Spinodal decomposition in fluids: Diffusive, viscous, and inertial regimes

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Using a Langevin description of spinodal decomposition in fluids, we examine domain growth in the diffusive, viscous, and inertial regimes. In the framework of this model, numerical results corroborate earlier theoretical predictions based on scaling arguments and dimensional analysis. [S1063-651X(96)05505-5]

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The dynamics of phase transitions in binary fluids quenched into the coexistence region has been the subject of considerable study in recent years [1,2]. It is generally accepted that long after the quench, the phase separation dynamics can be characterized by a single time dependent length scale, $R(t)\sim t^{\alpha}$. As a result, much attention has focused on how domains grow in time — specifically what is the growth exponent α?

Scaling and dimensional analyses due to Siggia [3], Furukawa [4], San Miguel, Grant, and Gunton [5] and more recently Bray [2] address this question. Experimental [6] and numerical [7–14] studies, however, have not necessarily supported these theories, sometimes providing conflicting results [15]. Often overlooked in spinodal decomposition in binary fluids is that several stages of growth can occur, in each of which a different transport mechanism dominates. This fact has been reemphasized in [2,4,17,18]. Individual experiments and numerical simulations typically access only a particular regime. Lacking has been a clear demonstration of (1) the existence of these distinct regimes within a single model and, subsequently, (2) quantitative results in these regimes which validate theoretical predictions [2–5]. In this paper we address these points.

To simulate phase separation in a binary fluid, we used the Langevin model of Farrell and Valls [7]. The order parameter ψ is the difference in the concentration of the two fluid components. Its evolution and that of the fluid velocity are given by

$$\partial_t\psi=\Gamma^2\mu-\lambda\nabla\cdot[\psi\rho\mathbf{u}], \tag{1}$$

$$\rho\partial_t\mathbf{u}=\eta\nabla^2\mathbf{u}+\sigma\nabla(\nabla\cdot\mathbf{u})-\lambda\nabla\cdot(\rho\mathbf{uu})-\lambda\psi\nabla\mu, \tag{2}$$

where ρ is the average mass density, Γ is an order parameter diffusion coefficient, and η is the shear viscosity. Here $\sigma=\eta(1-2/d)+\zeta$, where ζ is the bulk viscosity, and d is the spatial dimension. The dimensionless constant λ couples the order parameter to the fluid velocity and is also the strength of the convective flow. The chemical potential $\mu=\delta F/\delta\psi$ where F is the free energy of the system at equilibrium given by $F[\psi,\mathbf{u}]=\frac{1}{2}\int d^d\mathbf{r}[\rho u^2+\frac{1}{2}a\psi^4-b\psi^2+\beta K|\nabla\psi|^2]$. The strength of the interfacial energy is βK. Below the critical temperature, a and b are positive constants.

After the fluid is quenched, single phase droplets form and grow. In the coarsening process a competition between hydrodynamic and thermodynamic effects can lead to three dynamical regimes: the diffusive, viscous, and inertial [2,4]. We discuss these briefly, using dimensional analysis based on Eqs. (1) and (2).

In the diffusive regime, the fluid velocities are small, and the advective term in (1) is negligible compared to the order parameter diffusion. Therefore (1) becomes $\partial_t\psi\sim\Gamma\nabla^2\mu$. Since the chemical potential $\mu\sim\kappa/R$ where κ is the surface tension and R is the characteristic length scale in the system (i.e., domain size), we have $R(t)\sim(\Gamma\kappa)^{1/3}t^{1/3}$. The coefficient $\Gamma\kappa$ implies that the growth in this regime is driven by diffusion and surface tension. In two dimensions, for example, the surface tension κ is given by $\kappa=4/3(2\beta K)^{1/2}$ [4].

In the viscous regime, hydrodynamics becomes relevant. In particular, in the velocity Eq. (2), the viscous term dominates the inertial terms. If one ignores the inertial and bulk viscosity terms, the shear stress term is balanced by the force due to the gradient in the chemical potential. Thus $\eta\nabla^2\mathbf{u}\sim\lambda\psi\nabla\mu$ so that $R(t)\sim\lambda\kappa/\eta t$. This is the linear growth law predicted by Siggia [3]. The coefficient $\lambda\kappa/\eta$ indicates growth driven by the surface tension and controlled by the viscous force in the fluid. The length-scale R_d and time-scale t_d at which the system crosses over from the diffusion regime to the viscous regime is given by setting $(\Gamma\kappa)^{1/3}t_d^{1/3}\sim\lambda\kappa/\eta t_d$. Thus $t_d\sim(\Gamma\eta^3/\kappa^2\lambda^3)^{1/2}$ and $R_d\sim(\Gamma\eta/\lambda)^{1/2}$.

In the inertial regime, inertial effects dominate over the viscous forces so that $\rho d\mathbf{u}/dt\sim\lambda\psi\nabla\mu$. This leads to $R(t)\sim(\lambda\kappa/\rho)^{1/3}t^{2/3}$, as predicted by Furukawa [4] (see also [2]). The coefficient here indicates that the growth is driven by the surface tension and controlled by the inertial effects. The crossover between the viscous regime and the inertial regime thus occurs at length-scale R_h and time-scale t_h where $\lambda\kappa/\eta t_h\sim(\lambda\kappa/\rho)^{1/3}t_h^{2/3}$ so that $t_h\sim\eta^3/\rho\lambda^2\kappa^2$ and $R_h\sim\eta^2/\lambda\rho\kappa$. Similarly, the length R_i and time t_i for crossover from diffusion directly to inertial are given by $R_i\sim(\Gamma^2\kappa\rho/\lambda)^{1/3}$ and $t_i\sim\Gamma\rho/\lambda$, respectively. This would correspond to the inviscid flow case.

To facilitate growth of domains in each of these regimes and to access each of them within the framework of a single

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model, we vary R_d and R_h (relative to system size) by adjusting the parameters η, λ, and β. For convenience, the actual (dimensionless) numerical equations we solve are the following:

$$\partial_t \phi = \nabla^2[\phi^3 - \phi - \beta\nabla^2\phi] - \hat{\lambda}\nabla\cdot[\phi\mathbf{v}] + \mu, \tag{3}$$

$$\partial_t v_i = \hat{\eta}\nabla^2 v_i + \hat{\sigma}\sum_k \nabla_i\nabla_k v_k - \hat{\lambda}\phi\nabla_i[\phi^3 - \phi - \beta\nabla^2\phi]$$

$$-\hat{\lambda}\sum_k [\nabla_k(v_i v_k) + v_k\nabla_i v_k] + w_i . \tag{4}$$

The rescaled order parameter and transport quantities are given in terms of those used in (1) and (2) by $\phi = (a/b)^{1/2}\psi$, $\mathbf{v} = (a/b\rho K)^{1/2}\mathbf{u}$, $\hat{\eta} = \eta/\rho\Gamma K$, $\hat{\sigma} = \sigma/\rho\Gamma K$, $\hat{\lambda} = \lambda(b/\Gamma^2 a\rho K)^{1/2}$. Space and time are rescaled by $\mathbf{r}\to\mathbf{r}$, $t\to\Gamma K t$. The dimensionless crossover lengths are given by $R_d = (\hat{\eta}/\hat{\lambda})^{1/2}$, and $R_h = \hat{\eta}^2/\hat{\lambda}\hat{\kappa}$, where we have set $\rho = 1$. In two dimensions, the surface tension, $\hat{\kappa} = 4/3(2\beta)^{1/2}$, so that by varying β, we can control the surface tension.

We studied deep, critical or symmetric quenches with $\langle\phi\rangle = 0$ throughout the course of the simulations, where $\langle . \rangle$ denotes an ensemble average or space average. The order parameter and velocity are initially taken as Gaussian fields with $\langle\phi\rangle = \langle v_i\rangle = 0$, and $\langle\phi^2\rangle = \langle v_i^2\rangle = 0.005$. The grid size Δx used was 1.7 and the time step Δt was chosen as 0.05 in two and 0.02 in three dimensions, respectively. The numerical integration scheme is the same as in [7,11]. The average domain size was defined as the first zero of the equal time correlation function $G(r,t) = \langle\phi(\mathbf{x},t)\phi(\mathbf{x}+\mathbf{r},t)\rangle$, the Fourier transform of which is the structure factor $S(k,t)$. The fields μ and w_i were Gaussian, white noise with covariance given by the fluctuation-dissipation relation [7,11]. We found that adding noise does not alter the growth exponent in the scaling regime. However it introduces curvature in the early growth so that longer times are required to reach the scaling regime. The results we report here were obtained in the absence of noise and in all cases were averaged over 3 or 4 independent runs.

In two dimensions, on a 1024^2 system, we let $\hat{\eta} = 1$, $\hat{\lambda} = 1$ and $\beta = 1$. Thus $R_d \sim R_h \sim 1$ (in lattice units) are both small compared to the lattice size $L = 1024$ so that for domain size $R(t) \gg R_h$, the system will favor droplet growth in the inertial regime. The data represented by ($\square$) in Fig. 1 shows that $R(t)$ has a behavior consistent with $\alpha = 2/3$. In order to have a viscous regime, one requires $R_d \ll R(t) \ll R_h$. This is satisfied by choosing, for example, $\hat{\eta} = 20$, $\hat{\lambda} = 1$ and $\beta = 1$ so that $R_h \sim 120$ and $R_d \sim 3$. In Fig. 1 the symbol ($\times$) shows the growth under these conditions. It is consistent with $\alpha = 1/2$ growth over a time interval spanning about 1.5 decades. The exponent of $\alpha = 1/2$ in two dimensions was predicted in [5]. Since $R_h \sim 120$, the inertial force would not be expected to influence the growth until at late times when $R(t)$ is comparable with R_h. To indicate how the $\alpha = 1/2$ growth could yield to the $\alpha = 2/3$ growth, we changed parameters to make R_h smaller so that the crossover from the viscous regime to the inertial regime can happen earlier. The symbols ($\diamond$) and ($+$) in Fig. 1 show data for $R_h \sim 30$ ($\hat{\eta} = 11$, $\hat{\lambda} = 1$, $\beta = 1$) and $R_h \sim 7$ ($\hat{\eta} = 5$, $\hat{\lambda} = 1$, $\beta = 1$), respectively. As R_h (and R_d) decreases, the data shows that the viscous growth and a later, faster inertial growth occurs progressively earlier. Finite size effects and the need for very long times to see adequate viscous and inertial growth make quantitative analysis of growth in the crossover regimes difficult. The time evolution of the Reynolds number Re, the ratio of inertial to viscous effects, is consistent with the behavior of $R(t)$ as R_h decreases. Corresponding to the parameters for domain growth, the insert to Fig. 1 shows Re how changes from its behavior in the viscous regime, where Re<1 and is essentially constant, to that in the inertial regime where it increases as $t^{1/3}$ [4]. We find that for $\eta \geqslant 11$, the system lies well within the viscous regime until the influence of inertial flow at very late times. The scaled correlation functions $G(\xi)$ and $\xi^2 G(\xi)$ [8] are shown in Fig. 2, for $\hat{\eta} = 20$, $\hat{\lambda} = 1$, $\beta = 1$, where $\xi = r\langle k\rangle$ and $\langle k\rangle = \int kS(k,t)dk / \int S(k,t)dk$. The data collapses well for several times, indicating that the $\alpha = 1/2$ growth is in the scaling regime. The scaling behavior for $\alpha = 2/3$ was shown in [11].

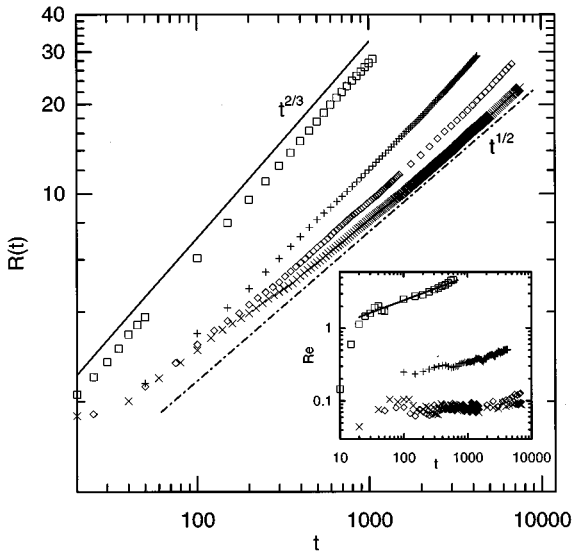

FIG. 1. The domain growth $R(t)$ vs time t in *two* dimensions for different crossover lengths R_h showing the change from growth in the inertial regime ($t^{2/3}$) to the viscous regime ($t^{1/2}$). The errors in the data due to different initial conditions are of the order of the size of the symbols. The inset shows the Reynolds number Re $= \tilde{v}R(t)/\hat{\eta}$ as a function of time, where $\tilde{v}$ is the characteristic velocity calculated as dR/dt [4]. The data are consistent with Re $\sim t^{1/3}$ in the inertial regime and Re$\sim$const in the viscous regime. The straight line has slope 1/3. The symbols represent $\hat{\eta} = 20$, $\hat{\lambda} = 1$, $R_h \sim 120$ ($\times$), $\hat{\eta} = 11$, $\hat{\lambda} = 1$, $R_h \sim 30$ ($\diamond$), $\hat{\eta} = 5$, $\hat{\lambda} = 1$, $R_h \sim 7$ ($+$) and $\hat{\eta} = 2, \hat{\lambda} = 1$, $R_h \sim 1$ ($\square$). The surface tension controlling parameter $\beta = 1$ for all cases.

Using this model in two dimensions, we previously [11] examined the behavior of α as a function of the coupling constant, $\hat{\lambda}$ ($0 < \hat{\lambda} < 1$), by fixing $\hat{\eta}$, β and ρ. For this one parameter system, $R_h \sim 1/2\hat{\lambda}$ and $R_d \sim 1/\hat{\lambda}^{1/2}$. For $1/2 < \hat{\lambda} < 1$, $R_h \sim R_d \sim 1$, so that only the inertial growth survived. For $\hat{\lambda} \to 0$, the domain size $R(t) < R_d$ and the dominant mechanism was diffusion. It was the first attempt to show within a single model different regimes, however, the one-

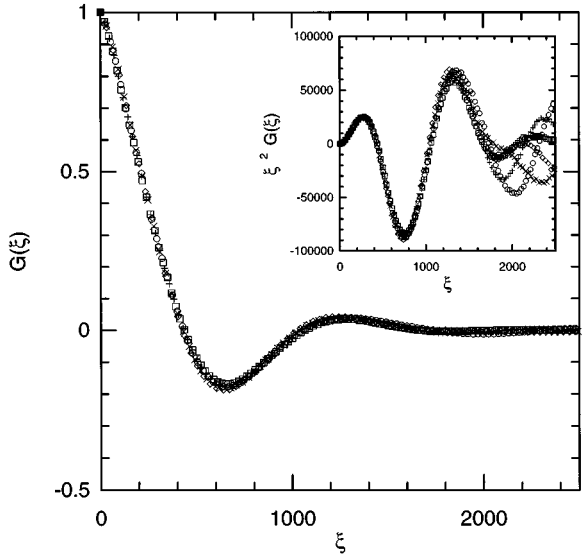

FIG. 2. The scaled and normalized correlation function $G(\xi)$ vs ξ, where $\xi = r\langle k\rangle$ and the first moment $\langle k\rangle = [\int kS(k,t)dk]/[\int S(k,t)]$, for $\hat{\eta}=20$, $\hat{\lambda}=1$, and $\beta=1$ on 1024×1024 lattices, at $t=2500$ ($\diamond$), 3000 ($\times$), 4000 ($\bigcirc$), 5000 ($+$), and 6000 ($\square$). The inset shows $\xi^2 G(\xi)$ versus ξ for the same times and since $\langle k\rangle \sim 25$, scaling is good for ~ 80 lattice units.

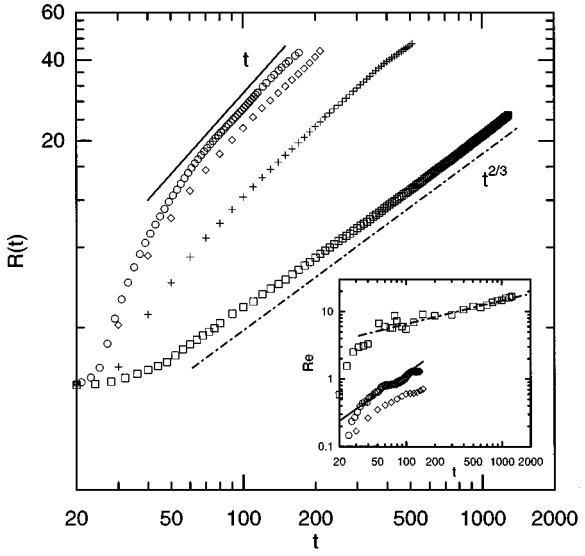

FIG. 3. The domain growth $R(t)$ vs time t in *three* dimensions for values of crossover lengths R_h showing the change in α from inertial ($t^{2/3}$) to viscous (t) regime. The errors are of the size of the symbols. The inset shows that the behavior of the Reynolds number Re is consistent with $t^{1/3}$ in the inertial regime and t in the viscous regime. The straight lines have slopes 1/3 (– - –) and 1 (——). The symbols represent $\hat{\eta}=25$, $\hat{\lambda}=25$ ($\bigcirc$), $\hat{\eta}=20$, $\hat{\lambda}=20$ ($\diamond$), $\hat{\eta}=8$, $\hat{\lambda}=8$ ($+$), $\hat{\eta}=1$, $\hat{\lambda}=1$ ($\square$). The surface tension controlling parameter $\beta=1$ for all cases.

parameter system was limited in how well it could capture all three regimes. The competing mechanisms of viscosity, inertial force, and surface tension appear to demand a system with two parameters. Two-dimensional lattice Boltzmann and lattice gas simulations seem to be carried out primarily with relatively small R_h, thus the $\alpha=2/3$ estimates are consistent with growth in the inertial regime [9,10,17]. The results from molecular dynamics are controversial. It has been pointed out [18] that the $\alpha=1/2$ growth obtained in [14] may be attributed to droplet coalescence. Velasco and Toxvaerd [15] observed $\alpha=1/2$ crossing over to $\alpha=2/3$ in their two-dimensional molecular dynamics simulations. A recent experimental study of near-critical two-dimensional phase separated polymer solutions obtained an early growth of $t^{1/3}$ followed by a $t^{2/3}$ at late stage [16].

Three-dimensional simulations were carried out on Eqs. (3) and (4) using a system with 256^3 lattice sites and show behavior analogous to that observed in two dimensions. As above, we set $\beta=1$. If $\hat{\eta}=1$ and $\hat{\lambda}=1$, $R_h \sim R_d \sim 1$ and are small compared to the domain size $R(t)$. One thus expects inertial growth with $\alpha=2/3$ at late times, and this is seen by the data represented by ($\square$) in Fig. 3. If $\hat{\eta}=\hat{\lambda}$ (with $R_d \sim 1$), the system should favor growth in the viscous regime for sufficiently large $\hat{\eta}$. The symbols ($\times$) and ($\diamond$) in Fig. 3 show growth for $\hat{\eta}=25$, $\hat{\lambda}=25$, and $\hat{\eta}=20$, $\hat{\lambda}=20$, respectively. As $\hat{\eta}$ increases, the growth becomes consistent with $\alpha=1$. The crossover between the viscous regime and the inertial regime can be simulated through decreasing R_h, while keeping R_d small (~ 1). The symbols ($+$) in Fig. 3 used $\hat{\eta}=12$, $\hat{\lambda}=12$ and show that a regime with a growth exponent of 1 gradually yields to a slower growth regime, a 2/3 type growth. Figure 3 (inset) shows that the behavior of the Reynolds number Re is consistent with the growth for appropriate parameters in the inertial and viscous regimes.

Finite size effects are more pronounced in three dimensions, so that the inertial regime is difficult to access as R_h increases. In Fig. 4 is plotted the scaling of the correlation functions $G(\xi)$ and $\xi^2 G(\xi)$ (inset) for the inertial regime in three dimensions. The quality of the collapse of the data in Fig. 4 for several times indicates that the $\alpha=2/3$ growth is in the scaling regime.

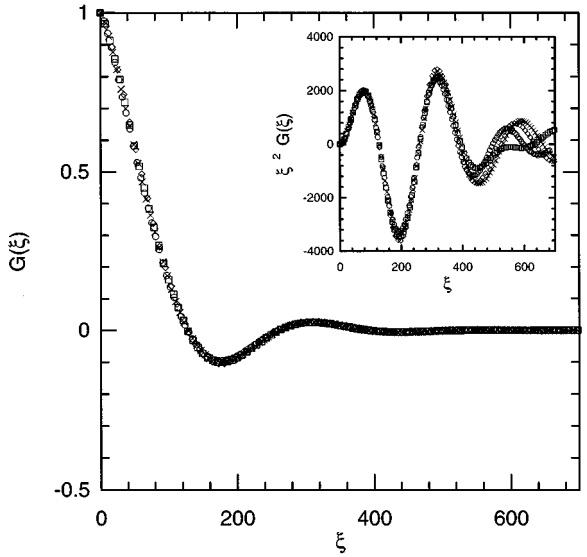

FIG. 4. The scaled and normalized correlation function $G(\xi)$ vs ξ for $\hat{\eta}=\hat{\lambda}=1$ and $\beta=1$ on 256^3 lattices, at $t=600$ ($\diamond$), 800 ($\square$), 1000 ($\times$), and 1200 ($\bigcirc$). The inset shows $\xi^2 G(\xi)$ vs ξ for the same times. Since $\langle k\rangle \sim 6$, the times scale well to ~ 40 lattice units.

Earlier work by Farrell and Valls [7] on the same model was carried out on an 81^3 lattice with $\hat{\eta}\sim 1$, $\hat{\lambda}\sim 1$, and $\hat{\sigma}=2$ so that $R_h\sim 1$. Their estimate of $\alpha\sim 1$ was based on an extrapolation of a time-dependent, effective exponent in terms of an inverse droplet size. Puri and Dunweg [12] used a cell dynamical system model and obtained $\alpha\sim 1$ on a model (with 80^3 lattices) without the convective term in the velocity equation and with $\hat{\eta}=1$, $\hat{\lambda}=2$, and $\hat{\sigma}=2$. Using their parameter values *with* the convective term on a 128^3 lattice, we find an early $\alpha\sim 1$ growth that crosses over to a slower $\alpha\sim 2/3$ growth at later times. Shinozaki and Oono [8] and Koga and Kawasaki [13] obtained $\alpha\sim 1$ at late times with their models (Model H), ignoring the inertial terms. It was noted in [8] that for larger values of viscosity there is a crossover from $\alpha\sim 1/3$ to $\alpha\sim 1$ growth. Such a crossover can occur because a larger viscosity increases R_d which then favors the diffusive growth for domain sizes $R(t)<R_d$. Lattice Boltzmann simulations provide linear growth estimates [9,10]. A recent lattice gas simulation in three dimensions finds evidence for a 2/3 growth [19]. The model we have used allows for compressibility [7]. However it has been shown that in the viscous regime α does not change with the incompressible condition [8,13]. To our knowledge, the $\alpha=2/3$ in the inertial regime has not been observed in an experiment.

In summary, we have used a single model system to probe the hydrodynamic regimes that a phase separating fluid can undergo. In particular, we have shown how domain growth can be favored to take place in these regimes by an appropriate choice of the crossover lengths R_d and R_h within a finite size simulation. Moreover, we have obtained values for the growth exponent α in these regimes in two and three dimensions that are in agreement with the predictions of scaling and dimensional arguments. Our work helps to explain the estimates of growth exponents α obtained in a number of previous studies.

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