

Thermodynamically driven incompressible fluid mixtures

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Abstract: We compare two models describing the dynamics of phase separation of incompressible mixtures: A local model proposed by de Gennes, and a nonlocal model proposed by E and Palffy-Muhoray. We find that in the interfacial regime, the local model gives rise to interfacial motion via the Mullins-Sekerka law for moderate quenches, and surface diffusion for deep quenches. The interface dynamics is slowed down sharply as the quench depth is increased. The nonlocal model, on the other hand, has an additional convective mechanism which gives rise to motion by Hele-Shaw dynamics. This additional mechanism is insensitive to the quench depth. While both models explain qualitatively the observed pinning phenomenon for deeply quenched off-critical mixtures, only the nonlocal model predicts the correct dependence of the coarsening rate on the quench depth.

1. Introduction

The purpose of this paper is to compare two models: a local model proposed by de Gennes in order to study the onset of spinodal decomposition [1], and a non-local model proposed by E and Palffy-Muhoray [2], for the dynamics of incompressible fluid mixtures driven by thermodynamic forces. After presenting the two models, we will study the predictions of these models on the dynamics during the spinodal decomposition of polymer-polymer mixtures, with special attention to the pinning phenomena observed in such systems [3, 4]. While leading to the same linear theory for the early stage of the spinodal decomposition, the two models predict very different behavior for the intermediate regime dominated by interfacial dynamics: As the quench depth increases, the non-local model predicts a change from the Mullins-Sekerka interfacial motion to the Hele-Shaw, whereas the local model predicts a change from the Mullins-Sekerka motion to surface diffusion. Since surface diffusion leads to a $t^{1/4}$ coarsening law compared with $t^{1/3}$ given by Mullins-Sekerka and Hele-Shaw motions, the local model predicts a slow-down of the coarsening dynamics as the quench depth increases. Finally, we

will compare these predictions with the experimental work done on the spinodal decomposition of polymer-polymer mixtures. Our work casts doubts on the validity of an earlier theory by Kotnis and Muthukumar [4] on the pinning of the coarsening process.

2. The local and nonlocal models

Consider a fluid mixture of N components. Let ϕ_i be the volume fraction density of the i -th component and ϕ_0 be the volume fraction density of the free volume. By definition, the total volume fraction density sums up to 1

$$\sum_{i=0}^N \phi_i = 1 \quad \text{everywhere in the sample.}$$

We are interested in the case when the free volume is small

$$\phi_0 \ll 1$$

so that the limit $\phi_0 \rightarrow 0$ describes an incompressible mixture:

$$\sum_{i=1}^N \phi_i = 1 \quad \text{everywhere in the sample.} \quad (1)$$

To study the dynamics of such incompressible mixtures, we will restrict ourselves to the following situation:

- The system is driven by chemical potential gradient. More precisely, the spatial gradient $\nabla\mu_i$ of the chemical potential of the i -th component is the force acting on the particles of the i -th component
- The dynamics is purely frictional, meaning that the force on particles of the i -th component is proportional to the velocity of these particles; the constant of proportionality D_i being the “bare” mobility of the i -th component,

These lead to the continuity equation:

$$\partial_t \phi_i + \operatorname{div}(\phi_i D_i (-\nabla\mu_i)) = 0. \quad (2)$$

The remaining issue is how to deal with the constraint imposed by (1). In the following, we will discuss two main competing proposals for dealing with this constraint.

2.1. The local model

De Gennes [1] postulates that the fluxes J_i in the continuity equation $\partial_t \phi_i + \text{div} J_i$ sum up to zero

$$\sum_{i=1}^N J_i = 0, \quad (3)$$

which clearly preserves (1). His ansatz is that there is a force f which acts on all particles such that the fluxes

$$J_i = \phi_i D_i (-\nabla \mu_i - f)$$

satisfy (3). Solving for f leads to

$$\partial_t \phi_i + \text{div}(\Gamma_{ij}(-\nabla \mu_j)) = 0,$$

where the concentration-dependent Onsager coefficients Γ_{ij} are given by

$$\Gamma_{ij} = \delta_{ij} D_i \phi_i - \frac{D_i \phi_i D_j \phi_j}{\sum_{k=1}^N D_k \phi_k}.$$

Although de Gennes was originally motivated by studying the onset of spinodal decomposition, this local model has since been used quite extensively for studying regimes beyond the onset.

2.2. The nonlocal model

In contrast, E and Palffy-Muhoray [2] started from the compressible model in which ϕ_0 is finite and derived their model for incompressible mixtures by performing an asymptotic analysis in the limit as $\phi_0 \rightarrow 0$. They obtain from (2)

$$\partial_t \phi_i + \text{div}(\phi_i D_i (-\nabla(\mu_{0i} + p))) = 0 \quad (4)$$

along with (1). Here μ_{0i} is the chemical potential w. r. t. the free energy F_0 of the incompressible system. In this model, a Lagrange multiplier — the

pressure p — arises from the incompressibility constraint (1). Notice that the pressure is such that the fluxes

$$J_i = \phi_i D_i (-\nabla(\mu_{0i} + p))$$

satisfy

$$\operatorname{div} \left(\sum_{i=1}^N J_i \right) = 0.$$

As opposed to the above model (3), this model only requires the *divergence* of the sum of the fluxes to vanish. From the view point of lattice models, the above model corresponds to a Kawasaki type of pair exchange dynamics, whereas this model corresponds to a ring exchange mechanism involving possibly more than two lattice points. In the case when vacancies are abundant, events involving more than two points are rare. Therefore the difference between the two mechanisms is small. However, this difference becomes important when almost all lattice sites are occupied which is the case of interest here.

We observe that (4) together with

$$\operatorname{div} \left(\sum_{i=1}^N \phi_i D_i (-\nabla(\mu_{0i} + p)) \right) = 0 \quad (5)$$

uniquely define dynamics for ϕ_1, \dots, ϕ_N which preserve the incompressibility constraint (1). Because p has to be determined from the elliptic equation (5) and hence depends nonlocally on ϕ_1, \dots, ϕ_N , we call this the *nonlocal* model.

2.3. Two-component mixtures

For simplicity, we will henceforth consider the case of two component mixtures of the same bare mobility $D = D_1 = D_2$. In this case, both the local and nonlocal models can be compactly reformulated in terms of $\phi := \phi_1 = 1 - \phi_2$ and the difference of the chemical potentials $\mu := \mu_{01} - \mu_{02}$, which is the variational derivative of F_0 , considered as a functional of ϕ .

The local model can be written as:

$$\partial_t \phi + \operatorname{div}(D \phi (1 - \phi) (-\nabla \mu)) = 0, \quad (6)$$

which is the conventional Cahn–Hilliard equation with the ϕ -dependent mobility $D \phi (1 - \phi)$. In contrast, the nonlocal model becomes:

$$\partial_t \phi + \operatorname{div}(D \phi \mathbf{P} [(1 - \phi) (-\nabla \mu)]) = 0, \quad (7)$$

where \mathbf{P} denotes the Helmholtz projection, i.e. the orthogonal projection onto the space of irrotational vector fields. Since $\mathbf{P}[(1 - \phi)(-\nabla\mu)] = (1 - \phi)(-\nabla\mu) + (\mathbf{I} - \mathbf{P})[\phi(-\nabla\mu)]$ (where \mathbf{I} is the identity operator), (7) can be rewritten as

$$\partial_t \phi + \operatorname{div}(D\phi(1 - \phi)(-\nabla\mu)) + \operatorname{div}(\phi u) = 0, \quad (8)$$

where $u = (\mathbf{I} - \mathbf{P})(D\phi(-\nabla\mu))$ is the divergence-free part of $D\phi(-\nabla\mu)$. We now see that compared to (6) there is an additional term of convective nature.

An important first observation is that the nonlocal term in (8) provides an *additional* energy dissipation mechanism. In fact, it can be easily computed that

$$\frac{d}{dt} F_0 = \left\{ \begin{array}{ll} -\int D\phi(1 - \phi)|\nabla\mu|^2 & \text{for the local model} \\ -\int D\phi(1 - \phi)|\nabla\mu|^2 - \int |u|^2 & \text{for the nonlocal model} \end{array} \right\}. \quad (9)$$

The first term in the energy dissipation weakens as ϕ approaches 0 or 1. In contrast, the new energy dissipation mechanism generated by the term $\operatorname{div}(\phi u)$, is not affected by the degeneracy of the mobility $D\phi(1 - \phi)$ for ϕ close to 0 and 1. This fact will be of crucial importance to our discussions below.

2.4. The nonlocal model is a gradient flux

(9) shows that F_0 is a Liapunov functional for both the local and nonlocal models. It is more remarkable that the nonlocal model can be considered as the gradient flux of the free energy functional. It is doubtful whether the local model can be understood in a similar way.

More precisely, (4, 5) is the steepest descent of F_0 , restricted to the set of all incompressible configurations (ϕ_1, \dots, ϕ_N) (i.e. satisfying (1)), provided we endow this set with the following notion of distance: The distance between two configurations $(\phi_1^{(0)}, \dots, \phi_N^{(0)})$ and $(\phi_1^{(1)}, \dots, \phi_N^{(1)})$ is given by

$$\left(\sum_{i=1}^N \frac{1}{D_i} d(\phi_i^{(0)}, \phi_i^{(1)})^2 \right)^{\frac{1}{2}},$$

where $d(\phi^{(0)}, \phi^{(1)})$ denotes the Wasserstein distance between the densities $\phi^{(0)}$ and $\phi^{(1)}$ (for more details on this notion of distance, see [5]).

The Wasserstein distance is a natural notion of distance between particle densities. Loosely speaking, the square of the Wasserstein distance $d(\phi^{(0)}, \phi^{(1)})^2$ is the minimal “cost” of transferring the particles from an arrangement described by the density $\phi^{(0)}$ to an arrangement described by the density $\phi^{(1)}$. Here the cost of transferring any particle from location x to location y is the squared euclidean distance between x and y .

3. Spinodal decomposition of polymer melts

We will study the spinodal decomposition of a polymer-polymer mixture quenched to the unstable regime. We use the Flory–Huggins–de Gennes free energy functional for a saturated melt of two species of polymers (type A and B) of identical degree of polymerization:

$$F_0(\phi) := \int \left\{ f(\phi) + \frac{a^2}{36 \phi (1 - \phi)} |\nabla \phi|^2 \right\} \quad (10)$$

with coarse grained free energy

$$f(\phi) := \frac{1}{N} (\phi \ln \phi + (1 - \phi) \ln(1 - \phi)) + \chi \phi (1 - \phi). \quad (11)$$

Here N is the degree of polymerization and a is the effective segment size per monomer (for both A and B). χ is the effective Flory interaction parameter between the A - and B -monomers, normalized by kT ; χ can be controlled by the temperature. We refer to section 4.3 for a discussion of the various terms in the free energy. When χ is above the critical value $\chi_{crit} = \frac{2}{N}$, f is non-convex. Otherwise it is convex. In the non-convex case, f has two minima $\phi_- < \phi_+$ which are symmetric with respect to $\phi = \frac{1}{2}$: $\phi_- = 1 - \phi_+$, and $f(\phi_-) = f(\phi_+)$.

We now consider the case when a homogeneous mixture is suddenly quenched into the spinodal region. That is, we assume that $\chi > \chi_s$ for $t > 0$ and that ϕ is equal to a constant value $\phi^0 \in (\phi_-, \phi_+)$ at $t = 0$. We are interested in the regime when

$$\frac{1}{N} < \chi \ll 1.$$

For simplicity, we measure the strength of the quench by the quench depth for a critical mixture (that is $\phi^0 = \frac{1}{2}$)

$$\epsilon = \frac{\chi - \chi_{crit}}{\chi_{crit}} = \frac{N\chi - 2}{2}.$$

3.1. The early stage

When linearized around a homogeneous state, the local and non-local models coincide. Hence the two models do not differ substantially in the early stages of spinodal decomposition.

3.2. The interfacial regime

After the initial stage, the mixture approaches a state where ϕ is close to its equilibrium values ϕ_- , ϕ_+ except at very thin layers which can be thought of as being interfaces separating the bulk phases. This is the interfacial regime. In the interfacial regime, the dynamics of spinodal decomposition can be reduced to the motion of the interface. We will compare the local and the nonlocal model in the interfacial regime.

Let us first describe the common features of the two models in the interfacial regime. The profile of ϕ across the interfacial layer is approximately described by the one-dimensional stationary point $\phi^*(x)$ of F which links ϕ_- at $x = -\infty$ to ϕ_+ at $x = +\infty$. The corresponding Euler equation is

$$\frac{a}{6} \frac{d}{dx} \phi^* = (\phi^* (1 - \phi^*) [f(\phi^*) - f(\phi_-)])^{\frac{1}{2}}. \quad (12)$$

From this we see that the free energy is approximately proportional to the interfacial area:

$$F_0 = c_0 \times \text{area of } \Gamma + f(\phi_-) \times \text{volume of sample}, \quad (13)$$

where for definiteness we choose Γ to be the level set $\phi = \frac{1}{2}$. The multiplicative constant c_0 is the excess free energy of ϕ^* , which can be calculated with the help of (12)

$$c_0 = \frac{a}{3} \int_{\phi_-}^{\phi_+} \left(\frac{f(\phi) - f(\phi_-)}{\phi(1 - \phi)} \right)^{\frac{1}{2}} d\phi.$$

(13) suggests that μ , the variational derivative of F_0 w. r. t. ϕ , is related to the mean curvature κ of Γ by

$$(\phi_+ - \phi_-) \mu = c_0 \kappa \quad \text{in the interfacial layer.} \quad (14)$$

On the other hand, we infer from (6) or (8) that μ is harmonic away from the interfacial layer

$$\Delta \mu = 0 \quad \text{in the bulk phases} \quad (15)$$

So far, both models agree.

The local model in the interfacial regime

The local model is pure diffusion: Polymer chains of type A diffuse from regions of high chemical potential to regions of low chemical potential (a similar statement also holds for the chains of type B). In the interfacial regime, this means that the A -chains “evaporate” at the interface of the A -rich bulk region where this interface has high (positive) mean curvature, diffuse through the B -rich bulk region and “condensate” again at part of the interface of the A -rich bulk region with lower (possibly negative) curvature. This is the so-called “evaporation–condensation” mechanism. As mentioned above, the local model dissipates free energy F while conserving the volume $\int \phi$. In view of (13), it thus reduces interfacial area while preserving the volume of each bulk phases $\phi = \phi_+$ and $\phi = \phi_-$ in the interfacial regime. Hence this mechanism coarsens the bulk domains. It is intuitively clear from this picture that the speed at which this mechanism operates is proportional of the mobility of the chains in the bulk. As can be seen from (6), this mobility is equal to $D \phi_- (1 - \phi_-) = D \phi_+ (1 - \phi_+)$.

In order to make this more precise, we characterize the interfacial motion using a model proposed by Mullins and Sekerka. Consider the idealization of a sharp interface Γ separating the two bulk phases $\phi = \phi_+$ and $\phi = \phi_-$. From (6) we infer that the velocity V of Γ in its normal direction is given by

$$(\phi_+ - \phi_-) V = D \phi_- (1 - \phi_-) [\nabla \mu \cdot \nu], \quad (16)$$

see [6] for a careful analysis. Here $[\cdot]$ denotes the jump of the quantity in the brackets across Γ in the direction of its normal ν . Combining (16) with (14), we obtain

$$(\phi_+ - \phi_-)^2 V = D c_0 \phi_- (1 - \phi_-) \mathcal{MS}, \quad (17)$$

where \mathcal{MS} is the normal velocity of the Mullins–Sekerka interfacial motion:

$$\mathcal{MS} := [\nabla \psi \cdot \nu],$$

with the potential ψ uniquely determined by the position of Γ via

$$\Delta \psi = 0 \text{ except on } \Gamma \quad \text{and} \quad \psi = \kappa \text{ on } \Gamma.$$

Notice that for deep quenches $\epsilon \gg 1$, $\phi_- = 1 - \phi_+ = \exp(-(2\epsilon + 1))$. The crucial observation is that already for moderately deep quenches, ϕ_- and

thereby the *bulk mobility is very small*. Hence bulk diffusion is very slow. Therefore a second mechanism may dominate: diffusion along the surface. Within the interfacial layer, the mobility is of order D as opposed to $D\phi_-(1-\phi_-)$ in the bulk. Hence ϕ may diffuse freely along the interface (more precisely within the interfacial layer), again from regions of high chemical potential μ to regions of low chemical potential.

To better study surface diffusion, we assume that bulk diffusion is effectively suppressed by $\phi_- \ll 1$. Surface diffusion then operates in the following way: The gradient of the chemical potential along the interfacial layer creates a flux of the molecules along the interfacial layer, making the interfacial layer eventually move. In the idealization of a sharp interface we obtain

$$V = D c_1 \Delta_\Gamma \mu,$$

see [7] for a careful asymptotic analysis. Here Δ_Γ denotes the surface Laplacian on Γ and c_1 is obtained by integrating $\phi^*(1-\phi^*)$ from $x = -\infty$ to $x = +\infty$:

$$c_1 = \frac{a}{6\chi^{\frac{1}{2}}} \quad \text{for } \epsilon \gg 1.$$

Hence we have

$$V = D c_0 c_1 \mathcal{SD}, \tag{18}$$

where \mathcal{SD} is the normal velocity of the interfacial motion by the surface Laplacian of the mean curvature:

$$\mathcal{SD} = \Delta_\Gamma \kappa.$$

Evidently, bulk diffusion and surface diffusion scale differently. The interfacial velocity due to bulk diffusion is proportional to $\phi_-(1-\phi_-)/L^2$, where L is typical lengthscale of the bulk regions. The interfacial velocity due to surface diffusion is proportional to l/L^3 , where $l \ll L$ is the thickness of the interfacial layer. Hence surface diffusion should dominate bulk diffusion when $l/L \gg \phi_-(1-\phi_-)$.

Let us now express our findings on the local model in its natural nondimensionalized form obtained by rescaling time and the spatial variables in such a way that the linearization of the equation around the homogeneous state $\phi^0 = \frac{1}{2}$ does not depend on D, a, χ, N . More precisely, we rescale the variables in such a way that the most unstable wavelength and its growth

rate are the units for length and time. To achieve this, one has to measure time in units of $\frac{a^2 N^2}{D \epsilon^2}$ and length in units of $(N a^2 \frac{1}{\epsilon})^{\frac{1}{2}}$. This nondimensionalization is related to the “scaling hypothesis” of [8]. Aside from some absolute constants the nondimensionalized form of (17) for $\epsilon \gg 1$ is

$$V = \exp(-(2\epsilon + 1)) \mathcal{MS}$$

and the nondimensionalized form of (18) for $\epsilon \gg 1$ is

$$V = \mathcal{SD}.$$

Note that in a statistically self-similar sharp interface regime, the typical length scales like $t^{\frac{1}{3}}$ for \mathcal{MS} and $t^{\frac{1}{4}}$ for \mathcal{SD} . Since the prefactor of \mathcal{MS} is very small, coarsening may be dominated by \mathcal{SD} in the beginning. However, because of the different self-similar scaling, \mathcal{MS} eventually takes over. In any case, *the speed of coarsening decreases strongly with increasing quench depth*. This effect is not due to a decreasing of driving force (in fact, the driving force for bulk diffusion does not depend on ϵ for $\epsilon \gg 1$ in this nondimensionalization), but rather due to a strongly decreased mobility and hence is of kinematic nature.

The nonlocal model in the interfacial regime

The nonlocal model has an *additional* mechanism to reduce free energy (interfacial area in the interfacial regime): convection. Molecules of type A are convected by the incompressible velocity field u from regions of high chemical potential μ to regions of low chemical potential within one connected component of the bulk phase. As can be seen from (9) and (13), this convection mechanism by itself also reduces interfacial area while preserving the total volume of the bulk phases.

The dynamics of the interface due to this additional convective component can be described by the Hele-Shaw model for the flow of two viscous, immiscible fluids between two narrowly placed glass plates. In the notation used earlier, (17) changes to

$$(\phi_+ - \phi_-) V = D \frac{c_0}{\phi_+ - \phi_-} \phi_- (1 - \phi_-) \mathcal{MS} + (\phi_+ - \phi_-) u \cdot \nu$$

where u is the divergence-free part of $D \phi(-\nabla \mu)$. Since the difference of $D \phi(-\nabla \mu)$ and $D \nabla \phi \mu$ is a gradient, u can also be written as the divergence-free part of $D \nabla \phi \mu$. In the interfacial regime, $D \nabla \phi \mu$ is approximated by

the distribution $D c_0 \kappa \nu \delta_\Gamma$ where δ_Γ is the surface delta function. From this one can infer that

$$u \cdot \nu = D c_0 \mathcal{HS}$$

where \mathcal{HS} is the normal interfacial velocity in the Hele–Shaw interface motion

$$\mathcal{HS} = \nabla q \cdot \nu,$$

with the potential q uniquely determined by the position of Γ via

$$\Delta q = 0 \text{ outside of } \Gamma \quad \text{and} \quad [q] = \kappa, \quad [\nabla q \cdot \nu] = 0 \text{ on } \Gamma.$$

Hence we have

$$(\phi_+ - \phi_-)^2 V = D c_0 \left(\phi_- (1 - \phi_-) \mathcal{MS} + (\phi_+ - \phi_-)^2 \mathcal{HS} \right). \quad (19)$$

The result expressed in (19) allows us to assess the relative importance of diffusion vs. convection mechanisms in the nonlocal model. Observe that both convection and diffusion are driven by the same force, the spatial gradient of the chemical potential, and that both reduce the free energy. For shallow quenches, i.e. $\phi_+ - \phi_- = 1 - 2\phi_- \ll 1$, diffusion dominates convection and the nonlocal model does not differ much from the local one. For deep quenches, that is $\phi_- \ll 1$, convection dominates diffusion. To be more precise, we nondimensionalize the nonlocal model in the same way as we did with the local model. We obtain for $\epsilon \gg 1$

$$V = \exp(-(2\epsilon + 1)) \mathcal{MS} + \mathcal{HS}.$$

Hence we see that the convection mechanism does not weaken with increasing quench depth as the diffusion mechanism does.

4. Pinning: Percolation to droplet transition

4.1. Predictions of the models and numerical results

In order to see how a quench depth enforced shift from \mathcal{MS} to \mathcal{SD} (for the local model) or to \mathcal{HS} (for the nonlocal model) affects qualitative aspects of the coarsening, we now compare the interfacial motions \mathcal{MS} , \mathcal{HS} and \mathcal{SD} . We first observe that all three reduce the interfacial area while preserving the volume of each phase. We also notice that in a self-similar regime, \mathcal{MS} and

\mathcal{HS} lead to the same scaling: The typical lengthscale L is proportional to $t^{\frac{1}{3}}$; whereas for \mathcal{SD} , L scales like $t^{\frac{1}{4}}$.

On the other hand, there is a qualitative difference between \mathcal{MS} on one side and \mathcal{HS} , \mathcal{SD} on the other side. In \mathcal{HS} , the convectional mechanism, and \mathcal{SD} , the surface diffusion mechanism, there is no transfer of A -molecules from one connected component of the A -rich phase to another connected component of the A -rich phase. In \mathcal{MS} , the diffusional mechanism, connectivity plays no role. More specifically: In \mathcal{HS} and \mathcal{SD} , a collection of multiple size spherical nuclei of the A -rich phase immersed in a matrix of the B -rich phase is stationary. In \mathcal{MS} , the larger nuclei grow at the expense of the smaller ones — the mechanism of Ostwald ripening. This observation is not surprising: As pointed out earlier, \mathcal{HS} describes a surface tension driven fluid flow — where a collection of spherical droplets immersed in a matrix of the other phase is obviously stationary. Loosely speaking, \mathcal{HS} and \mathcal{SD} have more conserved quantities than \mathcal{MS} : The volume of *each* connected component of both phases is conserved. In \mathcal{MS} , only the overall volume of both phases is conserved. We observe though, that the number of connected components may change over time in all three interfacial motions.

This leads to the following predictions for a deep quenched system when coarsening due to bulk diffusion (that is via \mathcal{MS}) is effectively suppressed. In this case coarsening proceeds by convection (\mathcal{HS}) for the nonlocal model or surface diffusion (\mathcal{SD}) for the local model. For an off-critical mixture, as phase separation proceeds, the minority phase will cease to be continuous and break up into clusters (droplets), an event which has been called percolation-to-cluster transition by Hashimoto et. al. [3]. After that, the droplets will rapidly relax to spherical shape and coarsening is effectively stopped. In this sense, coarsening is said to be *pinned*. Notice that both the local and the nonlocal model predicts pinning.

On the other hand, for critical mixtures, the morphology will stay bicontinuous. In this case, the \mathcal{HS} resp. \mathcal{SD} mechanism acts over the whole extent of these structures and drives the coarsening. As mentioned earlier, in the self-similar regime, we have $L = t^{\frac{1}{3}}$ for the nonlocal model and $L = t^{\frac{1}{4}}$ for the local model.

We have numerically simulated the dynamics of the nonlocal model. (8) was discretized using a finite difference method on the domain $[0, 2\pi] \times [0, 2\pi]$. Although the results we present below were computed on a 400×400 grid, we checked that the same results can already be obtained on a 256×256

grid. In Figure 1, we plot the correlation length as a function of time for two mixtures, one with a 0.5/0.5 composition (the upper curve) and one with a 0.3/0.7 composition (the lower curve). It is clear from Figure 1 that while for the critical mixture, the morphology continues to coarsen, the coarsening has effectively stopped for the off-critical mixture after $t = 1$. The slight growth of the correlation length for the off-critical mixture can be attributed to the finite size of a in the free energy: decreasing a leads to slower growth. In Figures 2 and 3 we compare the morphologies obtained for the two cases. We see that the morphology for the critical mixture is bicontinuous (and remains to be bicontinuous), the minority phase in the off-critical mixture has broken into almost circular droplets.

Even though our theory predicts that the same qualitative behavior should exist for the local model, it would be much more difficult to observe this numerically since the coarsening process in the local model is sharply slowed down for deep quenches (surface diffusion acts on a much slower time scale). Numerical work on the local model can be found in [10] and [11].

4.2. Comparison with experiments

It is well established that the early stages of spinodal decomposition in polymer melts are adequately described by the linearization of the local model [12], which coincides with the linearization of the nonlocal model.

The phenomenon of pinning for strongly quenched off-critical polymer blends has been reported by Hashimoto et. al. [3] with light scattering experiments. Comparing the measured structure factor to structure factors of bicontinuous morphologies and droplet morphologies, they came to the conclusion that pinning occurs when the percolation-to-cluster transition takes place. Lauger et. al. were able to confirm this by optical microscopy [13]. As we have argued above, both local and nonlocal model explains this phenomenon qualitatively.

On the other hand, Hashimoto et. al. report that the rate of coarsening does not depend strongly on the quench depth. In the nondimensionalization introduced above, the $\ln L - \ln t$ -plot does not depend on ϵ for ϵ ranging from 2.19 to 2.94 [14]. This is consistent with the nonlocal model, whereas the local model predicts a noticeable shift downwards of this plot for ϵ changing from 2.19 to 2.94.

4.3. Remark on the work of Kotnis and Muthukumar

Kotnis and Muthukumar proposed that it is an entropic barrier that suppresses the bulk diffusion mechanism [4]. To outline their theory let us first identify the entropic and enthalpic contributions to the free energy. The entropic contribution to the free energy is twofold: the translational and the conformational entropy of the polymer chains. We treat the translational entropy first: Observe that in saturated melt, $\frac{\phi}{N}$ is proportional to the concentration of A -chains and $\frac{1-\phi}{N}$ is proportional to the concentration of B -chains (our attention is on the N -dependence here). Hence the mean field approximation of the translational entropy of a mixture of A and B -chains is given by

$$\begin{aligned} & \int \left\{ \frac{\phi}{N} \ln \frac{\phi}{N} + \frac{1-\phi}{N} \ln \frac{1-\phi}{N} \right\} \\ &= \int \frac{1}{N} \{ \phi \ln \phi + (1-\phi) \ln(1-\phi) \} + \text{const}. \end{aligned}$$

For the conformational entropy: Observe that ϕ is proportional to the concentrations of A -monomers. Because of the chain connectivity, variations of ϕ on lengthscales of the order a reduce the number of possible chain conformations. Various methods of coarse graining of this conformational entropy lead to the term

$$\int \frac{a^2}{36\phi} |\nabla\phi|^2.$$

Taking into account the polymers of type B and incompressibility, we get that the entire entropic contribution to the free energy is given by

$$\int \left\{ \frac{1}{N} (\phi \ln \phi + (1-\phi) \ln(1-\phi)) + \frac{a^2}{36\phi(1-\phi)} |\nabla\phi|^2 \right\}.$$

Within this square-gradient coarse grained description, the enthalpic contribution would be

$$\int \{ \chi \phi(1-\phi) + \chi \lambda^2 |\nabla\phi|^2 \},$$

where λ is the range of the interactions between monomers, which is assumed to be of the order a . Two observations are immediate: In the regime $\frac{1}{N} \leq \chi \ll 1$, bulk contribution of the enthalpy tends to dominate the bulk contribution of the entropy. On the other hand, the gradient part of the enthalpy is negligible compared to the gradient part of the entropy. Neglecting this gradient part leads to (10).

In the deep quench regime, that is $N\chi \geq 1$, the interfacial thickness $\frac{a}{\chi^{\frac{1}{2}}}$ is of the order of or smaller than the radius of gyration $aN^{\frac{1}{2}}$ of a polymer chain. Kotnis and Muthukumar argue that because of the loss of conformational entropy of a chain at the interfacial layer, there exists an entropic barrier proportional to N for chain transport across the interface. They further argue that this entropic barrier prevents A -chains to be pulled out of the A -rich domain across the interface into the B -rich phase followed by the diffusion and further condensation into another A -rich domain — and thereby suppresses bulk diffusion. We believe this is not the right picture: Bulk diffusion operates not by pulling chains of type A out of the A -rich *bulk domain*, it operates by removing chains from the *interfacial layer*.

Our picture of bulk diffusion and its suppression is the following: At lowest order, there is a local equilibrium between evaporation and condensation of chains at the interface. Both A and B chains increase their conformational entropy if they move away from the interface. In the deep quench regime, the concentration of A -chains in the B -rich bulk is very small and vice versa. Because of the incompressibility, the only way chains can move away from the interface is if A -chains evaporate into the B -rich bulk while B -chains evaporate into the A -rich bulk. But this is counteracted by the repulsive interactions between A -monomers and B -monomers. Hence this is an equilibrium between enthalpy and conformational entropy.

We now describe the next order effect: At positively curved interfacial regions (convex w. r. t. the A -rich phase), A -chains are more likely to evaporate than to recondensate, as, on the average, the repulsive interactions are already rather numerous in their exposed condensed position. The opposite is true at negatively curved interfacial regions. In other words, there is a difference in chemical potential between these parts of the boundary. The issue is now if and how these distant interface parts communicate. Diffusion can be thought of as to operate in the following way: Two neighboring A and B chains exchange their position with a probability proportional to the difference in the chemical potential at these positions. Hence in a mean-field approximation, the net flux is proportional to the product of the concentration of A -chains, the concentration of B -chains and the local gradient of the chemical potential. But the concentration of A -chains in the B -rich bulk is very small for a deep quench, so that bulk diffusion is effectively suppressed.

To support their entropy barrier argument, Kotnis and Muthukumar [4]

also present numerical simulations of the local model with a free energy, whose square gradient part is given by the entropy contribution

$$\int \frac{a^2}{36 \phi (1 - \phi)} |\nabla \phi|^2, \quad (20)$$

and a free energy, whose square gradient part is given by the enthalpic contribution

$$\int \chi \lambda^2 |\nabla \phi|^2 \quad (21)$$

only, as it would be for ordinary binary fluids. In an appropriate nondimensionalization, they found pinning for (20) in off-critical mixtures and under deep quench conditions, but they found no pinning for (21).

We question the finding that a change from (20) to (21) makes a difference w. r. t. pinning. Indeed, Glotzer et. al. [10] have shown that approximate solutions of the local model may get artificially pinned by a lack of numerical resolution. This might apply to the numerical simulation in [4], which is based on a $32 \times 32 \times 32$ lattice. In addition, our prior discussion shows that a change from (20) to (21) should make no qualitative difference in the interfacial regime. Indeed, the only quantitative effect of a change from (20) to (21) seems to point in the opposite direction since (12) for the one-dimensional stationary point ϕ^* of F_0 has to be replaced by the more conventional

$$\chi^{\frac{1}{2}} \lambda \frac{d}{dx} \phi^* = (f(\phi^*) - f(\phi_-))^{\frac{1}{2}}.$$

Hence in the appropriate nondimensionalization, a change from (20) to (21) flattens the profile of ϕ across the interfacial layer, giving diffusion further away from the interface more room to act.

5. Conclusions

Let us summarize our most important observation regarding the nonlocal model in the nondimensionalized form. *In contrast to the local model, the nonlocal model does not predict indiscriminately a strong decrease in the rate of coarsening when the quench depth is increased.* More precisely, the coarsening rate of bicontinuous structures is not affected by an increase of the quench depth. On the other hand for off-critical mixtures in a deep quench, coarsening is effectively pinned after the morphology undergoes the percolation-to-cluster transition.

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