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Molecular dynamics of phase separation in narrow channels

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The results of molecular-dynamics simulations of the phase separation of binary fluids in narrow channels are presented. Two channel widths allowing for one or two fluids layers are considered. The one-layer case does not exhibit good scaling. The two-layer case does and the growth exponents are the same as that found earlier for bulk phase separation. Our results point to the importance of conservation laws and hydrodynamic modes in determining the growth dynamics.

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The physics of the phase separation of two initially well-mixed fluids is a scientifically rich phenomenon [1] with considerable technological importance in, for example, segregation processes, metallurgy, and polymer blends. It is recognized that the dynamics of the growth of the domains are influenced by the hydrodynamic modes and thus the bindary fluid case is not expected to be in the same universality class as the spinodal decomposition of an Ising ferromagnet with conserved magnetization. Most of the theoretical progress to date has been the development of heuristic scaling arguments based on dimensional analysis carried out on the Navier-Stokes equation for the velocity field at the interface between the two fluids [2]. Earlier molecular-dynamics (MD) studies [3] of the spinodal decomposition of bindary mixtures, containing up to 32 000 molecules, led to a growth exponent inconsistent with simple dimensional analysis. In the presence of walls, new features are introduced. First, as pointed out recently by Liu *et al.* [4], wetting phenomena play a significant role. Further, the microscopic flow is influenced by the presence of a solid boundary, which modifies the appropriate fluid modes and can possibility lead to new qualitative behavior.

In order to understand some of these issues better, we have carried out MD simulations of the spinodal decomposition of binary fluid mixtures in a narrow channel bounded by planar walls (the Hele-Shaw geometry). It is well known that fluids layer in the vicinity of walls—indeed, for the two widths of the channel we have studied, one or two layers of fluid are formed. Strikingly, the dynamics of the phase separation are different for the two cases. The two-layer case shows excellent scaling in the late-time limit and growth law is *quantitatively* the same as was found earlier for spinodal decomposition in the bulk. The value of the exponent is different from $\frac{1}{3}$, underscoring the importance of hydrodynamic modes, *even* in confined geometries. In order to probe the effect of the conservation laws on the growth dynamics, our simulations have been carried out at both constant T (temperature) and constant E (total energy)—different exponents are found in the two cases. Our calculations allow us to study the wetting effects of the walls.

On the experimental front, two recent reports on the influence of wetting on the dynamics of phase separation of bindary mixtures have appeared. They are in apparent disagreement with each other, presumably because of the different window of time scales studied. One study [5] finds a fast growth mode with a dynamical exponent of $\frac{1}{3}$, whereas the other [6] finds a growth law characterized by an exponent of 0.6 ± 0.16. While we have not found any evidence for the fast growth mode in our simulations, our results are in quantitative accord with that of the latter experiment. Finally, spinodal decomposition in the Hele-Shaw geometry has been studied by Shinozaki and Oono [7] using a cell-dynamical system. They found that the finite size coupled with the effect of incompressible flow had a severe accelerating effect on the growth law. However, layering effects observed in real fluids are *not* incorporated in such a calculation, nor are the effects of hydrodynamics taken into account in an *ab initio* manner.

The details of the MD simulation have been described in Ref. [3]. While periodic boundary conditions are maintained in the x and y directions, walls have been introduced in the z direction. As in our earlier studies, the A and B molecules interact with Lennard-Jones potentials—the AB attraction is turned off after initial equilibration to cause phase separation. The initial equilibration for constant T runs was done at a reduced temperature of $T^*=1.4$. After the quench, a constant temperature was maintained by rescaling velocities of the molecules every time step of the calculation. The constant energy runs were equilibrated at $T^*=1$. After the quench, the temperature increased due to transfer of energy from potential into kinetic—at late stages of the simulation T^* was roughly equal to 2. The bulk consolute temperature is about 8, so our quench is deep [3]. Some test runs were carried out for different large quench depths. The results were similar in all cases, except for a changing prefactor. Shallow quenches are not accessible by MD simulations due to computational time limitation. The force between the walls and the fluid molecules, in the simplest version of our calculations, is taken to be [8]

$$F_z=-F_W\left[-\frac{4}{z^{11}}-\frac{2}{5(z+0.72)^{10}}+\frac{4}{z^5}+\frac{3z^2+12z+14}{3(z+1)^6}\right], \tag{1}$$

where the constant F_W determines the overall strength of the interaction and z is the distance between the wall and the fluid. Note that this simplified force law incorporates the effect of a semi-infinite solid, but does *not* take into account the corrugation and the xy structure of the wall. Some runs with molecular walls were also carried out. The lateral size in this case corresponded to $25\sigma\times25\sigma$. The results in the two-layer case were similar (in terms of the exponent) to the uncorrugated wall simulation, but the amplitude of the growth law was smaller. The simulations are carried out in the constant-N (the number of molecules) and constant-volume ensemble.

Two different geometries (channel widths) were considered. A width of 3σ allowed for the formation of two layers, whereas a narrower width of 2σ resulted in just one layer of the fluid. In the former case, 3600 fluid molecules corresponding to a transverse area of $50\sigma\times50\sigma$ (1800 for A and 1800 for B) were considered, whereas the one-layer case was treated for two lateral sizes incorporating 1800 and 3200 (transverse area $70\sigma\times70\sigma$) fluid molecules, respectively. In all cases, five independent runs were carried out.

Our key results are summarized in Figs. 1–3. We begin with the two-layer case. Figure 1(a) shows the results for the scaling form of the single species radial distribution function $g(r,t)$ defined in terms of the correlation function

$$s(r,t)=\langle\eta(r,t)\eta(0,t)\rangle$$
$$=\langle\delta\rho_A(r,t)\delta\rho_A(0,t)\rangle/\rho_{0A}^2\equiv g(r,t)-1\ , \tag{2}$$

where the order parameter

$$\eta(r,t)=\rho_A(r,t)-\rho_B(r,t)/(\rho_{0A}+\rho_{0B})\ , \tag{3}$$

ρ_A and ρ_B are local concentrations whose global averages are ρ_{0A} and ρ_{0B}, respectively, and $\delta\rho_A$ and $\delta\rho_B$ are the deviations of the local concentration from the average values. The symbol D is from a configuration at $t=7$ (in reduced time units, τ). At this "early" time, the molecular nature of the fluid introduces a competing length scale since the domain size is still small. This accounts for the deviation from scaling. The data taken at $t=18$ (X's) and 40 (squares) overalp well, whereas the deviation of

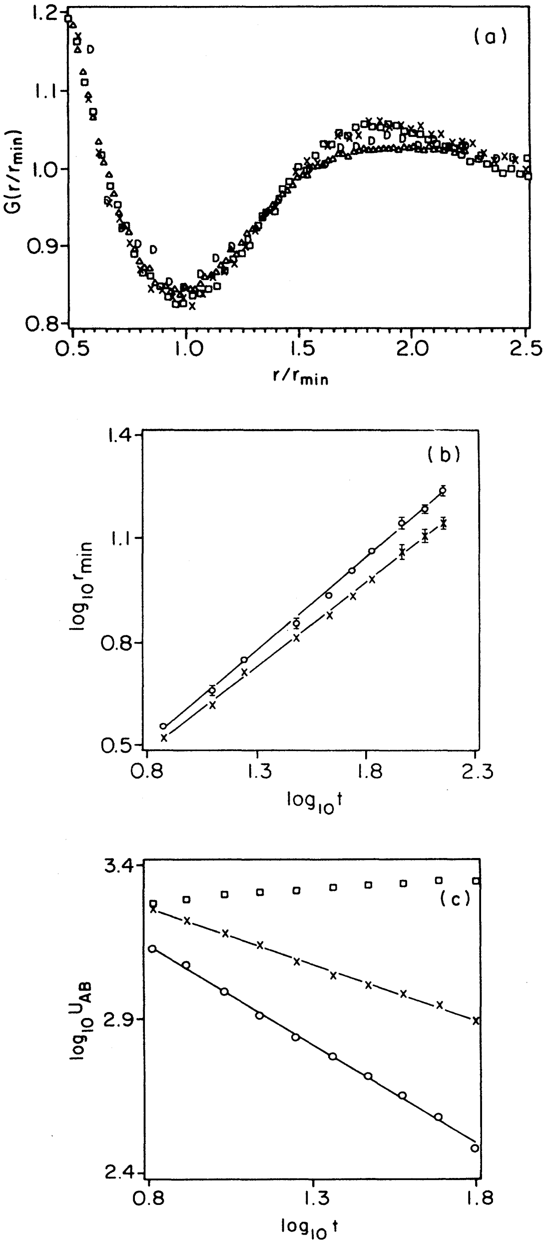

FIG. 1. (a) The scaling function $G(r/r_{\min})$ for two layers ($T=$const), obtained by overlapping data at $t=7\tau$ (D), 18τ ($\times$) 40τ ($\square$) and 90τ ($\triangle$). (b) A plot of the characteristic size $r_{\min}$ vs time. The upper and lower lines are the best fits for the two-layer system runs with $T=$const and $E=$const, respectively. (c) Plot of a repulsive potential energy between A-B species vs time for the system with two layers. The lower and upper lines represent the best fits for the runs with $T=$const and $E=$const, respectively. The squares denote the temperature as a function of time in the $E=$const runs ($3\times\log_{10}T$ vs $\log_{10}t$—T and t are in reduced units).

the data at $t=90$ (triangles) indicates the effect of the finite size of the simulation. Figure 1(b) shows a plot of $r_{\min}$ [a characteristic size of the growing domain obtained from the minimum of $g(r,t)$] as a function of time. The data were obtained by averaging over five runs. The upper line denotes the best fit to runs at constant T, whereas runs at constant E are fit by the lower line. The growth exponents in the two cases are 0.54±0.02 and 0.48±0.03, respectively. Note that typical experiments are carried out at constant temperatures.

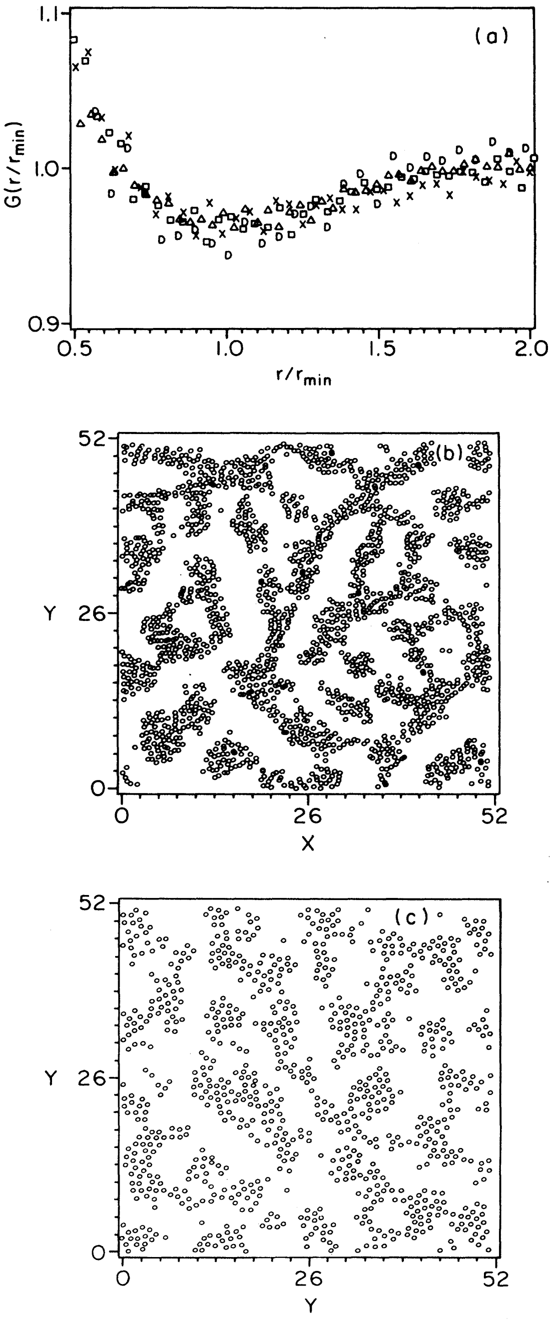

FIG. 2. (a) Attempt at scaling the radial distribution function $g(r,t)$ for a system with one layer with T=const. The symbols are as in Fig. 1(a). (b) Projection in a direction normal to the walls of the molecular positions at $t=20\tau$ for the two-layer system with T=cosnt. (c) Projection in a direction normal to the walls of the molecular positions at $t=25\tau$ for one-layer system with T=const.

The constant-energy exponent is somewhat lower than the constant-temperature one because of the continuous rise in temperature [Fig. 1(c)] in the former case leading to a smaller amplitude of the growth law. A similar difference has been noted for the case of liquid-vapor phase separation by Koch, Desai, and Abraham [9]. Figure 1(c) shows a log-log plot of the repulsive potential energy between the A and B molecules (circle, constant T; ×'s constant E) and the temperature (squares, constant E) versus time. The temporal decay of the repulsive energy fits a power law with an exponent of 0.64±0.02 (constant T) and 0.36±0.03 (constant E). The repulsive energy may be thought of as the product of a surface tension and a curvature (an inverse length scale). The exponents of the growth law of the domains and the decay of the repulsive energy are different from each other. The repulsive energy is a function both of the interfacial area and the mean A-B nearest-neighbor separation. We have found that while the former decreases, the latter increases with time (T=const) reinforcing the decay and leading to the larger exponent. The constant energy run leads to the energy decay exponent being smaller than the growth exponent, because the increase in the temperature causes the A-B distances to *shrink* in this case.

We now turn to the systems with one layer. Figure 2(a) shows an attempt at scaling the radial distribution function. Unlike Fig. 1(a), there is no evidence for good scaling in this case. The difference between the two-layer and one-layer cases is vividly seen in Figs. 2(b) and 2(c), which show the projections of the molecular configurations on a plane parallel to the walls. The times at which the snapshots are shown have been selected to match the degree of growth of the domains in the two cases. In the two-layer case, a well-defined domain structure is formed with one characteristic length scale—indeed an excellent degree of correlation exists between the ordering in the individual layers. On the other hand, the lack of scaling in the one-layer case arises from the absence of a dominant length-scale characteristic of the

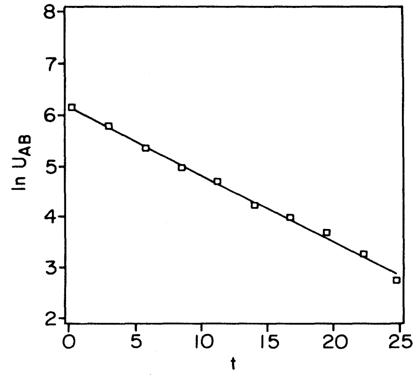

FIG. 3. Potential energy between A-B molecules present in the layer next to the A-wetting wall. The straight line represents an exponential decay.

ordering. This is due to the severe confinement of the fluid molecules—virtually no displacement of the molecules takes place in the direction normal to the walls leading to some of the molecules being stuck in metastable states for long times. In the two-layer runs, the rate of exchange between the two layers is high, being plausibly the major mechanism of avoiding metastable states observed in the one-layer case. Indeed when we increased the wall attraction we observed smaller amplitude of decomposition (but the same exponent) while the rate of the exchange between layers was decreased. The strength of the wall attraction in the one-layer case has little influence on the results since the fluid virtually does not move in the z direction and the xy structure of the walls has not been taken into account. The lack of scaling for the one-layer case is in sharp contrast to the behavior of a two-dimensional Ising spin system with Kawasaki dynamics [1], where excellent scaling is obtained.

The exponents obtained in the two-layer case are in agreement with the experimental results of Ref. [6]. In order to make a connection with the experiments of Wiltzius and Cumming [5], we have carried out MD simulations at constant T of broader channels (of width up to seven layers) with the "A" molecules preferentially attracted to one of the walls. Indeed, a "fast" mode (compared to spinodal decomposition) is observed originating due to this preferential attraction that results in a rapid enrichment of "A" molecules in the region near the wall. Figure 3 shows a plot of the repulsive A-B interaction energy within the first layer next to the wall. An exponential decay law is obtained that is inconsistent with the $t^{-1.5}$ algebraic law observed in the experiment. Two key differences between the simulations and experiments are the spatial extent of the wetting layer probed and the complexity of the molecules forming the fluids undergoing phase separation. The time constant of exponential decay decreases with growing strength of the wall attraction.

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