Thin diblock copolymer films on patterned surfaces: Computer simulations and the Frenkel-Kontorowa model

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We study by direct numerical integration of the dynamical evolution equation the equilibrium configuration of a diblock copolymer thin film melt on a patterned surface. The surface has a large number of stripes and the mismatch between the bulk diblock spacing and the stripe width is small. We investigate primarily the formation of small discommensurations in the incommensurate phase and compare the results with the predictions of an analogous model of solid-state physics, the Frenkel-Kontorowa model. [S1063-651X(99)13811-X]

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I. INTRODUCTION

Symmetrical diblock copolymers are made up of equal sized chains consisting of *A* and *B* monomers which are tethered together at one end. A bulk melt sample of such copolymers is theoretically predicted to microphase separate into lamellae [1] consisting of a layer of *A* followed by a layer of *B* successively. However, experimentally such a well aligned bulk sample is not observed, only in local regions of the sample are well defined lamellae seen. On the whole many defects and/or dislocations prevent the build up a layered structure throughout the material. Recently there have been experimental [2] and theoretical [3–5,7–11] efforts put towards understanding how a well aligned, lamellae sample may be produced. Such lamellae may have applications in lithographic masks and devices [12]. One possible solution is to place a thin film melt of diblock copolymers onto a periodically striped surface [2,12]. The stripes may prefer one or the other block alternatively. It is hoped that if the stripe-diblock potential is sufficiently strong it will induce the lamellae to align perpendicular and commensurate with the stripes. In such cases a well defined lamellae sequence should be produced throughout the thin film.

The physics of a thin melt film is quite different from that of a bulk melt sample because of surface interfacial tensions and confinement effects [13,14]. The added effect of a striped surface makes this a rich and complex physical system. Most of the previous numerical studies [3–5] have been devoted to smaller size systems, e.g., of the order of 10–20 stripes. These studies are necessarily small because they are three-dimensional and so computational limitations determine that the grids cannot be too large. In spite of these limitations these studies have led to some important characterizations of the system. For example, it is clear to obtain perpendicular, well aligned, commensurate lamellae one requires the mismatch between bulk equilibrium diblock spacing, L_b and stripe width λ to be as small as possible and the *A* block-upper surface (air) and *B* block-air interfacial tensions to be the same. It is also probably better to have $L_b > \lambda$ than $L_b < \lambda$ since in the latter case the lamellae interfaces can undulate to relieve the strain [5,8]. Recent experimental studies [2] have produced patterned surfaces with well defined stripes of a given period. These patterned surfaces are macroscopic and have a very large number of stripes. Thus there are some aspects of these large systems that the finite size studies [3–5] do not capture.

Apart from being of obvious interest to the polymer community this system should also be of interest to traditional solid-state physicists. This is because it is a one-dimensional (1D) example of mismatch between two different ''crystalline'' materials. Mismatch between two crystalline materials is a much-studied problem in solid state physics because it occurs at the interface between any two crystalline substances. In general, two different materials will have different lattice constants, and this leads to strain whenever a layer of one substance is deposited epitaxially on another. A classic model of this kind of system was proposed early on by Frenkel and Kontorowa (FK) [6]. This FK model considers what happens when a hypothetical 1D solid with preferred lattice spacing, a_p is placed in a potential with minima spaced a distance a_s apart. If the potential is very strong the particles sit in the lowest energy states of the potential wells and a commensurate state occurs, i.e., the particle positions are commensurate with the well minima. However, for a weaker potential a transition to a discommensurate phase can occur. In this phase the particles mainly sit at the bottom of the potential minima. However, periodically a discommensuration occurs where one or more of the particles sits well away from the minima. The FK model predicts that this transition is second order. Although this model is well known and much-studied there have been few, if any, experimental examples of FK systems in 1D. Most examples in practice occur in two dimensions, where an adsorbate is placed on a crystal surface. A symmetric diblock copolymer film on a striped surface is clearly a strong candidate for study as a 1D FK system, and indeed this was partly the motivation for two of our earlier studies [7]. There we showed that in a certain limit, i.e., $\delta \equiv L_b - \lambda$ is small, weak surface potentials and perpendicular alignment of the lamellae, the diblock-stripe system was analogous to the FK model. To obtain perpendicular alignment of the lamellae to the striped surface the diblock-air interfacial tensions should be the same. In this limit most of the lamellae align commensurate with the

stripes, but every so often discommensurations appear. When L_b is slightly larger than λ these discommensurations should be manifested as lamellae with periodic spacing slightly larger than λ. (Conversely for L_b slightly smaller than λ the discommensurations should appear as lamellae with spacing slightly smaller than λ.) The discommensurations set in at a critical value δ_c such that the commensurate to incommensurate transition is continuous (or second-order). The discommensurations are predicted to appear periodically across the surface with separation χ where $\chi \propto \ln[(\delta-\delta_c)^{-1}]$. Thus, one important practical conclusion of this study [7] is that it is important to have relatively strong striped surface potentials and L_b as close as possible to λ to overcome the formation of discommensurations. Of course, all of these predictions depend in part on the mapping between the diblock model and the FK model. This mapping is good, only in the limit mentioned above.

One aim of the present study is to determine the validity of our predictions and, in some sense, how close the diblock system is to the classical FK system. The two systems are different in detail, in that they each have different Hamiltonians, but we might expect some qualitative and semiquantitative features to be the same. In particular we would hope that the diblock system would show the presence of a periodic array of discommensurations. Besides direct experimental observations, simulation studies offer the best test of theory. Monte Carlo simulations are a possible technique, but due to the fact that we require a large grid we feel it is not a feasible technique for this problem. Other techniques that could be employed are the Scheutjens-Fleer self-consistent-field method [4] or direct numerical integration of the dynamical evolution equation [5,15,16]. Of these we numerically integrate the dynamical evolution equation, but to obtain as large as possible grid sizes we restrict our simulation to 1D. This restriction means we are limited to thin films, so there is little variation perpendicular to the surface. This also means we assume translational invariance along the stripes, so that the kind of undulational instabilities we have discussed previously [8,9,11] are ignored. The gain from these simplifications is great. We can explore systems with about 500 stripes and see clear evidence of discommensurations.

II. BLOCK COPOLYMER MODEL

The technique we will use is a well established method for studying phase separation and ordering in binary systems [15,16]. It has previously been used by Chakrabarti and coworkers to study various confined thin diblock copolymer film problems [5,17,18]. It is this formalism we use in our study, but we modify it for a 1D problem. In 1D we assume that the system is invariant in the y direction (along the stripes) and also in the z direction (perpendicular to the substrate) . We now write the free energy of the system in terms of the remaining spatial variable x (in the direction across the striped surface). The free energy is a function of the order parameter $\Phi(x,t) \equiv \rho_A(x,t) - \rho_B(x,t)$, where ρ_i is the density of the ith component. The free energy is then

$$\frac{F[\Phi(x,t)]}{k_B T} = h y_\infty \left\{ \int_0^{x_l} dx \left[-\frac{b}{2}\Phi^2 + \frac{u}{4}\Phi^4 + \frac{K}{2}(\nabla\Phi)^2 + B\int_0^{x_l} dx' G(x,x')\Phi(x,t)\Phi(x',t) \right] + \int_0^{x_l} dx Q \sin(\kappa x)\Phi(x,t) \right\}, \tag{1}$$

where h is the film thickness, y_∞ is the length of the system along the stripes, and x_l is the size of the system in the x direction. The parameters b, u, K and B are related to polymer size, etc. [5]. G is the Green's function satisfying $d^2G/dx^2 = -\delta(x-x')$. The striped surface-diblock interaction is accounted for by the last term and has a sinusoidal form with amplitude Q and wavelength $2\pi/\kappa$. Q is related to the preference of the striped surface for one block over the other. It is obtained as follows: The striped surface-A-block interfacial energy is $V_{AS} = V_0 + \sigma_A \sin(\kappa x)$, where V_0 and σ_A are constants in units of $k_B T$. A similar expression may be written for the striped surface-B-block energy. Subtracting the two expressions one finds the overall preference of the striped surface for one block over the other block is given by (neglecting unimportant constant terms) $V(x) = (\sigma_A - \sigma_B)\sin(\kappa x)$. This is the form of the surface energy term in Eq. (1). Thus we identify $Q h y_\infty \equiv (\sigma_A - \sigma_B)/k_B T$, so that Q is essentially the striped surface preference for one block over the other divided by film thickness.

Now to determine how the system evolves to equilibrium, below the order-disorder-transition (ODT), we use the Cahn-Hilliard equation

$$\frac{\partial\Phi}{\partial t} = M\frac{\partial^2\mu}{\partial x^2}, \tag{2}$$

where M is the mobility and $\mu(x)$ is the chemical potential at the point x. To determine $\mu(x)$ we take the functional derivative of the free energy [Eq. (1)] with respect to the order parameter. Thus applying the operation $M(\partial^2/\partial x^2)(\delta F/\delta\Phi)$ to Eq. (1) and rescaling, as done by Chen and Chakrabarti [5], we obtain the following equation, in dimensionless form,

$$\frac{\partial\Phi}{\partial t} = \frac{1}{2}\frac{\partial^2}{\partial x^2}\left(-\Phi + \Phi^3 - \frac{\partial^2\Phi}{\partial x^2} \right) - \alpha\Phi - A\kappa^2\sin(\kappa x) - \sqrt{\epsilon}\,\eta(x,t), \tag{3}$$

where $A \propto h^{-1}(\sigma_A - \sigma_B)/k_B T$. The last term on the right-hand side of the above equation is a random noise term [5] introduced to mimic the effect of thermal fluctuations. In practice it has an important effect in that it allows the system to escape from some metastable equilibrium states. The parameter ϵ is the magnitude of the fluctuations and is set here to 0.5. The distribution of $\eta(x,t)$ is determined by the fluctuation-dissipation theorem, i.e., $\langle \eta(x,t)\,\eta(x',t') \rangle = -\nabla^2\delta(x-x')\,\delta(t-t')$. Equation (3) is appropriately discretized and we use time steps of $\Delta t = 0.001$. We use lattice sizes up to 4800 lattice sites with periodic boundary conditions. The numerical integration begins at time $t=0$ and Eq.

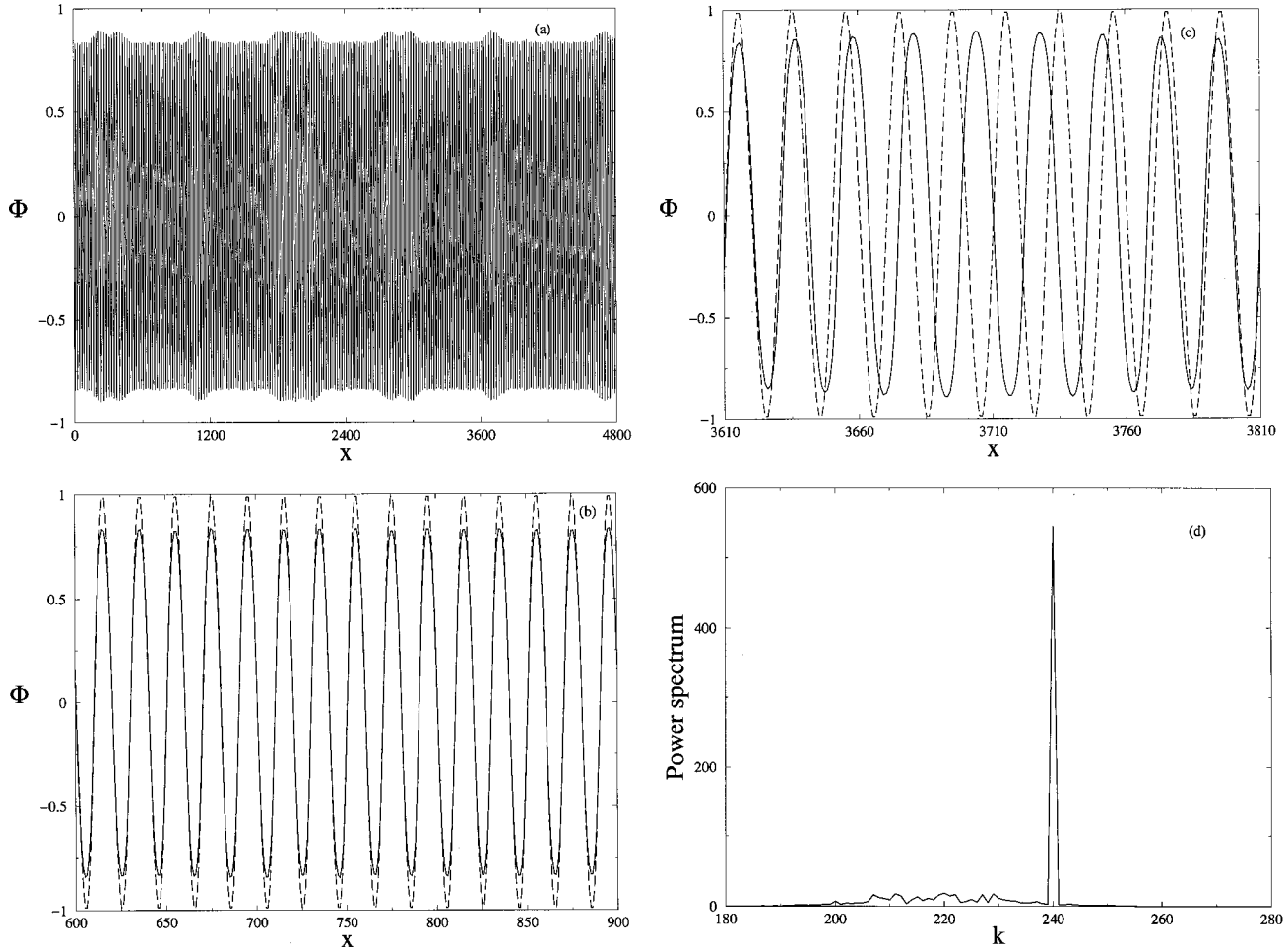

FIG. 1. (a) Equilibrium profile of the order parameter $\Phi(x)$ vs x (measured in units of lattice spacing) for stripes of width 10 lattice sites ($\lambda=10$) and $L_b=12$ in a system of $\mathcal{N}=4800$ lattice sites in total and $A=0.0009$. (b) Order parameter (solid line) for a commensurate region at a magnified scale compared with (a). The surface potential is shown as the dashed line (both lines overlap). (c) Order parameter (solid line) for a region enclosing a discommensuration at a magnified scale compared with (a). The surface potential is shown as the dashed line. At the edges of the discommensuration the order parameter aligns with the stripe potential, while within the discommensuration it does not. (d) Power spectrum vs k, averaged over 10 realizations, for $A=0.0009$.

(3) is iterated until a stable equilibrium solution is found, i.e., until there is no change in the order parameter. For systems of size $\mathcal{N}=4800$ lattice sites (results for which we show in this paper) we used 2×10^7 time steps. Initially Φ is in a randomly disordered configuration.

III. RESULTS AND DISCUSSION

The free energy functional in Eq. (1), except for the last integral, gives a qualitative phase diagram of a block copolymer melt close to the order-disorder transition [15]. The free energy functional is an expansion to fourth order in the order parameter and so is not quantitatively valid in the strong segregation limit (SSL). This is borne out by the order parameter profiles (see the figures), which have a sinusoidal rather than square-wave profile, as in the SSL [19]. This could be the cause of some quantitative discrepancies between our calculations and the FK results [7], which are valid in the SSL. Thus we alert the reader to the fact that our results only qualitatively describe the SSL, where both experiments [2] and theories [4,7–11] have been focused.

We use an α value of 0.01 which corresponds to a bulk (equilibrium) layer spacing of the lamellae of approximately $L_b=12$ lattice sites. We initially consider the results for a stripe potential of wavelength 20 lattice sites, i.e., $\lambda=10$ lattice sites, and an amplitude of $A=0.0009$. (Remember A is proportional to the striped surface preference for one block over the other divided by film thickness.) Thus $\delta=2$ which is positive, so the surface stripes attempt to compress the lamellae to a size smaller than the bulk value. Figure 1(a) shows the order parameter as a function of distance along the surface. The order parameter varies rapidly because of the large number of stripes in the sample. What is clear are a number of regions where the order parameter is of constant amplitude, separated by smaller regions of larger amplitude (the bumps). By expanding these two regions [Figs. 1(b) and 1(c)] it is clear these correspond to commensurate regions and discommensurate regions. Thus, within the flat regions the lamellae are commensurate with the surface, whereas at the bumps the lamellae are discommensurate with the surface and assume a spacing close to their bulk spacing. Our previous theory [7] for this case suggests the discommensurate lamellae should be stretched compared to λ. Indeed, we find within the discommensuration the lamellae are stretched

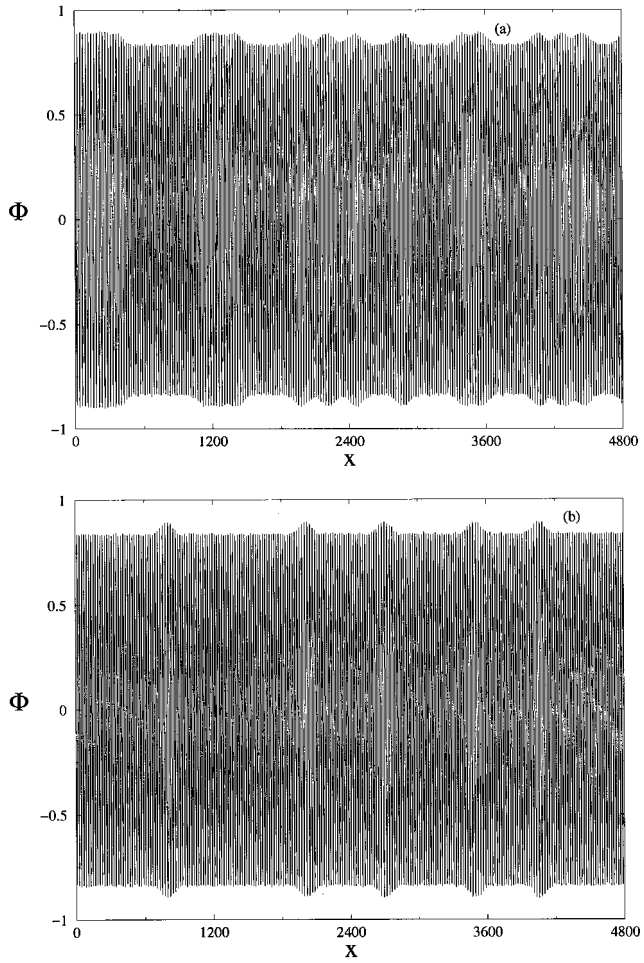

FIG. 2. Equilibrium profile of the order parameter $\Phi(x)$ vs x for stripes of width 10 lattice sites ($\lambda=10$) and $L_b=12$ in a system of $\mathcal{N}=4800$ lattice sites in total for (a) $A=0.0007$ and (b) $A=0.0011$.

compared to the stripe period, i.e., there are nine stripe wavelengths but only eight lamellar periods. By having these discommensurations with stretched lamellae, on the global scale, the lamellae (on average) are able to come closer to the bulk equilibrium spacing. Thus, one major result is that the system does show discommensurations. Figure 1(d) shows the time averaged power spectrum for the order parameter profile for the system shown in Fig. 1(a), averaged over 10 initial starting configurations. The power spectrum shows a large, sharp peak at $k=240$ corresponding to a wavelength of 20 units, and a much smaller, broader hump at $k\approx 220$ corresponding to a wavelength of 22 units. The large peak corresponds to lamellae aligning commensurate with the stripes in the majority of the lattice, while the smaller hump corresponds to lamellae attempting to achieve their bulk spacing in the discommensurations.

In Figs. 2(a) and 2(b) we show the order parameter profile for $\lambda=10$ (i.e., the same as Fig. 1) but with two different amplitudes, $A=0.0007$ and $A=0.0011$. For $A=0.0011$ we see fewer discommensurations compared to $A=0.0009$. Since the stripe potential here is stronger, many more of the lamellae align with the stripes and so only a few discommensurations appear. For $A=0.0007$ the converse is true. It is clear from the order parameter profiles that discommensurations do not appear perfectly regularly across the striped surface. The FK model implies that discommensurations should be equally spaced. We discuss reasons for this discrepancy in the conclusion.

In Fig. 3 we show the order parameter profiles and power spectra for two different stripe widths, both of them inducing compression of the lamellae. These are $\lambda=9.23$ or $\delta=2.77$ and $\lambda=10.91$ or $\delta=1.09$. In the case of $\delta=2.77$, which is relatively large, we find the critical amplitude, at which discommensurations first appear, is roughly 0.004. This is a much larger value than for $\delta=2$ (see Fig. 1), and confirms one's physical intuition that as the difference between lamellar period and surface potential wavelength increases, a much larger surface potential amplitude is required to align the lamellae. The power spectrum for this case shows two distinct peaks, one at $k=260$ corresponding to a wavelength of 18.46 units, i.e., the surface potential and one at $k\approx 195$ corresponding to a wavelength of 24.6 or the lamellar period. In the case of $\delta=1.09$ the discommensurations appear as tiny bumps (of slightly larger amplitude to the bulk amplitude) in the profile. This is due to the small surface potential amplitude that is needed to align the lamellae. The critical amplitude is roughly 0.0003, which is smaller than the previous cases, as expected. The power spectrum shows, once again, a large peak at the surface potential $k=220$ and much smaller peaks between 200 and 220.

These results show very clearly that discommensurations do exist and that their density behaves sensibly as a function of lattice mismatch and potential strength. It would however be useful to have a more quantitative idea of the dependence of discommensuration density on these parameters. According to the FK model [6,7] the number of discommensurations $\mathcal{D}$ that should appear is given by

$$\mathcal{D}\propto 1/\ln[(\delta-\delta_c)^{-1}]. \tag{4}$$

In the strong segregation limit we have previously argued [7] that the critical mismatch δ_c is related to the surface amplitude via

$$\frac{\delta_c^2}{L_b-\delta_c}=\left(\frac{16L_b^2}{3\pi^3 h\gamma_{AB}}\right)A, \tag{5}$$

We do not expect this result to hold exactly in the present study, since here we are dealing with a system that is not fully in the strong-segregation limit. Our order parameter profile is still close to sinusoidal, and not the square wave we would expect in strong segregation. Nevertheless, provided $\delta_c \ll L_b$ we expect $\delta_c^2\approx\tau^2 A$, where τ is a numerical constant. Thus, using the above two relationships we find that the number of discommensurations $\mathcal{D}$ scales with the amplitude A as

$$\mathcal{D}\propto 1/\ln[(\delta-\tau A^{1/2})^{-1}]. \tag{6}$$

In Fig. 4 we have plotted the number of discommensurations $\mathcal{D}$ versus the surface potential amplitude A for the case shown in Figs. 1 and 2. Since Eq. (6) is just a scaling relationship we cannot plot the numerical curve corresponding to this equation. However, the dashed curve has the same functional form as the scaling equation for $\mathcal{D}$. Figure 4 does

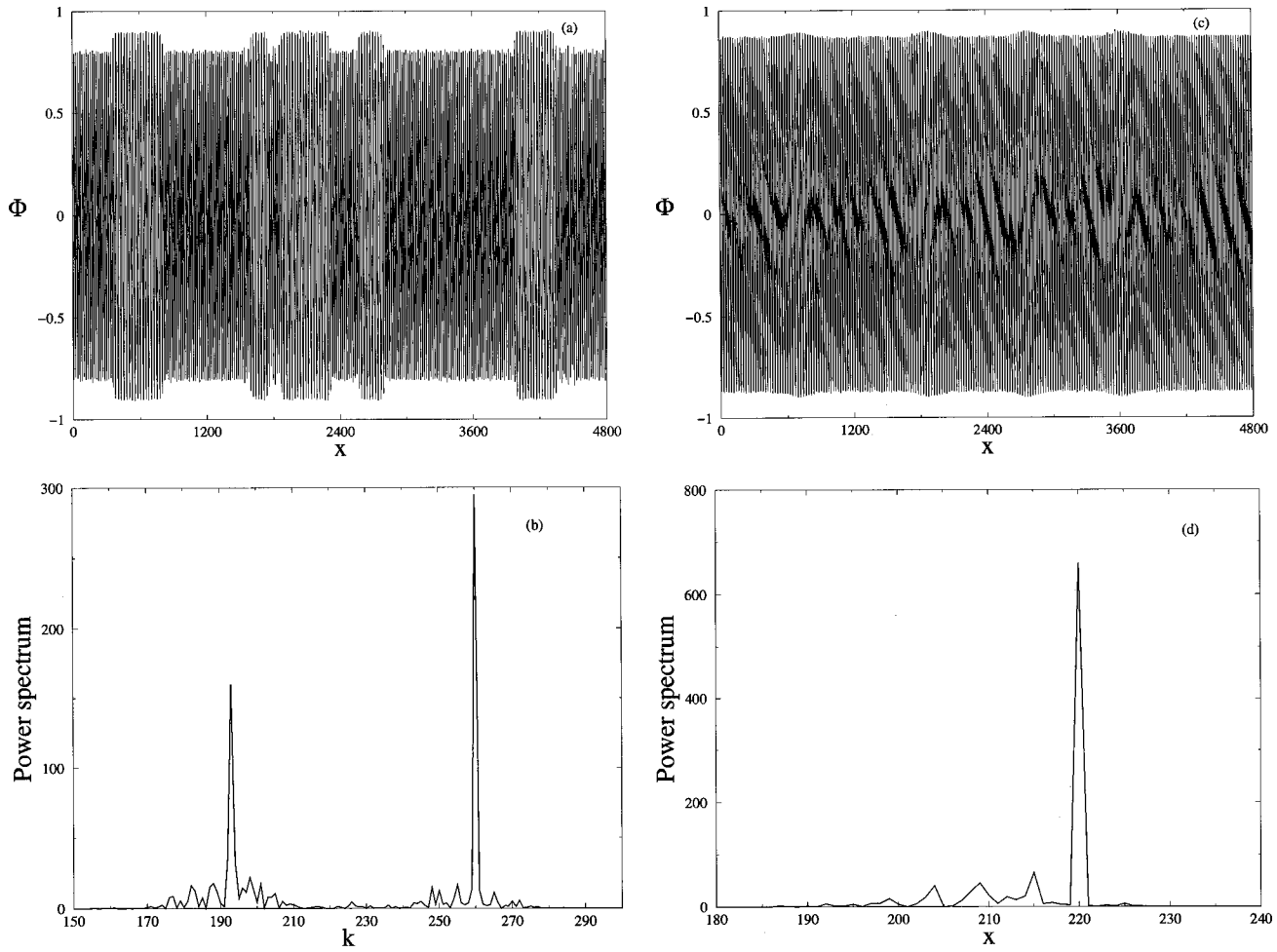

FIG. 3. Equilibrium profile of the order parameter $\Phi(x)$ vs x for stripes of width 9.23 lattice sites ($\lambda=9.23$) and $L_b=12$ in a system of $\mathcal{N}=4800$ lattice sites in total for $A=0.0044$. (b) Power spectrum for same case as in (a). (c) Same as (a) except $\lambda=10.91$ and $A=0.0004$. (d) Power spectrum for same case as (c). Note the power spectra are for only one realization each.

show that as the surface potential is increased the number of discommensurations decreases continuously, in keeping with the theoretical prediction that the incommensurate-commensurate transition is second-order [7,6].

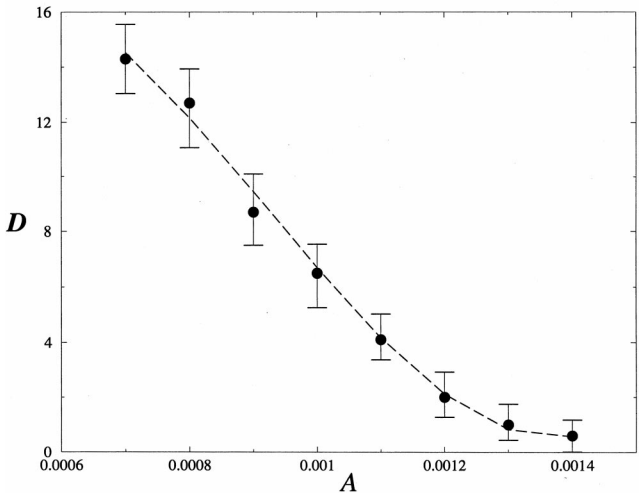

FIG. 4. Number of discommensurations $\mathcal{D}$ versus surface potential amplitude A for the case shown in Fig. 1. Points are averages of 10 realizations with 95% confidence intervals. The dashed curve is a guide to the eye.

So far we have only considered integrating the evolution equation for the case of $\delta>0$, corresponding to discommensurations where lamellae are stretched. In the converse case of $\delta<0$ we have previously shown [8] the diblock-striped system is unstable to a crinkling instability reminiscent of the Helfrich-Hurault effect [8,20]. We argued that this instability would have lower free energy than the undistorted state, and may indeed be the lowest free energy state of the system. Recent results for this system [5] seem to support this conclusion. However, for the sake of completeness we consider here what happens to the present 1D system in the limit of $\delta<0$. FK theory [6] predicts that once again discommensurations should appear regularly across the surface. These discommensurations should appear as lamellae which are compressed compared to the commensurate (surface) lamellae. Figure 5 shows the order parameter profile for the case of $\lambda=12.5$ or $\delta=-0.5$. The discommensurations are now smaller amplitude waves (indents), compared to the remainder of the profile. If one were to magnify the region encompassing a discommensuration we would see fewer stripe wavelengths than lamellar periods, and so the lamellae are compressed in a discommensuration. The power spectrum shows a large peak at $k\approx 190$, corresponding to a wavelength of 12.5, or the stripe width and smaller peaks in the neighborhood of $k=204$, corresponding to the bulk lamellar

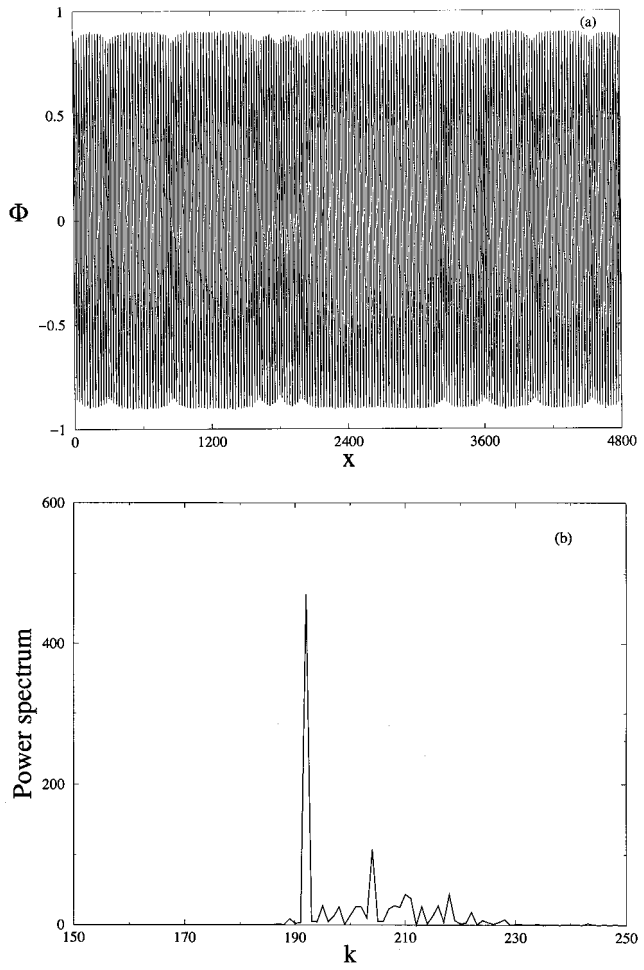

FIG. 5. Equilibrium profile of the order parameter $\Phi(x)$ vs x for stripes of width 12.5 lattice sites ($\lambda = 12.5$) and $L_b = 12$ in a system of $\mathcal{N} = 4800$ lattice sites in total for $A = 0.0004$. (b) Power spectrum for same case as in (a). Note the power spectrum is only for one realization.

wavelength. We have also made runs for $\lambda = 14.03$ ($\delta = -2.03$) with similar qualitative results to Fig. 5(a).

IV. CONCLUSION

We have used a numerical integration of the dynamical evolution equation to study the equilibrium configuration of a diblock copolymer melt on a periodically striped surface. This technique is useful in that it allows a ''hands-off'' approach to studying the system; we just start from some random initial condition and let the system evolve. We have restricted ourselves to the limit of small difference between lamellar period and stripe width. Our results are one dimensional so that we can model systems with a relatively large number of stripes. We thus concentrate on a specific situation, i.e., surface tensions between blocks and upper surface are large and similar. Thus, the top surface should remain flat and the AB lamellar interface should also be flat. By making the system 1D we also do not consider the possibility of mixed (parallel and perpendicular) lamellae forming [4,5,9].

We have seen that for relatively large surface potentials the lamellae align with the surface stripes (commensurate state), with a spacing of λ units. For small surface potentials the lamellae take on their bulk equilibrium spacing, i.e., L_b units. In between these two limits the lamellae can relieve their strain by forming small discommensurations, in which the lamellae are stretched ($\delta > 0$) or compressed ($\delta < 0$). It is the former case that we concentrate on here, since we believe in this case such lamellar configurations may indeed be the lowest free energy state. Our system is analogous to the FK system of solid-state physics, and indeed we find many similarities between our results and the results predicted by the FK model. In particular we find the presence of discommensurations. However, we do not find that these discommensurations are evenly spaced as they would be in the FK model. There are at least three possible explanations for this difference. The first is simple; our system is not exactly the same as the FK system and hence, one does not expect all the details of that model to hold. This is in some sense unsatisfactory, since on symmetry grounds we would expect the defects to be evenly spaced. A second explanation concerns the size of our system. Although the number of stripes is very large, the number of discommensurations is small, of order 10. It may well be that the finite size of the system ruins the strict periodicity expected from the FK model. The third, and most likely explanation concerns the equilibration time. It is well-known that in solitonic systems, of which the FK model is an example, the interactions between the defects decays exponentially. Indeed in the FK model the defects repel exponentially, with a decay constant which is of the order of the stripe width [6]. In our system, this means that the interaction between discommensurations is very weak, since they are often separated by about 50 stripes. This implies that discommensurations, once formed, do not see each other and have no way of organizing into a periodic array. This is particularly true in the presence of thermal noise, which might destroy any order. In any case, the dynamics of such organization is likely to be very slow. This may have important consequences for the experimental observation of defects, since response times in polymer systems are already very long. Thus, from an experimental point of view individual discommensurations might be more readily observed than a periodic array of them.

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[1] F. S. Bates and G. H. Fredrickson, Annu. Rev. Phys. Chem. **41**, 525 (1990).

[2] L. Rockford, Y. Liu, P. Mansky, T. P. Russell, M. Yoon, and S. Mochrie, Phys. Rev. Lett. **82**, 2602 (1999).

[3] D. Petera and M. Muthukumar, J. Chem. Phys. **107**, 9640 (1997).

[4] D. Petera and M. Muthukumar, J. Chem. Phys. **109**, 5101 (1998).

[5] H. Chen and A. Chakrabarti, J. Chem. Phys. **108**, 6897 (1998).
[6] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1995), p. 601.
[7] G. G. Pereira and D. R. M. Williams, Phys. Rev. Lett. **80**, 2849 (1998); Macromolecules **31**, 5904 (1998).
[8] G. G. Pereira and D. R. M. Williams, Europhys. Lett. **44**, 302 (1998).
[9] G. G. Pereira and D. R. M. Williams, Macromolecules **32**, 758 (1999).
[10] G. G. Pereira and D. R. M. Williams, Langmuir **15**, 2125 (1999).
[11] G. G. Pereira and D. R. M. Williams, J. Chem. Phys. **110**, 9223 (1999).
[12] M. Muthukumar, Curr. Opin. Colloid Interface Sci. **3**, 48 (1998).
[13] M. W. Matsen, Curr. Opin. Colloid Interface Sci. **3**, 40 (1998).
[14] M. S. Turner, Phys. Rev. Lett. **69**, 1788 (1992).
[15] T. Ohta and K. Kawasaki, Macromolecules **19**, 2623 (1986); L. Liebler, *ibid.* **13**, 1602 (1980).
[16] M. Bahiana and Y. Oono, Phys. Rev. A **41**, 6763 (1990).
[17] G. Brown and A. Chakrabarti, J. Chem. Phys. **101**, 3310 (1994).
[18] G. Brown and A. Chakrabarti, J. Chem. Phys. **102**, 1440 (1995).
[19] M. W. Matsen and F. S. Bates, Macromolecules **29**, 1091 (1996).
[20] W. Helfrich, Appl. Phys. Lett. **17**, 531 (1970); J. P. Hurault, J. Chem. Phys. **59**, 2068 (1973).