PHYSICAL REVIEW E VOLUME 49, NUMBER 5 MAY 1994

Phase separation dynamics of model thin films

Michael A. Vaksman
Department of Chemistry, University of Detroit Mercy, 4001 West McNichols Road, Detroit, Michigan 48219-0900

William E. McMullen
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

(Received 27 December 1993)

We numerically study the dynamics of a finite, binary film quenched to temperatures at which a single phase does not exist in bulk. Within the scope of the time-dependent, Landau-Ginzburg equation, our calculations monitor the density order parameter from a homogeneous, high-temperature initial state to the final equilibrium density profile in one dimension. We also obtain partial solutions in two dimensions. The presence of confining boundaries causes the one-dimensional (i.e., noiseless two- or three-dimensional) Landau-Ginzburg equation to approach equilibrium in a stepwise fashion. During each step, the order-parameter profiles vary negligibly in time. We demonstrate that the addition of noise and a second dimension accelerates the relaxation toward equilibrium for thick enough films while for thin films, relaxation still proceeds in a stepwise manner.

PACS number(s): 68.15.+e, 68.10.Cr, 68.45.Gd, 64.70.Ja

I. INTRODUCTION

A bulk, homogeneous mixture of two fluids A and B will spontaneously separate into distinct A-rich and B-rich phases upon reducing the mixture's temperature to a point inside the spinodal region. In a mean-field description of the dynamics, the temperature quench brings the mixture into a condition of absolute instability where it can no longer exist as a single phase. This process, often referred to as spinodal decomposition, has been the subject of numerous theoretical, experimental, and simulation studies [1]. Less is understood about phase-separation dynamics in the presence of surfaces or free boundaries. However, recent experiments [2–4] on polymer fluids and numerical calculations [5,6] suggest that patterns that develop during the phase separation differ qualitatively near a surface from those occurring in bulk. The consequences of pattern interference in the region *between* a pair of surfaces is a largely unexplored subject. The present article provides some preliminary results that we hope will inspire future studies of the way that surfaces affect relaxation to equilibrium in simple kinetic models of thin films.

The so-called time-dependent, Landau-Ginzburg equation provides a simple mathematical model for exploring the dynamics of the diffusive stages of phase separation. During the latest stages of the process, transport in fluid systems occurs principally through hydrodynamic flow, and one must supplement the Landau-Ginzburg equation with a second constitutive relation that introduces the transverse velocity field into the phenomenology [7]. In spite of these limitations, studies of the purely diffusive model serve as useful first numerical and theoretical attempts at examining the segregation processes occurring in complicated liquid systems. Later, once techniques exist for analyzing the diffusive stages of the phase-separation, hydrodynamic effects can be included in the model to better describe the late-stage segregation processes. Of course, for binary systems such as magnetic films that relax entirely diffusively, hydrodynamic modes do not contribute to the dynamics, and the diffusive model provides a reasonable description of the kinetics all the way to equilibrium.

The present report describes some preliminary calculations of the relaxation of a confined, binary system to equilibrium following a rapid temperature quench from the one-phase region of the phase diagram to a state where the single phase is absolutely unstable. Thermal fluctuations are sufficient to initiate segregation of an initially homogeneous *bulk*, binary liquid under these conditions. The components's preferential adsorption to boundaries can also initiate the segregation process. However, in this case, the boundaries have a coherent rather than random effect on the phase-separation dynamics. Thus, for quenches well below the critical point where density fluctuations are small, the surfaces bounding a confined fluid may prove more effective than fluctuations at initiating and influencing the diffusive aspects of fluid phase separation.

II. THEORETICAL BACKGROUND

Consider an incompressible, binary fluid of average composition f and define the order parameter $\psi(\mathbf{r},t)$ whose value denotes the local deviation of the composition from f. We model the thermodynamics of this model using a simple Landau free energy supplemented by surface terms that phenomenologically account for preferential adsorption or desorption of components. The bulk contribution to the free energy is

$$F[\psi]=\int dz\left[\frac{a}{2}\psi^2+\frac{u}{4}\psi^4+\frac{c}{2}(\nabla\psi)^2\right], \tag{1}$$

with a,b,c phenomenological coefficients whose precise values depend on the molecular model from which Eq. (1) derives. A binary mixture generally has a cubic term in

1063-651X/94/49(5)/4724(4)/$06.00

Eq. (1); for simplicity, we discuss only symmetric, binary systems for which the cubic term vanishes.

As others have done [5,8], we introduce surface contributions to the free energy of the form

$$F_s = -H_l\psi_l + \frac{\alpha_l}{2}\psi_l^2 - H_r\psi_r + \frac{\alpha_r}{2}\psi_r^2 \ . \tag{2}$$

The H's and α's in Eq. (2) provide a rough measure of the attractions and repulsions of the system components to confining walls. In Eq. (2), $H_l > 0$ implies that, relative to a homogeneous bulk state, the left-hand surface favors adsorption of the order parameter. Similar arguments apply to H_r and the right-hand surface. α_l and α_r are positive restoring coefficients that limit the magnitude of ψ at these boundaries.

The order parameter varies in time as

$$\frac{\partial\psi(\mathbf{r},t)}{\partial t} = \nabla\cdot M\nabla\frac{\delta F}{\delta\psi(\mathbf{r},t)} \ , \tag{3}$$

with M a (possibly) ψ-dependent mobility. In the present work, we assume a constant value for M, although more refined studies—especially those involving polymer fluids [9–11]—should allow for nonlocalities in M. Scaling the order parameter, coordinates, and time according to

$$\psi \rightarrow \left[\frac{|a|}{u}\right]^{1/2} \psi_{\text{rescaled}} \ , \tag{4a}$$

$$\mathbf{r} \rightarrow \left[\frac{c}{|a|}\right]^{1/2} \mathbf{r}_{\text{rescaled}} \ , \tag{4b}$$

and

$$t \rightarrow \frac{c}{Ma^2} t_{\text{rescaled}} \tag{4c}$$

leads to

$$\frac{\partial\psi}{\partial t} = \nabla^2(\pm\psi + \psi^3 - \nabla^2\psi) + \eta(\mathbf{r},t) \ , \tag{5}$$

where we have introduced the thermal noise $\eta(\mathbf{r},t)$ on the right-hand side of Eq. (5). The form of the surface free energy leads to the boundary conditions

$$\hat{\mathbf{n}}_0\cdot(\nabla\psi)_{z=0} = H_0 - \alpha_0[\psi(\mathbf{r},t)]_{z=0} \tag{6a}$$

and

$$\hat{\mathbf{n}}_L\cdot(\nabla\psi)_{z=L} = H_L - \alpha_L[\psi(\mathbf{r},t)]_{z=L} \ . \tag{6b}$$

In Eqs. 6(a) and 6(b), $H_{0,L}$ and $\alpha_{0,L}$ are rescaled surface terms that vary as $1/a$ and $a^{-1/2}$, respectively. At each surface, the no-flux conditions

$$[\hat{\mathbf{n}}\cdot\nabla(\pm\psi + \psi^3 - \nabla^2\psi)]_{z=0,L} = 0 \tag{7}$$

hold with $\hat{\mathbf{n}}$ the surface normal at $z=0$ and $z=L$. Puri and Binder [12] have proposed alternatives to Eqs. 6(a) and 6(b) that contain explicit time derivatives of the order parameter near a surface. More recently, Diehl and Janssen [13] have presented a rigorous, formal analysis of the stochastic dynamics of phase-separating fluids near a surface. They reach the conclusion that Eqs. 6(a) and 6(b) are the only contributions relevant to the boundary

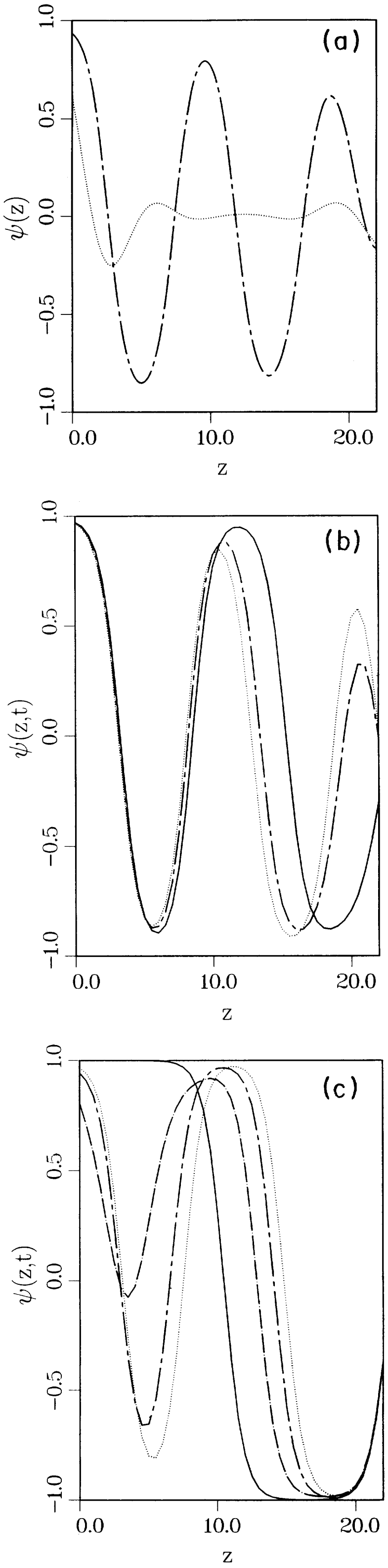

FIG. 1. Evolution of the order parameter with time for $L=22$ and one representative choice of surface parameters ($H_0=0.25$, $H_L=0.15$, $\alpha_{0,L}=0.25$): (a) early stages (· · · ·) $t=2$, (——–——) $t=50$; (b) intermediate stage, (· · ·) $t=310$, (——–——) $t=360$, (———) $t=410$; (c) transition to equilibrium, (· · ·) $t=1810$, (——–——) $t=2160$, (—·—) $t=2310$, (———) $t=2810$.

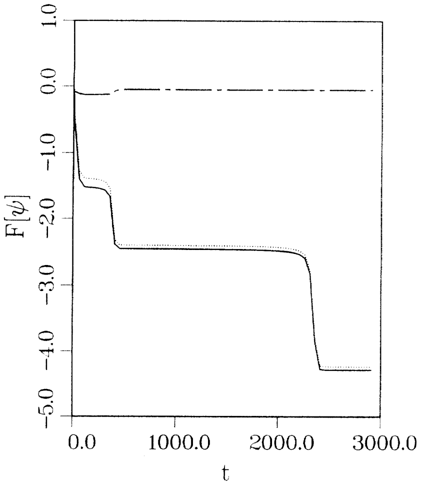

FIG. 2. Free energy vs time for the order-parameter evolution in the film of Fig. 1: (— — —) surface free energy contribution F_s; (· · ·) bulk free energy contribution F_b; (——) total free energy F. Each sharp decrease of F corresponds to a rapid change in the order-parameter profile.

conditions. This justifies our use of the simpler, equilibriumlike boundary conditions.

When $\eta(\mathbf{r},t)$ is nonzero, segregation may occur parallel to the confining boundaries of a two- or three-dimensional film. Assuming Gaussian statistics, $\eta(\mathbf{r},t)$ obeys the fluctuation-dissipation relation [1]

$$\langle \eta(\mathbf{r}_1,t_1)\eta(\mathbf{r}_2,t_2)\rangle = -B\delta(t_1-t_2)\nabla^2\delta(\mathbf{r}_1-\mathbf{r}_2) \ , \qquad (8)$$

with $B=2ua^{d/2-2}c^{-d/2}$. The noise has no qualitative effect on the intermediate- and late-stage dynamics of small-molecule *bulk* phase separation, its principal effect being the initiation of the segregation process. In the present work, we take Eq. (8) to apply at all times after a quench, and the noise plays a much more dominant role in determining the dynamics of thin films since it serves to drive the system over free energy barriers. One should recall, however, that Eq. (8) derives from linear-response theory as applied to a system extremely close to *equilibrium*. Its applicability for determining the random force in the generalized-Langevin equation [Eq. (5)] when the system is far from equilibrium is somewhat tenuous.

III. NUMERICAL CALCULATIONS AND DISCUSSION

First consider the one-dimensional solution of Eq. (5) in the absence of noise. Figs. 1(a)–1(c) show the order-parameter profile at various times following a quench from $T=\infty$ [where $\psi(\mathbf{r},t)=0$] to a low temperature where $B\approx 0$. Figure 2 plots the free energy as a function of time as the order parameter approaches equilibrium. After the quench, the system rapidly develops density oscillations that relax toward equilibrium only slowly with time. When relaxation finally occurs, it does so in a stepwise fashion as Fig. 2 shows. However, between relaxation events, the profile remains almost stationary. Furthermore, the time scales of the relaxation events are generally small compared to the time spent on each of the

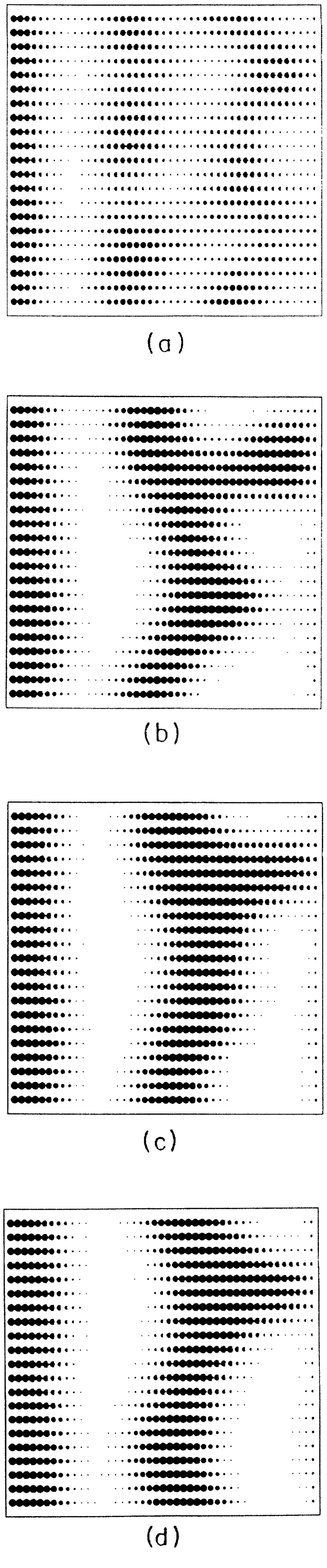

FIG. 3. Evolution of the two-dimensional analogue of the film in Figs. 1 and 2: ($L=22$; $H_{0,L}$, and $\alpha_{0,L}$ are as in Fig. 1): (a) $t=10$; (b) $t=100$; (c) $t=150$; (d) $t=300$; (e) y-averaged profiles (· · ·) $t=10$, (— — —) $t=100$, (— · —) $t=150$, (——) $t=300$.

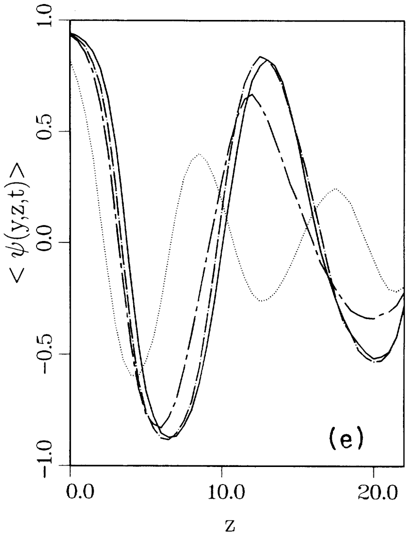

FIG. 3. (*Continued*).

free energy plateaus of Fig. 2. The occurrence of stepwise relaxation to equilibrium is in accord with recent mathematical analyses of Eq. (5) [14].

We have repeated these calculations in two dimensions for moderate noise levels that initiate segregation parallel to the confining surfaces. Figs. 3(a)–3(e) show one run of a typical "numerical experiment" for $B=0.01$ [note that not B but $\sqrt{B}$ appears in Eq. (5), so that the noise amplitude is 0.1]. The three-peaked profile that persists in Figs. 1 and 2 until $t=350$ rapidly relaxes to a two-peaked profile in Fig. 3. However, the two-peaked structure then lasts at least until $t=300$. In the presence of long-range, van der Waals interactions, we find that the order parameter profiles may differ quantitatively from those depicted in Figs. 3(a)–3(e), but the observation of a stepwise relaxation to equilibrium remains intact. These findings agree with previous studies of thicker fluid films [5,6] where density oscillations initiated at a single surface propagate into the bulk fluid. In the present case, the close proximity of the two surfaces causes the density oscillations to interfere and leads to the nonmonotonic approach to equilibrium.

We note that the occurrence of almost metastable states and the slow approach of the model film to equilibrium depends somewhat on the film thickness and the surface parameters. For extremely thin films ($L<5$), different stationary profiles obeying Eqs. 6(a) and 6(b) have very different free energies or else only one such profile exists. Then the approach to equilibrium occurs monotonically, and the free-energy-versus-time curves do not exhibit plateaus. Modifying the surface properties corresponds to adjusting the H's and α's of Eqs. 6(a) and 6(b), and this, in part, determines whether or not the equilibrium is achieved in steps. The most dramatic effects occur when the surfaces have similar but slightly different affinities for one of the film components. In Eq. (2) this means that, for example, H_l is slightly greater than H_r with both greater than 0.

Clearly the presence of thermal fluctuations and a second dimension offers the system another channel by which it can relax toward equilibrium. We thus expect that in three dimensions, relaxation toward equilibrium, for a given noise strength, proceeds more readily than in two dimensions. However, at a given distance from the critical temperature, the noise amplitude decreases upon passing from two to three dimensions. Real films may thus be observed to relax to equilibrium in a stepwise fashion provided they are thin enough and the confining surfaces exhibit strong preferences for the different components. We have, in fact, repeated the calculations summarized by Figs. 1–3 upon reducing the film thickness to $L=10$ (from $L=22$) while keeping $B=0.01$. In this case, the noise has a negligible affect on the dynamics, which proceeds as in the one-dimensional case. As we have already remarked, hydrodynamics should play an important role in the late-stage dynamics of films. Future studies will numerically couple the velocity fields to the evolving order parameter. Such calculations will require more efficient numerical algorithms for solving the resulting dynamical equations or perhaps generalizations of cell dynamical models [6,15].

ACKNOWLEDGMENTS

M.V. is grateful to Professor Jacob Klein for turning his attention to surface-directed spinodal decomposition. This research is supported, in part, by the Robert A. Welch Foundation (Grant No. A-1175) and by the donors of the Petroleum Research Fund administered by the American Chemical Society (Grant No. 25613-AC7B).

---

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8.

[2] R. A. L. Jones and E. J. Kramer, Philos. Mag. B **62**, 129 (1990).

[3] R. A. L. Jones, L. J. Norton, E. J. Kramer, F. S. Bates, and P. Wiltzius, Phys. Rev. Lett. **66**, 1326 (1991).

[4] F. Bruder and R. Brenn, Phys. Rev. Lett. **69**, 624 (1992).

[5] R. C. Ball and R. L. H. Essery, J. Phys. (Leipzig) **2**, 10 303 (1990).

[6] J. F. Marko, Phys. Rev. E **48**, 2861 (1993).

[7] G. Brown and A. Chakrabarti, Phys. Rev. A **46**, 4829 (1992).

[8] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[9] P. G. de Gennes, J. Chem. Phys. **72**, 4756 (1980).

[10] P. Pincus, J. Chem. Phys. **75**, 1996 (1981).

[11] K. Binder, J. Chem. Phys. **79**, 6387 (1983).

[12] S. Puri and K. Binder, Phys. Rev. A **46**, R4487 (1992).

[13] H. W. Diehl and H. K. Janssen, Phys. Rev. A **45**, 7145 (1992).

[14] P. W. Bates and P. C. Fife, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **53**, 990 (1993), and references therein.

[15] Y. Ohno and S. Puri, Phys. Rev. Lett. **58**, 836 (1987).