RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 1993-I

Hydrodynamic spinodal decomposition: Growth kinetics and scaling functions

F. J. Alexander, S. Chen, and D. W. Grunau
Center for Nonlinear Studies and Theoretical Division and Earth and Environmental Sciences,
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 6 January 1993; revised manuscript received 5 April 1993)

We examine the effects of hydrodynamics on the late-stage kinetics in spinodal decomposition. From computer simulations of a lattice Boltzmann scheme we observe, for critical quenches, that single-phase domains grow asymptotically like t^{α}, with $\alpha \approx 0.66$ in two dimensions and $\alpha \approx 1.0$ in three dimensions, both in excellent agreement with theoretical predictions.

The understanding of phase-segregation kinetics has been enhanced over the last two decades by the development of dynamic renormalization-group methods, an increase in computer resources, and a host of experimental results with which to compare.[1,2] Despite this progress, there remain many open questions, especially regarding the growth of single-phase domains and the scaling properties of the correlation or structure functions. Since phase segregation, either spinodal decomposition or nucleation, is a highly nonlinear process, theories rely mostly on approximation schemes, and exact results have been obtained only in certain limiting cases.[3] Simulations designed to address these issues typically require extensive computational effort and have not, in our opinion, provided conclusive answers to many of the most fundamental questions.

Phase segregating systems fall into two classes: those with hydrodynamic interactions (fluids) and those without (binary alloys, glasses). The latter class, has received far more attention both by computer simulations and by theory.[1,2] Only recently have there been attempts to carry out computer simulations of phase segregating systems with hydrodynamic interactions. These include molecular-dynamics (MD) simulations,[4] direct numerical simulation of time-dependent Ginzburg-Landau (TDGL) equations,[5] cell-dynamical systems (CDS) (Refs. 6 and 7), and lattice gas (LG) (Refs. 8 and 9) and lattice Boltzmann (LB) models.[10]

While MD simulations accurately represent the dynamics of real fluids, they are computationally demanding and at present may not be able to access the late stage (scaling) regime of spinodal decomposition. The TDGL approach eliminates the exact Newtonian particle dynamics in favor of a stochastic evolution governed by a coarse-grained phenomenological free energy functional. One then solves the concomitant system of Langevin equations which couple order parameter fluctuations to hydrodynamic currents. This approach requires extensive numerical computation and sacrifices both the Navier-Stokes behavior of the fluid and the interface phase dynamics. CDS methods further abstract the phase segregation process by replacing the Langevin equations with a much less numerically intensive dynamical map for the order parameter. The hydrodynamics they incorporate, however, have either been approximated by an Oseen tensor or by a coupling of the velocity field to pressure and order parameter fluctuations.

LG and LB models, on the other hand, provide alternative computational environments with which to study hydrodynamic phase segregation phenomena without the introduction of *ad hoc* relations between the order parameter fluctuations and the fluid dynamics. What makes these schemes so appealing is the natural way in which they can simulate the fluid properties, the phase segregation and the interface dynamics simultaneously. One drawback in the model presented here is that fluctuations only appear in the initial conditions. To make LB models more realistic tools with which to analyze phase transition kinetics probably involves the introduction of some type of thermal noise.

Several groups[8–10] have used LG and LB models to simulate phase segregation phenomena, but their work focused primarily on the *qualitative* features and did not address the details of dynamical scaling of the structure function.[11] In this paper we focus on domain growth kinetics and scaling properties of the phase segregation process. We present the results of large-scale numerical simulations of one such immiscible LB model and make quantitative comparisons with theory.

The LB method is a discrete, in space and time, microscopic, kinetic equation description for the evolution of the particle distribution function of a fluid.[12] The scheme described here is a modified version of the immiscible fluid model introduced by Gunstensen *et al.*[10] In this model the fluid has two components represented, for example, by the colors red and blue. The microscopic dynamics of the particle distribution function consists of four steps: (1) free streaming, (2) collision, (3) interface perturbation, and (4) recoloring.

In free streaming the fluid (both red and blue components) moves to neighboring sites along the links of the underlying lattice. During the collision step these densities then relax toward a local equilibrium state. In LB schemes one is free to specify the local equilibrium state, and the particular choice for this state is one which leads to the Navier-Stokes equations in the long-wavelength and low-frequency limit.

Let $f_i(\mathbf{x},t)$, $f_i^r(\mathbf{x},t)$, and $f_i^b(\mathbf{x},t)$ be the distribution functions for the total fluid, red (r) fluid and blue (b) fluid, respectively, at site $\mathbf{x}$ and time t moving along the link in the i direction. Here $f_i(\mathbf{x},t)=f_i^r(\mathbf{x},t)+f_i^b(\mathbf{x},t)$, where $i=0,1,\ldots,N$, and where N is the number of velocity states at each site. The $i=0$ state represents the portion of the fluid at rest. The kinetic or "lattice Boltzmann" equaton for f_i is written

$$f_i(\mathbf{x}+\mathbf{e}_i,t+1)-f_i(\mathbf{x},t)=\Omega_i^c(\mathbf{x},t)+\Omega_i^p(\mathbf{x},t)\ , \tag{1}$$

where Ω_i^c is the term representing the rate of change of f_i due to collisions, and Ω_i^p is the term representing the color perturbation. The vectors $\mathbf{e}_i$ are the velocity vectors along the kinks of the lattice.

In this paper we use a triangular lattice ($N=6$) for two-dimensional simulations with $\mathbf{e}_i=\{\cos[2\pi(i-1)/6], \sin[2\pi(i-1)/6]\}$, and a body-centered-cubic lattice ($N=14$) in three dimensions with $\mathbf{e}_i\in(\pm1,0,0)$, $(0,\pm1,0)$, $(0,0,\pm1)$, and $(\pm1,\pm1,\pm1)$. For computational efficiency, we have used the single time relaxation model[13] with the linear collision operator

$$\Omega_i^c=-(1/\tau)(f_i-f_i^{(\mathrm{eq})})\ , \tag{2}$$

where τ is the characteristic relaxation time, and $f_i^{(\mathrm{eq})}$ is the local equilibrium distribution given in two dimensions by

$$f_0^{(\mathrm{eq})}=\rho/7-\rho\mathbf{u}^2\ , \tag{3}$$

and

$$f_i^{(\mathrm{eq})}=\frac{\rho}{7}+\frac{\rho}{3}\mathbf{e}_i\cdot\mathbf{u}+\frac{2\rho}{3}(\mathbf{e}_i\cdot\mathbf{u})^2-\frac{\rho}{6}\mathbf{u}^2\ , \tag{4}$$

and in three dimensions by

$$f_0^{(\mathrm{eq})}=\rho/8-(\rho/3)\mathbf{u}^2\ , \tag{5}$$

$$f_i^{(\mathrm{eq})}=\frac{\rho}{8}+\frac{\rho}{3}(\mathbf{e}_i\cdot\mathbf{u})+\frac{\rho}{2}(\mathbf{e}_i\cdot\mathbf{u})^2-\frac{\rho}{6}\mathbf{u}^2\ , \tag{6}$$

for $\mathbf{e}_i$ along the lattice axes, and

$$f_i^{(\mathrm{eq})}=\frac{\rho}{64}+\frac{\rho}{24}(\mathbf{e}_i\cdot\mathbf{u})+\frac{\rho}{16}(\mathbf{e}_i\cdot\mathbf{u})^2-\frac{\rho}{48}\mathbf{u}^2 \tag{7}$$

for $\mathbf{e}_i$ along the links to the corners of the cube. In the above equations $\rho(\mathbf{x},t)=\sum_i f_i(\mathbf{x},t)$ and $\rho\mathbf{u}(\mathbf{x},t)=\sum_i f_i(\mathbf{x},t)\mathbf{e}_i$ are the local density and momentum, respectively.

The detailed forms of the coefficients in Eqs. (3)–(7) are determined by the conservation of mass and momentum, the constraints of Galilean invariance, and a velocity-independent, isotropic pressure tensor. It can be shown[14] that the macroscopics of (1)–(4) and (1), (2), and (5)–(7) correspond to the incompressible Navier-Stokes equation in two and three dimensions, respectively:

$$\partial_t\mathbf{u}+(\mathbf{u}\cdot\nabla)\mathbf{u}=(-1/\rho)\nabla P+\nu\nabla^2\mathbf{u}$$

$$\nabla\cdot\mathbf{u}=0\ ,$$

where P is the pressure, and ν is the kinematic viscosity. In two dimensions $\nu=(2\tau-1)/8$, and in three dimensions $\nu=(2\tau-1)/6$.

Defining the local order parameter as $\psi(\mathbf{x},t)=\sum_{i=0}^{N}[f_i^r(\mathbf{x},t)-f_i^b(\mathbf{x},t)]$, and the local color gradient $\mathbf{G}(\mathbf{x})$ by

$$\mathbf{G}(\mathbf{x})=\sum_{i=1}^{N}\mathbf{e}_i\{\psi(\mathbf{x}+\mathbf{e}_i)\}\ , \tag{8}$$

we add the surface-tension inducing perturbation

$$\Omega_i^p=A|\mathbf{G}|\cos2(\theta_i-\theta_G) \tag{9}$$

to facilitate segregration and stabilize interfaces. Here θ_i is the angle of lattice direction i, and $\theta_G=\arctan(G_y/G_x)$ is the angle of the local color gradient. The constant A sets the surface tension σ through $\sigma\sim A\tau\rho$. Note that $\mathbf{G}$ is perpendicular to red-blue interfaces and its magnitude large there, while in a homogeneous (color) region it approaches zero. In the recoloring step we then maximize the color flux $\mathbf{H}=\sum_{i=1}^{N}(f_i^r-f_i^b)\mathbf{e}_i$ in the direction of the color gradient $\mathbf{G}$ by maximizing $\mathbf{H}\cdot\mathbf{G}$. Recoloring conserves the individual color components and hence the total density of the fluid. It has been shown[10] that Laplace's law holds for this model.

For our simulations we perform critical quenches with $\sum_x\psi(\mathbf{x},t)=0$. The largest systems we simulated were $(2048)^2$ in two dimensions and $(128)^3$ in three dimensions. Although we have investigated the domain growth and scaling properties for a variety of lattice sizes and parameters, we report on the domain growth and dynamical scaling properties for only one set of parameters in both two and three dimensions. The results obtained with smaller lattices and different parameters (surface tension and initial fluctuations) are consistent with the data presented here.

We initialize the lattice (in both two and three dimensions) with $\langle\psi(\mathbf{x})\rangle=0$ and $\langle\mathbf{u}\rangle=0$ with small local fluctuations, where the angle brackets $\langle\ \rangle$ signify an average over the lattice. The system then evolves according to the dynamics outlined above. In two dimensions the surface tension inducing parameter $A=0.01$, and the average fluid density per site is $\rho=2.1$, and in three dimensions $A=0.001$ and $\rho=2.4$. As the system evolves, single-color domains form and grow while the total fluid undergoes a Navier-Stokes evolution. In Fig. 1 we show a "snapshot" [for a system of size $(256)^2$] of a two-dimensional system at time $t=1000$.

One convenient way to characterize the growth kinet-

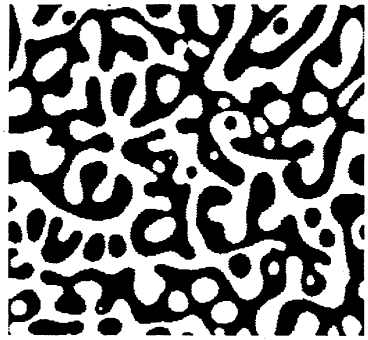

FIG. 1. Typical configuration for the two-dimensional model at time $t=1000$. The system size is $(256)^2$, and the other parameters are as in the text. The black region represents sites with positive order parameter.

ics during the segregation process is through the order parameter correlation function $G(\mathbf{r},t)=\langle\psi(\mathbf{r})\psi(0)\rangle-\langle\psi\rangle^2$ averaged over shells of radius r. One can then define the domain size $R(t)$ as the first zero of the function $G(r,t)$. The Fourier transform of G is then the structure factor $S(k,t)$. As time evolves the structure factor becomes more sharply peaked, and its maximum moves to smaller values of the wave number k. In a wide variety of phase segregating systems $S(k,t)$ has been observed to follow the dynamic scaling relation at late times:[1]

$$S(k,t)\approx R^d(t)F(x)\ , \tag{10}$$

where $x=kR(t)$, d is the spatial dimension, and $F(x)$ is the structure factor.

In Fig. 2(a) we plot $R(t)$ for the two-dimensional model. The data indicate that $R(t)\sim t^{0.66}$. This exponent is in excellent agreement with the generally accepted theoretical prediction of $t^{2/3}$ (Ref. 2) and the numerical simulations of Ferrel and Valls,[5] which find $R(t)\sim t^{\alpha}$, where $\alpha=0.65$ and $\alpha\approx0.69$ for systems with and without thermal modes, respectively.

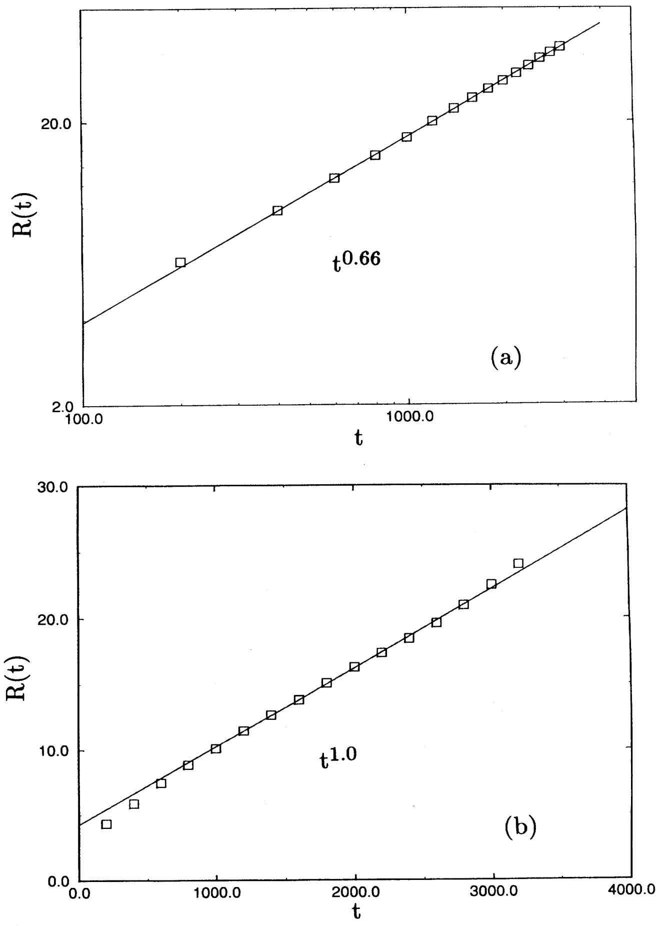

FIG. 2. Time dependence of average domain size for (a) two-dimensional and (b) three-dimensional systems. Both two- and three-dimensional data are averaged over two independent runs.

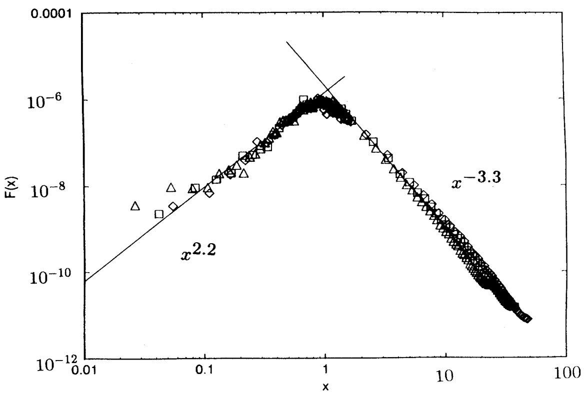

FIG. 3. Scaled structure function $F(x)$ for two dimensions at various times: $t=1000$ (△); $t=2000$ (□), and $t=3000$ (◇). The data are averaged over two independent runs.

In Fig. 3 we show the scaled structure factor $F(x)$ for our two-dimensional simulations. For $x>2$ we find that $F(x)\sim x^{-3.3}$, in reasonable agreement with Porod's law which predicts that $F(x)\sim x^{-(d+1)}$ in this region. However, for $x<1$, we observe that $F(x)\sim x^{2.2}$. This is in sharp contrast with the theoretical arguments of Furukawa[2] and Yeung[15] which predicts that $F(x)\sim x^4$. Our findings for $x\ll1$ appear to corroborate other recent numerical simulations of hydrodynamic spinodal decomposition in two dimensions. Shinozaki and Oono in their CDS model observe that $F(x)\sim x^2$. They conjecture that this might be a result of finite-size effects coupled to fluctuations of domain walls due to long-range hydrodynamic interactions.

In Fig. 2(b) we plot $R(t)$ for our three-dimensional model. Here we find that the domain growth is approximately linear in time with $R(t)\sim t^{1.0}$. This is in excellent agreement with the theoretical predictions of Furukawa[2] and Siggia[16] and with the (TDGL) numerical simulations of Ferrel and Valls and the CDS simulations of Koga and Kawasaki. It disagrees, however, with recent MD simulations of Ma *et al.*,[4] who observe a domain growth $R(t)\sim t^{0.55\pm0.05}$. This latter exponent may not reflect the growth in the asymptotic time regime.

In Fig. 4 we plot $F(x)$ for the three-dimensional model.

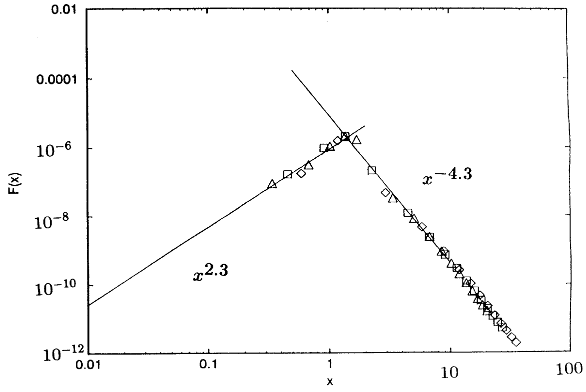

FIG. 4. Scaled structure function $F(x)$ for three dimensions at various times: $t=1200$ (△); $t=2400$ (□), and $t=3200$ (◇). The data are averaged over two independent runs.

As in two dimensions we find good agreement with Porod's law with $F(x) \sim x^{-4.3}$ for $x > 3$. Again, though, we find marked disagreement with the small x predictions of $F(x)$ which call for $F(x) \sim x^4$. In particular we find that $F(x) \sim x^{2.3}$. This result is consistent with recent light scattering data from spinodal decomposition of isobutyric acid and water[17] which also indicates a reduced exponent (≈ 2), but differs from the results of Bates and Wiltzius.[18]

We summarize by pointing out that the results of our simulations tend to be consistent with existing theories of domain growth in both two and three dimensions. There is also good agreement with Porod's law in both of these cases. However, we find a marked discrepancy with the theoretical predictions of Yeung[15] and Furukawa[2] for the small x behavior of the scaled structure factor. Moreover, there seems to be a consistent deviation from these theories among some recent numerical[6] and some experimental work.[17] In light of these results, we believe that the question of the small x behavior of the scaled structure factor is still open and that it is necessary to develop a more complete theory of dynamical scaling which includes hydrodynamic interactions.

The current model simulates fluids for deep (near zero temperature) quenches. As a result, this precludes an analysis of binary fluids near their critical points. To study critical dynamics of binary fluids requires some notion of temperature. An extension of the model described here might include a stochastic term which mimics the effects of thermal noise (Landau-Lifshitz fluctuating hydrodynamics)[19] or a kinetic temperature as in Ref. 20 with which one can control the segregation process by a local temperature. Without such a noise term it is unlikely that this model can simulate off-critical quenches.

The model in this paper is ideally suited for the simulation of hydrodynamic phase segregation in high Reynolds number flows.[14] Moreover, the LB scheme can easily simulate spinodal decomposition in systems with complicated boundaries, stirring, and the effects of wettability.

We thank K. L. Diemer, G. D. Doolen, K. G. Eggert, G. L. Eyink, S. Habib, S. A. Janowsky, J. L. Lebowitz, R. Mainieri, and J. D. Sterling for useful discussions. Eugene Loh was involved in the original CM-2 code development. This work was supported by the U.S. Department of Energy at Los Alamos National Laboratory. Numerical simulations were carried out using the computational resources at the Advanced Computing Laboratory at the Los Alamos National Laboratory.

---

[1] See the following and the extensive list of references contained therein. J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983); G. F. Mazenko, Phys. Rev. B **43**, 8204 (1991).

[2] H. Furukawa, Adv. Phys. **34**, 703 (1985).

[3] A. Coniglio and M. Zannetti, Europhys. Lett. **10**, 575 (1989); Phys. Rev. B **42**, 6873 (1990); A. J. Bray, Phys. Rev. Lett. **62**, 2841 (1989); A. J. Bray and K. Humayun, *ibid.* **68**, 1559 (1992).

[4] W. J. Ma, A. Maritan, J. R. Banavar, and J. Koplik, Phys. Rev. A **45**, R5347 (1992).

[5] J. E. Farrell and O. T. Valls, Phys. Rev. B **40**, 7027 (1989); **42**, 2353 (1990); **43**, 630 (1991); O. T. Valls and J. E. Farrell (unpublished).

[6] A. Shinozaki and Y. Oono, Phys. Rev. A **45**, R2161 (1992).

[7] T. Koga and K. Kawasaki, Phys. Rev. A **44**, R817 (1991).

[8] D. H. Rothman and J. M. Keller, J. Stat. Phys. **52**, 1119 (1988).

[9] C. Appert and S. Zaleski, Phys. Rev. Lett. **64**, 1 (1990); S. Chen, G. D. Doolen, K. Eggert, D. Grunau, and E. Y. Loh, Phys. Rev. A **43**, 245 (1991).

[10] A. Gunstensen, D. H. Rothman, S. Zaleski, and G. Zannetti, Phys. Rev. A **43**, 4320 (1991).

[11] Recently H. J. Bussemaker and M. H. Ernst (unpublished) have reported results for domain growth in a two-dimensional LG. Their results are consistent with those presented here.

[12] G. McNamara and G. Zanetti, Phys. Rev. Lett. **61**, 2332 (1988); F. Higuera, S. Succi, and R. Benzi, Europhys. Lett. **9**, 345 (1989).

[13] P. L. Bhatnagar, E. P. Gross, and M. Krook, Phys. Rev. **94**, 511 (1954); S. Chen, H. Chen, D. O. Martinez, and W. H. Matthaeus, Phys. Rev. Lett. **67**, 3776 (1991); H. Chen, S. Chen, and W. H. Matthaeus, Phys. Rev. A **48**, R5339 (1992); Y. H. Qian, D. d'Humieres, and P. Lallemand, Europhys. Lett. **17**, 479 (1992).

[14] S. Chen, Z. Wang, X. Shan, and G. D. Doolen, J. Stat. Phys. **68**, 379 (1992).

[15] C. Yeung, Phys. Rev. Lett. **61**, 1135 (1988).

[16] E. D. Siggia, Phys. Rev. A **20**, 595 (1979).

[17] K. Kubota, N. Kuwahara, H. Eda, and M. Sakazume, Phys. Rev. A **45**, R3377 (1992).

[18] F. S. Bates and P. Wiltzius, J. Chem. Phys. **91**, 3258 (1989).

[19] A. J. C. Ladd, Phys. Rev. Lett. **70**, 1339 (1993).

[20] F. J. Alexander, S. Chen, and J. D. Sterling, Phys. Rev. E **47**, R2249 (1993).