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Kinetics of liquid-liquid phase separation of a binary mixture in cylindrical pores

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We have performed molecular dynamics simulations of the liquid-liquid phase separation of a binary mixture confined in two different sizes of cylindrical pore. In these systems, the interactions between the two fluids and the pore wall are identical so that no wetting occurs and the fluid separates into a series of pluglike domains after a temperature quench. In the larger pore the fluid separation is characterized by bulklike growth exponents until the average domain size is comparable with the pore diameter, after which the growth slows dramatically. In the smaller pore domain sizes reach the pore diameter very quickly, after which the growth proceeds faster than in the large pore system. [S1063-651X(97)51302-X]

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The phase separation of binary liquids in confined geometries has been a topic of some interest to both simulators [1–4] and experimentalists [5–9]. Many studies indicate that under quenching conditions these systems rarely achieve macroscopic phase separation, instead ‘‘freezing’’ into a structure of microscopic domains that are kinetically prevented from further condensation. Early predictions that random pore networks would be described well by the random-field Ising model have had some success, but have been largely supplanted by predictions based on the ‘‘single pore model’’ of Liu *et al.* [10]. This theory is based on macroscopic considerations and predicts a ‘‘plug-tube-capsule’’ phase diagram for the phase-separated liquid. In the plug and capsule ‘‘phases’’ the kinetics of late-time phase separation will be very slow because of the collective motions required. That is, in a single pore filled with pluglike domains there is an enormous kinetic barrier to condensing two domains, since the separating quantity of the other phase has to be removed first, which can only be done by creating more interface. Furthermore, the free energy driving force toward condensation in one-dimensional pores decreases quickly with increasing domain size, since the effective attraction between two ‘‘like’’ plugs decreases exponentially with their separation [11]. Monette, Liu and Grest [12,13] performed Monte Carlo simulations of the confined Ising model using Kawasaki spin-flip dynamics, and observed this slowing down in a qualitative way.

Müller and Paul [14] performed extensive Monte Carlo simulations of the Ising model in a two-dimensional strip geometry using Glauber dynamics, which do not conserve the order parameter. These simulations show that phase separation in this system is entirely diffusive and can be described well by an ‘‘annihilating random walk’’ model, and that the average domain size grows in time as $t^{1/2}$. Unfortunately, these dynamics do not describe real liquids very well, and we do not expect this picture to hold for more realistic models.

Relatively few molecular dynamics simulations of phase separation in pore systems have been made. There have been several studies of two-dimensional mixtures of simple spherical particles [1,4,15,16]; these systems usually have an entirely repulsive interaction between unlike species. This unphysical potential speeds up the initial spinodal decomposition process, but in situations where diffusion of interfaces is important these systems may be slowed since the interfacial tension is very high and fluctuations in the shape of domains will be small.

Zhang and Chakrabarti [17] used molecular dynamics to study the phase separation of a two-dimensional fluid of this type in narrow channels. They found that the interfacial energy relaxed in time according to a power law with an exponent near -0.3 for times up to 1000 time units (τ), which is attributed to purely diffusive growth. In simulations in unevenly shaped pores they found a crossover to a faster late-time growth which was attributed to hydrodynamic modes becoming important in the larger parts of the pores. Using a lattice-Boltzmann approach, Grunau *et al.* [18] also studied the phase separation of a binary fluid in a strip geometry. These calculations qualitatively support the prediction of the single-pore model that phase separation slows dramatically when the domain size becomes as large as the pore size.

There have been few simulations of phase separation in cylindrical pores in three dimensions. Zhang and Chakrabarti [3] studied a mixture of the type described above in a pore of dimensions $R=8.7\sigma$ by $l_z=69.6\sigma$ and observed the breakup of the initial configuration into four alternating plugs that stretched entirely across the pore. Because of the small length-width ratio in this system we expect that effects due to the periodic boundary conditions may be important here, since the domains quickly grow to sizes comparable to the box size. No attempt to quantify the domain growth behavior was made during this study.

We have used molecular dynamics to study a mixture of Lennard-Jones fluids adsorbed in two different cylindrical pores. The Lennard-Jones mixture used is symmetric [19]: $\sigma_{11}=\sigma_{12}=\sigma_{22}=\sigma$ and $\epsilon_{11}=\epsilon_{22}=\epsilon$, with the ‘‘unlike’’ pair interaction energy given by $\epsilon_{12}=0.65\epsilon_{11}$; all intermolecular potentials were cut and shifted at $r_c=3\sigma$. The pore was a cylindrical hole of radius R cut out of a continuum Lennard-Jones solid with parameters $\epsilon_w/\epsilon=1.277$, $\sigma_w/\sigma=1.094$, and $\rho_w\sigma_w^3=0.988$. The potential in this geometry is not analytically integrable, but can be evaluated with a lookup table [20]. These parameters have historically been used to model argon in pores of CO_2 [21]; we have used them in order to facilitate comparison with earlier studies. The potential interaction between the pore wall and the liquid was not truncated.

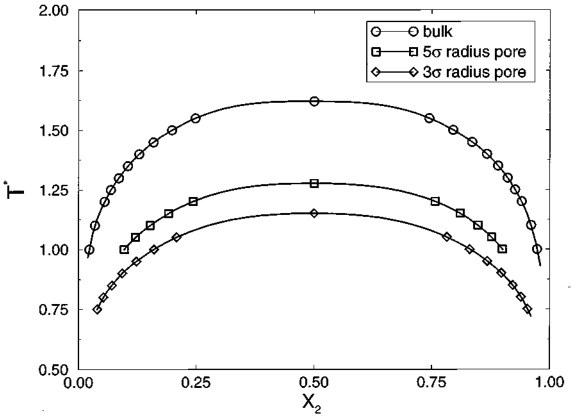

FIG. 1. T, X phase diagrams for 3σ and 5σ radius pore systems, and a bulk system at $\rho = 0.83$. These data were obtained by multicanonical simulation in the semigrand ensemble. Errors for points are less than 1%, the size of the symbols used; the critical temperature is accurate to approximately 3%.

The two pores we simulated were of radii $R = 5\sigma$ and $R = 3\sigma$. The 5σ system contained 10 000 particles (at 0.5 mole fraction) in a cylinder of length $l_z = 182.5\sigma$. This gives an effective reduced density $\rho_{\mathrm{eff}} = 0.83$, where $\rho_{\mathrm{eff}} \simeq \pi l_z (R - \sigma/2)^2$. The smaller pore contained 9258 particles at 0.5 mole fraction with a pore length of 562.5σ, for the same effective pore density. [We stress that these densities are approximate measures of the state of the fluid; in confined systems the density is dependent on the arbitrary choice of the pore volume. However, it is reasonable to assume (in this case) that the excluded volume in the pore is approximately an annulus of thickness $\sigma/2$, which leads to the above definition.]

For each simulation, we equilibrated the liquid for at least 30 000 time steps at a reduced temperature $T^* = 5.0$, and then quenched in one step to $T^* = 1.0$ and followed the phase-separation process in time. Simulations were performed with a time step of 0.005τ using a third-order Gear integrator and a Gaussian isokinetic thermostat [22]. We have compared results for *equilibrium* systems using this integrator and using a fifth-order Gear integrator with the same time step and found no difference. For the 3σ pore system we performed eight independent runs of 2.25 million time steps after the quench (11250τ; approximately 25 ns). For the 5σ pore system we performed nine independent runs of one million time steps (5000τ, or 11 ns). We used a parallel molecular dynamics code based on a one-dimensional domain decomposition algorithm; the calculations were done on the Cornell Theory Center's IBM SP2 using 15 or 20 processors per run. The total CPU time used by this study was approximately 7000 hours for each pore system.

The coexistence curves for the two systems we have studied (and a bulk system at similar density) are shown in Fig. 1. These curves were obtained in recent simulations [9] using multicanonical simulation and histogram reweighting [23] in the semigrand ensemble [24]. These simulations were quite successful, and are presently being extended to consider finite-size effects in these pore systems. The effects of confinement in small pores on the phase diagram are clearly visible in this plot; the critical temperature is depressed, and the coexistence region is narrowed. These effects are more prominent for smaller pores; for sufficiently small pores phase separation is entirely suppressed.

Snapshots of some configurations from two of our simulations are shown in Figs. 2 and 3. The phase separation is visible even at relatively short times after the quench; over long times the domains grow and the boundaries between domains sharpen. The 3σ pore system (Fig. 2) appears more disordered than the larger pore system; this is partially due to the larger saturation solubility in the smaller pore, and partially due to larger fluctuations in the structure of the interfaces between domains; since the interfaces themselves are smaller, motions in the liquid disturb them more.

We have used two different measures to monitor the phase separation process. The first is $E(t) - E_0$, the total potential energy per particle of the system relative to a fully relaxed state, the homogeneous phase at saturated concentration. After an initial decay of transients this quantity effectively measures the interfacial area in the system, which is inversely proportional to the domain size. The reference state energy for each pore system was determined in a separate simulation. The second measure is the average domain size. We can define a local selectivity (dependent on time and the z coordinate) by

$$\eta(z,t) = \frac{\rho_1(z,t) - \rho_2(z,t)}{\rho_1^0 + \rho_2^0}, \tag{1}$$

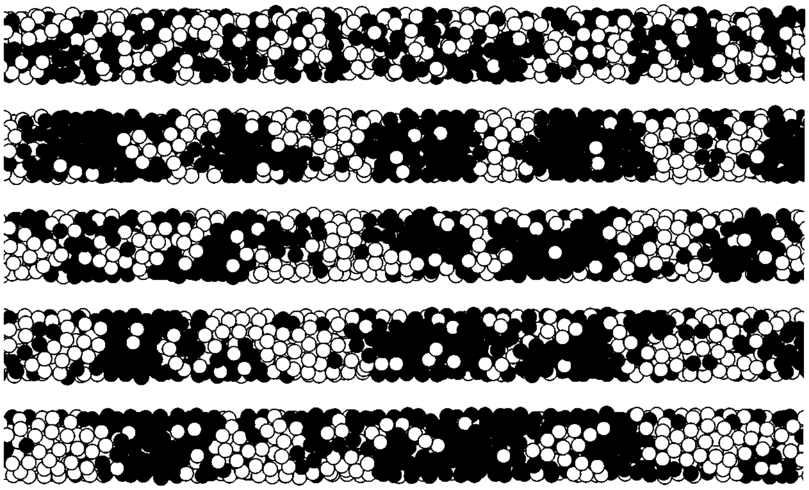

FIG. 2. Molecular dynamics "snapshots" of phase separation in the 3σ radius pore system. These snapshots were taken at $t = 0\tau$, 750τ, 1500τ, 2250τ, and 3000τ (6.5 ns) reading from top to bottom, from a single simulation.

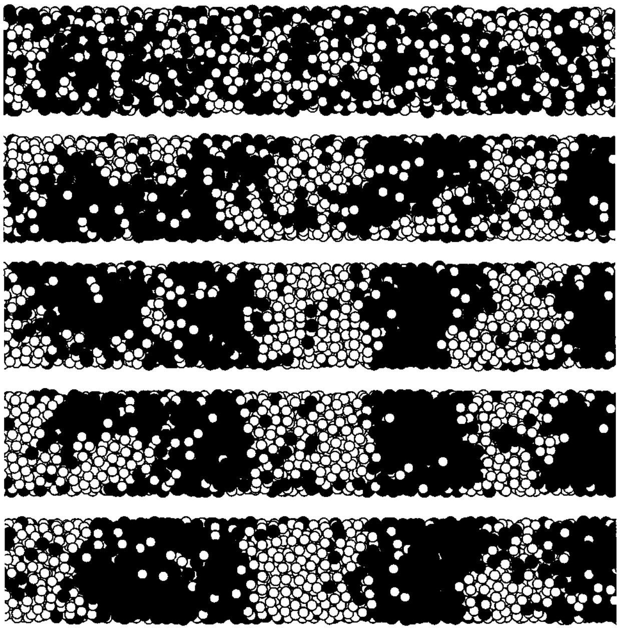

FIG. 3. Molecular dynamics ''snapshots'' of phase separation in the 5σ radius pore system. These snapshots were taken at $t=0\tau$, 500τ, 1000τ, 1500τ, and 2000τ (4.3 ns) reading from top to bottom, from a single simulation.

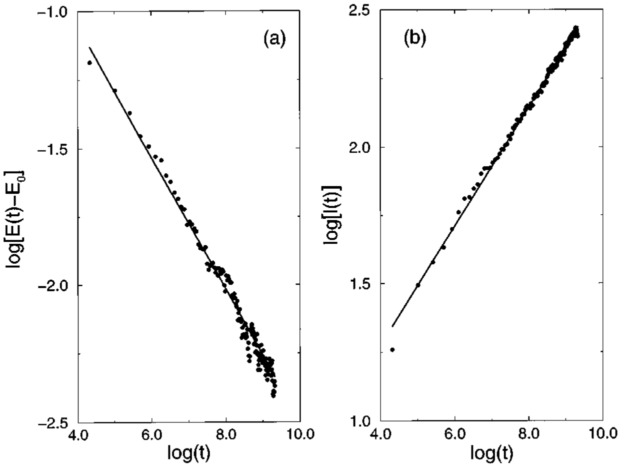

FIG. 4. Two measures of the time dependence of the average domain size for the 3σ cylinder calculations: (a) relaxation of the potential energy in the system, and (b) geometric measure of the domain size from the local selectivity autocorrelation function. Lines are fits from a nonlinear regression analysis and points are averages over eight separate trajectories.

where $\rho_1(z,t)$ is a short-time-averaged density of component 1 at position z, ρ_1^0 is the system-averaged density of component 1, etc. We then look at the autocorrelation of this function in the z direction, e.g., $\langle \eta(z,t)\eta(0,t)\rangle$. The position of the first minimum of this function, referred to as $l(t)$, is characteristic of the domain size, and is the one-dimensional analog of the scaling form used in two and three dimensions [1]. Many runs were required for both pores because the energy and $l(t)$ data are very noisy for these system sizes. We have attempted to use cluster-counting routines [22] to determine the distribution of domain sizes, but found that because of the diffuse interfaces and the relatively small number of domains these definitions were extremely sensitive to cutoff parameters and were not reliable.

Our main results are presented in Figs. 4 and 5. In Fig. 4 we give the energy relaxation data and $l(t)$ data averaged for the 3σ runs. The lines have been fit by a nonlinear regression to the original data with the heteroscedasticity of variance fit with the power-variance model [25]. The power law fit to energy data gives a relaxation exponent of -0.242 ± 0.004; the $l(t)$ data is best fit by a growth exponent of 0.218 ± 0.004, in reasonable agreement. (The exponents should be of opposite sign and the same magnitude, since they correspond to inversely proportional measures.) The data is fit well over this time range by simple power laws, indicating that no slowing-down events occur. The domain growth proceeds slower than in bulk systems, which are predicted to have a (diffusive) growth exponent of 1/3 [26].

The data from the 5σ radius pore (Fig. 5) are not fit well by simple power laws (or logarithmic functions [11]). At later times both the energy and $l(t)$ deviate significantly from their early-time power law behavior. We are unable to determine the late-time functional form of the growth from this data; much longer runs and better statistics would be required. These results are consistent with the single-pore model predictions. However, the single-pore model also predicts that such effects should be more dramatic for narrower pores, which is not true for these systems. The early-time growth exponent in the 5σ cylinder obtained from the $l(t)$ data is 0.272 ± 0.019, and that from the energy relaxation data is -0.281 ± 0.007, again in reasonable agreement.

It has been pointed out [27] that there can be no bona fide phase transition in a system infinite in only one dimension, and that the phase-separation process we observe in these simulations should end at some *thermodynamically* stable average domain size. We are currently trying to estimate this domain size by Monte Carlo simulation. Our initial data indicate that the equilibrium length is quite large (hundreds of molecular diameters) for both of the systems that we have

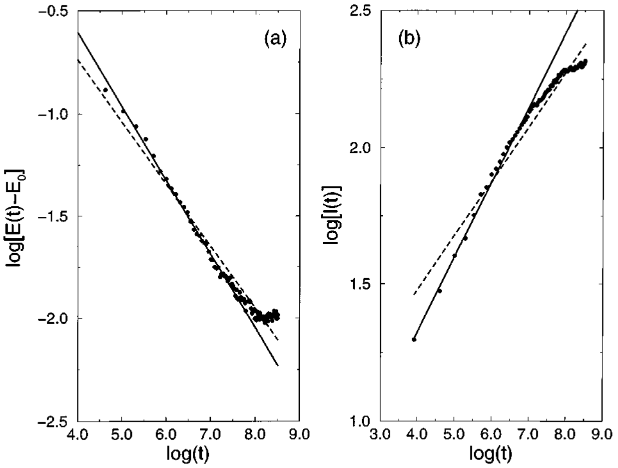

FIG. 5. Two measures of the time dependence of the average domain size for the 5σ cylinder calculations: (a) relaxation of the potential energy in the system and (b) geometric measure of the domain size from the local selectivity autocorrelation function. The dotted lines are fits from nonlinear regression analysis, points are averages over nine separate trajectories, and the full lines are visual fits to the short-time data.

studied, so that this should not affect the short-time behavior of these systems.

Our main conclusion from this work is that the picture of phase-separation kinetics obtained from the single-pore model appears to break down for sufficiently narrow pores. This may be due to the large fluctuations of domain shape observed in the small system. Over this range of times, these may allow for diffusive ''walking'' of the domains and simple power law growth behavior even for large plugs. Note that the domains in the smaller pore reach an average length of 12σ in our simulation, well into the asymptotic regime. The exponents measured in both pores are depressed from their bulk theoretical values of 1/3, indicating that confinement affects the coarsening process even at short times. We continue to study these systems, and are attempting to measure quantities such as the plugs' diffusion constants and potential of mean force between neighboring plugs in order to estimate the behavior at later times, which cannot be simulated directly.

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