

## Computer-Simulation Dynamics of an Unstable Two-Dimensional Fluid: Time-Dependent Morphology and Scaling

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From an isothermal molecular-dynamics experiment of an unstable two-dimensional fluid undergoing phase separation, two principal growth regimes are observed: (1) spinodal decomposition with a wavelike morphology followed by (2) a transition to cluster formation and growth due to atomic condensation and cluster coagulation. The time-dependent power-law behavior for the second growth regime is 0.5, in contrast to a constant-energy simulation which yields a power-law behavior of 0.33. Details of the phase-separation dynamics are discussed and compared with theory.

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Motivated by our interest in phase-transition phenomena in monolayer physisorbed films<sup>1</sup> and guided by our recent linear hydrodynamic-fluctuation theory for the early-time behavior of an unstable fluid,<sup>2</sup> we have simulated spinodal decomposition of a "two-dimensional" simple fluid by molecular dynamics, the dynamics of the phase-separation process being followed to very late times (450 ps) and for a very large number of particles (5041 Lennard-Jones atoms). Our computer experiment consists of solving the equations of motion for a classical fluid of 5041 Lennard-Jones (LJ) atoms by numerical integration with use of a fifth-order Nordsieck-Gear algorithm. Our system of atoms is enclosed in a parallelogram of density  $\rho\sigma^2 = 0.325$  and length  $L/\sigma = 133.8$ , with the standard periodic boundary conditions being imposed in order to simulate an infinite system.<sup>3</sup> We note that the periodic boundary condition prevents the occurrence of inhomogeneities of a size larger than the length of the computational box. The integration time step is chosen to be  $\epsilon\Delta t/\sigma^2 = 0.004636$ , or  $10^{-14}$  s for argon. The fluid is initialized by placing the atoms in a triangular lattice of density 0.325 (critical density for liquid-vapor coexistence) with a Boltzmann velocity distribution corresponding to a temperature  $kT/\epsilon = 0.45$ , which is slightly greater than the triple-point temperature. In this Letter, we present the simulation details of an "isothermal" computer experiment which was simulated by renormalizing the atomic velocity distribution at each time step, in order to fix the system's average temperature at 0.45. Our positional initialization guarantees that the system starts with a uniform distribution of atoms in a very unstable state of the two-dimensional fluid phase diagram. The memory of the triangular lattice is quickly lost (in approximately 3 ps).

We have also simulated the "constant-energy" phase-separation process (i.e., no renormalization of the velocity distribution) and will present the principal result after discussing the isothermal experiment.

In Fig. 1, a temporal sequence of atomic configurations and their respective radial distribution functions  $g(r)$  is presented for selected times during the dynamical phase-separation process. The experimental uncertainty in  $g(r)$  is comparable to the linewidth of the drawing, this high accuracy resulting from the large number of atoms in the simulation. We note the short-range, liquid-state atomic order represented by the pronounced small-period oscillations for a radial distance of  $5\sigma$ , this order becoming time invariant after approximately 30 ps. In addition, a damped oscillation with growing amplitude and period is evident for all times, representing a growing short-range order with a spatial scale that is time dependent; this is simply a consequence of the continuous partitioning of atoms into condensed-phase regions which grow in size. In terms of the Fourier transform of the radial distribution function (the structure factor), the short-range liquid peak appears at a wave number  $k\sigma = 5.87$  and saturates in amplitude after 30 ps. Also, a small  $k$  peak appears at  $k\sigma = 1.33$  after 4 ps and continues to grow in amplitude by over 2 orders of magnitude, eventually shifting in  $k\sigma$  to 0.1 after 450 ps of the phase-separation process. We obtain a coarse-grained radial distribution function  $g(r, t)$  by averaging over radial intervals greater than the period characteristic of the atomic short-range order, and arbitrarily take as a measure of the coarse-grain "average size" of the growing liquid regions the radial distance at which this distribution function first equals unity. In Fig. 2 (upper, left scale, dots)

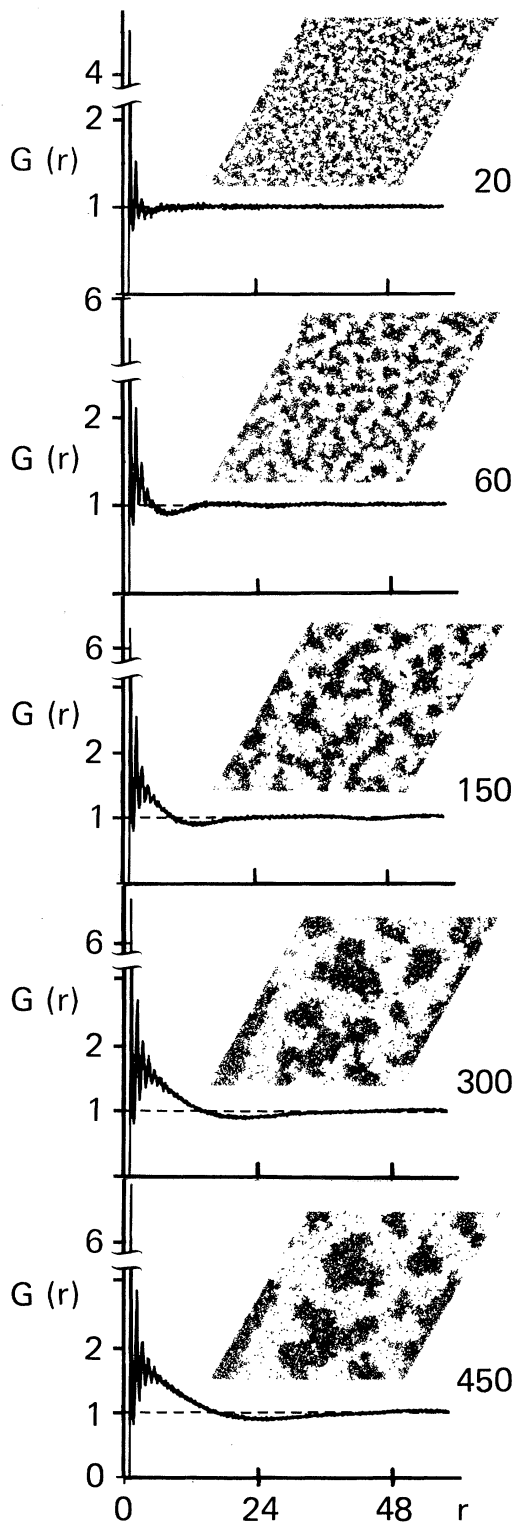


FIG. 1. Radial distribution function  $g(r)$  and atomic configurations for various times after quench ( $\tau$  in units of  $\sigma$ ). The experimental uncertainty is comparable to the linewidth of the drawing.

this average cluster size  $R(t)/\sigma$  as a function of time  $t$  is presented on a log-log plot. The number of points was chosen only to show the representative trend for the time variation, even though, in actuality, there is a point for each time step of 0.01 ps. By arbitrarily seeking power-law growth regimes, we find an approximate 0.20-power dependence during the early stage of the phase-separation process ( $0 < t \leq 30$  ps), followed by a change to a prominent one-half-power dependence for the remainder of the simulation ( $50 < t < 450$  ps). A careful examination of the time-developing interatomic morphologies for these different growth stages suggests that they may be characterized as “wave creation and growth” until local maxima in density approach the condensed-liquid density, followed by “wave necking” or breakup leading to the creation and subsequent growth of atomic clusters. One may correctly state that the “spinodal mechanism” comes to completion by about 30 ps since the density extremes have been achieved. After this early time, coarsening dynamics by vapor condensation and/or cluster coagulation are the governing mechanisms.

The two-stage growth of clusters is also substantiated by examining two further characteristics: (i) The magnitude of the minimum of  $g(r)$  versus time is shown in the lower part of Fig. 2. It clearly shows the two growth stages. (ii) From the atomic configurations (Fig. 1), we have also

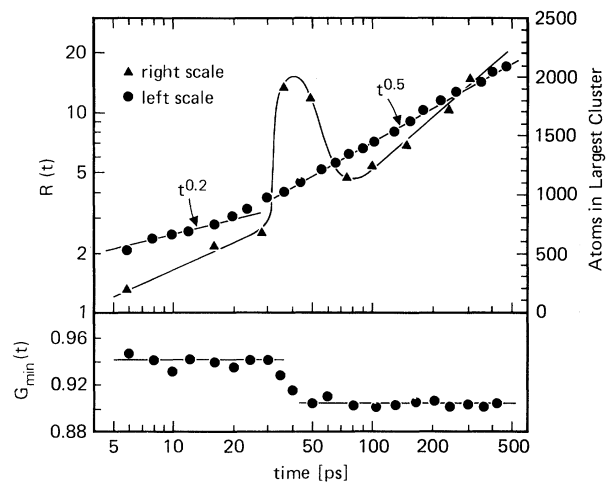


FIG. 2. Cluster size  $R(t)$  (dots, upper, left scale), minimum of radial distribution function  $G_{\min}(t)$  (dots, lower, left scale), and the number of atoms in the largest cluster (triangles, upper, right scale) as functions of time ( $R$  in units of  $\sigma$ ).

studied directly the cluster size distribution using the algorithm outlined by Stoddard.<sup>4</sup> In Fig. 2 (upper, right scale, triangles), we show the size of the largest cluster as a function of time. This demonstrates the phenomenon of “wave creation” up to about 30 ps, manifesting itself as the appearance of a very large growing cluster due to the highly interconnected morphology. Subsequently, there is a “wave necking” transition region around 40–50 ps. This is followed by “isolated” cluster growth (compare Fig. 1, insets).

A simple scaling of coarse-grained radial distribution functions with time is suggested if we hypothesize that the density morphology remains approximately topologically invariant during coarsening, but the actual spatial variation of density domains expands as  $R(t)$ . We conclude that within the framework of this picture, a time-invariant radial distribution function  $G(X)$  is obtained from the relation

$$G(X) = g(X, t), \quad X = r/R(t), \quad (1)$$

where  $g(r, t)$  is the measured coarse-grained distribution function at time  $t$ . In Fig. 3, the scaled function  $G(X)$  is presented for various times and for the two different growth regimes. We see very good scaling invariance for the two growth regimes; at later times the invariance breaks down for  $X > 2$ . This failure only reflects the fact that the average nearest-neighbor separation distance does not scale exactly with average cluster size  $R(t)$  when the system coarsens to a few large clusters, a consequence of conservation of total number of atoms. In actual fact, the scaled coarse-grained distribution function  $G(X)$  for distances  $X < 2$  reflects principally the structure of

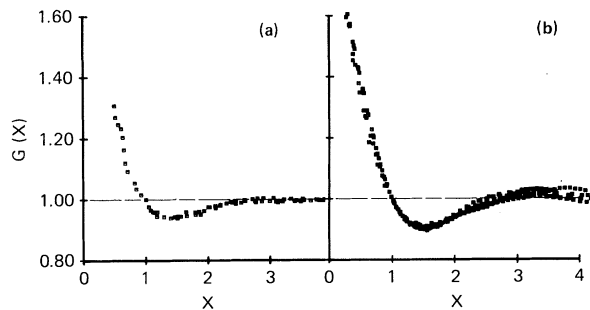


FIG. 3. Scaled radial distribution function  $G(X)$ , Eq. (1), for the two growth regimes at various times: (a) 12, 14, 16, 18, 20, 22, 24, and 26 ps and (b) 60, 80, 100, 200, 300, 400, and 450 ps.

an individual “average” cluster of normalized size  $X = 1.0$ , the cluster’s structure described by the peculiarities of radially averaging over atomic positions in the cluster.

A very simple model of the inhomogeneous density distribution for the phase-separating system contains the essential ingredients for describing  $G(X)$ . The model consists of a “mother cluster” of size  $R_1(t)$ , surrounded by a shell of vapor concentric with the mother cluster and of outer radius  $R_2(t)$ , which in turn is surrounded by a uniform fluid of mean density with which the system began its time evolution (and which “macroscopically” is always constant!). For simplicity, we assumed that the density variation in the model system is such that (i) within the mother cluster the density is  $\rho_1$ , the final equilibrium liquid density, (ii) the density in the vapor shell is zero, and (iii) the density in the outermost region is  $\rho_m$ , the uniform mean density. The conservation of the total number of atoms in the system implies that  $R_2 = (\rho_1/\rho_m)^{1/2}R_1$ . We conclude that  $G(X)$  is a rather insensitive measure of the system’s morphology and that it is not very astonishing that we find a scaling invariance for relation (1). This scaling behavior in  $G(X)$  is reflected in a scaling invariance for the growth peak in the structure factor  $s(k)$ ; i.e.,

$$S(K) - 1 = [s(k, t) - 1]/R(t)^2, \quad K = kR(t).$$

Similar scaling behavior for three-dimensional systems has been found for Ising binary lattices<sup>5</sup> and real glass,<sup>6</sup> where  $R^{-2}$  is replaced by  $R^{-3}$ .

We have also completed a “constant-(total)-energy” molecular-dynamics experiment on the two-dimensional Lennard-Jones fluid quenched to the unstable region of the phase diagram; i.e., this experiment is, in most respects, identical to our isothermal simulation except that the renormalization of the velocity distribution is not performed. We find that the late-stage growth law for this constant-energy experiment follows a time-dependent power-law behavior of  $\frac{1}{3}$ , in sharp contrast to the power-law behavior of  $\frac{1}{2}$  for the isothermal experiment. We have a theoretical argument supporting the different growth laws observed for the constant-temperature experiment and the constant-energy experiment, respectively, based on an asymptotic analysis of cluster growth in a one-component system.<sup>7</sup> Our analysis is similar to that done by Lifshitz and Slyozov<sup>8</sup> for binary mixtures.

To summarize, we find scaling of the coarse-grained radial distribution function (or structure

factor) with two principal growth regimes, spinodal decomposition until local density extremes approximate the densities of the thermodynamic coexisting phases but with a wavelike morphology of wave number equal to unity, followed by a transition to cluster formation and growth due to atomic condensation and cluster coagulation. For the later stage of the phase-separation process, the time-dependent power-law behaviors for the constant-temperature and constant-energy experiments are 0.5 and 0.33, respectively; these dependences may be rationalized from a theory for vapor accretion on two-dimensional clusters in a "one-component supersaturated vapor."<sup>7</sup> The  $t^{1/2}$  dependence also arises in the cluster coagulation mechanisms in two dimensions,<sup>9</sup> but the late-stage trajectory pictures suggest that this is not a governing coarsening process.

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<sup>3</sup>The parameter  $\sigma$  is the value of the interatomic separation for which the LJ potential is zero. The parameter  $\epsilon$  is the depth of the minimum of the LJ potential. The parameter  $m$  denotes the mass of an atom.

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## Dynamic Monte Carlo Simulation of an Entangled Many-Polymer System

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The dynamics of a system of long polymer chains is investigated numerically with Monte Carlo dynamics. By use of a lattice model of polymers interacting via hard-core potentials, much longer polymers have been investigated than has been possible previously. The correlation functions calculated are in agreement with de Gennes's "reptation" hypothesis, and differ strongly from Rouse-like behavior.

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Polymers of high molecular weight and at high concentrations exhibit unusual behavior in many of their properties. The viscosity<sup>1</sup> and diffusion coefficient<sup>2</sup> both exhibit power-law dependences on the molecular weight, whose exponents are independent of the chemical structure of the molecules. Furthermore, the viscoelastic behavior of such systems also appears independent of microscopic structure. In order to account for such phenomena, de Gennes<sup>3</sup> and Doi and Edwards<sup>4</sup> have constructed a semiphenomenological theory to explain the behavior of entangled polymers.<sup>2,5</sup> The theory assumes that a long polymer at high concentration has its motion restricted by a "tube" with diameter  $D$ , that is assumed independent of molecular weight, and is dependent on the chemical structure of the polymer. This is related to the notion of "entanglements." Between entanglements, the polymer moves as if it were

in a viscous fluid. That is, over short distances, the effect of all other polymers is modeled as a fluid. The distance between entanglements is approximately the tube diameter so that the "entanglement length"  $N_e$ , which is the average number of segments of polymer chain between two entanglement points, is  $D^2/a^2$ , where  $a$  is the step length of the polymer. The motion of a single polymer in a highly viscous fluid can approximately be described by the Rouse model.<sup>6</sup> It predicts that a portion of polymer chain  $n$  segments in length will relax in a time of roughly  $n^2/W$ , where  $W$  is a jump frequency. Thus for observation times shorter than  $N_e^2/W$  an entangled polymer should move much like a free one. The relaxation time for an entangled polymer with  $L$  segments is about  $L^2/W$ , which is the time it takes a "kink" to travel from one end of the tube to the other end. The transfer of kinks from one