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Phenomenological model for cross-linked polymer blends

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What is the distinction between the patterns made by quenched block copolymer melts and quenched cross-linked polymer blends? If we observe thin films under the condition without flow, it is unlikely that we can distinguish them in critical quench experiments. However, off-critical quenches and moving boundary conditions could exhibit a marked distinction. Such a conclusion is reached with a simple mathematical model of cross-linked polymer blends. [S1063-651X(97)08207-X]

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I. INTRODUCTION

de Gennes [1] first studied the problem of cross-linking a polymer mixture consisting of incompatible polymers A and B, and suggested that the system free energy is effectively that of a diblock copolymer melt [2,3]. From this, he asserted that the representative size of the segregated domain is of order $n^{1/2}$, where n is the intercross-link length in terms of monomer units. His result seems to have been experimentally confirmed by Briber and Bauer [4] except for the small-k behaviors of the form factors $S(k)$. This discrepancy stimulated further study of the cross-linked polymer blends. Benmouna *et al.* [5] ascribed this discrepancy to the frozen-in fluctuation due to cross-linking. These authors proposed a modification of de Gennes's theory using the interaction-dependent screening length. However, Read *et al.* [6] pointed out that this model does not properly take into account the pinning effect of cross-links. They introduced a simple single chain model to incorporate the pinning effect and derived the desired free energy functional with the aid of a generalization of the random phase approximation (RPA). Hashimoto *et al.* [7] demonstrated that pinning of the growing phase-separated domain structure can be achieved by cross-linking the polymers.

The main purpose of this paper is to raise a question: What is the major distinction between cross-linked polymer blends (CLB's) and diblock copolymer melts (DBC's) under segregation conditions? Needless to say, the CLB becomes an amorphous solid [8] under a sufficient density of random cross-links. It is a solid in the sense that no global flow is allowed. Therefore, for example, in the CLB it is very unlikely that globally ordered segregation patterns like lamellar or lattice structures are formed. In this sense, the distinction should be trivially there. Hence, obviously, de Gennes's effective Hamiltonian and its modification by Benmouna *et al.* without explicit pinning do not capture this crucial distinction.

The recent work by Read *et al.* seems to correct this defect. A remaining natural question is whether the pinning due to cross-links has effects on the segregation patterns or not. If a film is prepared without plasticizer or solvent, the flow effect is unimportant for not extremely long experiments (i.e., for most experiments) and the form factor for the DBC exhibits a marked enhancement for small k values as can be seen, e.g., in the result of Hashimoto *et al.* [9]. That is, the enhancement of $S(k)$ for small k is shared by DBC's and CLB's. Perhaps the enhancements in both cases may be different, but the current theories do not look sufficiently reliable to discriminate these two quantitatively. Hence we look for experimentally easily accessible distinction between DBC's and CLB's without hydrodynamic effects. We have found that the model proposed by Read *et al.* under realistic initial conditions tells us that CLB's and DBC's exhibit indistinguishable segregation patterns. This conclusion might be correct. However, since the model does not prohibit global ordering under equilibrium conditions, there is a good reason to believe that not all the pinning effects are captured in the model. We propose a simple model for CLB's which cannot form globally ordered lamellar structure. Our model suggests experimental methods to discriminate CLB's and DBC's even without fluid dynamic effects.

In Sec. II we begin by reviewing a computationally efficient model for DBC's. We then modify it in a minimal way to obtain a model of CLB's. In Sec. III we discuss the major differences between DBC's and CLB's, and propose how to best observe experimentally the difference between the two systems. We conclude with a discussion in Sec. IV.

II. MODEL OF CROSS-LINKED BLENDS

Some time ago, a simple DBC model dynamics was proposed [10] on a discrete lattice (to facilitate simulations) as a cell-dynamical system (CDS) model [10–12]:

$$\psi_{t+1}(n)=(1-B)\psi_t(n)+\mathcal{I}_t(n)-\langle\langle\mathcal{I}_t(n)\rangle\rangle, \tag{2.1}$$

where

$$\mathcal{I}_t(n)=\mathcal{F}(\psi_t(n))+D[\langle\langle\psi_t(n)\rangle\rangle-\psi_t(n)]-\psi_t(n); \tag{2.2}$$

$\psi(n)$ is the order parameter describing the local concentration difference between the two monomer units, $t\in\mathbb{N}$ is time, and $n\in\mathbb{N}^d$ is the lattice point of a simple cubic lattice in d space. D and B are positive constants, and $\langle\langle * \rangle\rangle$ is the isotropic spatial average: in two-space

$$\langle\langle\psi_t(n)\rangle\rangle=\frac{1}{6}\sum_{n'\in \mathrm{NN}}\psi_t(n')+\frac{1}{12}\sum_{n'\in \mathrm{NNN}}\psi_t(n'), \tag{2.3}$$

where Σ_{NN} denotes a sum over the four nearest neighbors and Σ_{NNN} over the four next-nearest neighbors. The map $\psi_{t+1}(n)=\mathcal{F}(\psi_t(n))$ controls the local dynamics of each cell. Its exact form is not important as noted in [13]. The map $\mathcal{F}(\psi)=A\tanh(\psi)$ is chosen here, with $A<1$ above the critical temperature and $A>1$ below. The equation corresponds to the Cahn-Hilliard equation [14] with a subtraction term $B\psi$:

$$\partial_t\psi=\Delta(-\tau\psi+u\psi^3-D\Delta\psi)-B\psi, \tag{2.4}$$

where τ, u, and D [different from that in Eq. (2.1)] are the usual phenomenological parameters and Δ is the Laplacian. It has been pointed out that this equation also models phase segregation in reacting systems [15] and surface melting due to laser heating [16]. Equation (2.4) can be written in the form

$$\partial_t\psi=\Delta\,\frac{\delta F}{\delta\psi}, \tag{2.5}$$

with the free energy F,

$$F(\psi)=\int d\mathbf{r}\left[-\frac{D}{2}(\nabla\psi)^2-\frac{\tau}{2}\psi^2+\frac{u}{4}\psi^4\right]+\frac{B}{2}\int\int d\mathbf{r}\,d\mathbf{r}'G(\mathbf{r},\mathbf{r}')\psi(\mathbf{r})\psi(\mathbf{r}'), \tag{2.6}$$

where G is the Green's function for Laplace's equation $-\Delta G(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}')$.

If we put the free energy of the DBC-derived random-phase approximation (RPA), theoretically by Kawasaki and Ohta [3], in the conserved time-dependent Ginzburg-Landau (TDGL) equation (2.5), we can ''almost'' obtain this equation [Eq. (2.4)]. Traditionally, polymer melts and blends have been described with the aid of the Flory-Huggins (FH) free energy. de Gennes [17], Pincus [18], and Binder [19] proposed various modifications of the Cahn-Hilliard equation compatible with the FH free energy which can describe polymer blend spinodal decomposition. All these models contain a composition-dependent factor in front of the spatial derivative term. It was noticed [20,21] that the model is over-coarse-grained, because the interface thickness should be independent of the polymer molecular weight and off criticality in fairly deep quenches, and [22] that this causes some problems in block copolymers. This feature due to over-coarse-graining can also be seen in the results of Read *et al.* [6]. Currently, there is no systematic way to correct this defect of the RPA approaches.

The model (2.1) [or (2.4)] does not have such a defect. If $B=0$, it is a standard spinodal decomposition model and has been demonstrated to explain polymer spinodal decomposition [23,24] quantitatively [21]. For $B>0$, as long as segregation occurs, the model gives segregation patterns indistinguishable from the actual film experiments of DBC's and does not exhibit composition-dependent interfaces. That is, the model (2.1) is physically more reasonable than the models derived with the aid of the RPA from microscopic models. However, the model (2.1) was not introduced through a physical consideration of DBC's, but through a purely mathematical requirement of stabilizing $\psi=0$, the interface. The argument is summarized here because the same idea suggests a simple albeit crude model of random cross-linked blends and because the RPA is currently incapable of deriving the above-mentioned model (2.4) without some *ad hoc* adjustment.

The distinction of DBC's and the ordinary blend of segregating polymers is that in the former the interface where $\psi=0$ is stabilized due to the covalent bonds between blocks. Hence the simplest model with enhanced stability of $\psi=0$ is Eq. (2.1) with $B>0$. The N (polymerization index) dependence of B can be fixed by considering that the subtraction term $B\psi$, which makes the final equilibrium state nonuniform, should represent the effect of the connectedness of each chain. The relevant length scale due to this effect is $N^{1/2}$. From dimensional analysis, we have $B=c/N^2$, with c a dimensionless parameter. Its continuum version (2.4) of Eq. (2.1) can be derived from the RPA free energy, if we correct its composition-dependent coefficient in front of the gradient term due to over-coarse-graining.

If we perform the stability analysis of Eq. (2.1), we realize that $|k|^2\sim c/N$ characterizes the dominant mode in the weak-segregation case. To realize this mode, for example, $k_x=0$, $k_y\sim 1/\sqrt{N}$ is admissible, so that a flat lamellar structure can be formed. This is possible for DBC's as is well known empirically, because all the molecules can move freely even without hydrodynamic modes (though slowly). In the actual solvent-cast experiments, the fluidity of the film precursor facilitates this ordering. This was demonstrated by a model with hydrodynamic interactions [20].

For CLB's just like DBC's, $\psi=0$ should be more stable than a simple blend. Hence there must be a term like $-(c/N^2)\psi$ in the CLB model, where N is now the inter-cross-link spacing in terms of the number of chain statistical units and c plays the role of an elasticity constant [1]. However, there should not be any long-range order, because polymers cannot move globally. In particular, there cannot be a globally ordered lamellar structure. This means that $|k|^2>\epsilon>0$ is not a sufficient constraint for CLB's in contrast to DBC's. Not only $|k_x|$, but also $|k_y|$ must be strictly larger than some positive number due to cross-links.

We must impose on the average that the dominant mode in the x and the y directions must be of finite wave number: $|k_x|>\epsilon$ and $|k_y|>\epsilon$. Notice that the inverse operator of $\langle\langle * \rangle\rangle - *$ in Eq. (2.1) [i.e., the inverse of the Laplacian Δ operating on $\delta F/\delta\psi$ in Eq. (2.5)] gives the effect of connectedness (in this case isotropic) [3]. The effect of cross-linking is not expected to be isotropic locally, so that the discrete Laplacian should be anisotropic, and its anisotropy must be spatially random.

The easiest way to realize this constraint is to assign a randomly anisotropic Laplacian to the quantity $\mathcal{I}_t(n)$ at each cell in the CDS model in place of the isotropic term $\langle\langle * \rangle\rangle - *$. If we assign annealed random anisotropy, this is an isotropic model with the constraints $|k_x|>\epsilon$ and $|k_y|>\epsilon$. In CLB's, however, the random preferred orientation may anneal only locally at most to the scale of the pattern correlation range, but cannot anneal globally, and so the preferred anisotropic directions (or preferred orientations of the normal to the level set corresponding to $\psi=0$) should be different from place to place (cell to cell in CDS's). In this paper we use a simple quenched anisotropy; we will note in Sec. III that the spatial correlation in random anisotropy does not change the properties of the system very much.

Thus the simplest model of CLB's we propose is given by Eqs. (2.1) and (2.2) with a random anisotropic Laplacian, where the direction of anisotropy is chosen randomly at each lattice site n. The Laplacian in Eq. (2.1) now becomes

$$\langle\langle \mathcal{I}_t(n)\rangle\rangle_\alpha = (1-\alpha)\langle\langle \mathcal{I}_t(n)\rangle\rangle + \alpha\langle\langle \mathcal{I}_t(n)\rangle\rangle_A, \tag{2.7}$$

where $\langle\langle * \rangle\rangle_A$ is chosen as follows: If the anisotropic direction is, e.g., x we choose

$$\langle\langle \mathcal{I}(\psi_t(n_x,n_y))\rangle\rangle_A = [\mathcal{I}(\psi_t(n_x+1,n_y)) + \mathcal{I}(\psi_t(n_x-1,n_y))]/2; \tag{2.8}$$

if the anisotropic direction is in the diagonal direction, e.g.,

$$\begin{aligned}\langle\langle \mathcal{I}(\psi_t(n_x,n_y))\rangle\rangle_A &= [\mathcal{I}(\psi_t(n_x+1,n_y+1)) + \mathcal{I}(\psi_t(n_x-1,n_y-1)) \\ &\quad + \mathcal{I}(\psi_t(n_x+1,n_y)) + \mathcal{I}(\psi_t(n_x-1,n_y)) \\ &\quad + \mathcal{I}(\psi_t(n_x,n_y+1)) + \mathcal{I}(\psi_t(n_x,n_y-1))]/6. \end{aligned} \tag{2.9}$$

$\alpha = 1$ is totally anisotropic, and $\alpha = 0$ is the usual isotropic Laplacian. Our model, which will be called the RA (random anisotropy) model, is

$$\psi_{t+1}(n) = \psi_t(n) - B[\psi_t(n) - 1 + 2f] + \mathcal{I}_t(n) - \langle\langle \mathcal{I}_t(n)\rangle\rangle_\alpha, \tag{2.10}$$

where f is to specify the off criticality, and does *not* satisfy the conservation law (the conservation is actually only weakly violated in this model). Strictly speaking, the condition must be imposed as done in the CDS model of Kawasaki exchange dynamics [25]. However, for the current crude purpose to learn about possible patterns, this simple model is sufficient (because the B term also plays a role of a chemostat). Notice that the strict enforcement of local conservation law simply slows down pattern formation and enhances the pinning effect, so that if the above model exhibits a distinct pinning effect in contradistinction to other models mentioned in the Introduction, we may conclude more strongly that the conservation-corrected model exhibits the pinning effect. For a more conventional justification of this model, see the last section.

The CDS version of the model proposed by Read *et al.* is

$$\psi_{t+1}(n) = \psi_t(n) - B[\psi_t(n) - \psi_0(n)] + \mathcal{I}_t(n) - \langle\langle \mathcal{I}_t(n)\rangle\rangle, \tag{2.11}$$

where $\psi_0(n)$ is the initial frozen-in fluctuation (the initial condition itself). We will refer to this model as the FC model (frozen-in concentration model). In the numerical experiments that follow in Sec. III, the frozen-in initial concentration $\psi_0(n)$ is taken (for each lattice point n) as a random number in the range $(-\psi_0,\psi_0)$, for some positive number ψ_0.

The concentration $\psi_0(n)$ is due to the freezing of a natural fluctuation in the system at the onset of cross-linking. The cross-linking is imposed before the quench in the disordered phase, presumably at a reasonable distance from the critical region. As such, one expects ψ_0 to be fairly small. Typical scattering intensities from [9] indeed show that the scattering maximum in the disordered state is much broader and weaker compared with the scattering maximum in the ordered phase. It is reasonable to assume that ψ_0 should not be more than 10% of $\psi_{\max}$ (value of ψ in a pure phase).

III. DBC's vs CLB's

If we ignore the difficulty due to the formation of lamellar structure in the equilibrium state, de Gennes's reduced free energy (which is identical to the DBC free energy) or its modification by Benmouna *et al.* is a reasonable one. In any case, almost equilibrium widths are realized far before ordering of the global pattern. From this, de Gennes predicted, as mentioned above, that the segregation size is proportional to $N^{1/2}$. This is identical to the simple dimensional analytic result. We know this is good only when the interface thickness is comparable to the pattern size (weak segregation case). In the strong segregation, the power should be $N^{2/3}$ as discussed by Ohta and Kawasaki [3] and as related to the growth exponent 1/3 of the spinodal decomposition [20,26]. The experimental data in [4] cannot discriminate these predictions as can be seen by replotting the data (their result was based on only three data points, and considering the error bar on each point, it is rather difficult to claim a 1/2 power law). CLB's with the 2/3 power law should be realizable with sufficiently large molecular weight of the intercrosslink segments.

This is a feature of CLB's we can understand with the DBC analogy due to de Gennes. We will not demonstrate this numerically, because it is well known that a very-large-scale simulation is needed to observe 2/3 in DBC simulations [20,27], although in real systems it seems easy. The computational difficulty of obtaining the 2/3 power could be, however, due to insufficient hydrodynamic effects. If this is the case, then cross-links would freeze the pattern determined by the initial unstable mode. Then the power law may be 1/2 and the equilibrium value 2/3 may never be observed. Although we believe 2/3 power is observable in CLB's, a critical study is needed.

What is the major distinction between CLB's and DBC's? It is the presence of quenched random links, which forbid global transport of matter and hydrodynamic effects. Consequently, ordered structures like lamellars should not be formed in CLB's in contrast to DBC's. However, in the film experiment, the flow effect is often minimal, so that this distinction is not easily observable. Furthermore, the small-k behavior of the form factors due to the frozen in fluctuations exist even for DBC's as mentioned in the Introduction. This should be obvious because the length scales affected by the frozen-in fluctuations are larger than the pattern width and because the freezing at such scales is obvious from the virtual impossibility of ordered lamellars in DBC films. Thus the question is whether there is an experimentally accessible clear distinction between DBC's and CLB's when hydrodynamic effects are minimal (as is often the case).

The critical quench patterns for three different models are in Fig. 1: the DBC, RA (with $\alpha = 0.5,1$), and FC (all started from the same random initial condition) models. In general, it is quite hard to see a real significant difference. Local rearrangement of the composition is allowed even with

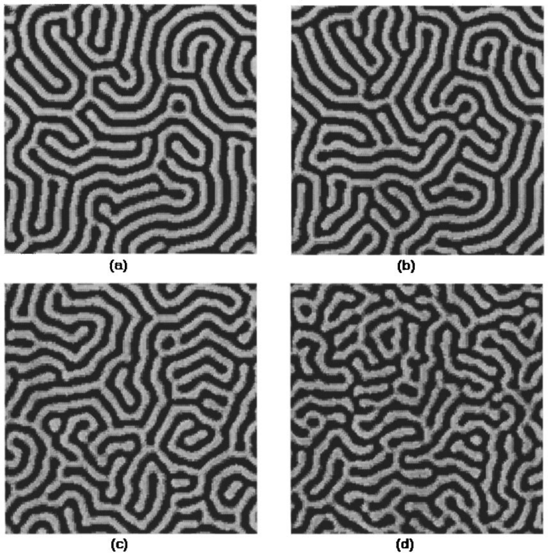

FIG. 1. Patterns for three different models: (a) DBC, (b) FC with $\psi_0 \in (-0.05, +0.05)$, (c) RA with $\alpha=0.5$, and (d) RA with $\alpha=1.0$. Parameter values are $A=1.3$, $D=0.5$, $f=0.5$, and $B=0.02$, after 10 000 iterations in a 128×128 lattice from the same random initial condition.

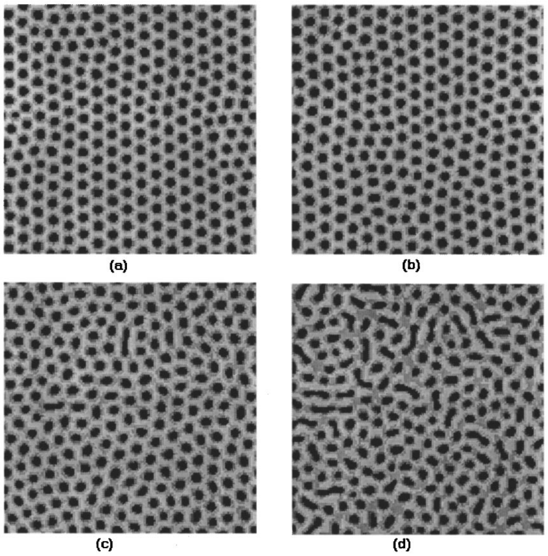

FIG. 2. Off-critical quench for $f=0.4$, $A=1.3$, $D=0.5$, and $B=0.02$, after 30 000 iterations in a 128×128 lattice from random initial conditions: (a) DBC, (b) FC with $\psi_0 \in (-0.05, +0.05)$; this corresponds to $\approx 10\%$ of $\psi_{\max}$. Even for 15% initial fluctuation, our conclusion does not change. (c) RA with $\alpha=0.5$ and (d) RA with $\alpha=1.0$.

cross-linking, so that the film pattern, which is largely due to local segregation, is not affected by the lack of global transport. There is a slight difference in that the domains in the RA ($\alpha=1$) model have larger curvature. The effect, however, washes away with time and on decreasing the parameter B. Therefore, DBC's and CLB's (whatever the model is) are close. Hence our prediction is that DBC's and CLB's cannot be clearly distinguished in the film critical quench experiment.

However, in the off-critical case, we may be able to detect the random cross-link effect more easily as illustrated in Fig. 2. This is, however, because the ordering in the DBC case is easier than in the critical case and also it is easy to detect irregularities against expected lattice structures. Notice that the FC model is much closer to the DBC model, in that the ordering is only slightly destroyed, in contrast to the RA case.

The effect of the boundary can be very different on the quenched patterns, because random cross-links prepare favorable conditions to one or the other phases locally, and such localized patterns cannot be dislodged easily. Perhaps the clearest experiment is the ''sliding cold block'' experiment [28]. In this experiment, the system is cooled from one edge and the cold region is advanced at some rate. As is already known, depending on the cooling rate, this procedure can help the ordering process [28,29]. For a slow rate, this condition coerces ordered patterns in DBC's. For a fast rate, there is no difference from quenching the whole system. If the pinning effect is well captured by the model, even under order-coercing conditions a disordered pattern should be observed.

In the numerical simulation, a free boundary condition is imposed on the right vertical boundary and periodic boundary conditions along the horizontal boundaries. On the left vertical end, free boundary conditions were used for the off-critical case; for the critical case, the order parameter was held fixed to $\psi=0.5$ to facilitate the ordering (in an actual experiment [30] a free edge is preferentially covered with one phase). The parameter A in the CDS map (see beginning of Sec. II) measures the quench depth, so that the cold front is mimicked by varying A along the (horizontal) length of the system. The temperature parameter A was taken to be $A=A_c>1$ (cold region) on the left end of the front and $A=A_h<1$ (hot region) on the right end of the front. The front is a strip between the cold and hot regions, where A is decreased linearly from A_c to A_h. Starting from the left vertical edge of the lattice, the front was advanced through the system by shifting it to the right after a fixed number of iterations. The temperature parameter varies as $A(n_x+1)=A(n_x)-0.01$ with $A_c=1.3$ and $A_h=0.9$ (front width of 40 lattice spacings). The result of the simulation was qualitatively the same for different front widths.

Figures 3 and 4 illustrate the difference in the three models, for both the critical and off-critical quench cases. The completely anisotropic random Laplacian model (our RA) clearly exhibits a sharp distinction in preventing the formation of a well-defined lamellar or lattice structure behind the front. The sharp distinction between the models persists upon decreasing the velocity of the front. Increasing the front velocity results in more disordered patterns in the RA case, whereas the FC model maintains a fairly ordered pattern up to some maximum velocity, beyond which the patterns start to become increasingly distorted.

The patterns in the sliding block experiment for different α in our RA model are shown in Fig. 5. A crossover from an ordered to disordered state occurs around $\alpha\approx0.5$ for the parameters values used in the simulation. While it is clear that our RA model does exhibit a clear distinction from DBC and FC models, we should note here that α is a phenomenological parameter in our model and we do not know the scale or range of α that is appropriate for a typical experiment. How-

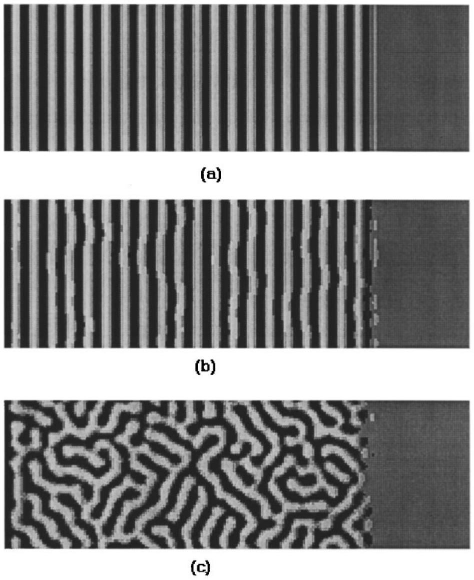

FIG. 3. Sliding block experiment, after 6000 iterations, for (a) DBC, (b) FC with $\psi_0 \in (-0.05,+0.05)$, and (c) RA with $\alpha=1.0$ (for the effect of α see Fig. 5). Parameter values are $D=0.5$, $f=0.5$, and $B=0.02$, on a 64×300 lattice, from random initial conditions. The front moves at a rate of 3 columns every 120 time steps. The temperature parameter variation in the front width is $A(n_x+1)=A(n_x)-0.01$, with $A_c=1.3$ and $A_h=0.9$. The fixed starting edge (left end) of the lattice is $\psi=0.5$.

ever, it should be noted that to impose the positivity condition for $|k_x|$ and $|k_y|$ strictly, we need $\alpha=1$. Furthermore, the positivity condition should be strict, because even in equilibrium, we cannot expect globally ordered lamellars. Therefore, we may expect that α must be fairly close to 1. In any case, our conclusion is that if DBC's and CLB's can be experimentally distinguishable at all, then the sliding block experiment must be the most convenient.

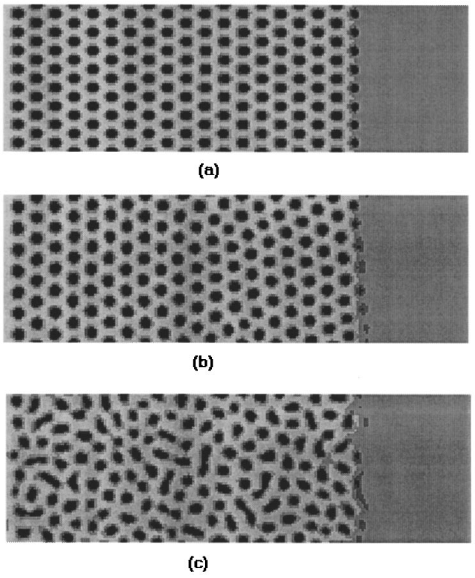

FIG. 4. Sliding block experiment for the off-critical case for (a) DBC, (b) FC with $\psi_0 \in (-0.05,+0.05)$, and (c) RA with $\alpha=1.0$. The same conditions as in Fig. 3, but with $f=0.4$.

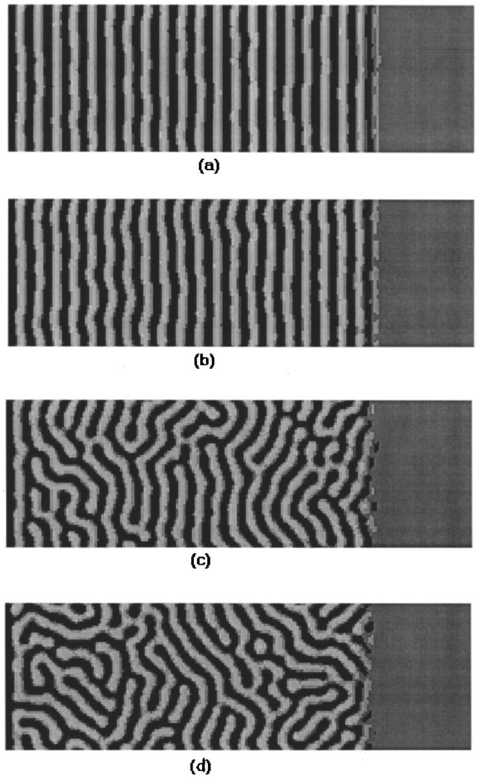

FIG. 5. Sliding block experiment for different values of α: (a) $\alpha=0.2$, (b) $\alpha=0.4$, (c) $\alpha=0.6$, and (d) $\alpha=0.8$. The same conditions as in Fig. 3.

As mentioned in Sec. II, the case of annealed randomness is not suitable in our model because the molecules should not be allowed to move globally. A numerical simulation of an annealed disorder, modeled in a simple way by choosing a random anisotropic Laplacian both in space [as in Eq. (2.9)] and time, resulted in no difference from the DBC case. We also performed simulations of quenched randomness correlated over a certain block size (by imposing a uniform anisotropic Laplacian [Eqs. (2.8) and (2.9)] over a number of cells$=2^b$, for $b=1$, 2, and 3). For the critical quench case, no real significant difference from the DBC case was observed. For the sliding cold block and off-critical experiments, however, the same disordering effect was observed in the blocked RA model as for the RA model with $b=0$. The qualitative features distinguishing the three models do not change when the randomness is correlated over a block size.

IV. DISCUSSION

We have demonstrated that the DBC and FC models are not distinguishable under the above simulated conditions. Should we conclude that there is no distinction between DBC's and CLB's from this? It is highly likely that the pinning due to cross-linking can prevent global ordering even under coercive conditions.

We have introduced a simple model (RA) of CLB's straightforwardly extending a successful model of diblock copolymer melts. The RA model captures the main effect of the inability of the network to move and form globally ordered spatial patterns. The model does not exhibit any global ordering even under coercive conditions. We can simply add to the RA model the effect of frozen-in initial fluctuations as the FC model without any significant effect. The FC model of CLB's introduced by Read *et al.* globally orders under coercive conditions. Hence we must conclude that under realistic conditions [i.e., reasonable amplitude for the frozen-in fluctuation (as discussed at the end of Sec. II)], the modeling of pinning with a random potential as in the FC model is not sufficient to distinguish CLB's and DBC's. However, even our RA model predicts that a simple critical quench experiment of a film cannot exhibit any difference of CLB's and DBC's. The clearest experimental distinction is predicted in the case of sliding cooling block experiments. We have also proposed a reexamination of the pattern size as a function of the inter-cross-link molecular weight.

Finally, we discuss a ''more microscopic'' justification of our model. As was discussed by Read *et al.*, for example, with the aid of the pinned chain model of Read *et al.* we can obtain a coarse-grained free energy RPA theoretically, which has the following form similar to Eq. (2.6), but with anisotropic Green's function G_α,

$$F_\alpha(\psi)=\int d\mathbf{r}\left[-\frac{D}{2}(\nabla\psi)^2-\frac{\tau}{2}\psi^2+\frac{u}{4}\psi^4\right]+\frac{B}{2}\int\int d\mathbf{r}\,d\mathbf{r}'G_\alpha(\mathbf{r},\mathbf{r}')\psi(\mathbf{r})\psi(\mathbf{r}'). \tag{4.1}$$

Alternatively, at a more phenomenological level, one can push the model by Benmouna *et al.* further to reach the above model by assuming that the long-range interaction is screened by a random anisotropic screening length.

Random cross-linking should also produce an anisotropic mobility coefficient γ_k (Laplacian in k space) in the phenomenological dynamics

$$\partial_t\psi=-\gamma_k\frac{\delta F_\alpha}{\delta\psi_k}, \tag{4.2}$$

derived in principle by a projection of a microscopic model with, say, quenched anisotropic chain confinement. Here $\lim_{k\to 0}\gamma_k=0$ due to conservation. In our RA model we choose this random anisotropic Laplacian to cancel the random anisotropic Green's function G_α [i.e., $-\Delta_\alpha G_\alpha=\delta(\mathbf{r}-\mathbf{r}')$], so that the subtraction term $-B\psi$ describes the random qualitative bonding effect:

$$\partial_t\psi=\Delta_\alpha(-\tau\psi+u\psi^3-D\Delta\psi)-B\psi. \tag{4.3}$$

This convenient choice may look very arbitrary, but at least the following qualitative universality argument justifies the use of the crude model for our qualitative purpose. Apart from the fact that this results in a very simple clean model, one should note that (1) if the cancellation is not complete and $\Delta_\alpha G_\alpha$ results in a local random operator in the dynamics, it is likely that there is no qualitative change, as seen in the case of adding frozen-in randomness to the RA model; (2) even if the incomplete cancellation produces a long-range interaction term as in the models extensively studied by Sagui and Desai [31], the extra long-range terms does not change the qualitative features of the DBC model.

Needless to say, we wish to have a more satisfactory ''derivation'' of more realistic models of CLB's. However, we must repeat that so far no RPA-type theory has been able to produce a satisfactory coarse-grained model.

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