Kinetics of Domain Growth and Wetting in a Model Porous Medium

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We report results from computer simulations of the kinetics of domain growth and wetting in a binary liquid mixture contained inside a model porous medium which has an interconnected and tortuous structure resembling Vycor glass. We find that the growth process slows down dramatically when the average size of the domains is comparable to the average pore radius and dynamical scaling breaks down at late stages. We argue that the random-field model cannot be invoked to explain these results. On the other hand, the single-pore model seems to be reasonably successful in explaining the source of this slow growth.

Macroscopic phase separation takes place when a binary liquid mixture is quenched rapidly from one-phase region to a point inside the coexistence curve [1]. For critical quenches, it has been found experimentally [2,3] that the intermediate stage can be described by a diffusive growth mechanism [4] while hydrodynamic effects [5] become important at late stages. It is also well established that when domain sizes are much larger than the interfacial thickness, there is only one dominant length scale in the system and this results in a time-invariant master curve for the scattering intensity.

The above course of phase separation is completely altered when the fluid mixture is contained inside a porous medium [6–9]. In this case, phase separation does not proceed to a macroscopic scale and many small micro-domains rich in either of the two components are formed. The theoretical understanding of this lack of macroscopic phase separation is incomplete. Two very different theoretical interpretations can be found in the literature. The first one suggests [10] that the preference of the random pore surface for one of the components of the mixture manifests as a random field in the problem, which gives rise to the metastability and the slow kinetics of domain growth seen in experiments. Recently, this random-field description has been criticized [11] to be inapplicable in the case of low-porosity media such as the Vycor glass. It has been argued theoretically that a single-pore model without any randomness can be used as a model system to understand various effects observed in experiments with Vycor glass. This single-pore model allows for various long-lived metastable configurations (called "plugs" and "capsules") depending on temperature and the strength of the interaction of the pore surface with one of the components of the mixture. Monte Carlo simulations have been carried out recently [12] which support the presence of these metastable configurations. Simulations in this single-pore model also suggest [13] that the kinetics of domain growth slows down radically when the average domain size and the pore radius become comparable.

The single-pore model does not seem to be a realistic description of the phase separation process in high-porosity medium (such as various gels) which is constituted of a dilute network of strands. There is some evidence from experiments that the random-field model may be applicable for phase separation in such a medium [14]. Even for a low-porosity medium, such as the Vycor glass, it is not clear *a priori* that the single-pore model contains all the necessary physics since the interconnected structure of the confining geometry might play an important role in the phase separation process by creating extra barriers to domain growth. These issues are, however, difficult to resolve completely in experiments since it is difficult to find real systems with a widely varying porosity, pore size, and surface affinity for one of the components of the mixtures. Clever computer simulations, on the other hand, could play a very important role by a systematic isolation of the important parameters controlling the growth process and morphology of the domains.

With this in mind, we have carried out large-scale simulations of the kinetics of domain growth process in a model porous medium of quite high porosity (about 75%). The novelty of this study is that the porous medium considered here has an interconnected and tortuous structure resembling Vycor glass, although the porosity of the model system is much higher than in commercially available Vycor glass. The binary mixture in our simulations is contained inside the pore region of this model porous medium. The kinetics of phase separation of such a mixture is then numerically studied using a Cahn-Hilliard description [1] with proper boundary conditions to incorporate the presence of the porous medium. We have studied the process of domain growth in both the presence and absence of surface fields which stands for the interactions of the pore surface with the components of the mixture. Our main result is that the interconnected and tortuous geometry of the porous medium creates barriers to domain growth. Even in the absence of any surface interactions we find that the domain morphology consists of a large number of plugs and the growth process slows down dramatically when the average size of the domains is comparable to the average pore radius, as predicted by the single-pore model [11]. We also find that there are many length scales present in the system and

that dynamical scaling breaks down at late stages. Since a prerequisite for the random-field description is the presence of a preferred attraction of one of the components to the pore surface, these results clearly demonstrate that the random-field model cannot be invoked to explain the nonalgebraic domain growth and the breakdown of the dynamical scaling in this case. On the other hand, the single-pore model seems to work reasonably well in explaining the slow domain growth seen in the simulations. We find similar results of slow domain growth and a breakdown of dynamical scaling when the surface field is present, although the domain configurations are quite different now showing the presence of a wetting layer.

An important ingredient in our simulations is the construction of the porous medium whose structure would resemble a real system. We followed *commercial methods* of making Vycor glass in this context. Vycor is made commercially by quenching a borosilicate glass into the spinodal region and then etching out the softer phase with acid such that all the pores are interconnected. In our two-dimensional model, we start from a 256×256 lattice consisting of a 50-50 mixture of two components and model the quenching process by a cell-dynamics [15] simulation method. We have stopped the phase separation process after a reduced time of $t = 1000$ and "etched out" one of the two phases. This creates an interconnected morphology of the "pores" if one uses a cutoff value of 0.97 for the order parameter for the "etching." We find that the "porosity" of this system is about 75% with an average pore radius of about 15 lattice spacing [16]. This model porous medium is shown in Fig. 1 where the white region corresponds to the pores and the black region corresponds to the solid material or "glass."
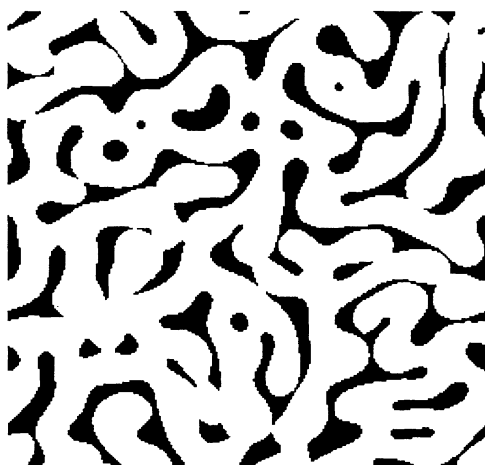
Once the porous medium is constructed, we start from

a critical mixture of two components A and B which is confined in the pore region. We then model the domain growth process in this porous medium by numerically integrating the Cahn-Hilliard equation for the order parameter. In the Cahn-Hilliard model, one considers a concentration field, $\psi(\mathbf{r},t)$, which represents the difference in the local concentration of the two components of the mixture. It is assumed that the time variation of this conserved field is governed by the functional derivative of a free-energy functional given in terms of a Ginzburg-Landau expression. After suitable rescaling of distance, time, and concentration field [17], the resulting equation of motion is
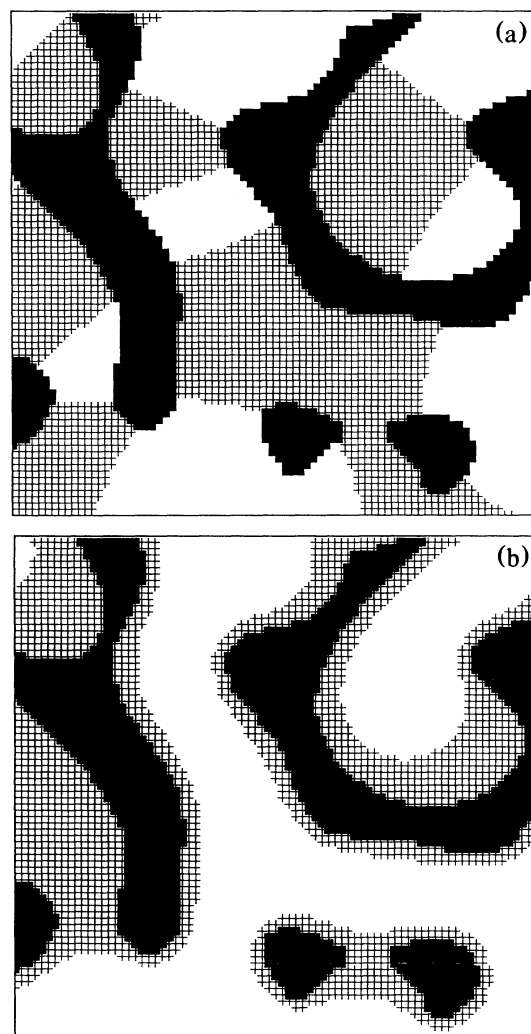

FIG. 2. (a) Domain morphology in an 80×80 section of the full 256×256 system in the absence of any surface field. The white and the shaded regions correspond to the two phases of the binary mixture and the black region corresponds to the "glass." The domains are formed in the shape of "plugs" (Ref. [11]). (b) Same as in (a) except in the presence of surface field of strength $h = 1$. Note the presence of a wetting layer around the "glass" surface.

FIG. 1. The model porous medium constructed by a cell-dynamics simulation [15] method (see text). The white region corresponds to the "pores" and the black region corresponds to the "glass." The "porosity" of this system is about 75% with an average pore radius of about 15 lattice spacings.

$$\frac{\partial \psi(\mathbf{r},t)}{\partial t} = \tfrac{1}{2} \nabla^2 [-\psi + \psi^3 - \nabla^2 \psi] , \qquad (1)$$

where we have not included thermal fluctuations in the above equation. Our results, then, would correspond to a very deep quench. The boundary conditions imposed are the following. First, no flux is allowed through the impenetrable glass region. This preserves the global conservation law for the order parameter. Second, the presence of a surface field is handled by imposing the following *mean-field* type boundary condition on the order parameter:

$$\nabla \psi \cdot \hat{\mathbf{n}} = h \qquad (2)$$

at the glass surface.

We have numerically integrated the above equations using a finite difference scheme with a mesh size $\Delta x = 1$ and a time step $\Delta t = 0.025$ up to a final rescaled time of $t_{max} = 50000$. The initial values of ψ are uniformly and randomly distributed between -0.1 and 0.1. We have considered two cases for the surface interactions—one with no surface field and the other with surface field strength $h = 1$. In each case the results are averaged over twenty realizations of the initial conditions. Domain morphology in an 80×80 section of the system is shown in Figs. 2(a) and 2(b). In the first case there is no surface field and the domains are formed in the shape of plugs at late times which slows down further growth. In the latter case $h = 1$ and a wetting layer around the glass surface is present. Domain growth is also slow in this case and dynamical scaling breaks down as well. It seems that, the presence of wetting layers around the random, interconnected geometry of the glass surface creates barriers to further growth process and leaves the system with many different length scales.

For a quantitative description of the kinetics of this domain growth process, we compute the pair-correlation function

$$g(\mathbf{r},t) = \langle \psi(\mathbf{r})\psi(\mathbf{0}) \rangle_t - \langle \psi \rangle^2 , \qquad (3)$$

where the average is with respect to different realizations of the initial conditions. We also compute the structure factor $S(\mathbf{k},t)$ which is the Fourier transform of the pair-correlation function. In the above computations, the order parameter is considered to have a value of zero at the location of the glass. As a measure of the average domain size we compute the location of the first zero (R_g) of the correlation function. In Fig. 3 we plot $\ln R_g$ vs $\ln t$ both in the absence and presence of the surface fields. In each case, growth becomes very slow and possibly slower than a power law as the average domain size becomes comparable to the average radius of the pore size. This has been predicted in the single-pore model [11] as a manifestation of the breakdown of the Ostwald ripening process [1,4].
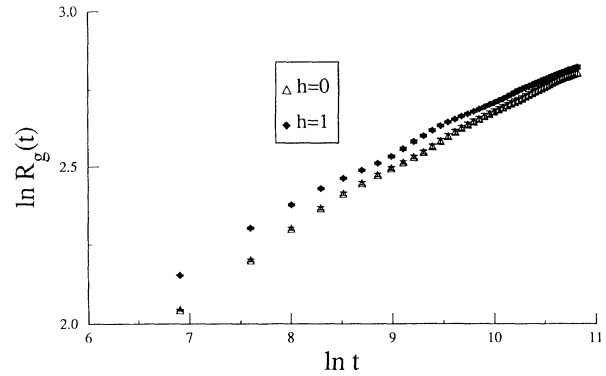
The nonalgebraic growth law seen above suggests that

FIG. 3. Log-log plot of the average domain size $R_g(t)$ vs t in both the absence and presence of the surface fields. In each case the growth seems to be slower than a power law when the average domain size is comparable to the average pore radius (about 15 lattice spacings).

there is more than one length scale in the problem due to the presence of the porous medium. This might lead to a breakdown of the dynamical scaling behavior. We have tested the scaling hypothesis [1] for the structure factor for $h = 0$ as shown in Fig. 4. It is clear from this figure that the data are quite scattered even in the late stages and curves for different times do not fall on a single master curve. Thus, the scaling hypothesis seems to break down during the growth process. We find a similar behavior in the case of $h = 1$.

To conclude, we have studied the kinetics of domain growth in a model porous medium of high porosity. When the domain sizes are comparable to the average pore radius, we find nonalgebraic domain growth and a breakdown of dynamical scaling behavior even in the absence of any surface fields. This arises due to the tortu-
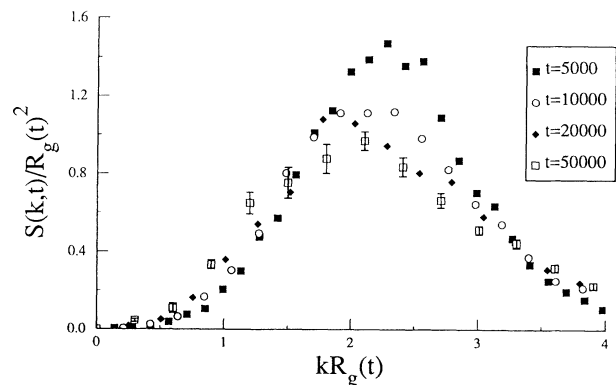

FIG. 4. The scaling hypothesis [1] for the structure factor is tested for $h = 0$ by plotting $S(k,t)/R_g(t)^2$ vs $kR_g(t)$ for various times during the evolution. Dynamical scaling seems to break down during the growth process.

ous geometry of the system which creates barriers to domain growth. In the absence of the surface field there is no preference for the surface by any one of the components and the basic mechanism for the random-field description of the growth process breaks down. This strongly suggests that the random-field model may not be applicable to explain slow domain growth kinetics in a porous medium even with this high porosity. On the other hand, the single-pore model seems to be reasonably successful in explaining the source of this slow growth as the absence of the evaporation-condensation (Ostwald ripening) mechanism when the average domain size becomes comparable to the pore radius. Although the simulations are carried out in two dimensions, we expect that the results will be applicable in three dimensions as well, since the same mechanism of breakdown of the Ostwald ripening will be present in three dimensions.

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[16] The average pore size can be controlled to some extent by stopping the phase separation process at various times. Our choice of 75% for the porosity partly arises from the fact that neither of the two theoretical models is expected to be applicable in this case. Experimentally also this seems to be an unexplored region.

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