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Kinetics of phase separation in fluids: A molecular dynamics study

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We present results from extensive three-dimensional molecular dynamics (MD) simulations of phase separation kinetics in fluids. A coarse-graining procedure is used to obtain state-of-the-art MD results. We observe an extended period of temporally linear growth in the viscous hydrodynamic regime. The morphological similarity of coarsening in fluids and solids is also quantified. The velocity field is characterized by the presence of monopolelike defects, which yield a generalized Porod tail in the corresponding structure factor.

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The nonequilibrium evolution of a phase-separating binary mixture, A+B, is a complex nonlinear process [1]. This problem has attracted much research interest both computationally [2] and experimentally [3]. The growth of A-rich and B-rich domains during phase separation is a scaling phenomenon. The two-point equal-time correlation function, $C_{\psi\psi}(r,t)$, which characterizes the domain morphology and growth, scales as $C_{\psi\psi}(r,t)=g[r/\ell(t)]$ [4]. Here, $g(x)$ is a scaling function independent of time. The average domain size $\ell(t)$ grows with time t as $\ell(t)\sim t^{\alpha}$.

The growth exponent α depends upon the transport mechanism which drives segregation. For diffusive dynamics, $\ell \sim t^{1/3}$, which is referred to as the Lifshitz-Slyozov (LS) law [1]. The LS behavior is the only growth law expected for phase-separating solid mixtures. However, for fluids and polymers, one expects faster growth at large length scales where hydrodynamic effects are dominant. For $d=3$, convective transport yields additional growth regimes [5] with

$$\alpha = 1, \quad \ell(t) \ll \ell_{\text{in}},$$

$$\alpha = 2/3, \quad \ell(t) \gg \ell_{\text{in}}. \tag{1}$$

In Eq. (1), the inertial length ℓ_{in} [$\simeq \eta^2/(\rho\gamma)$, η, ρ, and γ being the shear viscosity, density and interfacial tension] marks the crossover from a low-Reynolds-number viscous hydrodynamic regime to an inertial regime. There has been experimental evidence [6] for a crossover from diffusive to viscous growth. However, no experimental observation of an inertial regime has been reported.

While recent focus has turned to systems with realistic interactions and boundary conditions [2,3], our understanding of segregation kinetics in bulk fluids remains far from complete. The viscous regime has been observed in numerical studies using the phenomenological Model H [7,8]. Further, both viscous and inertial regimes have been observed in lattice Boltzmann simulations [9,10]. However, molecular dynamics (MD) methods, where hydrodynamics is automatically inbuilt, have rarely been used to study domain growth, primarily due to heavy computational requirements. To the best of our knowledge, the first MD study was by Ma *et al.* [11], who did not find a signature of viscous growth. In a later MD simulation, Laradji *et al.* [12] observed linear domain growth over a small interval in a binary Lennard-Jones (LJ) fluid. These first MD results have been obtained for low-density fluids over very limited time windows. More recently, Thakre *et al.* [13] used a similar model to study the crossover from diffusive to viscous dynamics. However, they do not observe linear growth in the postcrossover regime. In related work, Kabrede and Hentschke [14] found $\alpha \simeq 0.5$ in MD simulations of gas-liquid phase separation. In this communication, we present results from large-scale MD simulations in conjunction with a numerical renormalization procedure [15]. These state-of-the-art MD results provide the first unambiguous confirmation of viscous domain growth in fluids, and also explore the ordering dynamics of the velocity field. Our MD results strongly support the universal nature of domain growth morphologies in solid and fluid mixtures. This has important theoretical implications as obtaining the scaling form of the correlation function for phase-separating systems remains an outstanding problem in this area. These results will serve as a valuable reference for experimentalists and theorists.

Following Das *et al.* [16], we have employed a symmetric model where particles of diameter σ interact via the potential $V(r_{ij})=U(r_{ij})-U(r_c)-(r_{ij}-r_c)dU(r_{ij})/dr_{ij}|_{r_{ij}=r_c}$. Here $U(r_{ij})=4\epsilon_{\alpha\beta}[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6}]$ is the LJ potential; and $r_{ij}=|\vec{r}_i-\vec{r}_j|$, $r_c=2.5\sigma$, and α, β=A,B. We chose $\epsilon_{AA}=\epsilon_{BB}=2\epsilon_{AB}=\epsilon$, so that phase separation is favored energetically. All particles were assigned equal mass m. We set m, σ, ϵ, and k_B to unity. An incompressible fluid ($\rho=1$) is studied for which phase separation sets in at a critical temperature $T_c \simeq 1.423$ [16], well separated from the gas-liquid and liquid-solid transitions. In the case of compressible fluids, possible coupling between liquid-liquid and gas-liquid transitions can be problematic in the appropriate identification of domains and thus the understanding of the growth process. A total number of 262 144 particles were confined in a cubic box of size 64^3 with periodic boundary conditions in all directions. The MD runs were performed using the standard Verlet velocity algorithm [17] with a time step $\Delta t=0.01\tau$ [the LJ time unit, $\tau=(m\sigma^2/\epsilon)^{1/2}=1$], which provides integration error within acceptable limits. The temperature T was controlled by a Nosé-Hoover thermostat (NHT) [17], which is known to preserve hydrodynamics. Homogeneous initial configurations were

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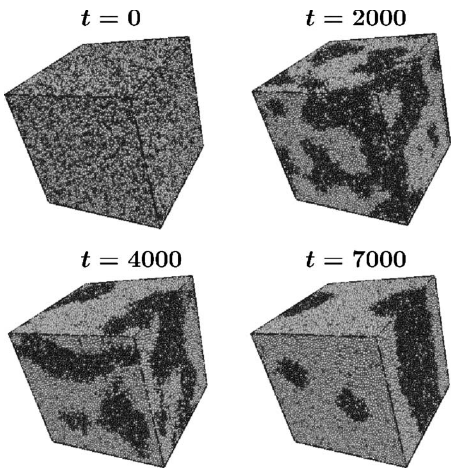

FIG. 1. Evolution snapshots for a 50:50 binary Lennard-Jones fluid after quenching from the high-temperature homogeneous phase to $T=0.77T_c$. The A and B particles are marked in black and gray, respectively.

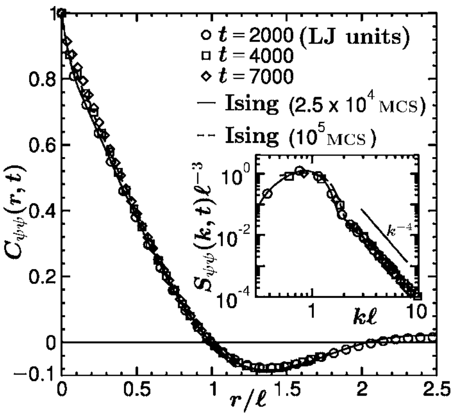

FIG. 2. Scaling plot of the correlation function, $C_{\psi\psi}(r,t)$ vs r/ℓ, for three different times. The inset shows the scaling plot of the structure factor $S_{\psi\psi}(k,t)$ for the same times. The solid and dashed lines, which almost coincide and are hard to distinguish, denote analogous data from the Kawasaki-Ising model.

prepared by equilibrating the system at $T=10$. At $t=0$, the system is quenched to $T<T_c$. All the results presented here were obtained by averaging over five independent runs at a quench temperature $T=0.77T_c$.

In Fig. 1, we present evolution pictures at different times. As expected for a symmetric (critical) composition, a bicontinuous domain structure is seen. The snapshot at $t=0$ corresponds to the homogeneous state immediately after the quench. The snapshot at $t=7000$ corresponds to the situation where the system has almost completely phase separated. Note that this time interval is more than an order of magnitude larger than earlier MD studies. While domains grow without encountering any perceptible size effects within this time window, finite-size effects are seen beyond it [18].

To characterize the domain morphology, we calculate the correlation function as

$$C_{\psi\psi}(r,t) = \langle \psi(0,t)\psi(\vec{r},t)\rangle / \langle \psi(\vec{r},t)^2 \rangle, \tag{2}$$

where the order parameter $\psi(\vec{r},t)[=x_A(\vec{r},t)-x_B(\vec{r},t)]$ is the local concentration difference between A and B species. The angular brackets in Eq. (2) denote statistical averaging. We use a coarse-graining procedure [15] to obtain the pure domain structure by eliminating thermal fluctuations in the snapshots of Fig. 1. Figure 2 shows the scaling plot of $C_{\psi\psi}(r,t)$ vs r/ℓ. The average domain size ℓ is defined as the first zero crossing of $C_{\psi\psi}(r,t)$, which is computed from the coarse-grained order parameter. Our correlation function data are comparable in quality to that obtained from a Langevin simulation [8]. The neat data collapse over an extended interval shows that a scaling regime is reached.

We would like to make a quantitative comparison of our MD results for $C_{\psi\psi}(r,t)$ with those for segregation in the Kawasaki-Ising model (KIM), where the structure and dynamics are much better understood. The lines in Fig. 2 denote $C_{\psi\psi}(r,t)$ vs r/ℓ, obtained from a Monte Carlo (MC) simulation of the KIM [19] with critical (50:50) composition. The MC scaling function is in excellent agreement with our MD data. In the inset of Fig. 2, we show the corresponding results for the scaled structure factor, $S_{\psi\psi}(k,t)\ell^{-3}$ vs $k\ell$, where $S_{\psi\psi}(k,t)$ is the Fourier transform of $C_{\psi\psi}(r,t)$. Again, a good data collapse is obtained confirming the scaling form, $S_{\psi\psi}(k,t)=\ell^d f(k\ell)$ [1]. The agreement with the corresponding KIM result is demonstrated again in the inset. Here, the decay of the tail with a power law, $S_{\psi\psi} \sim k^{-4}$, is consistent with the expected Porod's law [20,21], $S(k,t) \sim k^{-(d+n)}$, for ordering dynamics in $d=3$ with a scalar order parameter ($n=1$). (In an extended publication, we will present results for morphological characteristics such as the Tomita sum rule, Yeung-Furukawa law for $k \to 0$, etc.) The excellent agreement of the scaling functions confirms a close similarity of structures formed during phase separation in fluids with those for solid mixtures. In a related context, Puri *et al.* [22] have emphasized that domain growth morphologies are approximately independent of the kinetic mechanism of coarsening. These authors compared morphologies arising from bulk diffusion with those from surface (or interface) diffusion, and found that they were characterized by a universal correlation function. Our results in this paper show that this universality is of greater generality. This should be contrasted with a *Cell Dynamical Systems* study by Shinozaki and Oono [8], who argued that there were different scaling functions for phase separation in alloys and fluids.

Next, we focus on the time dependence of the domain size. In Fig. 3, we plot ℓ vs t. The growth at later times ($t > 2000$) is clearly linear, but the earlier-time data deviates somewhat. In fact, a least-squares fit to the form $\ell(t)=B+At^{\alpha}$ in the range $t \in [0,2000]$ gives an exponent $\alpha \simeq 0.75$. Essentially, the diffusive regime (with $\ell \sim t^{1/3}$) is very short lived at this temperature. A gradual crossover to the viscous regime (with $\ell \sim t$) starts very early, extending over a large fraction of the time window, where the effective exponent is rather high.

The top curve in the upper inset of Fig. 3 shows the instantaneous exponent $\alpha_i[=d(\ln \ell)/d(\ln \mathrm{t})]$ vs $1/\ell$. Because of the significantly large off-set value in ℓ as $t \to 0$, α_i tends to its asymptotic value in a linear fashion only in the limit $\ell \to \infty$ [18]. Without a knowledge of the functional form of α_i

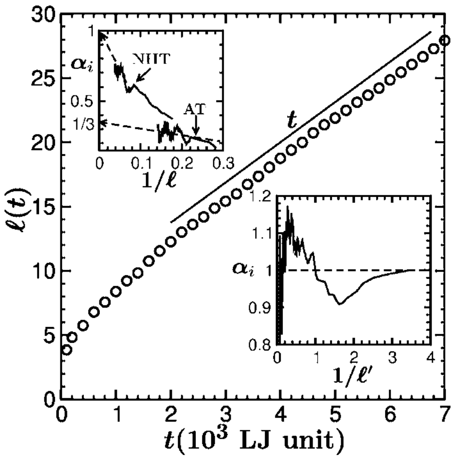

FIG. 3. Plot of average domain size, $\ell(t)$, as a function of time t. The insets show the instantaneous exponent α_i vs $1/\ell$ (upper) and α_i vs $1/\ell'$ (lower). A detailed explanation of the insets is provided in the text.

for the whole range of $1/\ell$, the dashed straight line serves as a guide to the eyes and suggests $\alpha_i \to 1$, justification of which will be clear from further analysis. The lower curve in this inset is obtained from the coarsening dynamics when an Andersen thermostat (AT) is used instead of an NHT. The AT, where T is controlled by letting the particles collide randomly with a heat bath, is stochastic in nature and does not model hydrodynamics. Thus, it is expected to provide a diffusive growth of domains with $\alpha = 1/3$. Indeed our result is consistent with that expectation, as shown by the dashed straight line which extrapolates to $\alpha = 1/3$ in the upper inset. This confirms the utility of the NHT in studying hydrodynamic phenomena in domain growth. We also emphasize that MD with an AT offers a more realistic way of modeling diffusive phase separation than the commonly used but unphysical KIM. Of course, one can preserve hydrodynamics better by using more advanced thermostats [23], like dissipative particle dynamics. However, for the system size used, NHT has been found to preserve hydrodynamics well. This was confirmed by comparing our results with those from other system sizes over smaller run lengths.

There is another instructive way of investigating α_i. In hindsight, we introduce a time t_0 [12,18] and assume that segregation kinetics follows a power-law behavior with time $t' = t - t_0$,

$$\ell'(t') = \ell(t) - \ell(t_0) = At'^{\alpha}. \tag{3}$$

Then, we calculate the exponent $\alpha_i = d(\ln \ell')/d(\ln t')$. For linear growth, Eq. (3) is invariant under an arbitrary choice of t_0. Thus, if t_0 is chosen appropriately, $\alpha_i \simeq 1$ for all values of t'. However, as noted by other authors [8,18], in computer simulations of finite systems one finds an oscillation of α_i as $\ell \to \infty$, with growing amplitude around the expected value. This is due to increasing separation between the domains of like particles, thus delaying collisions between domains of *large* size. The lower inset of Fig. 3 plots α_i vs $1/\ell'$ for $t_0 = 2500$, which lies in the linear region. Indeed, this plot is consistent with the above expectation, and α_i oscillates around the mean value $\alpha = 1$.

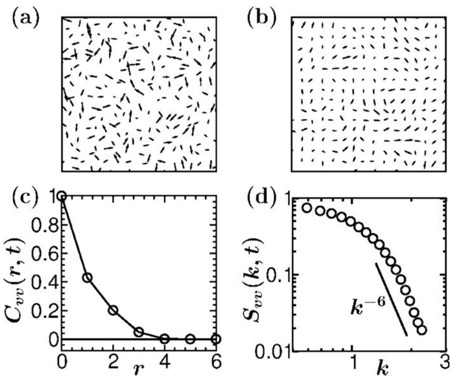

FIG. 4. Pattern formation in the velocity field at $t = 7000$. (a) Projection of velocity field onto a 2D cross section. (b) Same as (a) but for the coarse-grained velocity field. (c) Plot of correlation function, $C_{vv}(r,t)$ vs r, for the velocity field. (d) Plot of corresponding structure factor, $S_{vv}(k,t)$ vs k, on a log-log scale.

Finally, we turn our attention to the pattern dynamics of the velocity field. Figure 4(a) shows a two-dimensional (2D) cross section of the system at $t = 7000$, with particle velocities being projected onto this plane. While the orientations of velocity vectors look fairly random at the microscopic scale, structure starts emerging upon coarse-graining over larger length scales, as seen in Fig. 4(b). In Figs. 4(c) and 4(d), we present plots of the velocity correlation function $C_{vv}(r,t)$ and structure factor $S_{vv}(k,t)$ analogous to the density field. The decay of the structure factor tail as $S_{vv} \sim k^{-6}$ is consistent with the generalized Porod's law [21] for ordering of a three-component $(n=3)$ vector field in $d=3$. This is indicative of presence of monopole-like defects, which can be seen in the coarse-grained snapshots of the velocity field. To study growth in this ordering, if any, as seen in the lattice Boltzmann simulations [9,10], we need coarse graining over a larger length scale which is not accessible with the present system size. It would be more interesting, though challenging, to study the dynamics of velocity field in the vicinity of the domain boundaries.

In summary, our results from extensive MD simulations of a binary LJ fluid unambiguously confirm the linear growth law in the viscous hydrodynamic regime. We use a numerical renormalization technique to obtain noise-free data from our MD studies. Even though the growth mechanisms in fluids are different from solids, the domain morphologies are comparable in the two cases. Similar studies at higher quench temperatures will be useful to identify diffusion-driven growth and crossovers. Note that while our choice of system size was appropriate for understanding viscous growth, this size is not large enough to study dynamics in the inertial regime. To achieve the latter goal, sophisticated modeling at the multiscale level is required, in addition to usage of parallel programming and a graphics card.

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