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Composition waves in confined geometries

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The dynamics of spinodal decomposition in confined geometries is studied using molecular-dynamics simulations and the numerical integration of the exact equation of motion of soft Ising spins undergoing Kawasaki dynamics. We argue that, as long as there is a conservation law for the two species and a planar heterogenity is present in the initial conditions, composition waves with a wave vector normal to the heterogeneity should be observed. Our results indicate that hydrodynamic modes play a role in determining the dynamics.

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Recently Jones *et al.* [1] have studied the spinodal decomposition [2] of a polymer-melt-blend film with a free planar surface. They found that the presence of the surface resulted in composition waves (regions rich in one phase separated by regions rich in the other) with a wave vector normal to the surface. On the theoretical side, Ball and Essery (BE) [3] and Puri and Binder (PB) [4] have numerically solved the time-independent Ginzburg-Landau equation and have obtained surface-directed spinodal decomposition. The equations of BE involve two (unequal) temperatures, one of which fixes the coefficients of the Ginzburg-Landau free energy and thence the shape of the potential, whereas the other controls the strength of the noise. PB start with the continuum equations of Binder and Frisch [5], which are designed to produce the correct mean-field transition temperature, carry out some simplifications, and discretize the resulting equations. The BE and PB approaches start with continuum equations valid near the critical temperature. This is a matter of some concern since spinodal decomposition is governed by a $T=0$ fixed point [6]. The PB mean-field approach does not incorporate noise; the noise term of BE does not ensure the proper approach to equilibrium, nor do their boundary conditions hold in average—a requirement recently stressed by Diehl and Janssen [5].

In this Rapid Communication, we summarize the results of extensive studies of the effect of a surface on the spinodal decomposition process following a critical quench using several complementary techniques. Our focus is on the phase separation in a direction normal to the surface. We have carried out molecular-dynamics (MD) simulations of the phase separation of two immiscible Lennard-Jones fluids in the presence of molecular walls. These simulations incorporate hydrodynamic effects and the wetting properties of the walls can be controlled. Second, we carryout numerical integration of the equations of motion for an Ising spin system on a discrete lattice employing Kawasaki spin-exchange dynamics. These *ab initio* equations for a continuum field on a discrete lattice are exact at all temperatures, they incorporate the noise correctly, and they treat the boundary effects properly. They reduce to a mean-field approach on turning off the noise. Both cases yield composition waves—however, the time dependence of the wave vector of the Ising system (that does not include hydrodynamic effects) is different from that found in the MD simulations and experiment, which are in accord with each other, pointing to the importance of hydrodynamic modes even in confined geometries. We show analytically (both within a linearized approximation and taking into account the nonlinearities approximately within a Berlin-Kac [7] approach), and have confirmed numerically, that composition waves are produced even in the absence of a boundary as long as there is a planar inhomogeneity in the initial conditions and the conservation of the two species is maintained.

Three-dimensional systems of Lennard-Jones (LJ) molecules having 1372 and 2744 fluid molecules were studied. The first was a cube of edge 11.8σ (σ is the LJ length scale), while the second had one of the sides, parallel to the x axis, longer by a factor of 2. Two molecular walls made up of 648 fixed molecules each on a fcc lattice with the (100) surface exposed to the fluid were constructed normal to the x direction. Periodic boundary conditions were applied in the two other directions. The simulations were carried out at constant volume with a reduced fluid density of 0.8. A fifth-order predictor-corrector scheme with an integration time of 0.0025τ was employed, where $\tau=(m\sigma^2/\epsilon)^{1/2}$, m is the mass of the fluid molecule, and ϵ is the energy parameter of the fluid-fluid interaction. The systems were equilibrated prior to the quench at $T^*=1.4$. After preparation, one-half of the molecules were selected randomly and labeled A, and the other half B, and the attraction between A and B was turned off. The system was then evolved *isothermally* at $T^*=1.4$ (the consolute temperature of the binary fluid is approximately 8.0) by rescaling velocities every time step. Note that this procedure is simpler than a quench corresponding to a system cooled from the outside [3]—the complications of heat flow and temperature inhomogeneities are avoided.

It is well known that fluids undergo layering near a solid surface with molecular structure. The dynamics of layering does not play a role in our simulations, since the layers are well formed prior to the quench. Qualitatively similar results were obtained in the two cases that we considered: in both, the wall on the right had a purely repulsive interaction with both fluids and thus no preference for either fluid. In the first case the left wall was similar to the right wall, whereas in the second it had a regular LJ interaction with fluid A and a purely repulsive interaction with fluid B. The deep quench employed in MD leads to the phase separation being primarily driven by the immiscibility of the two fluids rather than the preference of the wall for one fluid over the other. Two consequences of this are the relative insensitivity of the results to the exact nature of the walls and the weak spatial decay of the amplitude of the composition wave (Fig. 1) in contrast to the experimental observations [1].

The temporal decay of the wave vector (normal to the surface), obtained as an average with weight $S(k,t)$, of the composition waves is shown in Fig. 2 for the two kinds of walls, averaged over 20 systems each for the larger system (similar results were obtained for the smaller system). The time dependencies of three length scales

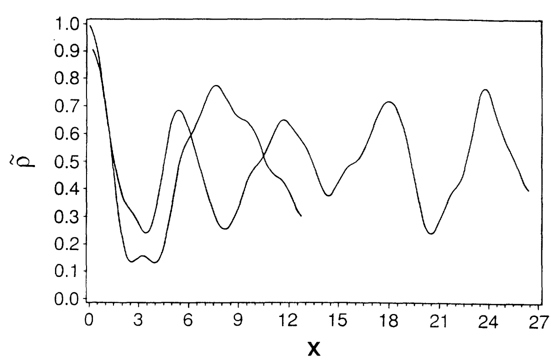

FIG. 1. Typical density profiles for two different sizes in the MD simulations. The wall on the left preferred fluid A and the other wall was repulsive to both fluids. Oscillations associated with layering have been removed using Fourier transform techniques. $\tilde{\rho}=\rho_A/(\rho_A+\rho_B)$. In the smaller system, the final state is metastable—no further evolution takes place. Note the resemblance to the experimental data in Ref. [1].

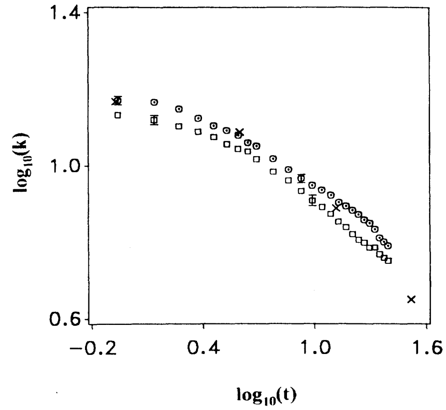

FIG. 2. The wave vector of the composition waves as a function of time. The squares denote a system having one wall preferring fluid A and the other wall repulsive to both fluids, whereas the circles correspond to both walls being repulsive. The data sets are an average over 20 runs each. The error bars correspond to variations arising from differing initial conditions. The ×'s denote the results from the experiment (Ref. [1]). The data were moved by arbitrary amounts in both the x and y directions to obtain the best fit on the log-log plot.

obtained from the first three moments of the structure factor $S(k,t)$ are virtually the same, showing that there is just *one* length scale characterizing the composition waves. While there is no clear algebraic behavior, the temporal dependence is in accord with the experimental data. Unlike bulk spinodal decomposition, the phenomenon of composition waves is essentially one involving boundaries. Our calculations have been carried out until the wavelength of the composition wave becomes comparable to the system size. At this state, the system remains stuck in a metastable state and little further evolution takes place.

We now turn to the spin system. We briefly review the derivation of the equations of motion. These are obtained for the Ising reduced Hamiltonian

$$\beta H=-\tfrac{1}{2}\sum_{x,y} K_{xy}S_xS_y-\sum_x h_xS_x\ , \tag{1}$$

where $K_{xy}=K$ when x,y are nearest neighbors and $S_x=\pm 1$, by making a Hubbard-Stratonovich transformation and writing the partition function

$$Z=\prod_x \int_{-\infty}^{\infty} dm_x e^{-F\{m\}}\ ,$$

with the effective Boltzmann weight given by [8]

$$F\{m\}=\tfrac{1}{2}\sum_{x,y} m_xK_{xy}m_y-\sum_x V\left[\sum_y K_{xy}m_y+h_x\right]\ , \tag{2}$$

with $V(\phi)=\ln\cosh\phi$. Note that the discrete lattice is maintained while the discrete spin variable S_x has been replaced by m_x that takes on values between $-\infty$ and $+\infty$. Following Chandrasekhar [9], we derive a Langevin equation for the dynamics of m:

$$\dot{m}_x=f_x\{m\}+\sum_{y,\alpha} g_{xy}^{\alpha}\zeta_y^{\alpha}(t)\ , \tag{3}$$

where we impose the conservation law that $\sum_x \dot{m}_x = 0$ by requiring that

$$\sum_x f_x = \sum_{x,y,\alpha} g^{\alpha}_{xy} \zeta^{\alpha}_y(t) = 0 \ , \tag{4}$$

where $\zeta^{\alpha}_y(t)$ is a white noise (with a Gaussian probability distribution), satisfying $\langle \zeta^{\alpha}_x(t)\zeta^{\beta}_y(t')\rangle = 2\delta_{\alpha\beta}\delta_{xy}\delta(t-t')$. $\alpha = 1,2,\ldots,d$, where d is the dimensionality. In order to obtain the correct equilibrium distribution with the weight given by (2), we choose

$$f_x\{m\} = -\sum_y \sum_{z,\alpha} g^{\alpha}_{xz} g^{\alpha}_{yz} \frac{\partial F\{m\}}{\partial m_y} \tag{5}$$

and

$$g^{\alpha}_{xy} = \delta_{y,x+\hat{\alpha}} - \delta^{(\alpha)}_{y,x} \ , \tag{6}$$

where $\hat{\alpha}$ is a unit vector in the αth direction, $\delta^{(\alpha)}_{x,y} = 1$ if $x = y$, and $x - \hat{\alpha}$ does not belong to the wall and zero otherwise. With this choice Eq. (4) is satisfied. In the naive continuum limit, Eq. (3) with the choice (5) and (6) reduces to the standard model [2] B in the bulk for T near T_c. The key advantage of our approach is that it is now straightforward to incorporate the boundary conditions because of the discreteness of the lattice. Furthermore, turning off the noise in (3) leads to a mean-field approach. (Unlike PB, our equations are *not* restricted to the mean-field limit.) In this limit, we recover the PB boundary conditions on taking the naive continuum limit [4,5]. The continuous variables m allow for more efficient averaging than the discrete Ising variables S. Note that we have only one temperature, the one entering in Eq. (1). We have numerically verified that the exact T_c of model (3) with f_x given by (5) is the same as for model (1).

The two fluid phases are represented by the up and down magnetization of the Ising model. The preferential attraction of the wall for one fluid is readily incorporated by choosing a nonzero fixed magnetization on the wall. We have integrated the equations of motion in two dimensions, with and without noise and the boundary condition $m(-L/2) = 1$, $m(L/2) = 0$; the walls are at $\pm l/2$. Composition waves are produced in both cases. The time dependence of the wave vector is shown in Fig. 3. We find that the noise term is crucial in preventing the system from getting stuck in a metastable state at early times. In contrast to the MD results, the behavior of the Ising case with noise leads to an exponent increasing with time reaching a value $\sim\frac{1}{4}$. Analogous runs with periodic boundary conditions lead to the expected exponent value of $\frac{1}{3}$, suggesting that the reduced value of $\sim\frac{1}{4}$ is caused by the presence of the walls. As in the MD simulations, the time scale of the runs was long enough to reach a metastable state in which the wavelength of the composition wave was comparable to the system size. Runs at different quench depths are similar to each other at late times.

Our results demonstrate the generality of occurrence of composition waves as long as a wall is present and a conservation law is operational. Indeed, we will now argue that such waves should be seen in even more general circumstances—when the wall is replaced by a planar heterogeneity in the initial condition. Our argument is based on taking the continuum limit of the equations of motion and neglecting higher-order terms in the magnetization and its spatial derivatives. In this limit, valid near T_c, the Glauber (G) and Kawasaki (K) -type dynamics [2] in suitably chosen units are given by

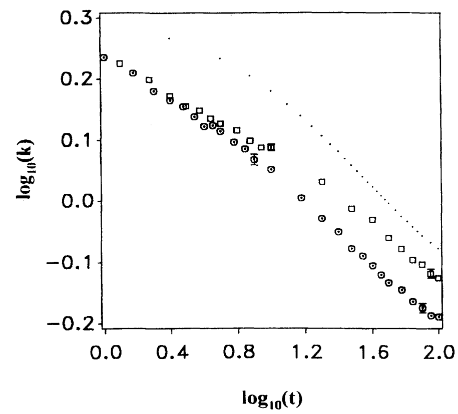

FIG. 3. Results for the Kawasaki spin dynamics: the time dependence of the wave vectors of the composition waves for the Ising spin systems of size 32×8 with noise [quenched to a coupling of 0.48 and 0.60 (squares and circles) averaged over 128 and 64 runs, respectively] and in a mean-field approximation [quenched to a coupling of $\frac{1}{8}$ (dots)—the critical coupling in mean field is equal to $\frac{1}{9}$—averaged over 32 initial conditions].

$$\dot{m}_G \simeq \nabla^2 m_G - a m_G \ , \tag{7a}$$

$$\dot{m}_K \simeq \nabla^2(a m_K - \nabla^2 m_K) \ , \tag{7b}$$

with $a \propto T - T_c$. The neglected cubic terms in Eqs. (7a) and (7b) have a coefficient equal to 1 in the chosen units. We choose the initial condition $m(x,t,=0) = m_0 \epsilon(x)$, where $\epsilon(x) = -1$ for $x < 0$ and $\epsilon(x) = +1$ for $x > 0$. For $T > T_c$ $(a > 0)$, the linearized equations yield the following solutions:

$$\frac{dm(x,t)}{dx} \sim \frac{m_0}{\sqrt{\pi t}} e^{-at - x^2/4t} \ \ (\mathrm{G}) \ , \tag{8a}$$

$$\frac{dm(x,t)}{dx} \sim \frac{m_0}{\sqrt{\pi t}} \frac{e^{-x^2}/4at}{\sqrt{a}} \ , \ \ at \gg 1 \ (\mathrm{K}) \ . \tag{8b}$$

For $T < T_c$ $(a < 0)$, the initial m_0 is chosen to satisfy $|m_0| \ll \sqrt{|a|}$, to allow the neglect of nonlinear terms. For the Glauber case, one finds that Eq. (8a) holds again with $a < 0$ and at early times no composition waves should be seen. This is in sharp contrast to the Kawasaki dynamics, where one finds [10]

$$\frac{dm(x,t)}{dx} \sim \frac{m_0}{k_0} \frac{1}{\sqrt{\pi t}} \exp[k_0^4 t - x^2/(16k_0^2 t)] \times [\cos(k_0 x) + 3x \sin(k_0 x)/16k_0^3 t) + O(1/t^2)], \tag{9}$$

where $k_0 = \sqrt{|a|/2}$ and $8k_0^2 t \gg 1$, showing the presence

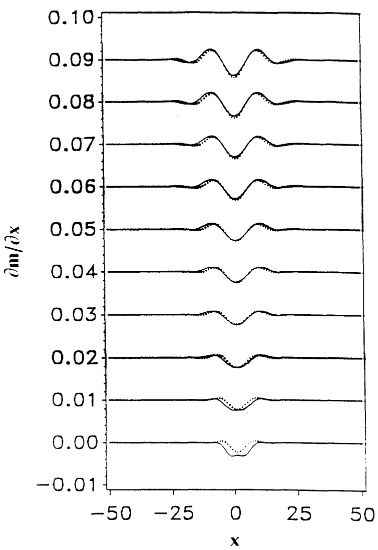

FIG. 4. Comparison of the integration of the full equation of motion (dots) and the analytic form (9) obtained in a linearized approximation (solid line). The curves shown (from top to bottom: $t = 200\tau, 180\tau, 160\tau, \ldots, 20\tau$) have been shifted for clarity.

of composition waves. Further, the wavelength of the aymptotic mode corresponds to the fastest growing mode in spinodal decomposition, in agreement with our numerical results. We have also verified that composition waves are indeed produced by direct numerical integration of the continuum version of the full nonlinear equations and that Eq. (9) is an excellent approximation for $t < 200\tau$, where τ is the characteristic time scale (Fig. 4). (It is important to note that while the composition wave associated with the wall grows out from it, the wave here is merely a transient density oscillation arising from the initial condition.)

Furthermore, an exact solution of a simplified Berlin-Kac [7] model taking into account the nonlinear terms leads to the same conclusion. The model is described by the equation

$$\dot{m}(x,t) = -\Gamma\left[-\frac{d^2}{dx^2} + a + \overline{m^2}(t)\right] m(x,t) , \qquad (10)$$

where the phenomenological parameter $a \sim T - T_c$, $\Gamma = 1$, and $-d^2/dx^2$ for Glauber and Kawasaki dynamics, respectively, $\overline{m^2} = (1/L)\int_{-L/2}^{L/2} dx\, m^2(x,t)$, and L is the length of the one-dimensional system. The value of $\overline{m^2}$ is determined self-consistently. Equation (10) can be solved in terms of the Fourier transform of $m(x,t)$, $\tilde{m}(k,t) = \tilde{m}(k,0)\exp\{-\gamma[(k^2+a)t + q(t)]\}$, where $q(0) = 0$ and $\dot{q}(t) = \overline{m^2(t)}$ and $\gamma = 1, k^2$ for Glauber and Kawasaki dynamics. As before, for the step initial condition and $a < 0$, composition waves are found in the conserved case and *not* for Glauber dynamics with the resulting equations being of the form [(9) and (8a)], respectively. Note that the Berlin-Kac model not only predicts the dynamical behavior at intermediate times but also produces the correct equilibrium limit at long times. More details will be presented elsewhere.

In conclusion, we have demonstrated that composition waves are generally produced when a binary mixture undergoes spinodal decomposition in the presence of a planar inhomogeneity, as long as the total amount of each fluid is conserved. The time dependence of the wave vector is found to be the same in molecular-dynamics simulations of Lennard-Jones fluids and in the experiment of Jones *et al.* [1] on polymer blends, but qualitatively different in Ising spin systems demonstrating the importance of hydrodynamic modes. It is likely that the phenomenon of composition waves will be useful for tailoring composite materials with novel properties and in biological applications [11].

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