Front propagation and selection in a two-space diblock copolymer melt

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The selection problem for propagating fronts is considered for a multiple-mode semilinear parabolic partial differential equation describing front propagation phenomena in a two-space diblock copolymer melt. Several regimes, defined by the value of a reduced temperature appearing in the equation, displaying qualitatively different types of behavior, are identified. It is found that for any value of the reduced temperature in a certain range there exists a unique selected solution. Outside of this range, however, for any value of the reduced temperature, there exist multiple physically realizable solutions. The mechanism responsible for this behavior is identified, and, based on its very generic nature, it is conjectured that similar behavior should be exhibited by a large class of systems. An experimental method for observing the front propagation phenomena is proposed.

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I. INTRODUCTION

Front propagation phenomena have been the focus of much study since 1937 when Fisher [1] and Kolmogorov, Petrovskii, and Piskunov (KPP) [2] published work on a class of semilinear parabolic partial differential equations which have come to be known collectively as the Fisher equation. Fisher considered these equations as models for the propagation of an advantageous gene through a population. He pointed out that such an equation possesses stable traveling wave solutions for all values of the propagation speed greater than or equal to some minimum value and speculated that, for his application, the meaningful one of these solutions (i.e., that which can be observed in an actual system modeled by the equation) is that with the smallest speed. KPP later proved that the slowest stable solution is indeed realized from initial conditions satisfying a certain set of constraints (most importantly that they vanish outside some bounded region) for a particular subclass of the Fisher equation. Since 1937, the "selection problem" has been studied in the context of semilinear parabolic as well as more complicated PDE's. For these equations, there exist multiple (usually a continuous family) stable propagating front solutions, while the physical systems they are used to describe display reproducible behavior corresponding to only one of these solutions. The problem is to determine a general method of identifying the so-called selected solution [3–7].

In this paper, the selection problem is considered for a multiple-mode semilinear parabolic PDE describing front propagation in a diblock copolymer (DBCP) melt. This system is interesting because it does not always possess a unique selected solution. It is found that in a certain regime there exist multiple physically realizable solutions of the equation used to model the dynamics of the DBCP system. The mechanism responsible for the appearance of multiple realizable solutions is identified, and based on the very generic nature of this mechanism, we conjecture that the behavior exhibited by this system is common to a large class of physical systems in which an ordered pattern invades a disordered region.

A diblock copolymer is a synthetic molecule composed of two homopolymer subchains a and b joined covalently at one end. We designate the monomers composing a and b as A and B, respectively. In general, A-B contacts will be energetically less favorable than will A-A or B-B. In addition, given even a weak repulsion between unlike monomers, unlike sequences will be strongly repelled. Thus a and b subchains tend to segregate as they are cooled below some microphase separation temperature T_{MST}. However, because of the covalent bond joining a and b, macrophase separation is not possible, and such a system, in equilibrium below T_{MST}, will thus consist of A-rich and B-rich mesoscale ordered domains.

In the present work, our focus will be on describing systems in the weak segregation limit. We consider front propagation processes in which stable phase separated (ordered) regions invade unstable homogeneous (disordered) regions. Roughly speaking, the fronts we describe consist of periodic ordered structure whose amplitude increases from zero to some equilibrium value. In the regime we study, the fronts contain many periods of ordered structure. For this reason, there exist well defined front *envelopes* representing the amplitude of the periodic structure. These envelopes assume simple forms, and we thus seek to describe the invasion processes in terms of them. We consider the invasion of lamellar and triangular ordered phases and treat the case in which the spatial dependence of the front envelope is confined to that dimension parallel to its velocity and for which we can speak unambiguously in terms of a front *profile* envelope function. Experimentally, such front propagation phenomena could be realized by applying a uniform perturbation (cooling, etc.) to one edge of a thin film sample, for example. Lamellar and triangular ordered structures are considered because, in the weak segregation limit, these are the only ones to appear in equilibrium, as predicted by mean-field theory [8,9].

This paper is organized as follows. In the following

section, the DBCP equation is introduced, and an abbreviated derivation of the equation of motion to be studied is given. In Sec. III, the selection problem for this equation is considered. Experimental investigation is discussed in Sec. IV. A summary and concluding remarks are given in Sec. V.

II. DBCP SYSTEM AND EQUATION OF MOTION

Front propagation in a DBCP system was first studied by Liu and Goldenfeld [10], and later systematically by Paquette [9] in a work we will refer to as I. In I, propagation of an ordered pattern into a metastable disordered region is considered. In the present work, we consider propagation into an unstable disordered region and find that here the DBCP system displays a much richer variety of behavior than that reported in I. The approach taken here will closely follow that of I, and the derivation of the equation of motion studied, as well as a detailed discussion of experimental feasibility and the validity of the mean-field approximation, can be found there. We will now briefly sketch the derivation given in I.

The problem undertaken in I is that of constructing propagating front solutions to the DBCP equation [11],

$$\frac{\partial\psi(\mathbf{x},t)}{\partial t}=\nabla^2[-\nabla^2\psi(\mathbf{x},t)-T\psi(\mathbf{x},t)+\sqrt{3(1-T)}\psi^2(\mathbf{x},t)+\psi^3(\mathbf{x},t)]+\left[z-\frac{T^2}{4}\right]\psi(\mathbf{x},t)\ . \quad (2.1)$$

$T\in[0,1]$ reflects the degree of asymmetry of the polymer. $T=1$ corresponds to a symmetric chain. z is a measure of the quench depth. With $z=0$, (2.1) represents a system at the spinodal. In I it is argued that (2.1) yields time dependent solutions of the form

$$\psi(\mathbf{x},t)=\sum_{n=1}^{\infty}\sum_{m=1}^{r(n)}c_{n,m}(T)[\epsilon W_m(\mathbf{x},t)]^n\cos(\mathbf{k}_{n,m}\cdot\mathbf{x})\ . \quad (2.2)$$

Here, the $c_{n,m}(T)$ are $O(1)$ functions of T. ϵ, a small parameter, is introduced for convenience and serves to parametrize the relationship between ψ and z. The relationship between ϵ and z is determined in the process of constructing solutions. W_m is the envelope function representing the amplitude of the mth mode of ordered structure. It is in terms of these envelope functions that the problem will eventually be cast. $\mathbf{k}_{n,m}$ represents the mth element of the $r(n)$ nth order reciprocal lattice vectors of the ordered structure defined by the $r(1)$ primitive vectors $\mathbf{k}_{1,1},\ldots,\mathbf{k}_{1,r(1)}$.

We are presently interested in the invasion of ordered structure into an unstable disordered region in two spatial dimensions. We consider a system prepared in the disordered $\psi=0$ state to which a perturbation is applied. If this perturbation takes the form of, for example, a uniform cooling applied to one edge of the system, we expect that a propagating front will form as the stable ordered region invades the unstable disordered region. Immediately after the application of the perturbation, modes of ordered structure (perhaps many) will be excited. Since we are considering the weak segregation regime, there will be a narrow ring of linearly unstable wave vectors. For simplicity, we assume that only the most unstable of these (those with magnitude k_0) are excited by the perturbation. (Discussion of this point is given in I.) Then, since in a real system, very closely lying wave vectors cannot be distinguished, we can think of the reciprocal space as being partitioned into a finite number of directions. To each of these directions there corresponds one of the most unstable modes. The equation of motion for the (a,β)th such mode can then be written as (the reason for adopting the double subscript is made clear below)

$$\frac{\partial W_{a,\beta}}{\partial t}=D_{a,\beta}\nabla^2W_{a,\beta}+W_{a,\beta}-sW_{b,\beta}W_{c,\beta}-\tfrac{3}{8}W_{a,\beta}^3-\tfrac{3}{4}W_{a,\beta}\sum_{i=-1}^{1}\sum_{j}W_{i,j}^2\ , \quad (2.3)$$

where $D_{a,\beta}=\cos^2\Theta_{a,\beta}$, and $\Theta_{a,\beta}$ is the angle made by the (a,β)th primitive wave vector and the propagation velocity. $s=[3(1-T)/4z]^{1/2}$ represents an effective temperature. For convenience, we break up reciprocal space into three regions of equal size $(-\pi/2,-\pi/6)$, $(-\pi/6,\pi/6)$, and $(\pi/6,\pi/2)$. Call these regions -1, 0, and 1, respectively. [Since (2.2) is unchanged if we replace $\mathbf{k}_{m,n}$ by $-\mathbf{k}_{m,n}$, we need only consider this half-space.] The first index of $W_{a,\beta}$ identifies the region to which this mode belongs. The second index identifies which position this mode occupies within its region. We choose a convention such that $W_{-1,\beta}$ can be obtained from $W_{0,\beta}$ by a rotation of $\pi/3$, etc. The wave vectors of the triplet of modes $\{W_{a,\beta},W_{b,\beta},W_{c,\beta}\}$ then form an equilateral triangle. For such modes, there is a direct second order coupling. This fact accounts for the second order term in (2.3). The sum in (2.3) is over all modes, excluding a,β. For later use, we now define $W_{0,0}$ to be that mode whose wave vector is parallel to the propagation velocity. Thus $\Theta_{0,0}=0$, $\Theta_{-1,0}=-\pi/3$, and $\Theta_{1,0}=\pi/3$.

As demonstrated in I and [8], depending on s, the equilibrium of this two-space DBCP system is either a lamellar phase (only one nonzero mode) or a triangular phase (only the three modes of a single triplet nonzero). Although it is not obvious from (2.3), we have found through our numerical studies that no "additional" modes appear in any fronts. That is, the only modes appearing in the steady-state traveling wave solutions are those that appear in the equilibrium phase. (See I for further discussion of this point.) Thus, given s and a set of initial conditions, there is a competition between modes, or between triplets, and eventually only one mode or triplet survives and evolves toward a steady-state traveling wave solution.

III. FRONT SELECTION

We have found that there are several distinct regimes, defined by s, in which qualitatively different front propagation behavior is exhibited. This behavior becomes progressively more complicated as s increases from 0.

A. $0 \leq s < 0.51$

As shown in I, in this regime the equilibrium phase is the lamellar. Here, the steady-state traveling wave solution is that of a single mode, and (2.3) reduces to

$$\frac{\partial W_{\alpha,\beta}}{\partial t} = D_{\alpha,\beta}\nabla^2 W_{\alpha,\beta} + W_{\alpha,\beta} - \tfrac{3}{8} W_{\alpha,\beta}^3 \ . \tag{3.1}$$

Then assuming that a particular mode $W_{a,b}$ invades the disordered region, it is well known that there exist stable traveling wave solutions to (3.1) corresponding to each speed $c \geq 2\sqrt{D_{a,b}}$. As proven by Aronson and Weinberger, any solution emerging from initial conditions that vanish outside a localized region propagates asymptotically at the minimum such speed. Since it is generally difficult to manipulate the initial conditions outside a compact set in any experiment (real or numeric), compact support is recognized as a necessary condition for the physical realizability of initial conditions. The result of Aronson and Weinberger has thus been interpreted as proof that the slowest stable traveling wave solution is selected for (3.1). In order to determine the selected speed in the regime in question, we must therefore identify the selected mode $W_{\alpha,\beta}$. This identification can be made through the following argument. If $W_{\alpha,\beta}$ in (3.1) is *not* the mode whose wave vector is parallel to the propagation speed, $W_{0,0}$, then the selected solution of this equation will be unstable with respect to small, localized perturbations by $W_{0,0}$. This is due simply to the fact that the propagation speed of a small disturbance of $W_{0,0}$, 2, is greater than $2\sqrt{D_{\alpha,\beta}}$ for all (α,β) distinct from (0,0). Thus $W_{0,0}$ is selected, and $c=2$.

B. $0.51 \leq s < 2.6$

In this regime (and in fact for all values of s greater than 0.51, as demonstrated in I), the equilibrium phase is the triangular, and thus (2.3) reduces to

$$\frac{\partial W_{a,\beta}}{\partial t} = D_{a,\beta}\nabla^2 W_{a,\beta} + W_{a,\beta} - sW_{b,\beta}W_{c,\beta} - \tfrac{3}{8} W_{a,\beta}^3 - \tfrac{3}{4}(W_{a,\beta}W_{b,\beta}^2 + W_{a,\beta}W_{c,\beta}^2) \ , \tag{3.2}$$

for each of the three coupled modes $W_{-1,\beta}$, $W_{0,\beta}$, and $W_{1,\beta}$. Again, we wish to identify the selected value of β. For this equation, there is no rigorous identification of the asymptotic solution resulting from physically realizable initial conditions. However, based on the hypothesis that the physically realizable behavior of (3.2) must be *structurally stable,* it has been shown that this behavior corresponds to a so-called "critical trajectory" in the flow field of the ordinary differential equation (ODE) obtained when a traveling wave solution is assumed for (3.2) [7]. As discussed in [7], it is believed that corresponding to each orientation of the invading ordered structure there is one such critical trajectory, and this represents the slowest invasion among the continuous set of stable (here using the ordinary sense of the word) traveling wave solutions for this orientation. In [7] and [12], the relation between these *apparently* independent criteria for physical realizability—structural stability and compact initial conditions—is considered, and it is concluded that, at least for the semilinear parabolic PDE's considered by Aronson and Weinberger, the two are equivalent. We believe that this equivalence holds for a much wider class of equations. Also in [7] and [12], the reason for this equivalence is discussed at length. There it is found that compact initial conditions produce solutions whose behavior is determined by the front's bulk. That is, the observable properties of the front are largely independent of the behavior of the tip. Because the nature of these solutions is determined by the bulk, which is stable with respect to structural perturbations, as opposed to the tip, which is unstable with respect to structural perturbations, these solutions are structurally stable. All other solutions are "tip determined," and therefore structurally unstable.

For the range of values of s considered here, if $\beta \neq 0$, the invasion described by (3.2) emerging from localized initial conditions propagates at a speed <2 (as determined numerically) and is once again unstable with respect to small, localized perturbations by $W_{0,0}$. The corresponding solution is thus not observable. Hence the selected triplet is given by $\bar{W}_0 \equiv \{W_{-1,0}, W_{0,0}, W_{1,0}\}$. Interestingly, the resulting solution consists of two traveling waves. $W_{0,0}$ leads the invasion with speed $c=2$, and it is followed by $W_{0,-1}$ and $W_{0,1}$ traveling together at a smaller speed (see Fig. 1). Here, the leading single-mode invasion corresponds to the critical trajectory of the ODE for this selected orientation.

The double-front behavior seen here, in which a region first orders into a lamellar pattern and later, as the slower trailing fronts pass, orders further into the equilibrium triangular pattern, is reminiscent of that described by Bechhoefer, Löwen, and Tuckerman [13] for a single-mode system. In the present case, however, this phenomenon is due strictly to the multiple-mode nature of the invasion and the fact that $D_{0,0} > D_{-1,0}, D_{1,0}$. As shown in Fig. 1, the difference between the speeds of the trailing and leading modes decreases as s increases and the coupling between modes becomes stronger. Finally,

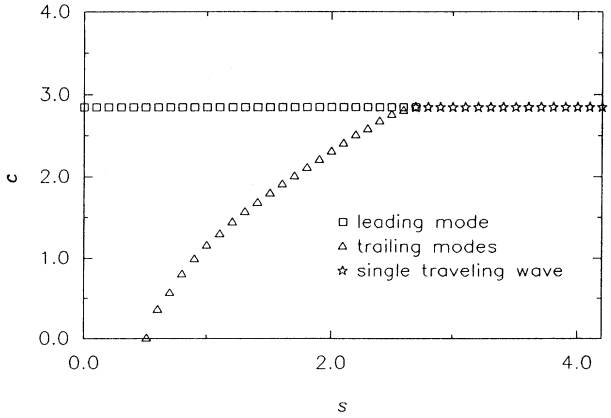

FIG. 1. Propagation speeds for the three modes $W_{-1,0}$, $W_{0,0}$, and $W_{1,0}$. For $s<2.6$, $W_{0,0}$ leads the invasion, traveling at a speed $c=2$, while $W_{-1,0}$ and $W_{1,0}$ trail, traveling together at some slower speed. For $s>2.6$, the three modes travel together at the same speed (for values of s shown here, this speed is 2).

we should point out that for any value of s in this regime, the double-traveling wave behavior cannot continue indefinitely. In the region which opens up between the leading and trailing fronts, the lamellar pattern will eventually undergo spontaneous ordering (that is, ordering which is not forced by the trailing fronts) into the triangular pattern. Near $s=0.51$, the lamellar state is metastable with respect to such ordering, while for larger s it is unstable.

C. $2.6 \leq s < 4.2$

Here again, it is found numerically that the asymptotic solution resulting from initial conditions with compact support (equivalently, the structurally stable solution) corresponding to any orientation other than $\tilde{W}_0$ travels at a speed <2. Thus again, the selected solution is the structurally stable one corresponding to $\tilde{W}_0$. In this regime, the coupling between modes represented by the second order term in (3.2) is strong enough that, in a sense, it negates the effect introduced by the relative difference in magnitude of the diffusion coefficients. Although the $W_{0,0}$ mode still leads the invasion, it travels together with the trailing modes at a speed $c=2$. Here, the critical trajectory for the selected orientation corresponds to this three-mode invasion. In this regime, increasing s only causes the trailing modes to further "crowd" the leading mode. For even larger values of s, as we will next see, the trailing modes actually "push" the leading mode, and the front propagates at a speed $c>2$.

D. $s \geq 4.2$

Until this point, the fastest structurally stable invasion has been that corresponding to the triplet $\tilde{W}_0$. The speed of this invasion has been independent of s and determined by only the linear order terms in (3.2). The same is not true, however, for the structurally stable solutions of all orientations. As an example, we consider the invasion of the triplet $\tilde{W}_{\pi/2}$, obtained from $\tilde{W}_0$ by a rotation of $\pi/2$ radians, ignoring the fact that such an invasion is unstable with respect to $W_{0,0}$, and thus not physically realizable in the regimes thus far considered. (We will refer to the speeds of triplets $\tilde{W}_0$ and $\tilde{W}_{\pi/2}$ as c_0 and $c_{\pi 2}$.) In Fig. 2, the speeds $c_{\pi/2}$ and c_0 are plotted as functions of s. We can see that near $s=2.5$, $c_{\pi/2}$ begins to acquire an s dependence and is no longer determined solely by the linear order terms in the equation of motion for $\tilde{W}_{\pi/2}$. Also note that near $s=4.2$, $c_{\pi/2}$ becomes greater than c_0. Below this value of s, $c_{\pi/2}$ represents the slowest propagation speed, while c_0 represents the fastest. Above $s=4.2$, $c_{\pi/2}$ represents the fastest propagation speed, while c_0 represents the slowest. We can associate an orientation with the βth triplet by defining Θ_β to be the smallest element of the set $\{|\Theta_{-1,\beta}|, |\Theta_{0,\beta}|, |\Theta_{1,\beta}|\}$. Propagation speed as a function of Θ_β is plotted in Fig. 3 for values of s both above and below 4.2.

The most important point here is not that c_0 becomes the slowest speed above $s=4.2$, but that the speed of the steady-state solution to (2.3) for any triplet $\tilde{W}_\beta$ becomes

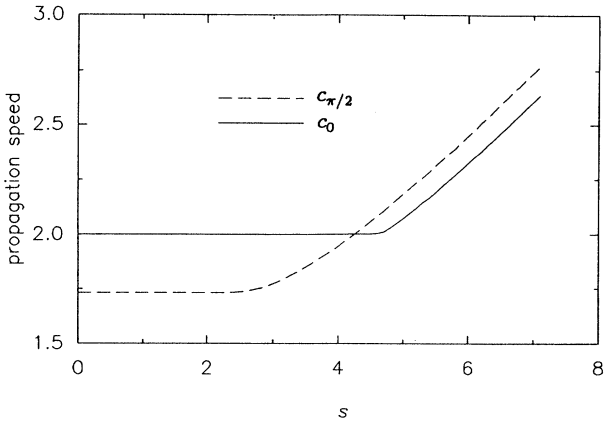

FIG. 2. Propagation speeds c_0 and $c_{\pi/2}$ for the triplets $\tilde{W}_0$ and $\tilde{W}_{\pi/2}$. Near $s=2.5$, $c_{\pi/2}$ begins to acquire an s dependence and is no longer determined solely by the linear order terms in the equation of motion for $\tilde{W}_{\pi/2}$. Near $s=4.2$, $c_{\pi/2}$ becomes greater than c_0 (and greater than the speed of $W_{0,0}$,2). At a slightly larger value of s, c_0 acquires an s dependence.

greater than that of small amplitude, localized disturbances of $W_{0,0}$. Due to this fact, each orientation is now stable with respect to $W_{0,0}$. In fact, each orientation is now stable with respect to all small, localized perturbations. The mechanism responsible for selecting $\tilde{W}_0$ has thus been lost, and there is now no unique selected solution. In this regime, to each orientation of ordered structure, there corresponds a physically observable solution representing the invasion of a triangular pattern.

Because small fluctuations are no longer effective in selecting an orientation, the outcome of a given experiment is determined by the initial conditions alone. Clearly, these can be chosen so that the propagating front solution corresponding to any desired orientation is realized.

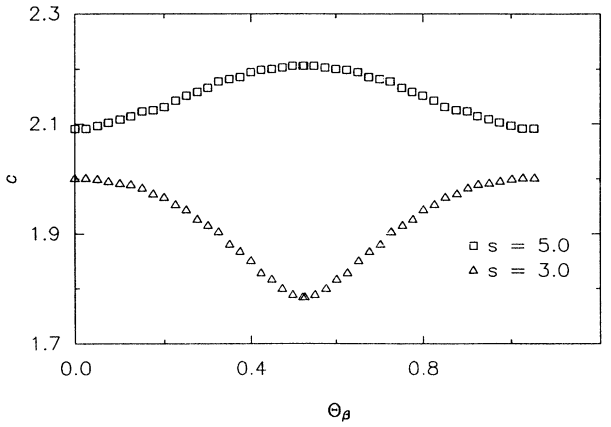

FIG. 3. Dependence of propagation speed on orientation of invading ordered structure for $s=3$ and 5. For each orientation, Θ_β represents the smallest element of the set $\{|\Theta_{-1,\beta}|, |\Theta_{0,\beta}|, |\Theta_{1,\beta}|\}$. $\Theta_\beta=0$ corresponds to the triplet $\tilde{W}_0$. $\Theta_\beta=\pi/6 (\approx 0.52)$ corresponds to the triplet $\tilde{W}_{\pi/2}$. For values of s below 4.2, c_0 is the fastest propagation speed and $c_{\pi/2}$ is the slowest. For values above 4.2, the opposite is true.

We have numerically studied the competition and selection that take place in this regime. Unfortunately, the structure of the domains of attraction in the space of initial conditions is not easily characterized. We thus were able to carry out only a rough and incomplete charting of this space. We found that for values of s between 4.1 and 4.9, the domains of attraction for all orientations are of approximately equal size. In general, as s increases, the domains of attraction corresponding to orientations near $\tilde{W}_{\pi/2}$ grow, while those corresponding to orientations near $\tilde{W}_0$ shrink.

We should note here that in a system of large spatial extent, there will be many local regions in which competition between orientations takes place. From each such local region, a particular orientation will emerge. Subsequently, each of these locally selected orientations will evolve toward fully developed fronts and as such will compete with each other. The whole problem of selection is obviously quite complicated. It is thus exceedingly difficult to make quantitative statements about the outcome of this competition.

IV. EXPERIMENTAL INVESTIGATION

There are two properties characteristic of polymer systems that are commonly cited as simplifying their study and making them attractive to both theorists and experimentalists. Although the connectedness of the polymer chains leads to rather complicated microscopic dynamics, at the level of mesoscopic phenomenology, this very connectedness simplifies the theory of phase separation dynamics. Extending the Ginzburg criterion [14] argument used by de Gennes [15] and Joanny [16] to demonstrate the validity of mean-field theory for critical phenomena of polymer systems, Binder [17] demonstrated the same for phase separation dynamics. He showed that the width of the temperature range over which such systems display non-mean-field behavior vanishes as $N^{-1/2}$. (This result is the same in the static case.) Thus the equation of motion we employ, derived using a mean-field approximation, can be used to model polymer systems even very close to the critical temperature. In I a particular physical system, subject to a critical quench, was considered, and it was found that our perturbative calculational method is valid well into the mean-field regime.

The second property of polymer systems alluded to above is relevant to the experimental investigation of their dynamics. In general, due to large viscosities, the dynamics of polymer systems proceed very slowly, and as a result, even the early stages of the phase separation process can be studied [18,19]. This is generally not the case with "ordinary" small molecule systems. This property is important for the present work because it allows a means by which the phenomenological parameters appearing in our model equation can be identified.

We now propose an experimental setup that should allow for the observation and measurement of front propagation phenomena. Suppose that we have an experimental system composed of two temperature regions separated by a moving boundary such that on one side of the boundary the homogeneous phase is stable, while on the opposite side an ordered phase is stable. Then imagine the situation in which a disordered-ordered front propagates behind this temperature boundary. If the speed of the boundary is greater than that of the front, a disordered region will open up between the two in which patches undergoing spontaneous phase separation will arise. These patches will eventually destroy the propagating front.

If we have a boundary moving and behind it a front propagating at the same speed $\mathcal{S}$, we can conclude that the natural speed of the front is at least as large as $\mathcal{S}$. If we now begin to increase the speed of the boundary, and if we can find the speed $\mathcal{S}_0$ at which the boundary first begins to "outrun" the ordered structure propagating behind it, this should be the natural speed of the front [20]. The goal is to determine $\mathcal{S}_0$.

Now, consider a front consisting of a particular ordered structure and a boundary moving together at the front's natural speed c. In the tip of the front, near the boundary, we can imagine spontaneous fluctuations appearing in which modes of all types (including those not present in the front) become excited. If these small disturbances propagate at speeds smaller than c, they will be overwhelmed by the oncoming front and eventually destroyed. If, however, some of these disturbance are able to propagate at speeds larger than c, the front will not be able to destroy them in this way. If the speed of the boundary were to remain equal to that of the original front, these disturbances would be held back by the boundary. If the boundary's speed were increased by a sufficiently small amount, however, they would be able to keep up. Thus if we are performing an experiment and trying to measure $\mathcal{S}_0$, the value we find must be at least as large as the speed of the fastest "small disturbances," i.e., the fastest linear mode that can be excited by localized fluctuations. Any fully developed front that is slower than this speed is not observable. If we produced such a front initially, it would eventually be destroyed by the fluctuations in its tip. All fronts that propagate at speeds at least as fast as any such fluctuations and that can be produced by localized initial conditions should be realizable with this type of experimental procedure.

Clearly in the case of an unstable disordered region, such a temperature boundary must be used in order to observe front propagation phenomena over an extended region. In the metastable case, however, this may not be necessary. As discussed previously, since polymer systems behave in close accordance with mean-field theory even when quenched very close to the spinodal, nucleation rates will be quite small, and we may not need to be concerned with the appearance of ordering patches ahead of the front.

V. CONCLUSION

In this paper, we have considered front propagation phenomena in a two-space diblock copolymer melt in which a stable ordered phase invades an unstable disordered phase. We have studied the multiple-mode semilinear parabolic PDE that can be derived from the DBCP equation, as demonstrated in I. It was found that, de-

pending on the value of a sort of reduced temperature appearing in this equation, the invading phase can possess either a lamellar or triangular structure. In the former case, the selected (i.e., physically realizable) wave vector of the invading ordered structure is parallel to the propagation velocity. In the latter case, there is a range of values of the reduced temperature for which there exists a unique selected orientation. Here, the wave vector of the *leading mode* of the selected invasion is parallel to the propagation velocity. For any value of the reduced temperature above this range, there is no unique selected solution. In this case, there exist realizable invasions corresponding to all orientations of ordered structure.

The behavior observed for the DBCP system should be quite general for systems in which an ordered pattern with an orientational degree of freedom (i.e., an ordered pattern in >1 dimensions) propagates into a disordered region. If the fastest speed present is that corresponding to small disturbances of a particular mode of ordered structure, the fluctuations in the leading edge of the front will allow the linear order terms to select their "favorite" orientation. When the speeds of the fully developed fronts are larger than that of these small disturbances, the fluctuations can no longer force such a selection, and assuming the nonlinear terms favor no orientation, there will be no unique selected solution.

Although it may be possible to construct a system for which this plausibility argument does not hold, for those systems, such as the DBCP, in which couplings between orientations lead to only stabilizing terms in the equations of motion, the argument clearly holds. Simply stated, in such cases, if a fluctuation cannot grow in the leading edge, where the front has effectively zero amplitude, it also cannot grow in a region of finite amplitude. Thus for such systems, if there is a unique selected solution, it is singled out from the other structurally stable solutions by a mechanism whose origin lies in the linear order terms. If the linear terms are able to produce no such mechanism, there will be no unique selected solution.

Finally, we wish to emphasize that the DBCP melt should provide an ideal system with which to observe front propagation phenomena. We hope that by using the experimental setup described above, the predictions made here can be successfully tested.

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[20] This assumes that the amplitude of the ordered structure near the boundary is small enough that the boundary only affects the shape of the front's tip. Then, by the "bulk driven" hypothesis explained in [7] and [12], such a perturbation should, as discretization in numerical studies, only slightly alter the front's speed.