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Adiabatic Spinodal Decomposition in Critical Binary Fluids

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ABSTRACT: We discuss early-stage spinodal decomposition in a near-critical binary fluid for a situation in which the system is quenched abruptly by changing the pressure and in which the subsequent phase separation occurs adiabatically. The resulting nonequilibrium situation has features that do not fit conventional theoretical assumptions. We find that changes in the effective temperature during the transition can account for the lack of agreement between earlier theories and recent experimental results of Bailey and Cannell.

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In a recent paper, Bailey and Cannell[1] (BC) have reported precise light-scattering measurements of early-stage spinodal decomposition in a near-critical mixture of 3-methylpentane and nitroethane ($3MP + NE$). Their experiment is, to our knowledge, the first fully quantitative observation of phase separation in a thermodynamically unstable state of a system for which all of the relevant properties and all of the control parameters are independently determined. Thus, their results provide a rigorous test for nonequilibrium theories of a kind that ultimately will be needed for reliable simulations of materials processes.

Although the BC experiments are uniquely well characterized, they are carried out in a way that is not consistent in some respects with conventional theoretical assumptions about the spinodal process. The most important of these differences is that BC quench their system into the unstable state by abruptly changing the pressure, not the temperature, and the subsequent unmixing of the two phases takes place very nearly adiabatically rather than isothermally. This procedure forces the theorist to face an unexpectedly fundamental question, specifically: What does one mean by "temperature" when a system is driven so far from equilibrium? Our purpose in this letter is to outline briefly our answer to this and some related questions, and to report that our calculations, with no adjustable parameters, are in excellent agreement with the experimental data. An account of this work may be found in Ref.(2); a complete report is being prepared for publication.

Our analysis is based on the theory of Langer, Bar-on, and Miller[3] (LBM) for the onset of isothermal spinodal decomposition in an Ising-like system with a conserved order parameter. This theory was designed to describe phase separation up to the point where the reaction has gone most of the way to completion but the characteristic length scale of the separation pattern is not yet very much larger than the correlation lengths ξ in the separated phases. LBM starts with a Cahn-Hilliard equation of the form[4]

$$\frac{\partial u}{\partial t} = M\nabla^2 \frac{\delta \mathcal{F}}{\delta u} + \text{thermal noise} \tag{1}$$

where $u(\mathbf{r},t)$ is the local deviation from the average concentration of one of the chemical constituents, M is a transport coefficient related to the diffusion constant, and

$$\mathcal{F}\{u\} = \int d\mathbf{r} \left[\frac{K}{2}(\nabla u)^2 + f(u)\right]. \tag{2}$$

Here, the gradient-energy coefficient K and the free-energy density $f(u)$ are quantities that can be determined from the equilibrium properties of the system. The function $f(u)$ also depends on temperature T and pressure P. For T and P such that the equilibrium state of the system is the uniformly mixed phase, $f(u)$ has a single minimum near $u = 0$. Unmixing occurs when $f(u)$ develops two minima at nonzero values of u.

It is very important for present purposes to note that u is a coarse-grained variable and $\mathcal{F}$ is a coarse-grained free energy. That is, u is a smooth function of position $\mathbf{r}$ that contains no Fourier components with wavenumbers k greater than some cutoff Λ, which we take to be of order ξ^{-1}; and the parameters in $\mathcal{F}$ have been renormalized by integrating over the rapidly equilibrating modes with $k > \Lambda$. We shall return to this point.

The process of interest here is one in which the most probable values of u are initially near zero in the unstable state but move toward the two minima of $f(u)$ as phase separation occurs. Eq.(1) is formally equivalent to a Fokker-Planck equation for a probability distribution in the space of functions $u(\mathbf{r})$; and this equation, in turn, is equivalent to a hierarchy of equations of motion for multi-point distribution functions of the form $P_N(u_1, u_2, ...u_N, t)$, where the symbols u_n denote values of u at points $\mathbf{r}_n$. The central feature of the LBM method is a simple truncation of this hierarchy that avoids the assumption, implicit in most low-order perturbation theories, that the distribution over values of u remains peaked near zero. Specifically, LBM assume that the time-dependent, two-point probability distribution function $P_2(u_1, u_2, t)$ can be written in terms of the one-point function $P_1(u,t)$ via the ansatz:

$$P_2(u_1, u_2) \approx P_1(u_1)P_1(u_2)\left[1 + \frac{u_1 u_2}{\langle u^2\rangle^2} S(|\mathbf{r}_1 - \mathbf{r}_2|)\right]. \tag{3}$$

Because $\langle u\rangle = 0$ by definition, it is easy to see that the function S in (3) is the two-point, equal-time correlation function $\langle u_1 u_2\rangle$ whose Fourier transform, $\hat{S}(k,t)$, is the structure factor that is measured in scattering experiments.

The ansatz (3) leads to an equation of motion for the structure factor that looks almost the same as the equation that one obtains by the most elementary linearization of the theory:

$$\frac{\partial \hat{S}(k,t)}{\partial t} = -2\,M\,k^2\left[\left(K\,k^2 + A(t)\right)\hat{S}(k,t) - k_B T\right]. \tag{4}$$

The only nonlinear feature of (4) is the time-dependent chemical potential $A(t)$, which is the statistical average of a one-point function:

$$A(t) = \frac{1}{\langle u^2\rangle}\langle u \frac{\partial f}{\partial u}\rangle, \tag{5}$$

and which therefore requires only a knowledge of $P_1(u,t)$ for its evaluation. Deriving an equation of motion for P_1 requires more work but no new assumptions; one simply uses (3) in the first of the hierarchy of equations of motion for the multi-point distribution functions. The result, which we shall not display here, looks as if the distribution P_1 is diffusing in a self-consistent time-dependent potential that, as expected, causes the initial peak in P at $u = 0$ to split into two peaks that signal the onset of phase separation.

The LBM theory originally was tested[3] against numerical simulations of the Ising model with Kawasaki spin-exchange kinetics. It also has been used in the analysis of X-ray and neutron scattering measurements of phase separation in alloys.[5] In order to apply the theory to fluids, however, one must include hydrodynamic degrees of freedom via a procedure introduced by Kawasaki and Ohta [6] (KO).

Because the length scales of interest here are very small, we need to consider only advection of the concentration gradient by overdamped viscous flow which, in turn, is driven by the same chemical-potential gradient that appears on the right-hand side of (1).

Accordingly, KO add to the right-hand side of (1) a term of the form

$$-2\int d\mathbf{r}'\,\nabla u(\mathbf{r})\cdot\mathbf{T}(\mathbf{r}-\mathbf{r}')\cdot\nabla' u(\mathbf{r}')\frac{\delta\mathcal{F}}{\delta u(\mathbf{r}')} \tag{6}$$

where $\mathbf{T}$ is the Oseen tensor whose components are

$$T_{\alpha\beta}=\frac{1}{8\pi\eta r}\left(\delta_{\alpha\beta}+\frac{r_\alpha r_\beta}{r^2}\right) \tag{7}$$

and η is the shear viscosity. When the LBM ansatz (3) is used in connection with this modified Cahn-Hilliard equation, the new equation of motion for the structure factor $\hat{S}(k)$ differs from (4) in two respects: the transport coefficient M is renormalized to include the hydrodynamic effects, and an additional term containing the Oseen tensor appears on the right-hand side.

For present purposes, we need not display these equations in detail, but we do need to be clear about one technical point. The quantity $A(t)$ in the hydrodynamic version of (4) is still defined by (5), but the distribution functions $P_1(u)$ implicit in that definition should be recomputed so as to be consistent with the changes in $\hat{S}(k)$ generated by the hydrodynamic forces. In their original paper, KO neglected this modification and simply took the function $A(t)$ from LBM[3]. It later was pointed out in an unpublished paper by A.J. Schwartz that the results of a fully self-consistent calculation are quantitatively different from those of KO. In collaboration with Bailey and Cannell, we have repeated and confirmed Schwartz's results. In what follows, we shall refer only to the self-consistent version of the theory.

The conclusion reached by BC, shown clearly in their Fig.3, is that their experimental data are in substantial disagreement with the KO theory, and that the self-consistent correction — if anything — makes the situation worse. We propose that the principal reason for this discrepancy is the assumption, implicit in the LBM and KO analyses, that the phase transformation takes place isothermally rather than adiabatically as is appropriate for the BC experiments.

Our adiabatic version of the LBM/KO theory is based on the following assumptions. We visualize the binary fluid as consisting of two distinct subsystems: (1) the relatively slow, coarse-grained modes described by the order parameter $u(\mathbf{r},t)$, whose behavior describes the phase separation, and (2) the rapidly equilibrating short-wavelength modes that we have integrated out of the equations of motion for $u(\mathbf{r},t)$, which serve as a thermal reservoir in contact with the slow modes. We assume that these subsystems, together, are thermally isolated from the outside world during the time in which measurements are being made. We further assume that the reservoir of fast modes effectively dominates the thermodynamic properties of the system as a whole. Because the reservoir equilibrates rapidly compared to any other changes in the system, it makes sense to talk about a reservoir temperature T_r, and we assume that T_r is the same as the temperature T that determines values of the parameters in the coarse-grained free energy $\mathcal{F}\{u\}$. Moreover, we assume that this coupling via T is the *only* explicit coupling between the reservoir and the coarse-grained modes.

In our picture of the adiabatic spinodal process, the initial pressure quench removes energy from the reservoir, thus lowering its temperature. The coarse-grained configuration remains unchanged at this instant. (The effects of the small change in the volume of the system are negligible.) The coarse-grained modes now see a lower temperature and, because they have fallen out of equilibrium, begin to undergo phase separation. During this process, they release energy which, according to our adiabatic assumption, can be absorbed only by the reservoir. Thus the system experiences what is known in the metallurgical literature as "recalescence"; the temperature rises and, as that happens, the kinetics of the phase transformation are modified.

These processes can be summarized by an equation of motion for the temperature T:

$$C_{pr}\frac{dT}{dt}=VT\alpha_{pr}\frac{dP}{dt}-\frac{\partial\langle\mathcal{E}\{u\}\rangle}{\partial t}, \tag{8}$$

where V is the volume and

$$\langle \mathcal{E}\{u\}\rangle = -\langle T^2 \left(\frac{\partial \mathcal{F}\{u\}/T}{\partial T}\right)_V \rangle \tag{9}$$

is the internal energy of the coarse-grained system computed using the time-dependent probability distributions obtained from the LBM ansatz.

The quantities α_{pr} and C_{pr} in (8) are, respectively, the isobaric thermal expansion coefficient and heat capacity for the reservoir, which must be computed by subtracting the singular contributions of the slow modes from the equilibrium values of these quantities in the critical region. In this connection, it is important to recognize the importance of the choice of the cutoff wave number Λ in these calculations. In principle, Λ is an artificial parameter that should cancel out of the final expressions for physically meaningful quantities. In fact, however, our choice of Λ is constrained by practical considerations. On the one hand, we need to choose Λ large enough so that what we call the "fast modes" do indeed equilibrate rapidly on the time scales that are of direct interest to us in specific experiments. On the other hand, we need to choose as small as possible a value of Λ so that essentially all of the thermodynamically important degrees of freedom are included in the reservoir, that is, so that we can easily determine the parameters in $\mathcal{F}$ by equilibrium measurements.

For example, the BC experiments are carried out by first allowing the system to come to equilibrium in a state just outside the two-phase region and then quenching abruptly to a state inside that region. Associated with each temperature T as the system undergoes decomposition are correlation lengths ξ and associated (T-dependent) relaxation times of order $\tau_T = 6\pi\eta\xi^3/k_BT$. Choosing Λ^{-1} to be less than but roughly comparable to the smallest of the ξ's assures both that the reservoir modes are "fast" and that the coarse-grained modes contain only just as many degrees of freedom as are necessary to describe patterns of phase separation. We also know that the coarse-grained modes with $k < \Lambda$

are too slow to undergo critical fluctuations at any stage of this experimental process, and thus we can formulate a self-consistent procedure for eliminating the critical singularities in computing α_{pr} and C_{pr}.

Eq.(8) simply expresses energy balance within the thermally isolated experimental sample. The first term on the right-hand side is the work done during the pressure quench, which is negative and therefore produces the initial drop in temperature. The partial pressure of the coarse-grained subsystem is negligible, thus the partial pressure of the reservoir is the same as P and remains constant throughout the later stages of the process. The second term is the contribution from the (decreasing) internal energy of the coarse-grained modes; it is this term that drives recalescence. The combination of (8) with the ingredients of the LBM/KO theory described in the preceding paragraphs produces a set of coupled nonlinear equations that is complicated but well suited to numerical integration.

To demonstrate the results of the adiabatic theory, we use equilibrium data for $3MP+NE^7$ and adopt the same experimental conditions as those used by BC.[1] We assume that all BC quenches were critical, that is, we set the average concentration to be the critical concentration. We introduce no adjustable parameters.

In Fig.1, we plot $\epsilon/|\epsilon_f|$ ($\epsilon \equiv (T-T_c)/T_c$) as a function of the reduced time $\tau = t/\tau_f$. Here, the subscript f denotes parameters evaluated in the final equilibrium state after the quench, and the subscript i denotes the initial state. For the quenches shown, $\epsilon_i/\epsilon_f = -5$, and $T_c\epsilon_f = -0.04$ mK, -0.4 mK, and -4.0 mK. We have set the scaled quench time τ_{quench} to be .01; thus the initial temperature drop does not appear on the graph. Clearly, the temperature undershoot is large; the temperature reached immediately after the quench is roughly $-2|\epsilon_f|$, with the smaller final temperatures giving the greater undershoot. Note also that there is not much difference in the scaled temperature trajectories even though the final unscaled temperatures differ by a factor of 100.

In Figure 2, we compare results of the adiabatic and isothermal theories with the

experimental data. Here we show the scaled structure factor $\tilde{S}(l) = \hat{S}(k)/\chi_f$ as a function of scaled wavevector $l = k/\xi_f$ for various times τ. The normalization factor χ_f is the susceptibility at $\epsilon = \epsilon_f$. The quenches shown all begin at $T_c\epsilon_i = 10$ mK and have final temperatures which range from $T_c\epsilon_f = -0.116$ mK to -10.37 mK. The solid and dashed curves denote results for the adiabatic and isothermal theories, respectively. For each time, the uppermost curve denotes the result for the deepest quench shown and the lower one denotes the shallowest. The effect of a finite quench time is included in these results; the scaled quench time τ_{quench} ranges from 2×10^{-3} for the shallowest quench to 11 for the deepest.

While lagging behind the data at early times, the adiabatic theory gives results for $\tilde{S}(l)$ which agree quite well with the data for times $\tau \simeq 20$ up to the largest time for which data is available, $\tau = 100$. A possible explanation for the lack of agreement at early times is that the actual temperature might have been farther below ϵ_f than predicted. Nonetheless, this good agreement is evidence that the temperature change during decomposition can be large for this class of systems. We conclude that, when modified to reflect actual experimental conditions, the LBM/KO theories of early stage spinodal decomposition can decribe experiment.

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FIGURE CAPTIONS

Fig.1. Scaled temperature $\epsilon/|\epsilon_f|$ as a function of scaled time τ for three adiabatic runs. The final temperatures are indicated in the figure and the initial temperatures are $\epsilon_i = 5|\epsilon_f|$. The straight line denotes the final equilibrium temperature.

Fig. 2. Scaled structure factor $\tilde{S}(l)$ as a function of scaled wavevector $l = k\xi_f$ at scaled times $\tau = 1, 5, 20, 50$ and 100. The initial temperature for all quenches was $T_c\epsilon_i = 10$ mK. The symbols denote the experimental results of Bailey and Cannell as follows: $T_c\epsilon_f =$ ($\triangle$) -0.116 mK, ($\bigcirc$) -0.219 mK, ($\square$) -0.538 mK, ($\times$) -1.036 mK, 2.079 mK, ($\bigcirc$) -2.079 mK, (∇) -5.156 mK, and ($\diamond$) -10.37 mK. The solid and dashed curves denote results of the adiabatic and isothermal theories, respectively. For each time, the upper curve denotes results for the deepest quench shown in that time frame, while the lower one is for the shallowest.