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.

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 \( \alpha \)?

Scaling and dimensional analyses due to Siggia [3], Furukawa [4], San Miguel et al [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 [2,4,16,17]. 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 Letter we address these points.

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

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

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

where $\rho$ is the average mass density, $\Gamma$ is an order parameter diffusion coefficient, and $\eta$ is the shear viscosity. Here $\sigma = \eta(1 - 2/d) + \zeta$, where $\zeta$ is the bulk viscosity, and $d$ is the spatial dimension. The dimensionless constant, $\lambda$, couples the order parameter to the fluid velocity and is also the strength of the convective flow. The chemical potential, $\mu = \frac{\delta F}{\delta \psi}$, where $F$ is the free energy of the system at equilibrium given by $F[\psi, u] = \frac{1}{2} \int d^d r [\rho u^2 + \frac{1}{2}a\psi^4 - b\psi^2 + \beta K|\nabla \psi|^2]$. The strength of the interfacial energy is $\beta K$. 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 Equations (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 $\kappa$ 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 $\kappa$ is given by $\kappa = \frac{4}{3}(2\beta K)^{1/2}$ [4].

In the viscous regime, hydrodynamics becomes relevant. In particular, in the velocity equation (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, $\eta \nabla^2 u \sim \lambda \psi \nabla \mu$ so that $R(t) \sim \frac{\Delta \psi}{\eta} t$. This is the linear growth law predicted by Siggia [3]. The coefficient $\frac{\Delta \psi}{\eta}$ 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 $(\Gamma \kappa)^{1/3} t_d^{1/3} \sim \frac{\Delta \psi}{\eta} t_d$. Thus, $t_d \sim \left(\frac{\Gamma \kappa^2}{a2\beta K} \right)^{1/2}$ and $R_d \sim (\Gamma \kappa)^{1/2}$. 
In the inertial regime, inertial effects dominate over the viscous forces so that $\rho \frac{du}{dt} \sim \lambda \psi \nabla \mu$. This leads to $R(t) \sim \left(\frac{\lambda \kappa}{\rho}\right)^{\frac{1}{3}} t^{\frac{2}{3}}$, 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 $\frac{\eta}{t_h} \sim \left(\frac{\lambda \kappa}{\rho}\right)^{\frac{1}{3}} t_h$ and $R_h \sim \frac{\eta^2}{\lambda \rho \kappa}$. Similarly, the length, $R_i$, and time, $t_i$ for crossover from diffusion directly to inertial are given by $R_i \sim \left(\frac{\Gamma^2 \kappa}{\rho \lambda}\right)^{\frac{1}{3}}$ and $t_i \sim \frac{\Gamma}{\rho \lambda}$ 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 model, we vary $R_d$ and $R_h$ (relative to system size) by adjusting the parameters $\eta$, $\lambda$ and $\beta$. For convenience, the actual (dimensionless) numerical equations we solve are the following:

$$\partial_t \phi = \nabla^2 \left[ \phi^3 - \phi - \beta \nabla^2 \phi \right] - \hat{\lambda} \nabla \cdot [\phi \mathbf{v}] + \mu, \quad (3)$$

$$\partial_t v_i = \hat{\eta} \nabla^2 v_i + \hat{\sigma} \sum_k \nabla_i \nabla_k v_k - \hat{\lambda} \phi \nabla_i [\phi^3 - \phi - \beta \nabla^2 \phi] - \hat{\lambda} \sum_k [\nabla_k (v_i v_k) + v_k \nabla_i v_k] + w_i. \quad (4)$$

The rescaled order parameter and transport quantities are given in terms of those used in (1) and (2) by $\phi = (\frac{\phi}{\psi})^{\frac{1}{2}} \psi$, $\mathbf{v} = (\frac{\rho \eta}{\kappa \rho \eta})^{\frac{1}{2}} \mathbf{u}$, $\hat{\eta} = \frac{\eta}{\rho \lambda}$, $\hat{\sigma} = \frac{\sigma}{\rho \lambda}$, $\hat{\lambda} = \lambda (\frac{b}{\rho \kappa})^{\frac{1}{2}}$. Space and time are rescaled by $r \rightarrow r$, $t \rightarrow \Gamma K t$. The dimensionless crossover lengths are given by $R_d = (\frac{\phi}{\lambda})^{\frac{1}{2}}$, and $R_h = \frac{\phi^2}{\lambda \kappa}$, where we have set $\rho = 1$. In two dimensions, the surface tension, $\kappa = \frac{3}{4} (2\beta)^{\frac{1}{2}}$, so that by varying $\beta$, 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 $\Delta x$ used was 1.7 and the time step $\Delta t$ 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 $G(r,t) = \langle \phi(x,t) \phi(x+r,t) \rangle$, the Fourier transform of which is the structure factor, $S(k,t)$. The fields, $\mu$ 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 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 ($\bigcirc$) and ($+$) in Figure 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 behaviour of $R(t)$ as $R_h$ decreases. Corresponding to the parameters for domain growth, the insert to Figure 1 shows how $Re$ 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 $\eta \geq 11$, 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 $\xi^2 G(\xi)$ are shown in Figure 2, for $\hat{\eta} = 20, \hat{\lambda} = 1, \beta = 1$, where $\xi = r\langle k \rangle$ and $\langle k \rangle = \frac{\int k S(k,t) dk}{\int S(k,t) dk}$. 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].

Using this model in two dimensions, we previously [11] examined the behavior of $\alpha$ as a function of the coupling constant, $\hat{\lambda}(0 < \hat{\lambda} < 1)$, by fixing $\hat{\eta}, \beta$ and $\rho$. For this one parameter system, $R_h \sim \frac{1}{2\hat{\lambda}}$ and $R_d \sim \frac{1}{\hat{\lambda}^{3/2}}$. 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-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 \cite{14}. The results from molecular dynamics are controversial. It has been pointed out \cite{17} that the $\alpha = 1/2$ growth obtained in \cite{14} may be attributed to droplet coalescence. Velasco and Toxvaerd \cite{15} observed $\alpha = 1/2$ crossing over to $\alpha = 2/3$ in their two-dimensional molecular dynamics simulations.

Three-dimensional simulations were carried out on Equations (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 (□) 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 (×) and (◆) 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 ($\sim 1$). 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 (insert) shows that the behaviour of the Reynolds number, $Re$, is consistent with 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 $\xi^2G(\xi)$ (insert) 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.

Earlier work by Farrell and Valls \cite{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 inverse droplet size. Puri and Dunweg \cite{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 $\eta = 1$, $\lambda = 2$, and $\sigma = 2$. 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 \cite{Shinozaki1991} and Koga and Kawasaki \cite{Koga1991} obtained $\alpha \sim 1$ at late times with their models (Model H), ignoring the inertial terms. It was noted in \cite{Shinozaki1991} 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 also provide linear growth estimates \cite{Levine1994}. The model we have used allows for slight compressibility. However, it has been shown that in the viscous regime $\alpha$ does not change with the incompressible condition \cite{Shinozaki1991, Koga1991}. To our knowledge, the $\alpha = 2/3$ in the inertial regime has not been observed in experiment or three-dimensional simulations.

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 $\alpha$ 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, $\alpha$, obtained in a number of previous studies.

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Figure Captions

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 insert 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 $dR/dt$. The data are consistent with $Re \sim t^{1/3}$ in the inertial regime and $Re \sim \text{constant}$ in the viscous regime. The straight line has slope $1/3$. The symbols represent $\hat{\eta} = 20, \hat{\lambda} = 1, R_h \sim 120(\times), \hat{\eta} = 11, \hat{\lambda} = 1, R_h \sim 30(\odot), \hat{\eta} = 5, \hat{\lambda} = 1, R_h \sim 7(+) \text{ and } \hat{\eta} = 2, \hat{\lambda} = 1, R_h \sim 1(\square)$. The surface tension controlling parameter $\beta = 1$ for all cases.

FIG. 2. The scaled and normalised correlation function $G(\xi)$ vs $\xi$, where $\xi = r\langle k \rangle$ and the first moment $\langle k \rangle = \int k S(k,t) dk / \int S(k,t) dk$, for $\hat{\eta} = 20, \hat{\lambda} = 1$, and $\beta = 1$ on 1024 $\times$ 1024 lattices, at $t = 2, 500 (\odot), 3000 (\times), 4000 (\circ), 5,000 (+) \text{ and } 6,000 (\square)$. The insert shows $\xi^2 G(\xi)$ versus $\xi$ for the same times and since $\langle k \rangle \sim 25$, scaling is good for $\sim 80$ 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 $\alpha$ from inertial ($t^{2/3}$) to viscous ($t$) regime. The errors are of the size of the symbols. The insert shows that the behaviour 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 $\hat{\eta} = 25, \hat{\lambda} = 25, (\circ), \hat{\eta} = 20, \hat{\lambda} = 20, (\odot), \hat{\eta} = 8, \hat{\lambda} = 8, (+), \hat{\eta} = 1, \hat{\lambda} = 1, (\square)$. The surface tension controlling parameter $\beta = 1$ for all cases.

FIG. 4. The scaled and normalised correlation function $G(\xi)$ vs $\xi$ for $\hat{\eta} = \hat{\lambda} = 1$ and $\beta = 1$ on 256$^3$ lattices, at $t = 600 (\circ), 800 (\square), 1,000 (\times), \text{ and } 1,200 (\odot)$. The insert shows $\xi^2 G(\xi)$ vs $\xi$ for the same times. Since $\langle k \rangle \sim 6$, the times scale well to $\sim 40$ lattice units.