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Percolation inversion in spinodal decomposition of mixtures with strong kinetic asymmetry

D. Sappelt and J. Jäckle*
Faculty of Physics, University of Konstanz, 78434 Konstanz, Germany
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It is shown that spinodal decomposition in thin films of mixtures of liquids of very different viscosity may exhibit an inversion of percolation of the low- or the high-mobility portions of the liquid. The condition is that the initial single phase lies in the low-mobility region. This result is derived from the non-linear Cahn–Hilliard equation with a strongly concentration-dependent mobility. Viscoelastic effects are neglected. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

In spinodal decomposition in thin films of polymer solutions and of polymer blends with components of very different viscosity often a change of morphology corresponding to percolation inversion has been observed[1]. In the early stage of decomposition small droplets of the low-viscosity liquid appear. In the late stage, however, droplets of the high-viscosity liquid of nearly circular shape are found, immersed in a sea of low-viscosity liquid. In the transformation region, as the droplets of the low-viscosity liquid expand, the volume of the high-viscosity portions shrinks to form a ramified network-like structure. Finally, the high-viscosity liquid breaks up into droplets of elongated shape, which become more and more circular at still later times. This process can be characterized as an inversion of percolation in which the role of the percolating majority phase and the non-percolating minority phase is interchanged between the low- and the high-viscosity portions of the liquid.

This peculiar course of phase formation has been ascribed to the effect of viscoelastic stresses occurring in the high-viscosity phase[1-3]. In part, this view is supported by recent theoretical work[4]. For a two-fluid model including viscoelastic stress relaxation in the network-forming fluid[5], patterns were found with a ramified structure of the high-viscosity phase. In the present paper we show how such percolation inversion can also result purely from kinetics if interdiffusion is very slow above a certain threshold of the concentration of the high-viscosity component, and if the following conditions are met: the threshold concentration must be lower than the concentration corresponding to the midpoint of the two-phase region; and the average concentration of the mixture must be chosen to lie in the window between threshold and midpoint concentration. This condition may be fulfilled for blends of polymer liquids of very different viscosity or for polymer solutions. The model for which this effect is studied is the non-linear Cahn–Hilliard equation for two dimensions with a concentration-dependent mobility coefficient modelled accordingly. Any influence of viscoelastic stress relaxation on the decomposition[1,4-6] is neglected. The effect is explained in

the next section. The applicability of the two-dimensional calculation to the decomposition of thin films follows from this explanation.

Model and results

The Cahn–Hilliard equation, after introducing dimensionless variables, can be written

$$\frac{\partial u(\vec{r},t)}{\partial t} = \vec{\nabla}(m(u)\vec{\nabla}(-u+u^3-\Delta u)) \tag{1}$$

where u is the scaled concentration of the high-viscosity component defined as $u = (c - c_0)/(c_0 - c_1)$, where c_0 is the critical concentration and c_1 is the concentration of the coexisting low-viscosity phase. $u = \pm 1$ holds for the coexisting high- and low-viscosity phase, respectively. $m(u)$ is the scaled concentration-dependent mobility coefficient, which is assumed to decrease rapidly with increasing u. For the qualitative treatment given here, we choose the convenient simplifying expression

$$m(u) = (\exp[\alpha(u-u_g)]+1)^{-1}+m_0 \tag{2}$$

We assume that this function near $u = u_g$ drops rapidly from a value of about one, corresponding to the high mobility in the low-viscosity liquid, to a small value $m_0 \ll 1$ at compositions of high viscosity. This is the case for $\alpha \gg 1$ (see *Figure 1*). To obtain percolation inversion in spinodal decomposition, the scaled average concentration $\bar{u}$, which corresponds to the initial single phase of the mixture, must lie in the low-mobility region, i.e.

$$\bar{u} > u_g \tag{3}$$

must hold. As explained below, equation (3) is necessary for the formation of small droplets of low-viscosity liquid, occupying only a small area fraction, in the early stage of decomposition. (Previously[7,8], we treated the opposite case $\bar{u} < u_g$, which models the intervention of a glass transition in spinodal decomposition. We note that equations (1) and (2) also provide a crude model for spinodal decompositon of a mixture which initially is in a thermoreversible, physical gel state. In this case u_g must be identified with the critical concentration for physical gelation. Our treatment by equations (1) and (2) is similar to the limiting case of the model
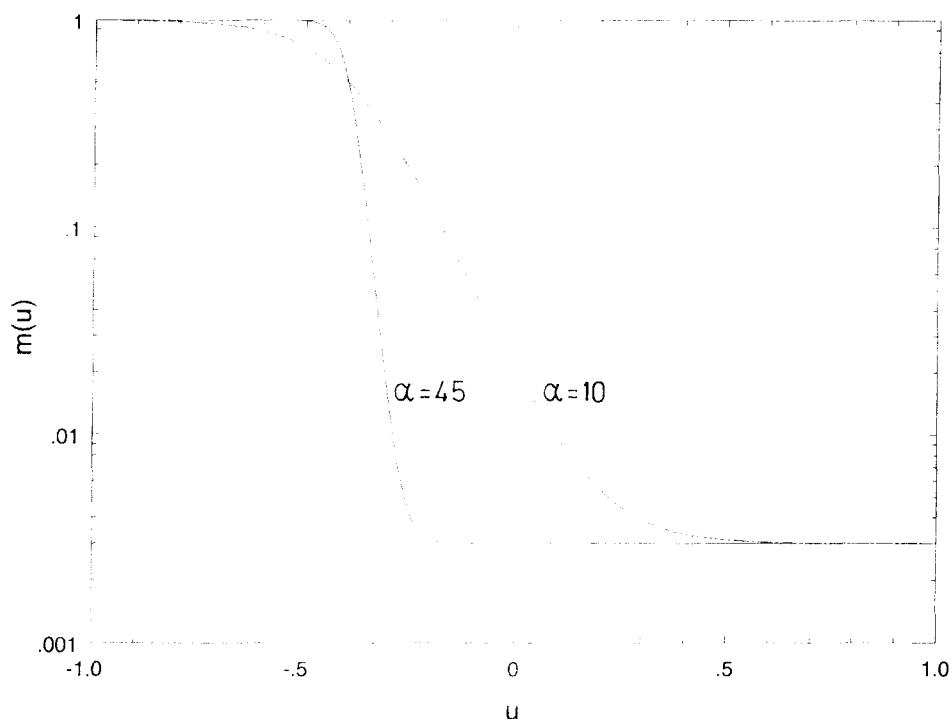
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* To whom correspondence should be addressed

Figure 1 Concentration-dependent mobility $m(u)$, equation (2) for two values of the parameter α used in the numerical solution of equation (1)

of Sciortino *et al.*[9] for the interference of phase separation and gelation, in which the gelation mobility M_c goes to infinity.)

To guarantee the inversion of this initial droplet pattern during the later stages of decomposition, the second condition

$$\ddot{u} < 0 \qquad (4)$$

is required. Equation (4) follows from the fact that in the late stage, when proper thermodynamic phases have been formed, their area fractions are given by $(1 \pm \bar{u})/2$, respectively, according to the lever rule. In two dimensions, the phase with the higher area fraction percolates, while the other phase occurs in isolated droplets. If equation (4) holds, the percolating phase is the low-viscosity phase. These considerations also apply to the decomposition of thin films, since there the late stage of decomposition is two-dimensional. Equations (3) and (4) together imply the condition for the threshold concentration

$$u_g < 0 \qquad (5)$$

We solved equation (1) numerically for two dimensions with an initial condition describing the random thermal concentration fluctuations in the initial mixed state. The technical details can be found elsewhere[8].

Figure 2a–f show the results of the calculation for a typical set of parameters: $u_g = -0.4$, $\bar{u} = -0.3$, $m_0 = 3 \times 10^{-3}$ and $\alpha = 45$. During the early stage of decomposition, first small droplets rich in the low-viscosity liquid, and of nearly circular shape, develop from the initial concentration fluctuations (*Figure 2a*). A necessary condition for the formation of such droplets in the early stage is a rapid drop of the mobility function $m(u)$ with increasing concentration u, as we assumed. If this condition holds, in the early stage concentration fluctuations into the range below the mobility threshold $(u < u_g)$, which occur in regions of small area fraction, progress rapidly towards the equilibrium phase $u \approx -1$ owing to the high mobility. Thereby small droplets

of low-viscosity liquid are formed. This mechanism is effective both in two and three dimensions. Therefore it also applies to the early stage of decomposition in thin films, which is three-dimensional. At later times, as the high-viscosity component is increasingly enriched in regions of decreasing area, and the area fraction of low-viscosity liquid increases accordingly, the portions of high-viscosity liquid assume a ramified channel-like structure (*Figure 2b–f*). At this intermediate stage, pattern formation is governed by two counteracting effects: the effect of surface tension, which tends to smooth out the interfaces; and the shrinking of area of the regions filled with high-viscosity liquid, which tends to make these regions more circular. After very long times the minority phase of high viscosity will finally form circular droplets, thereby completing the inversion of percolation in the concentration pattern. As *Figure 2f* shows, the channels of the high-viscosity phase have a very long lifetime in our calculation. However, in a laboratory experiment we expect the coarsening of the high-viscosity phase to be accelerated by hydrodynamic flow inside the low-viscosity phase, which is not taken into account in our calculation.

Similar results were also obtained for the parameter $\alpha = 10$, for which the mobility, equation (2), decreases more gradually with increasing concentration (dash-dotted curve in *Figure 1*).

Figure 3 shows the probability distribution $P_t(u)$ for the scaled concentration variable u at times $t = 2000$, 4000, 6000 and $20\,000$, which correspond to *Figure 2a, b, c* and *f*. The shift of area from the low-mobility liquid $(u > u_g)$ to the high-mobility liquid $(u < u_g)$ is apparent from this figure.

Discussion

The idea that a strong kinetic asymmetry of two unmixing fluids may lead to a ramified two-phase pattern is not new. Frank and Keller[10] had argued that the intervention of a glass transition in spinodal decomposition may lead to a
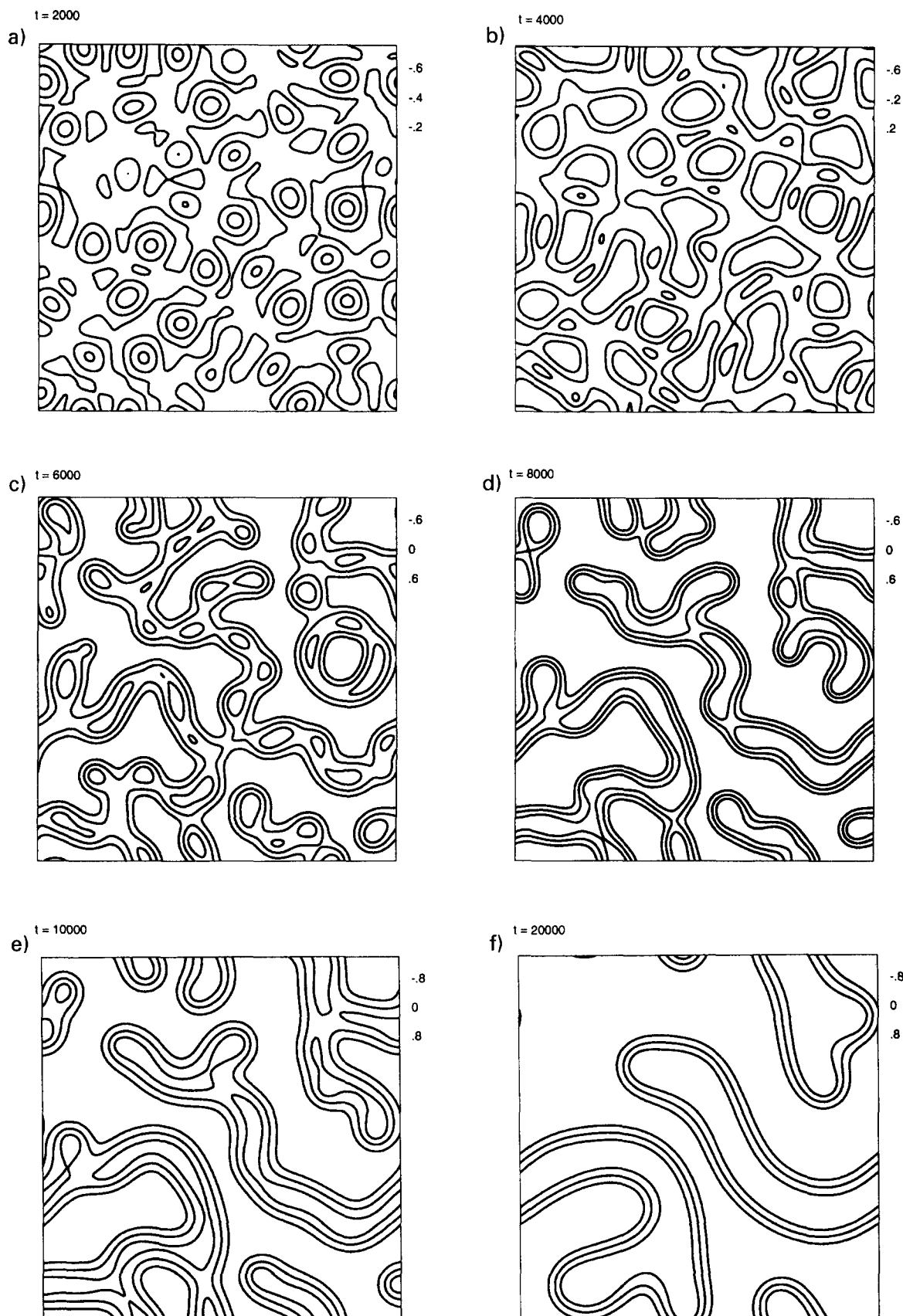
Figure 2 Evolution of concentration field $u(\vec{r},t)$ from numerical solution of equation (1). Drawn are lines of constant concentration at times $t = 2000$, 4000, 6000, 8000, 10 000 and 20 000 (a–f) for the u values noted at each figure. In (a) the nearly circular lines for $u = -0.6$ mark the liquid droplets (see text)
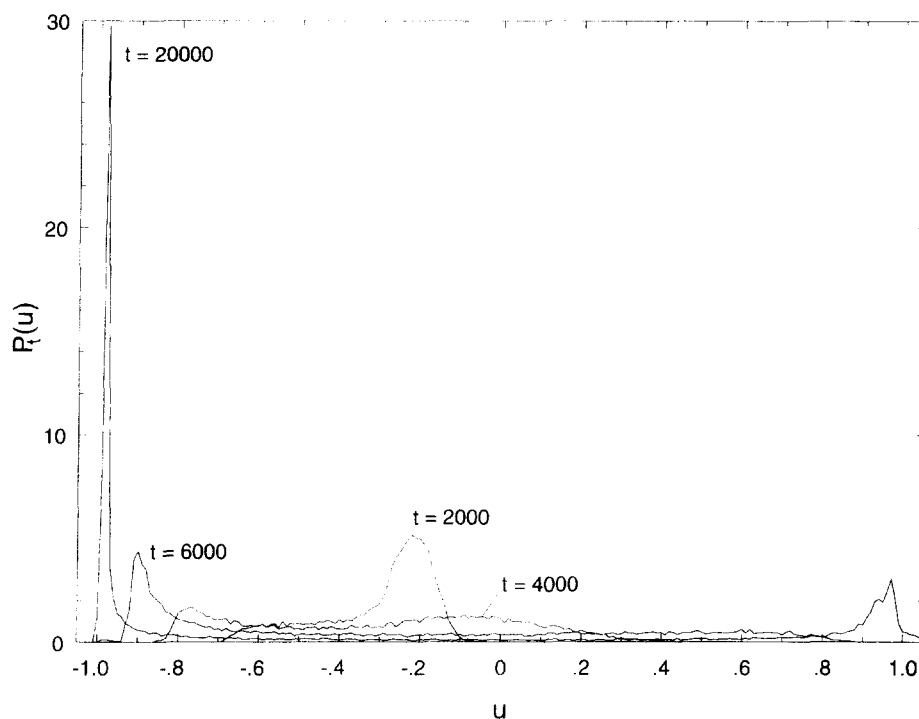
Figure 3   Probability distribution $P_t(u)$ of scaled concentration variable u at four times corresponding to *Figure 2a, b, c* and f

pattern of 'ramified aggregates' containing the glassy phase. This expectation was not borne out by our previous numerical solutions[7,8] of the Cahn–Hilliard equation (equation (1)) with a variable mobility modelling the glass transition as a function of concentration. There we concluded that our treatment lacks 'an ingredient of strong anisotropy', which would be required for a ramified glass structure to form. The results of the present paper show that in two dimensions a ramified structure of the high-viscosity phase may indeed exist for a long intermediate period of time, if the decomposition starts from a concentration in the low-mobility rather than the high-mobility region of the phase diagram. In this case, under the conditions specified above, the decomposition process takes a peculiar course, starting with the formation of small droplets of low-viscosity liquid, the subsequent growth of which forces the high-viscosity liquid into a ramified channel-like structure. We argued that the results of this two-dimensional calculation can be applied to the decomposition of thin liquid films, as studied experimentally[2,3].

The development of a unified treatment of the kinetic effects studied in the present paper and the effects of viscoelastic stresses elaborated previously[1,4] remains a challenge for future theoretical work.

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