Computer Simulation of Phase Separation in a Two-Dimensional Binary Fluid Mixture

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The spinodal decomposition and late-time domain growth in a two-dimensional binary fluid have been studied for the first time by computer simulation. The dynamical phase transition shows scaling, and evidence is found of a competition between different growth mechanisms. The scaling regime presents a time growth law with an exponent $\frac{1}{2}$, and a subsequent crossover to a faster growth, possibly mediated by a $\frac{1}{4}$ transient. Our results demonstrate that hydrodynamic modes play a decisive role in phase separation dynamics.

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The dynamics of domain growth in phase separating systems is an important technological problem, and also fundamental as an example of a highly nonlinear process far from equilibrium [1]. The phase separation takes place, e.g., when a fluid mixture is quenched to the unstable region of its phase diagram. Domains of the coexisting phases grow and coarsen in time, and in the late stages one expects all domain sizes to be much larger than all microscopic lengths. The growth law for the average domain size then has a power law of the form [2] $R(t)\propto t^n$, where n is called the growth exponent, and the correlation function shows a scaled form $g(r/R(t),t)=G(x)$, where $x=r/R(t)$. Much effort has gone into classifying different systems by distinct universality classes [3], characterized by specific exponents and scaled functions. It is believed that the conservation of the order parameter is a relevant criterion for such a classification. The case where the order parameter is conserved, however, still poses problems. Experiments on alloys [4] give an exponent $n=\frac{1}{3}$, whereas a subsequent crossover to linear growth is observed for fluid mixtures [5]. Monte Carlo experiments on Ising lattices [6] and Langevin models [7,8] reproduce the $\frac{1}{3}$ exponent. There are also some theoretical arguments [9] and computer simulation results [10,11] which suggest the importance of hydrodynamics in the phase separation of fluid mixtures. For two-dimensional fluids the situation is even more problematical since no clear experimental results are available and there are contradictory studies on the relevance of the hydrodynamics in late-stage growth [12–14], in particular as to whether a crossover to fast growth occurs. The lack of results from computer simulation adds to this uncertainty.

This work reports, for the first time, results of molecular dynamics (MD) and Monte Carlo (MC) computer experiments of phase separation in a binary fluid mixture in two dimensions. From a comparative study between the two techniques we demonstrate the paramount importance of hydrodynamic modes in the phase separation of the fluid: When they are suppressed (MC) a $\frac{1}{4}$ exponent is observed and no crossover, in contradiction with an MD study, which shows a rich growth behavior, with an early-time $\frac{1}{2}$ exponent going over to a faster growth, possibly mediated by $\frac{1}{4}$ transients. Until recently almost all simulations have been performed on lattice models via MC methods [6]. It is, however, well known that MC is not a suitable technique for studying fluid dynamics. The relevant simulation technique for spinodal decomposition is MD, but due to the very slow phase separation dynamics in dense fluids this technique might still seem prohibitive even with today's powerful supercomputers. This is, however, not the case, as we will show. The decomposition in a binary mixture is driven by the excess (free) energy of mixing, so by choosing a large interaction energy between molecules of different species it is possible to speed up the separation phenomenon. We have used extended range, Lennard-Jones-like potentials of the form

$$\begin{aligned} u_{AA}(r)&=u_{BB}(r)=4\epsilon((\sigma/r)^{12}-(\sigma/r)^3)\,,\\ u_{AB}(r)&=4\epsilon((\sigma/r)^{12}+(\sigma/r)^3)\,, \end{aligned} \tag{1}$$

where all potentials are truncated at 4.2σ and u_{ij} is the potential between molecules i and j of type A or B. The phase diagram for isotherms of such a system shows a wide miscibility gap, with a critical point located at low pressure [15]. One can therefore perform a deep quench to the unstable region, and still work at low density and pressure. (The quenches were performed at temperature $kT/\epsilon=2$ and density $\rho\sigma^2=0.4$ with a system pressure significantly higher than the critical pressure during all of the phase separations.) The implications of this are clear: The low density facilitates the separation dynamics and saves computer time, and the growth kinetics of relatively large systems can be studied up to the last times allowed by our finite systems.

Several measures of the domain size have been used. The value at which the radial distribution function $g_{ii}(r,t)$, for particles of the same species i, equals 1 for the first time is found to give the best measure of the average cluster size. Also, the AB potential energy is related to the length of the interface and thereby to the average domain size. Both measures give the same answer when the scaling regime is operative, which is in fact a strong test of the scaling regime. The size can also be determined from the structure factor $S(k,t)$, but, as also observed in other studies, we find that the domain

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TABLE I. Summary of simulation runs for the phase separation experiments. Each run is identified by a capital letter from A to H. N is the number of molecules in the system. Density is given in reduced units. The keywords for the simulation methods are as follows: MD, molecular dynamics; MC, Monte Carlo; NH, Nosé-Hoover thermostat; VRS, velocity rescaling; Gauss, Gauss isokinetic constraint; E=const, constant energy simulation. Time refers to the total time spanned by the simulation, in reduced units (the unit of time is $\tau = 10^{-14}$), except run H, which is given in MCS (Monte Carlo steps per molecule). Exponents are the exponents obtained from fittings to straight lines of the values of R as measured from the correlation functions. In all runs temperature was equal to 2 in reduced units.

Run	N	Density	Method	Time	Exponents
A	20000	0.40	MD NH	603	0.50→0.65
B	9800	0.40	MD VRS	550	0.52→0.24→0.59
C	9800	0.40	MD VRS	389	0.43
D	9800	0.40	MD Gauss	741	0.46→0.50
E	9800	0.40	MD NH	335	0.49→0.69
F	2450	0.40	MD VRS	335	⋯
G	9800	0.40	MD E=const	295	0.52→0.24→0.67
H	5000	0.38	MC	36200 MCS	0.24→log

size is most accurately obtained from $g(r)$. A constant temperature T was maintained in our MD experiments by different techniques. The popular velocity rescaling at every time step was used, but this technique does not ensure a canonical sampling of momentum. Thus we also used the Gaussian isokinetic [16] and the Nosé-Hoover thermostat [17], which both generate a Boltzmann sampling and thus are the sensible choice. In order to keep T constant, the thermostat must absorb the latent heat of the first-order transition sufficiently rapidly so as not to affect the phase separation dynamics or generate unwanted thermal fluctuations. In this respect the Gaussian thermostat is in principle more effective with strictly constant T at every time step.

We have performed a series of quenches at critical concentration for systems with different numbers of molecules, following the growth dynamics with the MD and MC techniques and measuring the associated exponents. Square systems with 2450, 5000, 9800, and 20000 molecules were studied, with periodic boundaries and starting from different initial configurations. Most of the MD runs were performed at constant temperature but one experiment was also done at constant energy. A summary is given in Table I, and a typical time sequence of molecule configurations is shown in Fig. 1. Our results for the domain size, as estimated from the radial distribution function, are presented in Fig. 2. Let us first concentrate on the MD constant temperature experiments. The (late times) domain growth dynamics is divided into three stages: early, medium, and late stages. All experiments performed using constant temperature techniques and different initial configurations give a $\frac{1}{2}$ for the exponent in the early stages, which shows that the law is not an artifact of a particular simulation technique. The same exponent is obtained from the decay with time of the AB energy. Therefore, the identification of the $\frac{1}{2}$ exponent is reliable, and constitutes the first confirmation by molecular dynamics simulation of ideas proposed by theoretical work based on phenomenological models [12].

Ideally one would like to average over many different experiments starting from different initial configurations and using a large number of molecules. This is clearly an impossible task given the limited computational resources available. However, we can obtain useful information from an examination of individual runs. From Fig. 2 it is seen that all runs show a regime of faster domain growth following the initial $\frac{1}{2}$ region, sometimes mediated by a

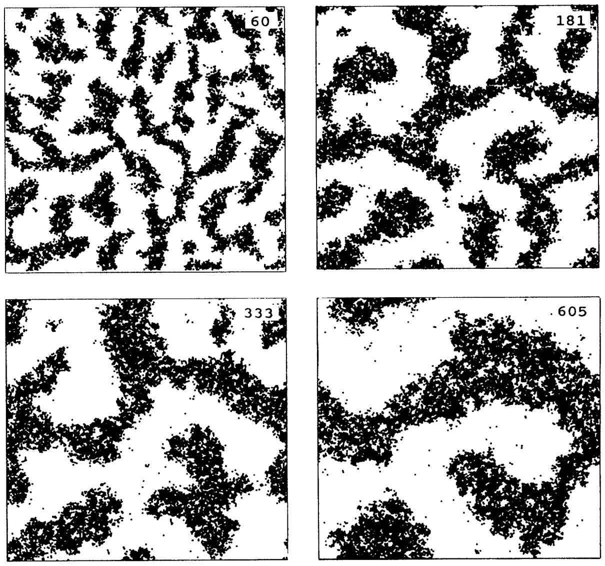

FIG. 1. A series of configurations corresponding to run A, with labels referring to time, in reduced units. Only particles of one type are represented.

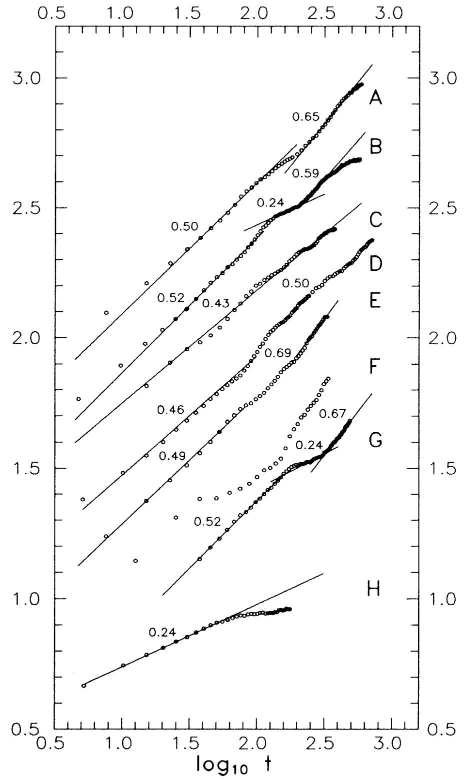

FIG. 2. Typical domain sizes R as estimated from the radial distribution functions, plotted against time t, in logarithmic form (a straight line in the figure means a power law for the growth with an exponent equal to the slope of the straight line). Curves are identified by a capital letter corresponding to the runs in Table I. The vertical axis is shifted for each set of data by a certain amount in order to made a direct comparison easier: Run H is not shifted, run G is shifted by 0.2, run F by 0.4, run E by 0.6, run D by 0.8, run C by 1.0, run B by 1.2, and run A by 1.4 units. Fitted straight lines are shown with their calculated slopes. Time in the MC run (run H) is arbitrarily given as Monte Carlo steps per molecule divided by 200.

considerably slow growth mode. The presence of a fast growth at the late stages is rather striking, and implies the existence of a crossover, as in three dimensions [9]. We do not obtain consistent values for the associated exponent in all the runs, but it is clear that this exponent is higher than $\frac{1}{2}$. Farrell and Valls [14] have recently studied a Langevin model and conclude that it is the presence of heat diffusion which makes the growth follow a law with an exponent 0.65. They do not obtain a $\frac{1}{2}$ exponent at the early stages, except when the heat diffusion terms are dropped and only pressure fluctuations are allowed, in which case a $\frac{1}{2}$ exponent is observed all the way. On the other hand, San Miguel, Grant, and Gunton [12] used linearized hydrodynamic equations to predict a $\frac{1}{2}$ law and no crossover. However, our MD results strongly support the $\frac{1}{2}$ exponent at the early stages and a crossover to faster growth at late times. Note that the evidence of a fast growth regime comes from the experiments with Nosé-Hoover dynamics (giving an exponent 0.65) and velocity rescaling (0.59). The Gauss isokinetic dynamics, which does not allow any fluctuation in the temperature, does not yield any evidence of such a high exponent. The Nosé-Hoover dynamics, on the other hand, allows for small scale fluctuations in temperature. This points to the relevance of heat diffusion, a genuinely hydrodynamic mode in the phase separation dynamics. If the fast exponent is due to thermal fluctuations, it will also appear in a microcanonical simulation, where the energy E is constant and temperature fluctuates. This effect is examined by first performing canonical MD until most of the latent heat is released and then letting the system evolve at constant E (label G in Table I and Fig. 2). Some indications have been obtained in the past [18] of a different growth law depending on the conditions on the system (constant E or constant T). There is, however, no evidence of a difference in the growth in the binary mixture as shown in Fig. 2. The microcanonical simulation with the strongest thermal fluctuations gives a late stage exponent 0.67 in accordance with Farrell and Valls [14].

The importance of hydrodynamic modes is also manifested when we compare our MD results with those obtained from an MC simulation of the same system (run H in Table I and Fig. 2). The MC technique does not take account of hydrodynamic modes due to its Markovian nature, and gives an Ising-like exponent of $\frac{1}{4}$. This is the predicted exponent for Markovian dynamics for a growth mechanism driven by particle diffusion along the interfaces [6], and the lattice dynamical calculations in [6] exhibit exponents of this magnitude. This growth, however, competes with the Lifshitz-Slyozov (LS) mechanism for growth driven by diffusion between clusters, which will dominate at (very) late stages, and gives an exponent of $\frac{1}{3}$. In our system diffusion across interfaces is greatly penalized due to the very repulsive AB interaction, and this makes the interfacial width relatively broad, facilitating transport along the interfaces. Thus it is likely that in our system the LS mechanism is not operative in either the MD or the MC simulation.

Figure 2 shows that the crossover to the high exponent in the MD systems is sometimes mediated by a considerably slow growth mode. This is more apparent in run A and especially in run B, with an exponent close to $\frac{1}{4}$. This exponent has, as mentioned, been associated with mass transport along domain boundaries [19,20], and has recently been observed experimentally [21]. The mechanism is always active when an interconnected structure is growing, and competes with the hydrodynamic motions and the LS evaporation-condensation process [22].

Finite size effects in the system were examined by performing simulations with different numbers of molecules. These effects are clearly visible at the end of the simulations, with the R versus t curve showing a break for R approximately one-third of the system size. The curve flattens off due to self-interaction of the clusters through the

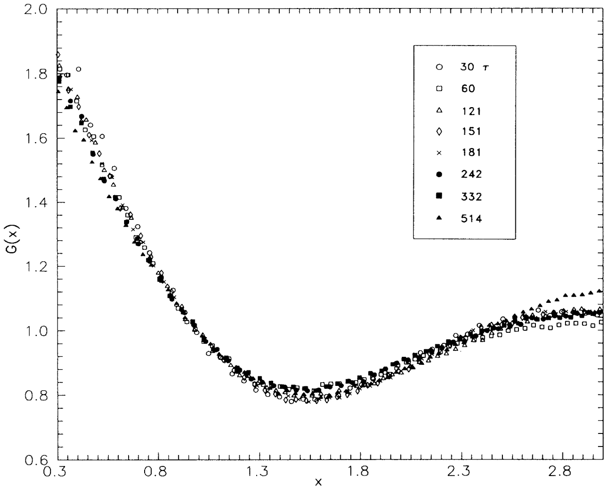

FIG. 3. Scaled radial distribution function for run *A* and different times, as a function of the dimensionless parameter $x = r/R(t)$. The inset gives the time associated to each curve, in reduced units.

periodic boundaries. The important point to stress is that most runs show the presence of all mechanisms, irrespective of the size. Therefore the different regimes we find and the crossover are genuinely intrinsic phenomena, not affected by size effect and driven only by the underlying growth mechanisms and statistical dispersion through the initial configurations. A closer comparison between runs *A*, *B*, *D*, and *F* (*A* denotes the large, *B*,*C* the intermediate, and *F* the small system) shows, however, that the time at which the curves begin to manifest a different growth behavior has a slight size dependence, increasing logarithmically with size.

The pair correlation function is shown in Fig. 3, to test the scaling hypothesis. In the scaling regime this function scales as $g(r/R(t),t) = G(x)$, except at very small distance, where scaling never holds. We can see from the figure that dynamical scaling is satisfied with scaling all the way up to finite size breakdown.

In conclusion, by enhancing the excess mixing energy, we have for the first time been able to perform molecular dynamics simulations of late stages of phase separation in two-dimensional binary fluid mixtures. We find a diffusive growth with an exponent $\frac{1}{2}$ which confirms results from corresponding Langevin models. However, a crossover to a higher exponent subsequently occurs, demonstrating the similarity between two- and three-dimensional systems and highlighting the importance of hydrodynamic motions in phase separation in two dimensions. The crossover is sometimes mediated by a transient $\frac{1}{4}$ law, which has been associated with diffusion along interfaces. Scaling of the correlation function is found in all regimes.

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