0, the amplitude of oscillation of the periodically oscillating substrate surface (see Figure 2), and λ, the wavelength of the oscillation. Consequently, following asymptotic limits of experimental interest are considered in this paper:

  (i) $\epsilon \ll 1, \lambda \ll \epsilon h_0$,
  (ii) $\epsilon \ll 1, \epsilon h_0 \ll \lambda \ll h_0$,
  (iii) $\epsilon h_0 \ll \lambda, h_0 \approx \lambda$, and
  (iv) $\epsilon \approx 1, \epsilon h_0 \ll \lambda$.

The case of large ϵ will be considered elsewhere since this regime is not relevant to the experimental results of interest.

II. MONOLAYER LAMELLAR FILMS IN PARALLEL ORIENTATION

In this section, we obtain expressions for free energy for lamellar monolayer films with oscillating (Figure 2) and flat (Figure 2) interface. We assume that the substrate surface has a sinusoidal profile with height h varying as a sine function
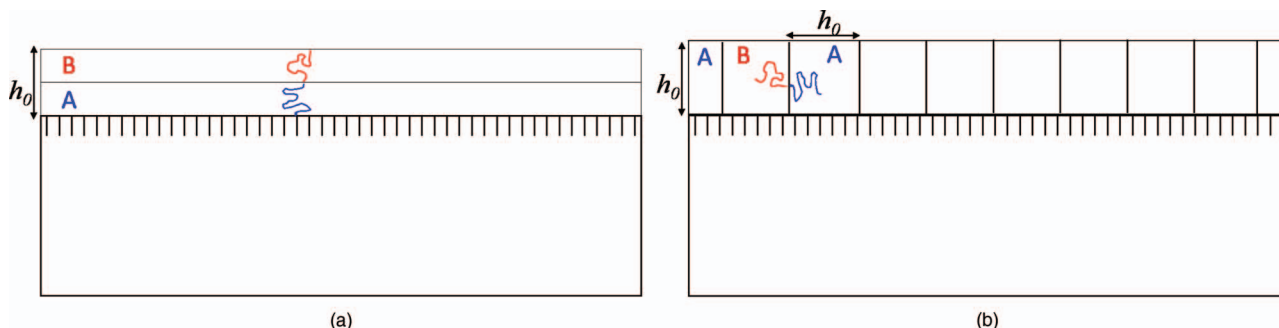

FIG. 1. Monolayer thick lamellar film on a flat substrate taken as a reference configuration for calculating the change in free energy. (a) and (b) have the same free energy given by the Eq. (1).
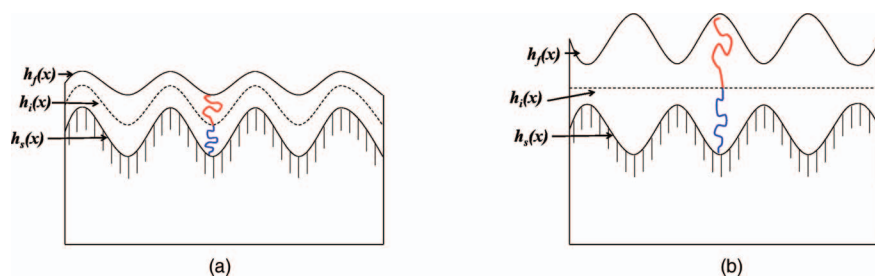
FIG. 2. (a) Geometry of monolayer lamellar film where the lamellae are arranged parallel to the substrate such that the monomer interface oscillates in phase with the substrate. (b) Geometry of parallel monolayer lamellar film with a flat interface. A representative diblock copolymer chain is also shown in each case.

along x-axis. The substrate surface height does not vary along y-direction. The lamellae are arranged such that the block interface lies on an average parallel to the substrate surface. The chains extending out from the AB interface assume brush like configuration under strong segregation, and the interface acts like the grafting surface of the brush. The grafting density of the interface and the brush height (which is half the domain spacing) are adjusted so as to minimize the sum of two competing energies: the chain stretching energy and the interfacial energy. We further assume the simpler case of an Alexander-de-Gennes (AdG) brush in which all chain-ends are acted upon by a fictitious force and are constrained to reside at the top surface of the brush. Free energy of such a brush on a flat surface is given by Eq. (1).

A. Oscillating interface

We first analyze the case of monolayer of lamellae such that the interface between the two blocks A and B conformally undulates along the substrate. In *absence* of surface undulations, such a brush would have an equilibrium height $h_0 = \sigma_0 N v$, where σ is number of molecules per unit area extending out from the interface, N the number of monomers in the chain, and v is the monomeric volume. This equilibrium brush height results from a balance between two competing effects of chain stretching energy and interfacial energy and the constraint of incompressibility.[8] The brush adjusts its σ to assume a minimum energy configuration.

The profiles for the substrate height $h_s(x)$, interfacial height $h_i(x)$, and the monolayer film height $h_f(x)$ are assumed to have the following forms:

$$h_s(x) = \frac{h_0}{2}\epsilon_s \sin(kx), \qquad (2)$$

$$h_i(x) = \frac{h_0}{2}\left(1 + \frac{\epsilon_s + \epsilon_f}{2}\sin(kx)\right), \qquad (3)$$

and

$$h_f(x) = h_0 + \frac{h_0}{2}\epsilon_f \sin(kx), \qquad (4)$$

such that $h_i(x) = (h_s(x) + h_f(x))/2$, that is, the block interface is positioned halfway between the film-top and the substrate. Various heights are measured from the mean surface height of the substrate. The brush heights at any x are equal on either side of the interface. The oscillation amplitudes $\epsilon_s h_0/2$ and $\epsilon_f h_0/2$ are much smaller than h_0 but are of the same order. In

general the two amplitudes of undulations $\epsilon_s h_0/2$ and $\epsilon_f h_0/2$ are assumed to be unequal. As a result the brush height also varies along the x-direction and the dependency is given by the following equation:

$$\begin{aligned} B(x) &= h_i(x) - h_s(x) = h_f(x) - h_i(x) \\ &= \frac{h_0}{2}\left(1 + \frac{\epsilon_f - \epsilon_s}{2}\sin(kx)\right) = \sigma(x)Nv, \end{aligned} \qquad (5)$$

where $\sigma(x)$ is the grafting density at a position x.

Next we calculate the stretching and interfacial energy contributions to the free energy per unit length along y direction. We consider a film with a lateral dimension of $\lambda = 2\pi/k$ along the x-direction. Interfacial energy per unit area between A and B microdomains is given by γ (in units of kT). The stretching energy per unit area is given by the energy per molecule times the number of molecules per area. The stretching energy of each molecule (in units of kT) can be estimated by using the Gaussian coil assumption and is given by

$$F_{\text{molecule}}(x) \approx \frac{B(x)^2}{Nb^2}, \qquad (6)$$

where b is the statistical segment length. The stretching energy per unit area is given by

$$\begin{aligned} f_{\text{stretch}} &= \frac{2}{\lambda}\int_0^\lambda dx\,\sigma(x)\frac{B(x)^2}{Nb^2} \\ &\quad \times \sqrt{1 + \frac{h_0^2}{4}\left(\frac{\epsilon_s + \epsilon_f}{2}\right)^2 k^2 \cos^2(kx)} \\ &= \frac{h_0^3}{4\lambda N^2 b^2 v}\int_0^\lambda dx\left(1 + \frac{\epsilon_f - \epsilon_s}{3}\sin(kx)\right)^3 \\ &\quad \times \sqrt{1 + \frac{h_0^2}{4}\left(\frac{\epsilon_s + \epsilon_f}{2}\right)^2 k^2 \cos^2(kx)}. \end{aligned} \qquad (7)$$

The interfacial energy contribution is given by the product of interfacial tension γ and interfacial area,

$$f_{\text{int}} = \frac{\gamma}{\lambda}\int_0^\lambda dx\sqrt{1 + \frac{h_0^2}{4}\left(\frac{\epsilon_s + \epsilon_f}{2}\right)^2 k^2 \cos^2(kx)}. \qquad (8)$$

Change in free energy is given by the $\Delta f = f_{\text{stretch}} + f_{\text{int}} - f_0$.

B. Flat interface

Since the interface where chains originate is assumed flat and the surface where they end is curved, the x-coordinate of

the first monomer of any chain should be different from that of the last monomer, unlike in a brush with a flat free surface. However, as has been argued by Turner and Joanny,[25] the deflection in the chain molecules along the course of its trajectory is of the order of ϵ^2. Therefore, in the present analysis, we ignore this small lateral deflections in the chains and assume them to be perfectly vertical, i.e., all the monomers on a chain have the same x-coordinates as depicted in Figure 2. With this assumption, the profiles for the substrate height $h_s(x)$, interfacial height $h_i(x)$, and the brush height $B(x)$ will have the following forms:

$$h_s(x) = \frac{\epsilon_s h_0}{2} \sin(kx), \tag{9}$$

$$h_i(x) = \frac{h_0}{2}, \tag{10}$$

and

$$B(x) = h_i(x) - h_s(x) = \frac{h_0}{2}\left[1 - \epsilon_s \sin(kx)\right], \tag{11}$$

where all heights are measured from the mean substrate surface position as before. We calculate the change in free energy value as done in Subsection II A. In the present case, there is no change in the interfacial energy since the interface remains flat as in the reference configuration. The change in the free energy is entirely due to stretching and is given by the following expression:

$$\Delta f = \frac{h_0^3}{4N^2 b^2 v}\left(\frac{1}{\lambda}\int_0^\lambda dx(1 - \epsilon_s \sin(kx))^3 - 1\right). \tag{12}$$

Next we consider these the cases of flat and oscillating interface lamellar monolayer films in various asymptotic limits.

C. $\epsilon \ll 1, \lambda \ll \epsilon h_0$

1. Oscillating interface

In this limit, the amplitude of oscillation is much smaller than the domain size, and the oscillation wavelength is much smaller than the oscillation amplitude. In practical terms, this limit is applicable to surfaces with highly oscillating surface but small RMS height. Simplifying the equations derived in Sec. II B, the change in free energy for an oscillating interface configuration can be written as

$$\Delta f \approx (f_0 + \gamma)\frac{h_0(\epsilon_s + \epsilon_f)k}{2\pi}. \tag{13}$$

2. Flat interface

For a flat interface, we obtain the following expression for the change in free energy,

$$\Delta f = \frac{3h_0^3}{16\pi N^2 b^2 v}\epsilon^2. \tag{14}$$

Comparing Eqs. (13) and (14) suggests that in large-k limit, a flat interface will be preferred and the free energy is given by the Eq. (14). This is physically plausible, because when

the oscillation in the substrate surface is fast enough, then the chains don't have to extend to large distances in order to place their ends at the surface, a constraint assumed in the definition of AdG brush. Therefore, chains can afford small stretching and thereby decrease their interfacial energy. Hence, in the large-k limit, the effect of interfacial energy dominates the chain stretching.

D. $\epsilon \ll 1, \lambda \gg \epsilon h_0$

1. Oscillating interface

In this limit, parallel lamellae with oscillating interface have the following free energy:

$$\Delta f \approx \frac{h_0^2 k^2 f_0 (\epsilon_s + \epsilon_f)^2}{128\pi} + \frac{3h_0^3(\epsilon_s - \epsilon_f)^2}{64\pi N^2 b^2 v}, \tag{15}$$

which, on minimizing with respect to ϵ_f yields the following ϵ_f:

$$\frac{\epsilon_f}{\epsilon_s} \approx \frac{24 - h_0^2 k^2}{24 + h_0^2 k^2}, \tag{16}$$

and the free energy is given by the following equation:

$$\Delta f \approx \frac{3h_0^3 k^2 f_0 \epsilon_s^2}{16\pi(6h_0 + k^2 N^2 b^2 v f_0)}. \tag{17}$$

It can be shown that, in the limit currently considered, the second term in the brackets in the denominator appearing in the above equation can dominate the first term when the following condition is met by ϵ_s:

$$\epsilon_s \ll \frac{1}{24}\left[1 + \frac{\gamma}{4 f_{0,\text{stretch}}}\right]. \tag{18}$$

When the above condition is satisfied, then for $k_1 \ll k \ll 1/(\epsilon_s h_0)$, where $k_1 = \sqrt{\frac{24 h_0}{h_0^3 + \gamma N^2 b^2 v}}$, the free energy becomes independent of the wave-vector and γ, and is given by

$$\Delta f \approx \frac{3h_0^3}{16\pi N^2 b^2 v}\epsilon_s^2 \quad \text{for } k_1 \ll k \ll 1/(\epsilon_s h_0). \tag{19}$$

For $k \ll k_1$,

$$\Delta f \approx \frac{3f_0}{16\pi}(\epsilon_s h_0 k)^2. \tag{20}$$

2. Flat interface

The free energy for flat interface lamellae is given by the following equation:

$$\Delta f \approx \frac{3h_0^3}{16\pi N^2 b^2 v}\epsilon_s^2, \tag{21}$$

which is independent of the wave-vector. Interestingly, this expression is the same as that obtained for oscillating lamellae satisfying Eq. (18), and given by Eq. (19). However, in order to compare whether lamellae with flat or oscillating interface survive in the limit of small ϵ and small k, one needs to compare the free energy Eqs. (20) and (21), which suggests that oscillating interface is favored in this limit. This result is physically plausible since for large wave-length modulations,
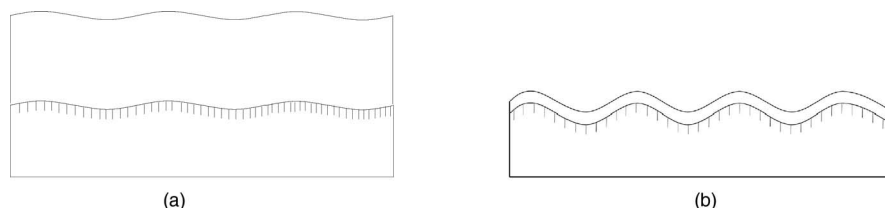
FIG. 3. The monolayer film in "fat" monolayer limit (a) and "thin" monolayer limit (b).

chains in the brush with flat interface will need to stretch strongly in order to place their chain-ends at the oscillating surface. This large stretching energetic penalty is avoided by the interface at the expense of small interfacial energy, by conformally following the substrate surface. Our analysis also predicts that, in this limit, the amplitude of modulation of the top surface of the monolayer film is smaller than the substrate amplitude (Eq. (16)). This implies that a diblock copolymer film of multiple lamellae will possess increasingly smaller amplitude of the film height modulation as the number of layers is increased. This is an effect known as planarization, an important step in microfabrication processes, and our model predicts that planarization is favored in a diblock copolymer thin film in the concerned limit.

E. $\epsilon \ll 1, \lambda \approx h_0$ ("fat" monolayer limit)

This special case depicted in Figure 3(a) is relevant to the experimental results to be discussed later.

1. Oscillating interface

Using the condition $h_0 k \approx 1$ in Eq. (17), we obtain the following expression for the free energy in "fat" monolayer limit:

$$\Delta f \approx \frac{3\epsilon_s^2 h_0 f_0}{4\pi (25h_0 + 4\gamma k^2 N^2 b^2 v)}. \tag{22}$$

For $\gamma \gg f_{0, \text{stretch}}$, the free energy is given by

$$\Delta f \approx \frac{3\epsilon_s^2 f_0}{4\pi} \quad \text{for} \ \gamma \gg f_{0,\text{stretch}}, \tag{23}$$

whereas for $\gamma \ll f_{0, \text{stretch}}$,

$$\Delta f \approx \frac{3\epsilon_s^2 f_0}{100\pi} \quad \text{for} \ \gamma \ll f_{0,\text{stretch}}. \tag{24}$$

2. Flat interface

For flat interface lamellae in "fat" monolayer limit, the free energy is given by

$$\Delta f \approx f_0 \epsilon_s^2. \tag{25}$$

These results suggest that lamellae with flat interface closely compete with those with oscillating interface, with the latter somewhat more stable than the former.

F. $\epsilon \approx 1, \lambda \gg h_0$ ("thin" monolayer limit)

In this limit, the amplitude of the surface modulation is large, and is comparable to the domain size. However, the modulation wave-vector is small. Therefore, from physical considerations, formation of flat interface lamellae can be ruled out. In this limit, we only consider lamellae with oscillating interface. This limit is also relevant to experimental results as will be discussed later.

1. Oscillating interface

Using Eq. (16), it can be seen that $\epsilon_f = \epsilon_s(1 + O(h^2 k^2))$. Therefore, the amplitude modulation is effectively undamped in this limit. The general expression for the leading correction in free energy in this limit is given by

$$\Delta f \approx \frac{3 f_0 h_0}{16\pi} \frac{h_0^2 k^2}{6h_0 + \gamma k^2 N^2 b^2 v}. \tag{26}$$

If $f_{0, \text{stretch}} \ll \gamma$, then it is possible to find an interval in wave-vector in which the free energy becomes independent of k. This interval is given by $k_2 \ll k \ll 1/h_0$, where $k_2 \approx \sqrt{\frac{6h_0}{\gamma N^2 b^2 v}}$, and the free energy in this range of wave-vectors is given by $\Delta f \approx \frac{3}{4\pi} f_{0,\text{stretch}}$. For $k \ll k_2$, the free energy is given by the following expression:

$$\Delta f \approx \frac{3 f_0}{96\pi} h_0^2 k^2. \tag{27}$$

III. PERPENDICULAR LAMELLAE

In this section, we analyze the case of a lamellar monolayer film having the same volume per unit area (and therefore the same thickness) as in the case of parallel lamellae. We calculate free energy for the same limiting cases and compare the values to determine whether parallel or a perpendicular lamellar film will be stable in each case.

A. $\epsilon \ll 1, \lambda \ll \epsilon h_0$

We employ results obtained by Kim and O'Shaughnessy[39] in order to analyze the case of vertically oriented lamellae at high k values. Kim and O'Shaughnessy considered nanoinclusions inside a brush and calculated the chain-stretching penalty for an equilibrated brush-particle system. It is possible to extend their results to the present problem of vertically oriented lamellae. The analogy is as follows. In vertically oriented lamellae, the extended chain molecules which are in immediate contact with the rough
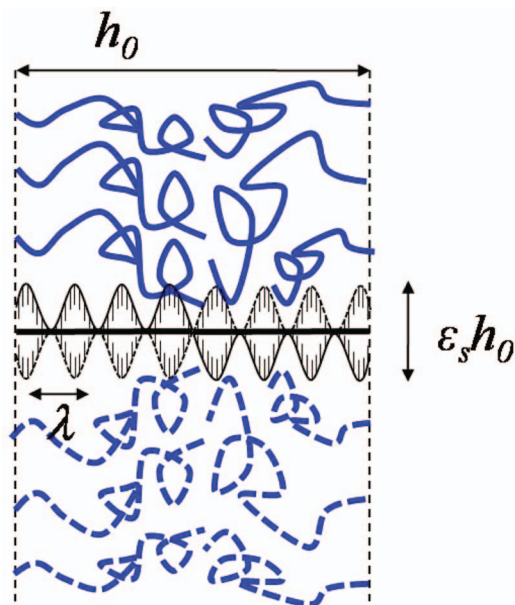
FIG. 4. Schematic of the method used for treating the problem of perpendicular lamellae on rough surface as one with brush containing nanoinclusions. The thick horizontal line is the mirror surface about which the original system of perpendicular lamellae on a rough substrate (depicted as hatched area bounded with a curved line) is reflected. Augmenting the original system on top with its reflection on bottom presents a system where the hatched area can be considered as nanoparticles immersed in a brush.

surface, are oriented along the surface and therefore their stretching is modified since the undulations and asperities can be treated as nanoinclusions immersed inside an unperturbed brush. The monomer interface that acts like a grafting surface stands perpendicular to the substrate, and these nanoinclusion laterally constraint the chain molecules. In order to be able to apply Kim and O'Shaughnessy's analysis, we consider a system prepared by augmenting our system of vertical lamellae arranged on a undulated substrate with its mirror image about the mean substrate position. The scheme is shown in Figure 4. The free energy of the chains lying on the modulated surface can be taken to be equal to that of the augmented system in which a line of particles with a hatched cross section area of $\approx h_0 \epsilon \lambda$ has been introduced inside an unconstrained brush. Thus we map our problem of interest to that of a brush containing a line of nanoinclusions. Note that the nanoinclusion results which assume a constant grafting density of the brush cannot be suitably extended for parallel lamellae since grafting density is not constant at the monomer interface, and is adjusted according to the available height in parallel lamellae. However, in the limit currently being considered, the height up to which the chains are perturbed should be on the order of ϵh_0, much smaller than the film thickness $\approx h_0$. Therefore, the grafting density in the interface can be assumed constant for the entire height of the interface.

Kim and O'Shaughnessy showed that the change in free energy due to a nanoinclusion of volume v_p at a height z where pressure is P, is of the order of Pv_p. We use this result to obtain the fractional change in free energy per unit area for two different cases. The pressure in the considered AdG brush is of the order of $h_0^2/(N^2 v b^2)$ in units of kT. Also, since for a molten brush the density and the film thickness ($\approx h_0$) remains
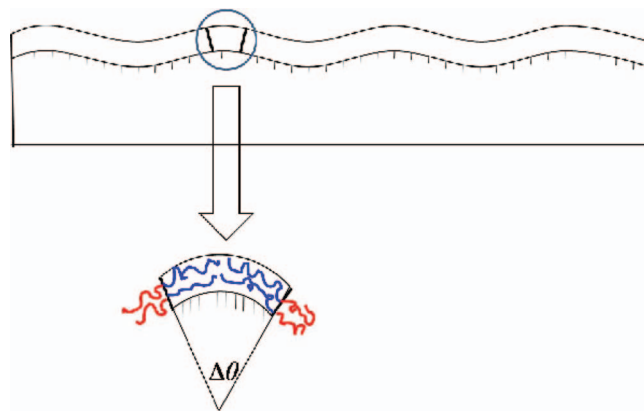

FIG. 5. The lamellar monolayer thin film oriented perpendicular to the substrate in small $\epsilon h_0 k$ limit. An enlarged view of one lamella is also shown.

the same, therefore the total interfacial area does not change as compared to the parallel arrangement. Therefore, the interfacial energy per unit area remains unchanged. Thus the free energy change per unit area is given by the following relation:

$$f - f_0 \approx \frac{h_0^2}{N^2 v b^2} \epsilon h_0 = 4\epsilon f_{0,\text{stretch}}. \tag{28}$$

A comparison with Eq. (14) shows that a parallel lamellar film with a flat interface will be more stable in this asymptotic limit.

In Sec. IV, we consider a diblock copolymer thin film on a fractal surface that possesses a range of length scales of modulations with a prescribed power spectral density, and compare the free energies of parallel and perpendicular arrangements of lamellae.

B. $\epsilon \ll 1$, $\lambda \gg \epsilon h_0$

This case is shown schematically in Figure 5. The free energy per lamella per unit length perpendicular to the plane (the section is also shown in the Fig. 5) is given by $\frac{3h_0^4}{4N^2 b^2 v} \Delta\theta^2$. Since $\Delta\theta \approx \epsilon h_0/\lambda$, we get the following expression for free energy per unit area:

$$\Delta f \approx \frac{3h_0^3}{4N^2 b^2 v}(\epsilon h_0 k)^2. \tag{29}$$

C. $\epsilon \ll 1$, $\lambda \approx h_0$ ("fat" monolayer limit)

For a perpendicular arrangement of lamellae in "fat" monolayer limit, the effect of surface undulations only persist up to a height ϵh_0 into the film. The chains in each lamella undergoes a stretching of the order of ϵh_0. Therefore, the free energy change per unit area is given as follows:

$$\Delta f \approx \frac{(\epsilon h_0)^2}{N b^2} \sigma \frac{\epsilon h_0}{\lambda} = \epsilon_s^3 \frac{h_0^3}{N^2 b^2 v}. \tag{30}$$

We note that in the "fat" monolayer limit, the leading correction to the the free energy for a perpendicular arrangement is cubic in ϵ. Comparing this expression for its counterpart for

parallel lamellae suggests that in this limit, a perpendicular arrangement is more stable.

D. $\epsilon \approx 1$, $\lambda \gg h_0$ ("thin" monolayer limit)

We can directly utilize the Eq. (29) to obtain the following expression for the free energy in this case:

$$\Delta f \approx \frac{3h_0^3}{4N^2b^2v}h_0^2k^2. \tag{31}$$

Next we compare some of our results with the experiments. As argued in Sec. IV, only the "fat" and "thin" monolayer limits are the most relevant limits for our comparison.

IV. COMPARISON WITH EXPERIMENTS

Here we utilize our results obtained for the asymptotic behavior of the diblock copolymer monolayer films on single frequency sinusoidal substrates to qualitatively explain some of the experimental results obtained by these authors on fractal surfaces. The favored configurations of a monolayer lamella in various asymptotic limits listed as (i)–(iv) at the end of Introduction can be summarized as follows based on our analysis:

(i) $\epsilon \ll 1$, $\lambda \ll \epsilon h_0$: A parallel arrangement with a flat interface is preferred. $\Delta f \approx \epsilon^2$.

(ii) $\epsilon \ll 1$, $\epsilon h_0 \ll \lambda \ll h_0$: For $k_1 \ll k \ll 1/(\epsilon h_0)$, a perpendicular arrangement is preferred whereas for $k \ll k_1$, perpendicular configuration closely competes with the parallel lamellae with an oscillating interface. $\Delta f \approx (\epsilon h_0 k)^2$.

(iii) $\epsilon h_0 \ll \lambda$, $h_0 \approx \lambda$: Perpendicular lamellar arrangement is preferred with $\Delta f \approx \epsilon^3$.

(iv) $\epsilon \approx 1$, $\epsilon h_0 \ll \lambda$: For $k_2 \ll k \ll 1/h_0$, perpendicular configuration is favored and for $k \ll k_2$, a parallel arrangement with oscillating interface closely competes with the perpendicular arrangement. $\Delta f \approx h_0^2 k^2$.

In order to apply our results to a fractal surface, we consider the surface to have a spectrum of wave-lengths. The PSD function, which is a Fourier transform of the correlation function of the height variation along a chosen line on the plane, is a measure of relative strengths of modulations with varying length-scales. A peak in the PSD curve for a given wavelength signifies a dominant length scale. The same curve can also used to estimate the fractal dimension of the surface.[34] By comparing the PSD curves of two different surfaces, we can qualitatively estimate the relative strengths of modulation in different range of wave-vectors and, subsequently, by incorporating our results from scaling analysis, qualitative conclusions can be drawn regarding the nature of self-assembled diblock monolayer films on the fractal surface. We also assume that the substrate surfaces are isotropic random fractals, that is, the statistical properties of their height variations are the same in any direction along the plane. Therefore, the plots of the PSD curves with wave-vectors will be expected to have the same characteristics irrespective of the direction of the wave-vector, and will be a function of only one vari-

able, which is the magnitude of the wave-vector. Therefore, our model which considers different range of wavenumbers in one-dimension could be satisfactorily applied to a two-dimensional fractal surface.

In the experimental study performed by Kulkarni *et al.*,[33] the morphology of PS-PMMA diblock copolymer thin films deposited on rough substrate surfaces were studied. We next describe their experiment in brief mentioning only those relevant parameters which are needed to justify our model when applied to their system. Authors in Ref. 33 used xerogels and SiO$_2$ nanoparticle coatings as means to control substrate roughness parameters. The substrate roughness was characterized by a power spectral density (PSD) analysis of the surface. For PSD analysis, 3 separate 5×5 μm^2 regions of each sample were scanned by AFM in tapping mode. The PSD from the topographic images was then calculated using an in-built software of in the AFM analysis program and averaged for all the three regions for each sample. The same analysis also gave the fractal dimensions of various surfaces. The AFM tip diameter was less than 20 nm (lateral resolution) with a vertical resolution less than 1 nm. In their experiments, addition of propyltrimethoxysilane to xerogels gives a handle to control the surface energy. By this technique, they were able to engineer a surface which was nearly neutral for the styrene and MMA monomers. This justifies our assumption of ineffective monomer-substrate interaction. The molecular weight of their PS-PMMA diblock was close to 60000 with molecular weights of individual PS and PMMA blocks respectively equal to 29 500 and 33 100. Readers are referred to Ref. 33 for further details.

One important finding of their work is that increasing the RMS height of the surface doesn't necessarily result into formation of perpendicularly oriented lamellae as efficiently as it does on a surface with smaller RMS height but with a different PSD spectrum. Summary of Kulkarni *et al.*'s results is shown in Figure 6. We will in particular address the qualitative aspects of the cases labeled 1, 2, and 3 in the Figure 6 which show a non-monotonic trend in formation of perpendicular lamellae with RMS height. These results evidently suggest that RMS height of the substrate is not solely responsible for
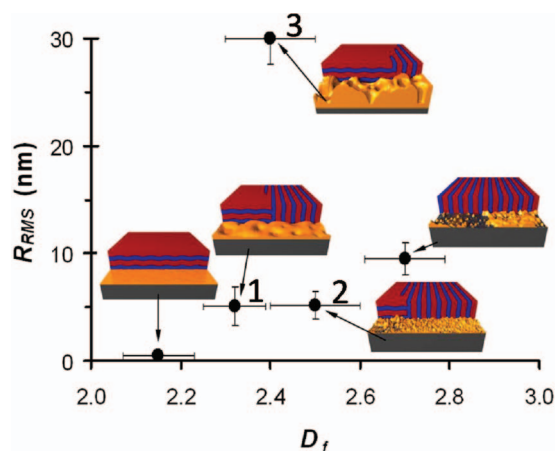

FIG. 6. Summary of results from Kulkarni *et al.* showing the percentage of perpendicular oriented lamellae as a function of substrate-surface parameters.

(a)   (b)
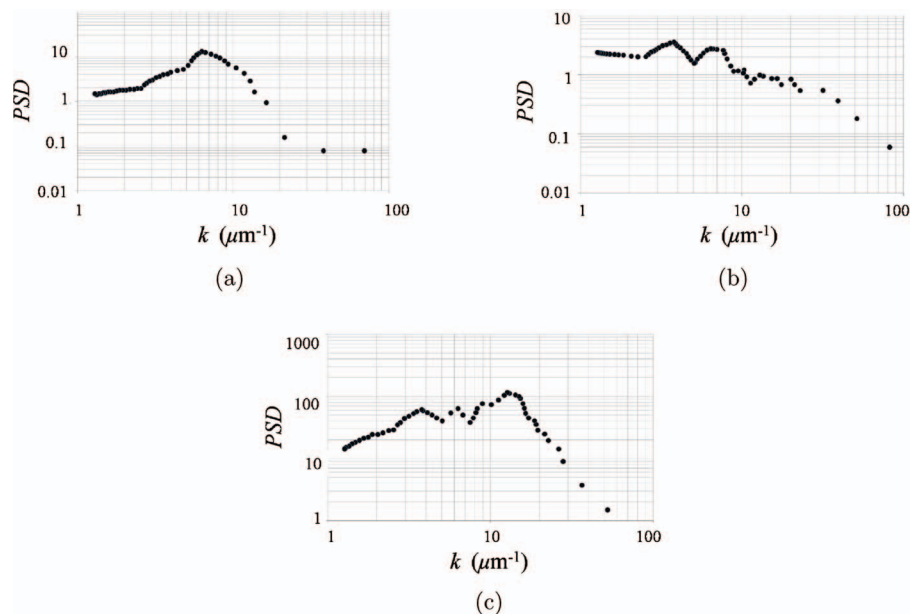

(c)

FIG. 7. Power spectra for three surfaces shown in Figure 6. (a), (b), and (c) correspond to cases labeled 1, 2, and 3 respectively in Figure 6.

reorientation of lamellae from parallel to perpendicular configuration. We show that the PSDs play an important role in effecting the morphology. The PSD curves for the surfaces 1, 2, and 3 as labeled in Figure 6 are shown in Figure 7.

Before applying our model to this system, it is necessary to make a numerical estimate of various quantities involved in the analysis. For the PS-PMMA system studied by Kulkarni *et al.*, we assume an average molecular weight of monomers to be 100 g mol^{-1}, such that $N \approx 600$, and b, the statistical segment length, is taken to be 1.8 nm.[40] γ can be evaluated using Helfand's theory[41] that predicts $\gamma \approx (\chi/6)^{1/2} \rho b kT$ where χ, the Flory interaction parameter between two monomers, has the value of 0.0375 (in units of kT), and the ρ, the density is taken to be 1 g cm^{-3}. Using these values yields $\gamma \approx 0.86$ nm^{-2}. The value of $f_{0, \text{stretch}}$, the unperturbed stretching energy per unit area, is close to 0.035 nm^{-2}. These numbers suggest that the free energy is dominated by the interfacial energy which is a consequence of the fact that this diblock system is strongly segregated. The corresponding χN is larger than 20. Therefore, our assumption of an AdG brush which implicitly assumes strong segregation is satisfied in this system. Other important parameters useful in analyzing the asymptotic behavior are the wavenumber scales k_1 and $1/h_0$ as noted in the beginning of this section. Their estimated values are respectively 10 μm^{-1} and 30 μm^{-1} for the diblock monolayer considered.

We first contrast the power spectrum of case 2, against those of 1 and 3 as labeled in Figure 6. Since formation of perpendicular lamellae is desirable for the purpose of micropatterning, we focus on the wavenumber range that favors formation of perpendicular lamellae. This range, as seen from our analysis, forms of $k_1 < k < 1/h_0$ which corresponds to approximately the wavenumbers ranging from 10 to 30 μm^{-1}. Hence we expect two surfaces drastically differing in their nature in this spectral range will effect a pronounced difference in the formation of perpendicular lamellae. Examining the power spectra of the surfaces of cases 1, 2, and 3 presented

in Figure 7 shows a marked difference in the PSD of case 2 as compared to the cases 1 and 3 in that the former has a nearly flat looking curve whereas the latter have sharply decreasing curves in this range. Therefore, it can be concluded that the case 2 will more effectively form perpendicular lamellae as compared to other two cases. This could be one explanation based why films in case 2 undergo stronger perpendicular orientation than in cases 1 and 3.

Next we contrast the case 1 against case 3. The wavenumber for $\lambda = h_0$ is around 200 μm^{-1}. The negative slope of the tail of the power spectrum for case 3 is much larger than the other. Therefore, in this range of wave-vectors, case 1 is more like lamellae in "fat" monolayer limit whereas the case 3 is closer to "thin" monolayer limit. As noted in our analysis, in fat monolayer limit, perpendicular configuration is more stable than the parallel and the trend is reverse in case of "thin" monolayer limit. Therefore, based on these arguments, the films are expected to have higher percentages of perpendicular lamellae in case 1 than in case 3, as observed in experiments. More generally, we can conclude that the amplitudes of the modulations with λ close to h_0 appears to govern the orientation of lamellae in Kulkarni *et al.*'s samples.

V. CONCLUSIONS

In summary, we have performed scaling analysis of monolayer thin films of diblock copolymer lamellae on sinusoidally oscillating surfaces within the framework of AdG brush theory. Various asymptotic limits of interest have been analyzed. Our scaling analysis predict some important results, for example, formation of flat interface vs. oscillating interface lamellae in various range of frequencies, which can be verified experimentally. The analysis results are then extended to qualitatively explain the orientation of diblock lamellar films on rough surfaces observed experimentally, by assuming the surfaces to be random isotropic fractal objects and

incorporating their PSD curves in our scaling results. Based on the comparison with experiments, we can conclude that on a fractal surface, the power spectral density of the surface plays very important role in determining the equilibrium orientation of the diblock copolymer lamellae forming the thin films.

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