Pinning of phase separation in a model of binary polymer blends

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The phase-ordering kinetics of a homopolymeric binary mixture is studied numerically in the framework of
the Flory–Huggins–de Gennes continuum model. For deep quenches the suppression of the evaporation-
condensation mechanism leads to slower growth, due to transport of molecules along the interfaces. When the
concentration of the minority phase is low all growth mechanisms are suppressed and the system exhibits a
temporary stop in the separation kinetics.

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When a binary mixture is quenched into the unstable re-
gion of the phase diagram it decays spontaneously toward a
thermodynamic state characterized by two coexisting phases
with different compositions. The way such a new equilib-
rium state is reached is highly nontrivial and is the subject of
intense investigation [1]. The general pattern of temporal
evolution is characterized by the initial formation of small
domains and their subsequent coarsening with an invariant
morphology. Polymeric blends in general share this qualita-
tive picture with other phase-separating systems. However,
they can exhibit a much richer phenomenology [2]. One re-
markable feature observed experimentally is the dramatic
slowdown in the growth of domains exhibited by some
blends when the concentration of the minority component is
sufficiently low [3]. This phenomenon has not been observed
in small-molecule systems and its physical origin is not com-
pletely understood. In particular, two possible interpretations
have been put forward. The first is related to the existence of
an enthalpic barrier inhibiting the usual evaporation-
condensation mechanism [4]. The second, the so-called per-
colation to cluster transition, is induced by hydrodynamics:
for off-critical quenches it would lead to a long crossover
between a fast viscosity-controlled coarsening and a slower
growth driven by evaporation and condensation or droplet
coalescence, producing an apparent pinning of the phase
separation [5]. Previous numerical studies [6,7] of continuum
models have not found evidence of pinning when hydrody-
namics is neglected. However in these studies only shallow
quenches [8] have been considered. In this Brief Report we
proceed one step further by considering deep quenches also.
We show that in this case a temporary stop is actually ob-
served when the concentration of the minority phase is low
enough to produce a dropletlike morphology. This result
shows that the continuum equation for polymer blends con-
tains sufficient physical ingredients for describing pinning in
the phase separation, even in the absence of hydrodynamic
interactions. In particular, it correctly models the suppression

of the bulk diffusion mechanism (evaporation-condensation)
due to enthalpic barriers at low temperatures.

The theoretical description of spinodal decomposition in
binary mixtures is based on the continuity equation

$$\frac{\partial \psi(\mathbf{x},t)}{\partial t} = \mathbf{\nabla} \cdot \left[M(\psi) \mathbf{\nabla} \frac{\delta(\beta F\{\psi\})}{\delta \psi} \right] \qquad (1)$$

for the order parameter $\psi(x)$, namely, the difference between
the concentration of the two species A and B, where $M(\psi)$ is
the mobility and $\beta = 1/k_B T$.

For linear homopolymers the usual choice [9] for the mo-
bility is $M(\psi) = ND(1-\psi^2)$ while βF is given by the
Flory–Huggins–de Gennes (FHDG) form

$$\beta F\{\psi\} = \int d\mathbf{x} \left[\beta f_{FH}(\psi) + \frac{\kappa(\psi)}{4} |\mathbf{\nabla}\psi(\mathbf{x},t)|^2 \right], \qquad (2)$$

with

$$\kappa(\psi) = \frac{\sigma_A^2}{18[1+\psi(\mathbf{x},t)]} + \frac{\sigma_B^2}{18[1-\psi(\mathbf{x},t)]} + \chi\lambda^2, \qquad (3)$$

where σ_A and σ_B are the Kuhn lengths of the two species, λ
is an effective interaction distance between monomers, and
the Flory-Huggins free energy is [10]

$$\beta f_{FH}(\psi) = \frac{1+\psi(\mathbf{x},t)}{2N} \ln\left[\frac{1+\psi(\mathbf{x},t)}{2} \right]$$
$$+ \frac{1-\psi(\mathbf{x},t)}{2N} \ln\left[\frac{1-\psi(\mathbf{x},t)}{2} \right] + \frac{\chi}{4}[1-\psi^2(\mathbf{x},t)]. \qquad (4)$$

We have assumed the same number of monomers N in
chains of type A and B; χ measures the repulsion strength
between unlike molecules and is inversely proportional to
the temperature. We will consider for simplicity a symmetric
blend, for which $\sigma_A = \sigma_B = \sigma$. The critical value $\chi N = 2$
separates stable states ($\chi N < 2$) from the thermodynamically
unstable region ($\chi N > 2$) where the mixture decays into two

separate phases. The evolution of the system is fully determined by the initial conditions, which are taken to be completely disordered $\langle \psi(\mathbf{x},0)\psi(\mathbf{x}',0)\rangle = \Delta \delta(\mathbf{x}-\mathbf{x}')$ with average concentration $\langle \psi(\mathbf{x},0)\rangle = \Psi_0$. A critical quench means $\Psi_0 = 0$.

The model introduced above differs from the usual Cahn-Hilliard (CH) description of phase-separating small-molecule blends [1] with respect both to the mobility and to the free energy functional. In particular, M is here order parameter dependent (whereas it is usually assumed to be a constant for small molecules), the local part of the free energy has a logarithmic expression [as opposed to the usual Ginzburg-Landau (GL) quartic form], and the square gradient coefficient $\kappa(\psi)$ is itself concentration dependent, while it is constant for small molecules. Of these three features, only the third is intimately related to the macromolecular nature of the blend components; the two others should be considered in principle in the study of phase separation in small molecule mixtures also. However, for small molecules, since N is of order 1, a large quench-depth parameter χN is not realistically feasible. In this situation the value $\pm \psi_0$ of the order parameter in the bulk of phase-separated domains, which corresponds to the minima of $f_{FH}(\psi)$, is small. Since $\psi^2 \ll 1$ everywhere, f_{FH} is well approximated by a quartic GL form and $M(\psi)$ and $\kappa(\psi)$ are essentially constant. Hence the model for polymer phase separation coincides in practice for shallow quenches ($\chi N \gtrsim 2$) with the usual CH description of small-molecule blends. Instead, when N is large, for low but accessible temperature one can have $\chi N \gg 2$ (deep quench). In this case a different behavior is expected because $\psi_0^2 \simeq 1$, producing strong variations of both the mobility M and κ between bulk and interfacial regions.

The numerical solution of Eq. (1) for critical shallow quenches was performed by Chakrabarti *et al.* [6], showing that the phase separation described by this model proceeds similarly to that exhibited by the usual small-molecule model. These studies were later extended to off-critical quenches, where, after some debate, it was recognized that the same pattern holds true [7]. In particular, the coarsening of domains is characterized by a power law increase $R(t) \sim t^{1/3}$ of the typical domain size, as for small molecules, and pinning is not observed. These results for shallow quenches are not surprising: The model for polymers coincides, in the limit $\chi N \to 2$, with the CH equation.

The possibility of a different behavior for deep quenches remained open, however. Recently this issue has been investigated by us with an analytical approach [11]. The equation of motion has been solved with the help of an approximation scheme, the large-n limit, which is of common use in phase-ordering problems. We have found that, for deep quenches, after the initial transient during which domains are formed, the system freezes for a time interval whose duration diverges in the limit $\chi N \to \infty$. For finite values of χN the system eventually leaves the pinned state and coarsening starts. For an intermediate stage, domains grow with a time dependence, that corresponds to $t^{1/4}$ in the physically relevant case of a scalar order parameter. Eventually a crossover leads to a growth law corresponding to $t^{1/3}$ in the scalar case. These findings suggest that the deep quench condition strongly inhibits the usual coarsening mechanism of evaporation and condensation (associated with an exponent 1/3) [4] and more

weakly the competing interface diffusion (giving 1/4) [12]. Within the analytical approach the pinning in the evolution occurs for unphysically large values of χN and with no crucial dependence on the concentration. However, the mean field nature of the large-n approach does not take into account properly the effects of the morphology of phase-separating domains. In particular, when the quench is sufficiently off-critical the minority phase forms a pattern of nonpercolating droplets dispersed in the matrix of the majority phase: in these conditions interface diffusion is suppressed for geometrical reasons. One question then arises naturally: can this suppression, together with the deep quench condition inhibiting evaporation from droplets, lead to a pinning phenomenon for physically reasonable values of χN in off-critical quenches?

In order to address this issue we have solved Eq. (1) numerically with the Euler first order discretization scheme on square lattices of linear sizes ranging from 256 to 512 mesh points. The deep quench condition introduces strong limitations in the choice of the time step Δt: When $\chi N \to \infty$ the minima of the potential f_{FH} are exponentially close to ± 1, while $f'_{FH}(\psi)$ becomes very large near such minima. As a result Δt must be very small to prevent $|\psi|$ from becoming accidentally larger than 1 due to numerical noise. The small value of Δt has made it impossible so far to reach long times in the numerical solution. Here we circumvent this difficulty by two means. First we consider a two-dimensional system. On the basis of what usually occurs in other phase-ordering systems, we do not expect the behavior to change qualitatively depending on the dimension. Second, we perform most of our simulations with $\sigma^2 = 0$, a choice that allows much larger values of the time step Δt. We have checked that relevant features do not change when this condition is relaxed. In the following we will present results for three quench conditions: a shallow critical quench ($\chi N = 2.1, \Psi_0 = 0$), a deep critical quench ($\chi N = 10, \Psi_0 = 0$), and a deep off-critical quench ($\chi N = 10, \Psi_0 = 0.7$). In the initial state the field ψ is given by Ψ_0 plus uncorrelated fluctuations distributed between -0.01 and $+0.01$. D and λ have been taken equal to 1. The inverse of the first moment of the structure factor

$$k_1(t) = \frac{\int dk\, k\, C(k,t)}{\int dk\, C(k,t)} \qquad (5)$$

is commonly used as a measure of the typical size of phase-separating domains. The time dependence of $1/k_1$ is reported in Fig. 1, where data are plotted with space rescaled by the factor $(\chi - \chi_s)^{1/2}$ and time rescaled by $D(\chi - \chi_s)^2/\chi_s$ ($\chi_s = 2/[N(1-\Psi_0^2)]$ is the mean field spinodal line), in order to make easier the comparison between different cases. Immediately after the quench, $1/k_1$ exhibits a smooth growth followed by a slight decrease. This corresponds to the linear regime, i.e., the formation of domains on a typical wave vector $k_0 = [[\chi N - 2/(1-\Psi_0^2)]/(2N\{\chi \lambda^2 + \sigma^2/[9(1-\Psi_0^2)]\})]^{1/2}$. When the linear regime ends, the behavior in the three cases is markedly different. For the shallow quench coarsening starts and the typical size quickly reaches the
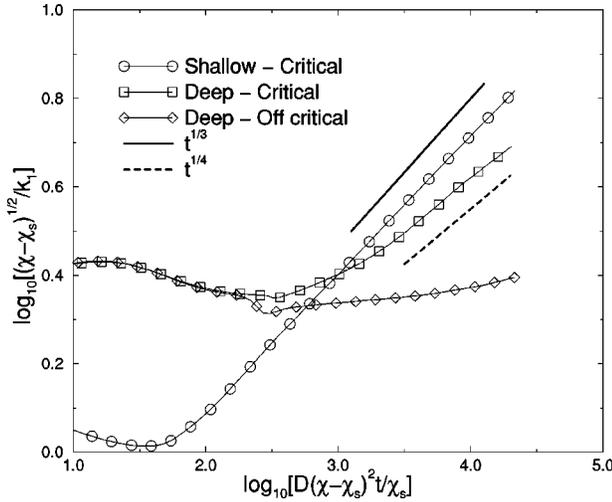
FIG. 1. Plot of the inverse of the rescaled first moment of the structure factor as a function of rescaled time, for the three types of quench performed.

FIG. 3. Plot of the time evolution of the structure factor for the deep off-critical quench (thin solid lines) along with the expression for the pinned structure factor computed in the large-n limit (thick dashed line).

asymptotic growth law $t^{1/3}$. This evolution is the same found for the CH equation and indicates that the dominating mechanism is the usual evaporation and condensation of molecules. For the deep critical quench, the time dependence of $1/k_1(t)$ is similar to the previous case, with the remarkable difference that the asymptotic time exponent is very close to $1/4$. This points out that coarsening is taking place via diffusion of molecules along interfaces [12]. A different behavior is found for the deep strongly off-critical quench: After the linear regime, $k_1(t)$ remains practically constant; only for the longest times of our computation can a very moderate increase in the typical size be spotted. This proves that both coarsening mechanisms are strongly inhibited in this region of the phase diagram. The slight final increase is very likely the first sign of a crossover to an asymptotic power law growth due to the residual evaporation. The difference between critical and off-critical deep quenches is made more evident in the snapshots presented in Fig. 2: While the bi-
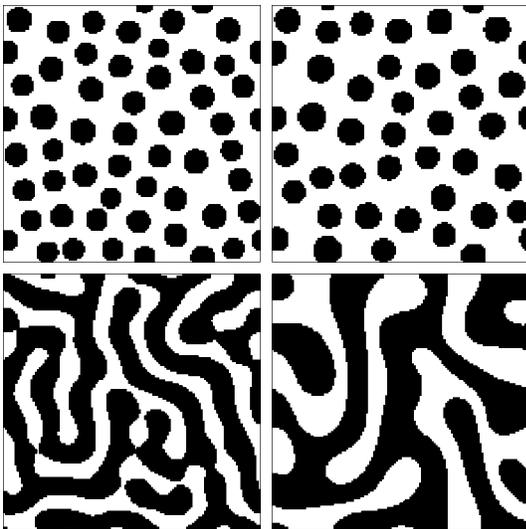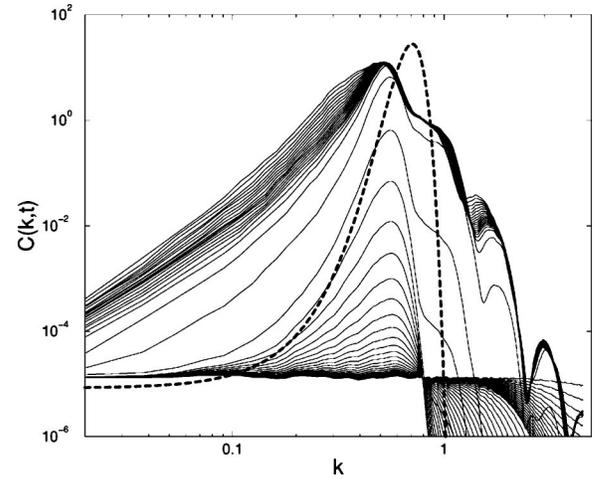
continuous structure of the symmetric composition coarsens in time, during the same time interval droplets remain almost unaltered in the off-critical case. The evolution of the structure factor in the deep off-critical quench is plotted in Fig. 3, along with $C_{pin}^{\infty}(\vec{k})$, the analytic expression for the structure factor in the pinned stage of the large-n limit [11]. One clearly sees that, after the linear stage where the position of the growing peak is fixed, the evolution stops and $C(\vec{k},t)$ remains practically constant. Only for the longest times considered does an appreciable evolution resume for small momenta. The duration of the pinning phenomenon grows when the quench depth is increased. The agreement between the forms of the pinned structure factor in the simulation and in the analytical computation is only partial. This is explained by the fact that $C_{pin}^{\infty}(\vec{k})$ is computed in the limit $\chi N = \infty$, while $\chi N = 10$ in the simulation. The agreement is expected to improve as deeper quenches are considered. For instance, the position k_0 of the maximum of $C(\vec{k},t)$ in the simulation converges, as χN goes to ∞, to the peak position $k_0^{\infty} = 1/\sqrt{2}$ of C_{pin}^{∞}.

The numerical results presented above contribute to the clarification of an issue that has originated some debate in recent years: the behavior of a phase-separating mixture described by the FHDG free energy and in particular the possibility for such a model to exhibit a noticeable slowdown for sufficiently off-critical quenches. The results confirm the physical picture obtained from the large-n approximate solution: the continuum model for phase separation with the FHDG free energy functional can undergo a temporary pinning during its time evolution. The crucial additional condition which was not taken into account by previous studies is that deep off-critical quenches must be considered. When the quench is deep the evaporation-condensation mechanism, which usually governs phase-separation, is strongly suppressed. For critical quenches this suppression leads to the dominance of the other growth process, diffusion along interfaces, and is reflected by the change in the growth exponent from $z=3$ to $z=4$. For sufficiently off-critical concentrations interfacial diffusion is also inhibited, because

FIG. 2. Snapshots of a system for times corresponding to $D(\chi -\chi_s)^2 t/\chi_s$ around 10^3 (left column) and 10^4 (right column) in the deep critical (bottom) and deep off-critical (top) cases.

droplets of the minority phase formed during the linear regime are isolated and almost spherical, so that no reduction of the interfacial free energy can be obtained via simple diffusion of molecules along domain walls. As a consequence, phase separation is pinned.

Once the issue of the existence of a pinned stage in this model has been settled and we know the parameters controlling the occurrence of the slowdown, it is natural to compare our findings with recent experimental studies [3,5] that reported pinning in phase-separating polymeric blends. It turns out that some features differ between the behavior of the model and real systems. The most relevant difference is the value of the exponent for domain growth. Experiments show a fast growth, with z close to 1, for critical quenches and also for off-critical quenches before pinning sets in. This is at odds with the behavior of the present model, which exhibits much smaller values of $1/z$ for critical quenches and no coarsening at all before the onset of pinning for off-critical concentrations. The absence of domain growth in the latter case is caused by the neglect of thermal noise in the equation of motion (1); its inclusion would lead to a $t^{1/4}$ growth law during the linear regime. However, the much faster growth law in experiments signals that in real systems different coarsening mechanisms are at work. In particular, the large value of the exponent suggests that advection may be important. Therefore hydrodynamical effects must in some way be included to have an accurate modeling of experimental results. Progress in this direction has been accomplished recently [13].

In summary, our results show that a stopping of phase separation in binary polymer blends can be produced by the continuum model based on the FHDG free energy, and predict the possibility of observing pinning even in extremely viscous polymer mixtures, where hydrodynamics can be neglected. It would be very interesting to find out whether it is possible to devise an experimental system exhibiting a pinning phenomenon of the type predicted by the present model.

[1] J. D. Gunton, M. San Miguel, and P.S. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1983) Vol. 8; A.J. Bray, Adv. Phys. **43**, 357 (1994).

[2] K. Binder, Adv. Polym. Sci. **112**, 181 (1994).

[3] T. Hashimoto, M. Takenaka, and T. Izumitani, J. Chem. Phys. **97**, 679 (1992); M. Takenaka, T. Izumitani, and T. Hashimoto, *ibid.* **98**, 3528 (1993); J. Läuger, R. Lay, and W. Gronski, *ibid.* **101**, 7181 (1994); T. Hashimoto, in *Material Science and Technology: Phase Transformations in Materials*, edited by P. Haasen (VCH, Weinheim, 1993), Vol. 12, p.251.

[4] I.M. Lifshitz and V.V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1961); C. Wagner, Z. Elektrochem. **65**, 581 (1961).

[5] H. Takeno and T. Hashimoto, J. Chem. Phys. **107**, 1634 (1997); **108**, 1225 (1998).

[6] A. Chakrabarti, R. Toral, J.D. Gunton, and M. Muthukumar, Phys. Rev. Lett. **63**, 2072 (1989); J. Chem. Phys. **92**, 6899 (1990); J.D. Gunton, R. Toral, and A. Chakrabarti, Phys. Scr. **T33**, 12 (1990).

[7] C. Castellano and S.C. Glotzer, J. Chem. Phys. **103**, 9363 (1995).

[8] Shallow or deep quenches correspond to equilibrium states near the boundaries or well inside the miscibility gap, respectively.

[9] J.S. Langer, M. Bar-on, and H.D. Miller, Phys. Rev. A **11**, 1417 (1975); K. Kitahara and M. Imada, Prog. Theor. Phys. Suppl. **64**, 65 (1978); P.G. de Gennes, J. Chem. Phys. **72**, 4756 (1980).

[10] P.J. Flory, J. Chem. Phys. **9**, 660 (1941); *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953); M.L. Huggins, J. Chem. Phys. **9**, 440 (1941).

[11] C. Castellano and F. Corberi, Phys. Rev. E **57**, 672 (1998).

[12] A.M. Lacasta, A. Hernandez-Machado, J.M. Sancho, and R. Toral, Phys. Rev. B **45**, 5276 (1992).

[13] H. Chen and A. Chakrabarti, J. Chem. Phys. **108**, 6006 (1998).