

# Spinodal decomposition, power laws, and wetting at a triple point

C. Varea

*Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, 01000 Mexico Distrito Federal, Mexico*

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We study numerically the dynamics of phase separation in ternary mixtures at a triple point. For the full range of compositions and for different interaction parameters, the long time growth is in accord with a universal law. The early time behavior is governed by the structure of the spinodal region, including the possibility of a two step separation and decomposition originating at a surface and propagating into the bulk. The appearance of the domains is governed by the wetting properties of the mixture and the growth of a wetting layer follows again the universal law; a result that we can interpret with a simple phenomenological model.

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## I. INTRODUCTION

Interesting and new phenomena appear when three phases coexist. The phenomenological pioneering work of Widom [1] and Cahn [2] uncovered the now well known wetting transitions [3]. When the system is in the partial wetting regime three interfaces form and meet, forming definite dihedral angles, at a line with an excess free-energy, or line tension [4]. The most significant effort to obtain a statistical-mechanical description of the wetting transition and of the line tension has been the study of model systems with one bulk order parameter in contact with an inert phase, which exerts an attraction to one of the phases and may be long ranged in character. Also the growth of the wetting layer with time has been studied [5,6] when the system, with one order parameter is quenched into the spinodal region of a two-phase system in presence of a wall.

Spinodal decomposition occurs when a mixture is quenched from the one-phase region into the immiscibility gap, and the unstable homogeneous state decays via wave fluctuations that are amplified. In one component systems, the dynamics of the subsequent nucleation and growth of domains follows a scaling behavior where the domain patterns, at later times, look statistically similar to those at earlier times [7,8]. In off-critical quenches of a binary fluid, droplets of the minority phase are formed in a sea of the majority phase. When this system is in the presence of a wall that preferentially attracts the minority phase, a wetting layer is rapidly formed creating a depletion zone near the surface where droplets are absent [5]. Further growth of the wetting layer is by diffusion through this depletion zone and the growth rate of the wetting layer, at early times, depends on the range of the surface potential and in the case where surface potential is short-ranged early time behavior is logarithmic with a cross over to the universal Lifshitz-Sylozov law [9], where there is a single length characterizing the domain pattern [10]. Near a symmetric composition [6] wetting effects are strongly delocalized by hydrodynamic effects unique to bicontinuous phase separation and, more interestingly, the phenomenon of retarded wetting-induced secondary phase separation is observed.

In compressible binary fluids, the phase behavior is more complex and some mixtures show liquid-vapor equilibrium

followed by triple points at lower temperatures where liquid-liquid-vapor coexistence occurs. Then a droplet of unmixed liquid in contact with its vapor may be quenched into the three-phase region. In some cases phase separation shows up first at the surface and propagates into the droplet at the same time that fingers of the vapor penetrate into the droplet [11].

In this work, we explore the behavior of the spinodal decomposition into a three-phase region when the three phases are represented by two order parameters and contrast this behavior with the case when the three phases are represented by a one-order parameter system in the presence of a wall. The model that we use presents a very rich behavior of phase separation, including three-phase separation with various wetting properties. The global thermodynamic behavior of model mixture that we use is well known and, in Sec. II, we compose a brief reminder of its properties including the wetting behavior into the three-phase region. In Sec. III we present our results. In particular we find that the early time behavior may be in two steps. In the first step two fluids form with droplets, or labyrinthine structures depending on concentration. At a later stage the droplets or one region in the bicontinuous regions decomposes into two phases. We show that this behavior is related to the properties of the spinodal region. At late times the growth is such that universal Lifshitz-Sylozov law is always obeyed, even in the case where a two-phase planar interface is quenched into the three-phase region forming a wetting layer, a result that we can interpret theoretically. In Sec. IV we summarize our results.

## II. THE MODEL

To model the mixture we use the Furman Dattagupta and Griffiths three component model [12], extended to include inhomogeneous states [13]. In the squared gradient approximation, appropriate to short-ranged interactions, the grand potential density is,

$$\begin{aligned} \omega = & kT[u \ln u + v \ln v + w \ln w] + avw + b w u + c u v \\ & + \frac{1}{2} (a \nabla v \cdot \nabla w + b \nabla w \cdot \nabla u + c \nabla u \cdot \nabla v) - \mu_u u \\ & - \mu_v v - \mu_w w, \end{aligned} \quad (1)$$

where  $(u,v,w)$  are the concentrations of components  $(UVW)$ ,  $(\mu_u, \mu_v, \mu_w)$  the chemical potentials for the mixture with interaction parameters  $(a,b,c)$ . We will consider only the case  $a=b$  with the usual normalization condition  $a+b+c=1$ , that sets the temperature scale, in what is called the symmetric part of the *principal energy triangle* ( $a>0, b>0$ , and  $0.5>c>0$ ). We also assume that the mixture is incompressible so that  $u+v+w=1$ . The mixture is then characterized only by the temperature  $T$ , the parameter  $c$  and the concentrations  $u$  and  $v$  of the mixed fluid before the quench.

The diffusive evolution of such nonequilibrium system can be described by the Cahn Hilliard model [8] with two independent and conserved order parameters  $u(\mathbf{r},t)$  and  $v(\mathbf{r},t)$ . The equations of evolution are of the form

$$\frac{\partial u(\mathbf{r},t)}{\partial t} = \frac{\delta \Omega[u,v]}{\delta u(\mathbf{r},t)}, \tag{2}$$

$$\frac{\partial v(\mathbf{r},t)}{\partial t} = \frac{\delta \Omega[u,v]}{\delta v(\mathbf{r},t)}.$$

Here  $\Omega[u,v] = \int \omega[u,v,(1-u-v)] d\mathbf{r}$  is the grand potential and we have absorbed the two, equal, transport coefficients into the time scale. We have not considered thermal noise since it has been shown to be irrelevant by renormalization group techniques [7].

The structure of the uniform equilibrium phase diagram of the model differs for different values of the interaction parameter  $c$ . In the region of the principal triangle, studied here, there are 3 sections all of them with triple points with phases  $P_U, P_V$ , and  $P_W$  (rich in components  $U, V, W$ ) in coexistence. This regions are characterized by the way the triple points end as the temperature is raised. For  $c < 0.29$ , in region I, a line of triple points ends in a two phase  $(P_U, P_V)$  critical point in equilibrium with the third phase  $(P_W)$  at a temperature  $T_1$ , leaving two pairs of phases in coexistence  $(P_W, P_{U-V})$  ( $P_{U-V}$  is a liquid poor in the  $W$  component with  $U$  and  $V$  unmixed), and  $(P_U, P_V)$ . Coexistence of  $(P_U, P_V)$  with low concentrations of  $W$  ends at a line of critical points  $T_c(w)$ . The  $(P_W, P_{U-V})$  equilibrium at high concentrations of  $W$  ends at an ordinary critical point  $T_c$  [see Fig. 1(a)]. In this mixtures the three phases below  $T_t$  are in a partial wetting regime with  $\gamma_{UW} = \gamma_{VW} < \gamma_{UV}$ , where  $\gamma_{UW}$  is the surface tension of the  $U-W$  interface. In the second region II, the so called *shield region*, ( $0.29 < c < 0.346$ ) there is equilibrium of four phases at one temperature  $T_4$ , three of them end at a tricritical point  $T_t$  which continues with a line of critical points  $T_c(w)$  and two at an ordinary critical point  $T_c$  [see Fig. 1(b)]. For the region III ( $0.346 < c < 0.71$ ) the model mixture presents also lines of triple points ending in a tricritical point, followed by  $T_c(W)$ . In regions II and III, and at low temperatures, each of the three phases below  $T_t$  partially wets the interfaces between the other two and have a wetting transition at  $T_w$  where  $\gamma_{UW} + \gamma_{VW} = \gamma_{UV}$  [14],  $T_w$  decreases as  $c$  increases and in the special case  $c=0.5$ ,  $P_W$  wets the interface between  $P_U$  and  $P_V$  at all temperatures. In Fig. 2 we show a plot of the spreading coefficient  $S = \gamma_{UV}$

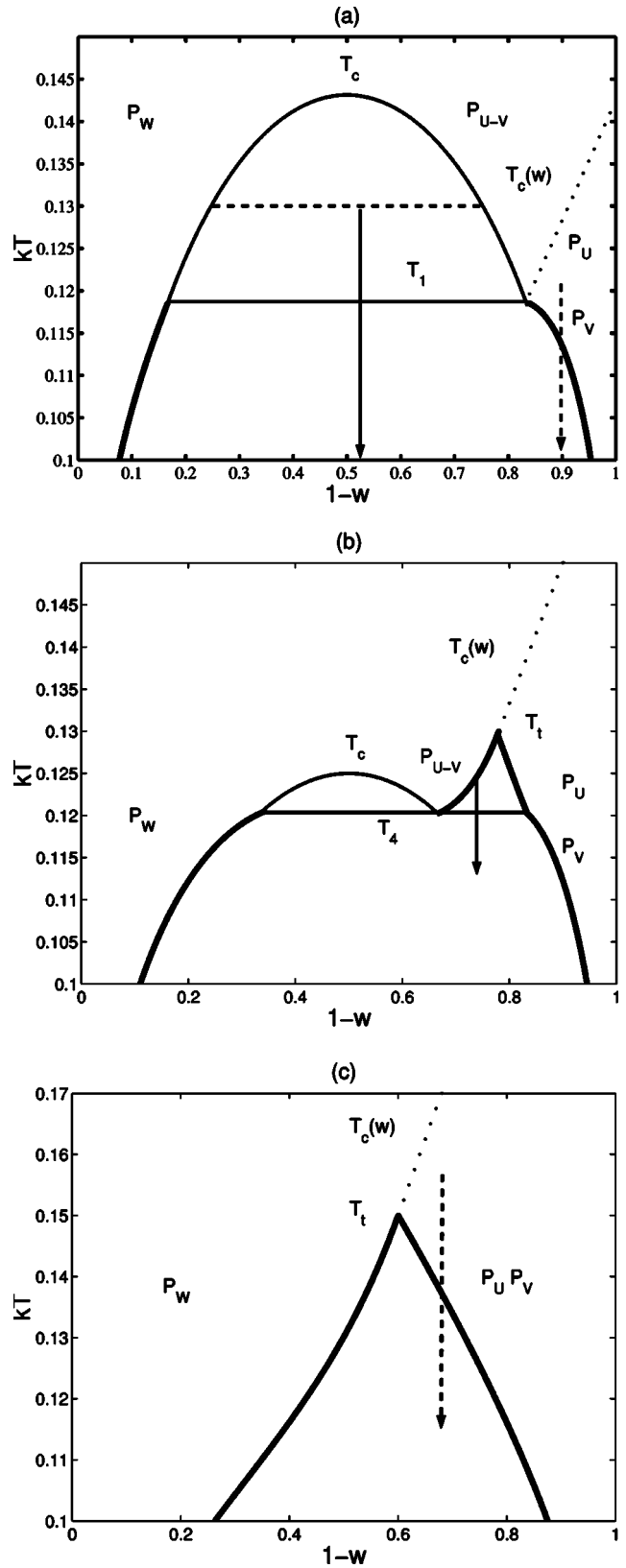


FIG. 1. Phase diagrams for the three component mixture for different values of the interaction parameter  $c$ . The temperature scale is in units of the interaction parameter  $J = a + b + c$ .

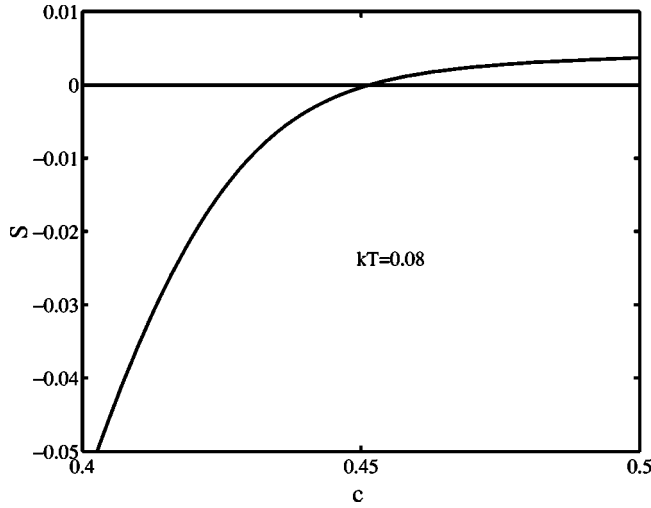


FIG. 2. Spreading coefficient (in arbitrary units) at constant temperature as a function of the interaction parameter  $c$ .

$-(\gamma_{VW} + \gamma_{UV})$  as a function of the interaction parameter  $c$  at constant temperature below the four-phase equilibrium temperature  $T_4$ . In the early stages of the evolution, in this mean field theory, the structure of the spinodals becomes relevant. For small fluctuations of the form  $\delta u = \delta u_0 e^{-\omega t + i\mathbf{k} \cdot \mathbf{r}}$  from a uniform state with concentrations  $(u, v, 1 - u - v)$  and for small wave vector  $\mathbf{k}$  Eqs. (2) become

$$\begin{aligned} \omega \delta u_0 &= k^2 (\omega_{uu} \delta u_0 + \omega_{uv} \delta v_0), \\ \omega \delta v_0 &= k^2 (\omega_{uv} \delta u_0 + \omega_{vv} \delta v_0), \end{aligned} \quad (3)$$

where  $\omega_{i,j}$  is the stability matrix of the model, then when the eigenvalues of the stability matrix become negative for a value of  $u$  and  $v$  the state is unstable to fluctuations of long wavelength. In Fig. 3 we show the structure of the spinodals at low temperatures. Along the line  $u = v$ , the eigenvectors of the stability matrix are symmetric of the form  $\delta u_0 = \delta v_0$  and antisymmetric with  $\delta u_0 = -\delta v_0$ . In regions I and II of the symmetric part of the energy triangle the spinodals have a complex structure that divide the area of the concentration triangle into 5 regions. Three of these regions, near the vertices of the composition triangle, have positive eigenvalues and represent stable or metastable uniform states. The interesting central region has two negative eigenvalues for systems with  $c < 0.29$ , but for  $0.29 < c < 0.346$  the two negative eigenvalues at low temperature become positive at some temperature below  $T_4$ , the fifth region is unstable with respect to one of the two eigenvectors. In the symmetric part of the composition triangle, the eigenvalue of the symmetric eigenvector is negative for low values  $w$  but for large values of  $w$  the antisymmetric eigenvector is the unstable one.

This model may also be applied to a binary alloy with vacancies where the phase  $P_w$  represents the vapor phase in this context similar models have been investigated before, for low concentration of vacancies and  $c = 2/3$ , to study the growth law of domains when vacancies are present [15–18].

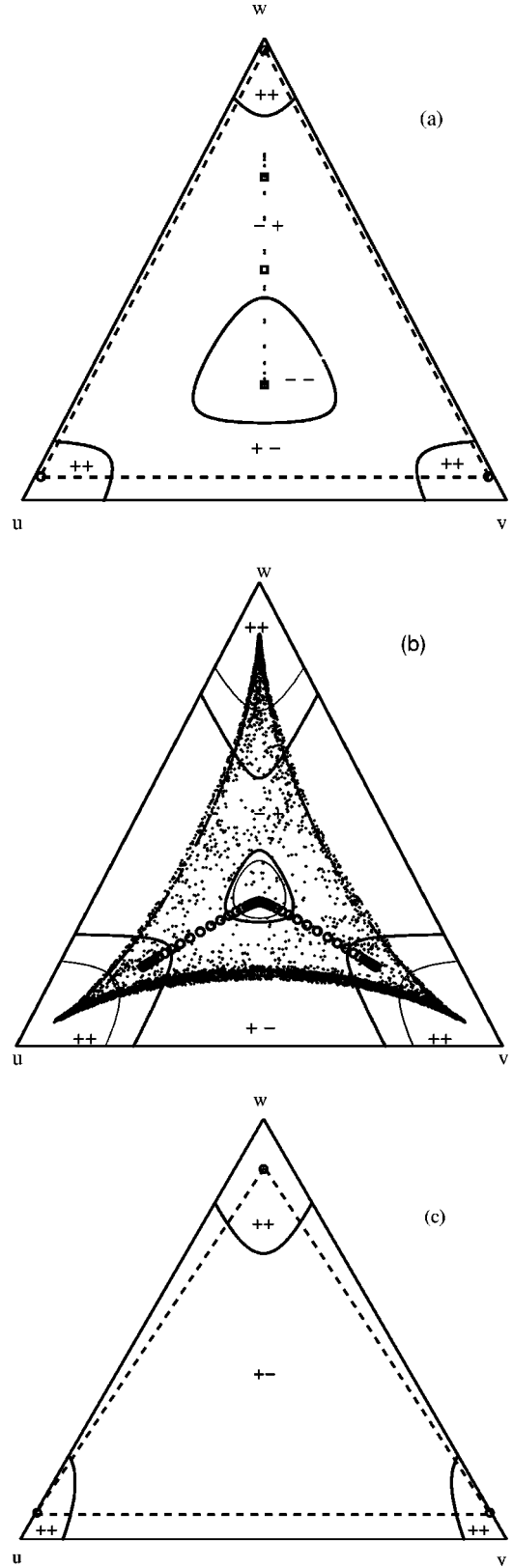


FIG. 3. Regions of stability and spinodal lines for mixtures with different values of  $c$  and  $kT=0.08$ . In (a)  $c=0.285$ , in (b)  $c = 1/3$ , and in (c)  $c=0.5$ .

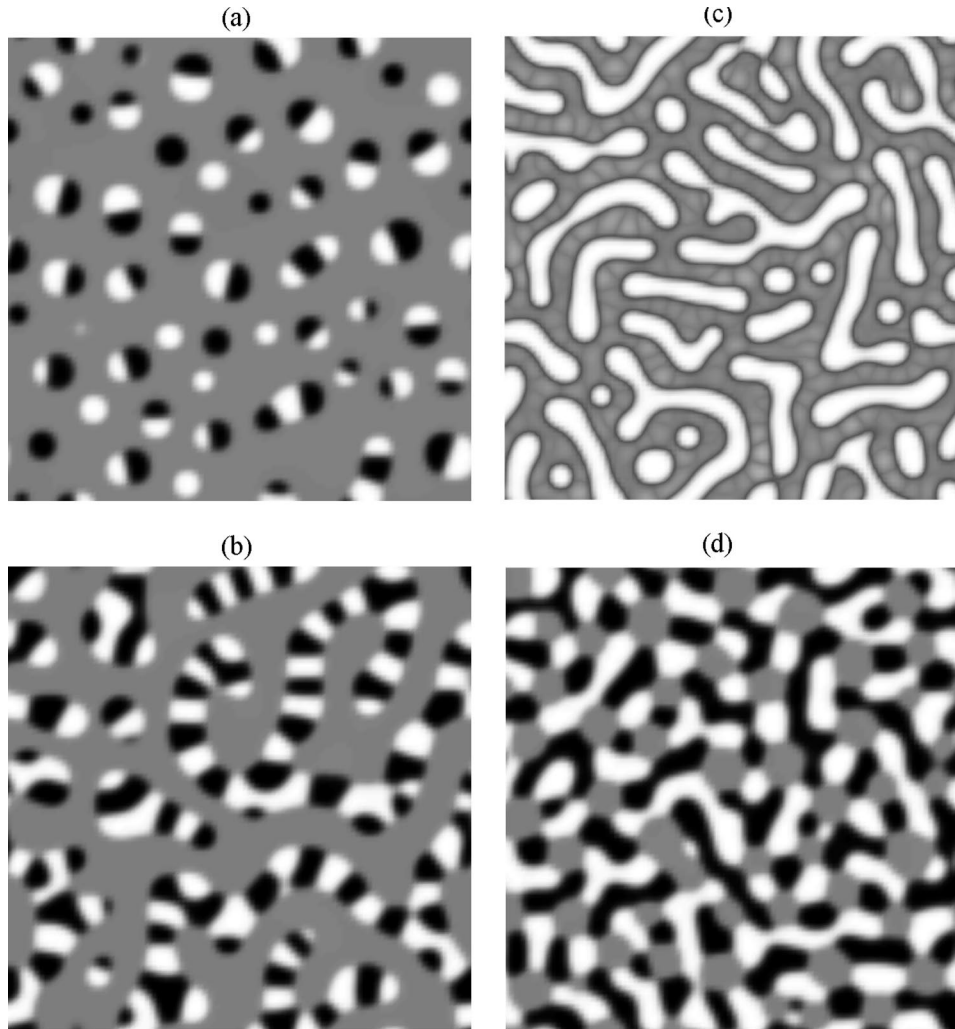


FIG. 4. Pictures obtained from simulation of the model for system  $S1$ , with a time step  $\Delta t = 0.0125$ . In (a) the concentrations of the uniform initial state are  $u_0 = v_0 = 0.14$  and the time is  $t = 130$ . In (b) the time is  $t = 6.7$  and global concentrations of the species are  $u_0 = v_0 = 0.25$ . In (c) and (d) two different contrasts of the case where  $t = 5.71$  and  $u_0 = v_0 = 0.37$ . In (c) shades of gray represent concentrations of  $u - v$  and in (d) concentrations of  $w$ . The time scale is arbitrary and the numbers are proportional to the number of iterations  $N$  ( $t = kT\Delta tN$ ).

### III. RESULTS

#### A. Quenches from a uniform initial state

The Cahn-Hilliard equations are solved by the simple Euler method with periodic boundary conditions in two dimensions on a  $100 \times 100$  lattice. The initial state is a uniform mixture of the three components with a random noise of small amplitude over the whole system to initiate the phase separation. As examples we show results for two systems. System  $S1$  is a mixture with  $c = 0.285$  close to the shield region in region  $I$  at a temperature  $kT = 0.08$ , the concentrations of the equilibrium states at the triple point are,  $P_U [0.9524, 0.0124, 0.0352]$ ,  $P_V [0.0124, 0.9524, 0.0352]$ , and  $P_W [0.0123, 0.0123, 0.9754]$  the temperature for the end of the triple line is at  $kT = 0.12$ . For this system (see Fig. 2) the three phases are in the partial wetting regime. System  $S2$  is a mixture with  $c = 0.50$  at a temperature  $kT = 0.08$  the concentrations of the equilibrium states at the triple point are,  $P_U [0.9539, 0.0028, 0.0433]$ ,  $P_V [0.0028, 0.9539, 0.0433]$ , and  $P_W [0.0845, 0.0845, 0.8310]$  the temperature of the tricritical point is at  $kT_t = 0.15$  and phase  $P_W$  wets the interface between the other two phases.

Figure 4 shows typical pictures for system  $S1$  for different concentrations, here we use shades of gray to represent

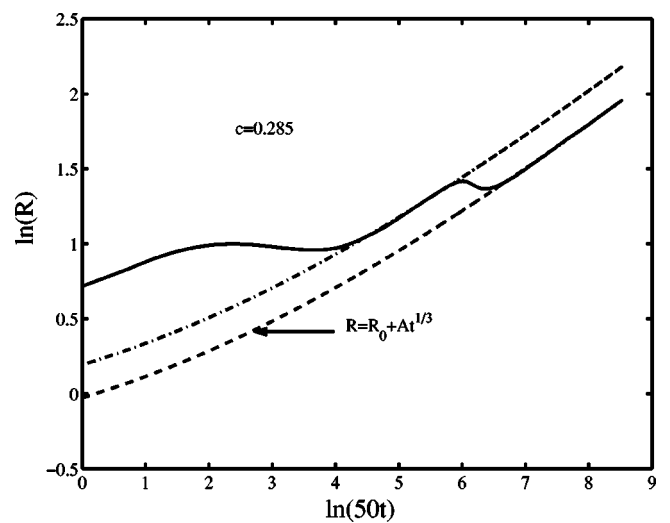


FIG. 5. In-ln plot of the time evolution of the first zero of the correlation function for the system shown in Figs. 4(b) and 4(c), the dotted lines are the best fits with  $R = R_0 + At^{1/3}$ .  $R$  is in units of the lattice constant and  $t$  as in Fig. 4.

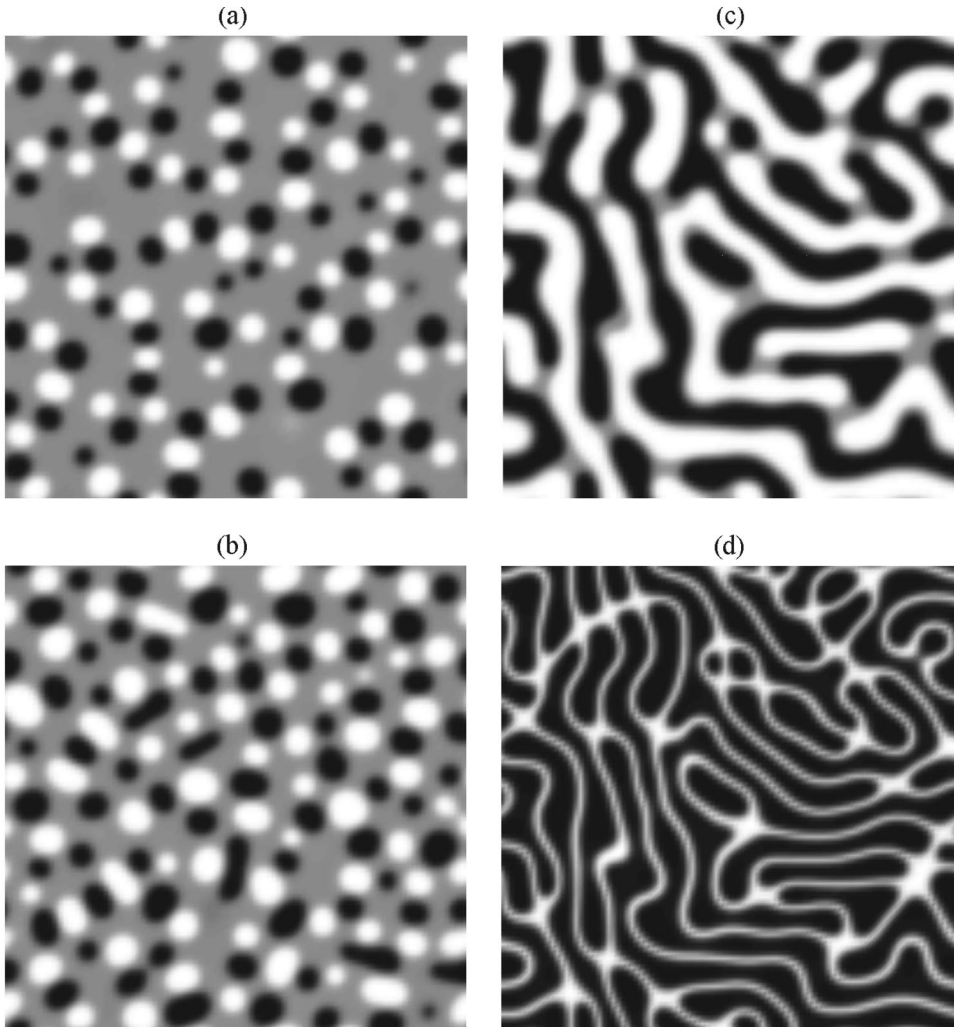


FIG. 6. Pictures obtained from simulation of the model for system S1, with a time step  $\Delta t = 0.0125$ . In (a) the concentrations of the uniform initial state are  $u_0 = v_0 = 0.14$  and the time is  $t = 130$ . In (b) the time is  $t = 6.7$  and global concentrations of the species are  $u_0 = v_0 = 0.25$ . In (c) and (d) two different contrasts of the case where  $t = 5.71$  and  $u_0 = v_0 = 0.37$ . In (c) shades of gray represent concentrations of  $u - v$  and in (d) concentrations of  $w$ .

the concentration of  $u - v$ . Figure 4(a) is the picture that results from the evolution of a uniform state with concentrations  $u = v = 0.15$  at a time corresponding to 80 000 iterations. We were forced to use a small time step of  $\Delta t = 0.006$  due to numerical instabilities brought about by the logarithmic terms in the kinetic equations. In this region of concentration, linear analysis shows the growth of fluctuations with  $\delta u = \delta v$  and small droplets of an unmixed fluid of the minority components forms in a sea of the majority phase. When the concentration amplitude of the droplets reaches the central spinodal region in Fig. 3(a) where fluctuations with  $\delta u = -\delta v$  become unstable the droplets start to decompose, as a result the two minority phases  $P_U$  and  $P_V$  condense into droplets that often are attached to each other forming a definite set of contact angles. The interfaces between the two droplets are straight because there is no pressure difference across that interface. We have measured the growth exponent for these droplets directly by measuring the area that each phase occupies and the number of droplets of each phase, the average radius  $R$  per droplet for long times satisfies a growth law of the form  $R(t) \propto t^x$  with  $x = 1/3$  i.e., of the Lifshitz-Slyozov form [9]. For an initial state with

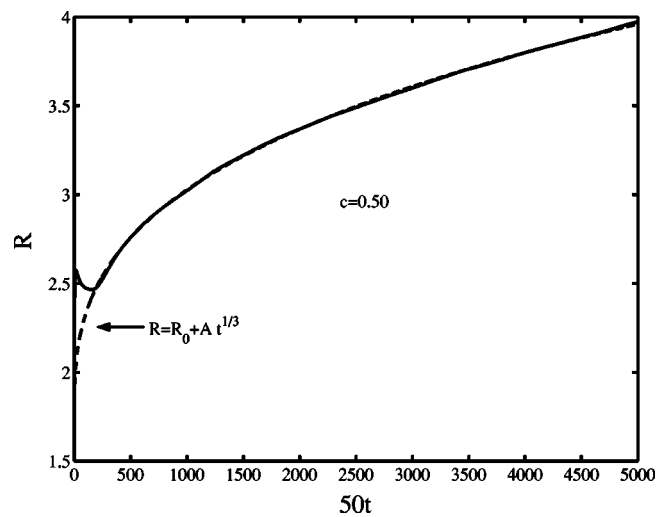


FIG. 7. Plot of the time evolution of the first zero of the correlation function for the system shown in Fig. 6(b). The dashed line is the best fit with  $R = R_0 + A t^{1/3}$ . Units as in Fig. 4.

concentrations  $u=v=0.275$  deep into the spinodal region but with still only one of the eigenvectors of the stability matrix unstable, the concentrations of  $u$  and  $v$  are large enough to form a labyrinthine structure where one of the phases is a mixture of the  $u$  and  $v$  components, and the other is rich in component  $W$ . Again when the concentration amplitudes reach the central spinodal region in Fig. 3(a) the stripes start to decompose into droplets. In Fig. 4(c) we show the appearance of the domains after 80 000 iterations. Here instead of growth of interconnected domains of two phases as in a two component mixture, we have the curious growth of strings of droplets with alternating  $P_U$  and  $P_V$  domains that percolate the lattice in a sea of the majority  $P_W$  phase. Here one of the contact angles is  $\sim \pi$  since  $\gamma_{UW} = \gamma_{VW} \gg \gamma_{UV}$ . It is easy to understand why the droplets alternate; at earlier times the system decomposes into a bicontinuous structure with regions rich in  $W$  and poor in  $W$ , as if it had only one order parameter [see Fig. 4(b)], when the value of  $w$  poor in  $W$  reaches the central spinodal region, the regions poor in component  $W$  start to decompose into droplets of the  $P_U$  and  $P_V$ , in addition there is a gain in free-energy creating interfaces with low surface tension. In this interesting case we analyzed the size of these structures by calculating the first zero of the angle averaged pair correlation function  $g_{ii}(r,t)$  for  $i=u$  and  $i=v$  [19]. This length  $R_i(t)$  was then averaged over 10 different random initial conditions and averaged over the index  $i$ . The growth is shown in Fig. 5 in a  $\ln(R) - \ln(t)$  plot. There, one can clearly observe the two regimes, formation of a labyrinthine structure followed by the formation of droplets. At the transition region the size of the structures decreases because the droplets formed on the stripes are smaller than the stripes themselves [see Fig. 4(c)]. When performing the same analysis to the growth shown in Fig. 4(a) we also find this two stages of growth except that, in this case, the decrease in  $R(t)$  upon reaching the central spinodal is smaller.

The two fits in Fig. 5 are in accord with Huse's theory [20] that assumes that at these high concentrations the rate of average domain size may be written as

$$\frac{dR}{dt} = C \left[ \frac{1}{R^2} + \frac{R_1}{R^3} \right] \quad (4)$$

the first term coming from diffusion between domains through the bulk and the second along the interface between domains. Interestingly, in this case, the same type of contribution could equally be interpreted as coming from the excess free-energy per unit length  $\lambda$  of the line tensions (here point tensions) that are formed in this configuration with  $R_0 = \lambda/\gamma$ . It is easy to show that for large  $R$ , the solution of this equation is of the form  $R = R_0 + At^{1/3}$ , with  $2R_0 = R_1$ . In Fig. 4(b) one can see that the growth is mainly due to coalescence of droplets of one phase that are closer to droplets of the same phase than when these droplets are placed at random. We observe that the coalescence occurs when two droplets surround the droplets of the other phase. It is interesting to notice that as in Monte Carlo simulations carried out using Kawasaki dynamics and for low concentrations of

component  $w$ , the Lifshitz-Slyozov regime is attained at late times and the analysis of the exponents is problematic [15]. At higher concentrations of  $u$  and  $v$  for an initial concentration  $u=v=0.375$  droplets of  $P_W$  are formed in a complex matrix of domains of phases  $P_U$  and  $P_V$  [see Fig. 3(d)]. These start forming in the boundaries of the droplets of  $P_W$  very much in the same way as Plapp and Gouyet describe [11]. The Lifshitz-Slyozov growth law, at late times, of the droplets of  $P_W$  is also applicable in this region of concentrations.

For system  $S2$  linear analysis shows only one unstable eigenvalue of the instability matrix with  $\delta u = -\delta v$  for all symmetric concentrations in the initial state. Figure 6 shows the typical appearance for the growing domains for system  $S2$ . In Fig. 6(a) the concentration of the initial uniform phase is  $u=v=0.2$  here well separated droplets of the two uniform minority phases are formed. Again the growth law for the average radius of this droplets is consistent with the exponent  $x=1/3$  for late times. In Fig. 6(b) we show the result of cooling down the system with an initial concentration  $u=v=0.25$ . Here instead of strings of alternating  $P_U$  and  $P_V$  droplets, the interfaces between  $P_U$  and  $P_V$  are wetted by the  $P_W$  phase, and the two kinds of domains become decoupled. In Fig. 7 we show the behavior of the radius of the domains as a function of  $t^{1/3}$  as measured by the average of the first zero of the pair correlation function. Again the value of  $R$  there, is the average over 4 runs, for the radii of the  $P_U$  and  $P_V$  droplets and for 250 000 iterations. As seen there, the fit to the behavior predicted by Huse is excellent. In Figs. 6(c) and 6(d) the appearance of the domains when the initial concentration is  $u=v=0.375$  is shown. In the early stages the kinetics is peculiar in the sense that the minority (according to the phase rule) phases  $P_U$  and  $P_V$  are formed with considerably higher concentrations of  $u$  and  $v$  than in the three phases in equilibrium. Component  $W$  spreads along the interface between  $P_U$  and  $P_V$  and starts to grow forming pockets of  $P_W$  in regions where four domains of the minority phases meet [see Fig. 6(d)]. In this configuration we used the first moment of the structure factor  $S_{ww}(k,t)$ , averaged over angles, to measure the typical size of the domains; this is again consistent with the Lifshitz-Slyozov law. Of course this implies that the wetting film that surrounds domains of  $P_U$  and  $P_V$  is growing at the same rate as the whole structure [5] for long times.

### B. Quenches from multiple phase equilibrium into multiple phase equilibrium.

To study the above mentioned behavior of the wetting layer we quenched the system from a double point at  $kT = 0.164$  to  $kT = 0.13$  with  $c = 0.45$  [see broken arrow in Fig. 1(c)]. The initial state has a planar interface between the phases  $P_U$  and  $P_V$ . After the quench, these phases become unstable and the minority phases start to nucleate so that droplets of  $P_V$  nucleate in phase  $P_U$  and domains of  $P_U$  nucleate in phase  $P_V$ . The other minority phase  $P_W$  wets all the interfaces formed. As seen in Fig. 8(a) a wetting layer, of thickness  $d(t)$ , and a depletion zone, of thickness  $D(t)$ , grows at both sides of the planar interface. In accord with

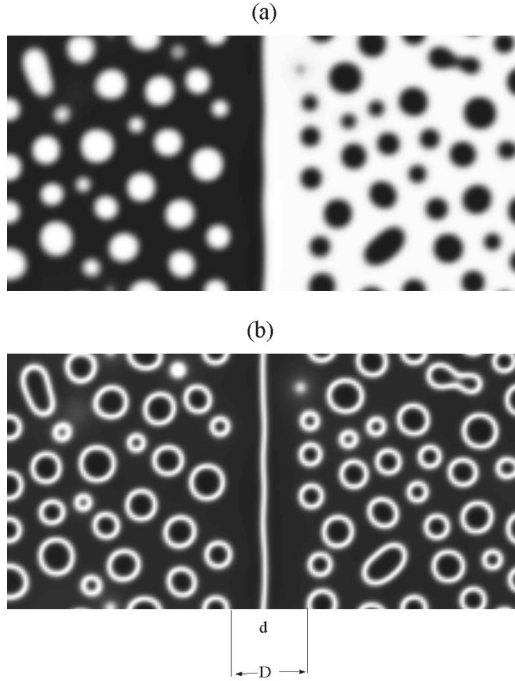


FIG. 8. Two different contrasts of the picture obtained from simulation of the model a system with  $c=0.45$ , at time  $t=3000$  with a time step  $\Delta t=0.125$ . The initial state consists of a planar interface between phases  $P_U$  and  $P_V$  at a temperature  $kT=0.154$  that is quenched to the temperature  $kT=0.13$  that is above the wetting temperature for this mixture.

Puri and Binder [5], since the diffusion from the boundary of the droplets to the wetting boundary is through the depletion zone, the current of component  $U$  at  $z=-d/2$  and at  $z=d/2$  is

$$J_z = \pm \frac{\gamma}{Ddu_w}, \quad (5)$$

where  $\gamma = \gamma_{wU} = \gamma_{wV}$  is the surface tension of the interface between the phase in the wetting layer and the two bulk phases at either side of the interface.  $u_w$  is the concentration of component  $U$  or  $V$  in the  $P_w$  phase. Since the global concentrations of the three components, in the wetting and depletion layers is conserved, we have  $d = 2D(u_U + u_V - 2u_0)/(u_0 - u_w)$ . Here  $u_V$  and  $u_0$  are the concentrations of  $U$  in the  $P_V$  phase and in the initial state, respectively. From this we obtain

$$2J_z = - \frac{2\gamma(u_0 - u_w)}{D^2 u_w (u_U + u_V - 2u_0)}, \quad (6)$$

giving way again to the universal law  $D(t) \propto d(t) \propto t^{1/3}$  for all times.

On the other side of the energy triangle for  $c=0.285$ , we cooled down a different kind of double point into the three-phase region, from a temperature of  $T=0.13$  to  $T=0.08$ . In Fig. 9 we show the values of  $u=v$  along the profile, there, we also show the eigenvalues of the uniform stability matrix had a uniform state acquired those values of  $u$ . Since the

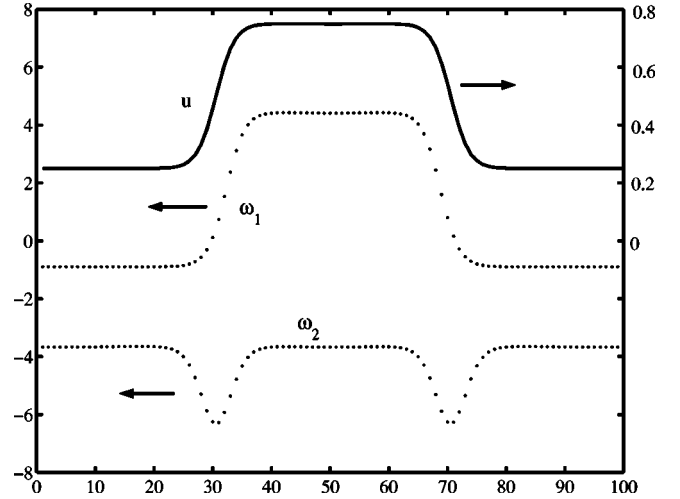


FIG. 9. Concentration profile  $u(r)=v(r)$  for two-phase equilibrium with  $c=0.285$  and  $kT=0.13$ . The dotted lines show the two eigenvalues of the stability matrix for those values of  $u$  along the profile.

most negative eigenvalues lie along the interface, the system that now consists of the interface between two unstable phases, starts to decompose along the interface [see Fig. 10(a)] [11]. At later times droplets of  $P_w$  are formed in a complex matrix of the  $P_U$  and  $P_V$  phases at one side of the original interface and pairs of droplets of the  $P_U$  and  $P_V$  phases form inside the other side of the original interface [see Fig. 10(b)]. Contrary to what Plapp and Gouyet find the interface remains flat because in this case the dihedral angle between the three phases is  $\sim \pi$  when  $P_w$  is the middle phase.

Finally we have cooled a system in a three-phase state,  $P_{U-V}$ ,  $P_U$ , and  $P_V$ , where one of the phases wets the other two into a different three-phase state  $P_w$ ,  $P_U$ , and  $P_V$ , in the partially wetting regime. For  $c=1/3$ , with an initial temperature of  $kT=0.122$  above the four-phase equilibrium temperature, and  $1-w=0.76$  the original concentration profile is shown in Fig. 3(b), upon cooling to  $kT=0.08$  the most unstable phase  $P_{U-V}$  so that alternating stripes of  $P_U$  and  $P_V$  are formed inside this phase. Meanwhile droplets of  $P_U$  grow into the original  $P_V$  phase while droplets of  $P_V$  grow into the original  $P_U$  phase. The original planar interfaces between  $P_U$  or  $P_V$  and  $P_{U-V}$ , has now undulations where there is a profusion of droplets with three equal dihedral angles in this completely symmetric mixture (Fig. 11).

#### IV. CONCLUSIONS

In conclusion it has been demonstrated numerically that in a three component mixture, for a quench deep into the triple point, all length scales grow with time as  $R(t) = R_0 + At^{1/3}$  at late times. The early time behavior is affected by the structure of the spinodals where we found that, in some cases, labyrinthine decomposition with some values of  $A$  and  $R_0$  is followed by decomposition into droplets with some other values of  $A$  and  $R_0$ .

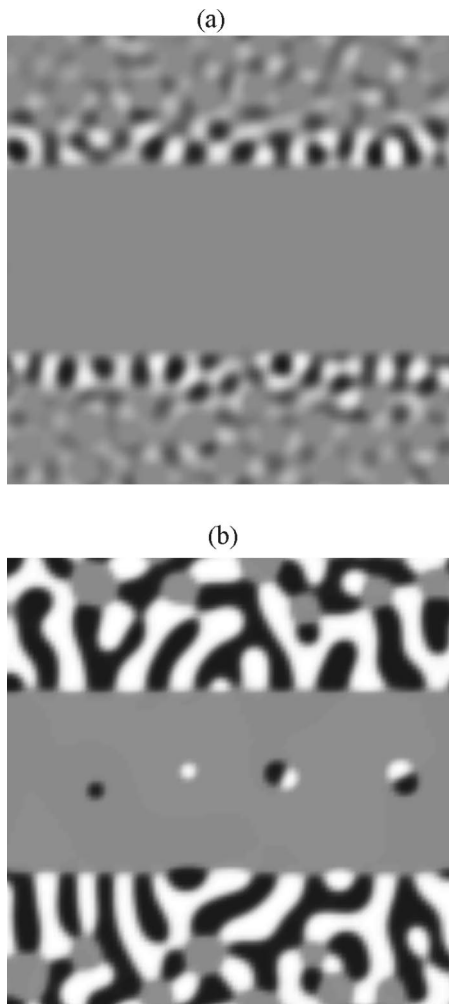


FIG. 10. Evolution of the concentration profile shown in Fig. 9 when the system is quenched to a temperature  $kT=0.08$ . In (a) the early time growth initiated at the surface and in (b) the later stages of the growth.

In these symmetric mixtures one can quench the interface between two phases in equilibrium at high temperature into the three phase region. In Fig. 1 we show two kinds of quenches; one in which the quench is from a double point  $P_W$  in equilibrium with  $P_{U-V}$  where the concentrations of both phases have the property  $u=v$ , and one in which the two phases in equilibrium are  $P_U$  and  $P_V$ . The first corresponds to the case discussed by Gouyet and Plapp [11] where the decomposition of one of the phases starts at the surface

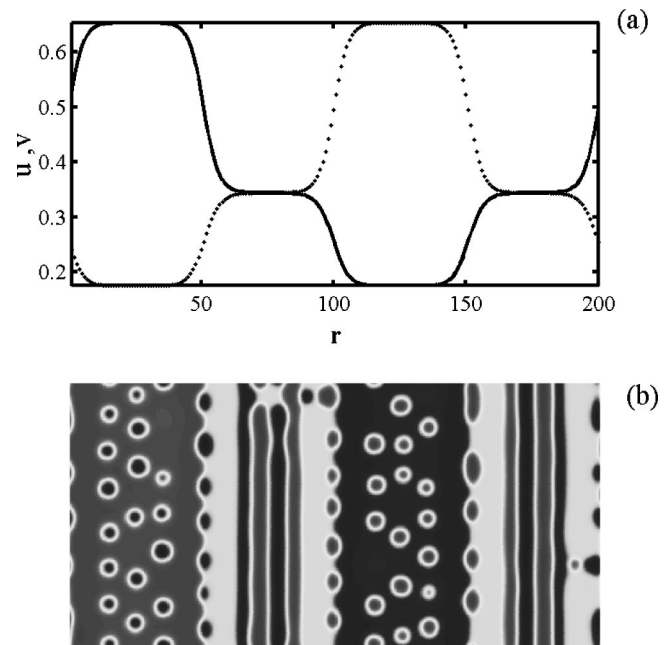


FIG. 11. (a) initial profile at a triple point with  $kT=0.122$  and  $c=1/3$  where the phase  $P_W$  wets the interface between the  $P_U$  and  $P_V$  phases. In (b) we show the evolution of the system after a quench at  $kT=0.08$  and 80,000 iterations.

so that the interface does not remain flat, we were able to track down this behavior to the spinodal properties that mixtures with  $0 < c < 0.346$  have. In the second case two symmetric phases become unstable when the system is cooled into the three-phase region. The interface remains flat when cooled into the three-phase region and we obtain two different behaviors. When below the wetting temperature, droplets of the third-phase  $P_W$  form into the two bulk phases, in the second case (above the wetting transition) droplets of  $P_W$  never form. The growth of the wetting layer at the surface follows the universal growth law at all times even for this model with only short-ranged potentials in contrast with the results of Puri and Binder for wetting at a solid wall. These results are likely to encourage new experiments on the spinodal decomposition in ternary fluids, solids, and polymer solutions.

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