Late stages of spinodal decomposition in binary mixtures

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The influence of hydrodynamic interactions on the coarsening rate r of a mist of droplets combining through diffusive coalescence is examined in detail. For a sufficiently rarified mist, the competing Lifshitz-Slyozov or evaporation-condensation mechanism is dominant, but the volume fraction of precipitate actually produced in most off-critical quench experiments probably favors direct coalescence. When the minority phase is continuous, as in a quench at the critical concentration, surface-tension effects lead to a crossover from $r \sim t^{1/3}$ to $r \sim t$, where t is the time.

I. INTRODUCTION

Spinodal decomposition is the process through which a thermodynamically unstable system separates into its components which can be either two phases of the same chemical species or phases of different composition. Cahn and Hilliard were the first to study this process in metallurgical systems.[1] The term nucleation is generally reserved for the decay of a metastable state, though the subsequent agglutination and organization of new phases, so produced, may be included under the rubric of spinodal decomposition. Phase separation is clearly a nonequilibrium and, except in its very, and possibly, unattainable stages, highly nonlinear phenomenon.

In this paper a number of new modes for phase separation unique to fluid systems are developed that typically will manifest themselves in the so-called later stages of spinodal decomposition. In addition, we collect all theoretical results, pertinent to "long" times and fluids and evaluate them with parameters appropriate for the two most widely studied systems. A number of critical parameters and regimes are isolated whose existence has been overlooked in the experimental literature.

Fluid systems are in certain respects more suitable for phase-separation studies then metallurgical ones when common physical processes occur and in addition, exhibit mechanisms inaccessible to solid systems.[1,2] Lattice mismatch and the concomitant strain effects, absent in fluids, are an additional complication that is seldom included in theories that treat the nonlinearities seriously. Time scales are very short in fluids and it is only by working near a critical point that interesting effects will occur over times of seconds to minutes. The quench process itself then frequently becomes by comparison instantaneous with consequent simplifications in the theory. Fluid mixtures possess a clear advantage over the well-

characterized liquid-gas systems near their respective critical points because the characteristic time; ξ^2/D, where ξ is a correlation length and D a diffusion constant or thermal diffusivity, is approximately 100 times longer in mixtures.[3] The smaller viscosity in the common liquid-gas systems is responsible.

Working near a critical point has other advantages. The correlation length greatly exceeds atomic scales and phenomenological free energies as well as hydrodynamics are frequently applicable. Certain material parameters change rapidly near T_c and varying the temperature is often the simplest and best controlled way to enhance one mechanism over another.

Most existing theories applicable to the early stages of spinodal decomposition begin with a phenomenological equation for a conserved Ising-like order parameter that is transferred diffusively in response to the gradient in the local chemical potential.[4,5] The chemical potential is written as the order-parameter derivative of a Ginzburg-Landau free energy. The stage or degree of evolution is expressed most naturally in terms of the wave number k_m at which the structure function $S(k, t)$ is a maximum. This characteristic wave number decreases monotonically with time and "early" times are typically those for which

$$0.1 < k_m \xi \lesssim 1.0. \tag{1.1}$$

The correlation length is defined in terms of the difference of the thermodynamic critical temperature T_c and a reservoir temperature that in most cases is spatially uniform and time independent. Binary mixtures near their critical point again possess an advantage over a single component system in that the thermal conductivity of the mixtures remains finite while near the liquid-gas transition it goes to zero.[6]

The upper bound on $k_m \xi$ in (1.1) merits comment since it excludes the earliest times. It is imposed in part because nonlinearities are treated within

a Ginzburg-Landau theory with critical fluctuations integrated out and incorporated into coefficients which generally assume their physical values. A gradient expansion of nonlocal terms should also converge for $k\xi < 1.0$.

The dynamics of a critical fluid are more complicated than kinetic Ising models because the velocity fluctuations strongly renormalize the transport coefficients.[6] If one attempted to model a fluid for $k_m\xi > 1.0$ out of equilibrium, it is not obvious what fluctuations enter the transport coefficients. It is also not obvious that the linear response hydrodynamic assumption that the current is the gradient of the local chemical potential retains any validity.[7,8] Might not the coefficient depend on the local order parameter for instance?

The Ginzburg-Landau equations together with hydrodynamics will hold for $k\xi$ arbitrarily small but become cumbersome and overly detailed when well defined regions of nearly equilibrium concentrations are established. The only quantitative theory for the early stages is due to Langer and co-workers.[4,5] For quenches at the critical concentration (or for zero net magnetization), they find that an order-parameter distribution that was spatially uniform at $k_m\xi = 1$ breaks down into a two peaked structure by $k_m\xi \sim 0.3$ with concentrations approaching their equilibrium values. Quenches with nonzero average magnetization evolve more slowly. Unfortunately, Langer's approximations fail around $k_m\xi \sim 0.3$ which is symptomatic of the theory's failure to approach the thermodynamically correct equilibrium and to describe the mixture when the domain size is very different from the interfacial thickness. It seems safe to assume that by $k_m\xi \sim 0.1$, i.e., the putative division between early and late stages, that the material consists of well defined patches in which the average order parameter is near its equilibrium value. Theories for the "late stages" of coarsening can work in terms of two distinct phases separated by sharp interfaces.

Kawasaki and Ohta have grafted the conventional mode coupling diagrams for a fluid onto the Ginzburg-Landau results of Ref. 5.[9] The velocity fluctuations are assumed to be Gaussian and in equilibrium. Apart from the limitations on this theory inherent in its application of Ref. 5, mode coupling will not correctly describe the hydrodynamic interactions between well defined regions of different phase on a scale k_m^{-1}.

Binder, whose intent was principally to understand the numerical experiments on kinetic Ising models,[10] has adopted a more microscopic starting point than Ginzburg-Landau theory.[11,12] By means of "cluster dynamics" he arrives at results for $k_m\xi \gg 1$ as well as for the early stages during which existing Ginzburg-Landau calculations would apply. In addition, he recovers the Lifshitz-Slyozov theory for long times. Many of Binder's published results follow from scaling and matching asymptotic forms.[11] For orientation, we estimate the duration of the early stages of spinodal decomposition in a binary fluid quenched through its critical temperature at its critical concentration. At room temperature, where all experimental work to date has been performed, the temperature can be controlled to about a mK leading to a reduced temperature ϵ of 3×10^{-6}. The characteristic time ξ^2/D is then 0.2 sec and at 3 mK from T_c it falls to 0.02 sec. The theories of Langer, Bar-on, and Miller and Kawasaki-Ohta work at best out to 100 times ξ^2/D.[5,9] Clearly, the regime $0.1 < k_m\xi < 1.0$ is difficult to attain and of limited duration. By contrast, the later stages of spinodal decomposition are accessible over a much wider range of conditions; and with a microscope, useful observations can be made out to times of an hour for certain parameters.

These characteristic times also necessitate rapid quench rates if the early stages are to be seen at all. The thermal response time of a mm^3 sample of the common binary fluid systems is ~10 sec independent of temperature near T_c. Simply immersing the sample in a bath will not suffice. Two techniques for a truly rapid quench have been developed. The first used by Wong and Knobler exploits a sudden change in pressure to raise T_c while keeping the actual temperature constant.[13] The second method, devised by Goldburg and collaborators, uses microwave radiation to uniformly heat a mixture, with an inverted phase diagram, into the spinodal region.[14,15]

It is convenient to classify experiments as critical or off-critical though the boundary between the two is not sharp. The former are quenches at the critical composition and lead to a 50-50 mixture of the two phases. Hydrodynamic effects are important here and we will argue that they are driven in succession by surface tension and gravity. Off-critical quenches begin with a system on the coexistence curve, removed an amount ΔT_i from T_c, and "cool" it through the nucleation or cloud temperature to a final temperature ΔT_f measured from T_c. Figure 1 illustrates our notation. For $\Delta T_f \gg \Delta T_i$ the composition ratio in the off critical quenches approaches one but in current experiments the minority phase ranges from about 2% to 20% of the total. At the lower end of this composition range, Lifshitz-Slyozov[16] (evaporation-condensation) and direct droplet recombination are of equal importance with the latter dominating in more concentrated mixtures. Experiment and theory agree regarding exponent and
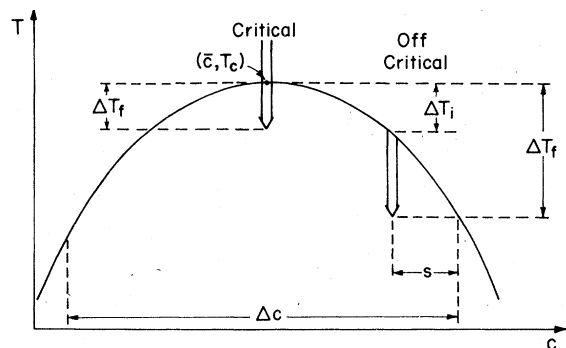
FIG. 1. Schematic plot of the temperature concentration plane for a binary mixture to illustrate our notation.

prefactor except where there is reason to believe initial transients have not relaxed.

In outline then, Sec. II contains an account of the influence of hydrodynamic interactions on droplet coalescence followed by an evaluation of the Lifshitz-Slyozov theory with parameters appropriate to the commonly studied binary mixtures. The Lifshitz-Slyozov mechanism is also shown to be resistent to a number of potential hydrodynamic instabilities. Our treatment of the hydrodynamic effects observed in critical quenches is at the level of dimensional analysis, but it does isolate several relevent parameters that had not been fully appreciated. The third section concludes with a synopsis of the experimental literature and a comparison with theory. Included is a partial explanation of the time dependence of the shape and magnitude of the k-dependent scattering intensity for off-critical quenches.

The picture that emerges, then, is a growth law $k_m^{-1} \sim t^{1/3}$ with a calculable coefficient throughout the late stages when the minority phase is sufficiently rarified that internal flow is impossible. Droplet coalescence, even with hydrodynamic interactions included, leads to more rapid growth than Lifshitz-Slyozov except for very dilute mixtures. For more nearly 50-50 mixtures, k_m^{-1} goes from approximately $t^{1/3}$ to t at a temperature-dependent length set by the surface tension. This length can logically be no less than ~10ξ since well defined interfaces are required for surface tension flow. Our crude theory, which is purely dynamical. does not require it to be any larger than 10ξ. The $t^{1/3}$ regime then properly falls into what we have called the "early stages" where Ginzburg-Landau theory is required,[5,9] though a naive application of our formulas for droplet coalescence[11,12] gives $t^{1/3}$ and a reasonable coefficient. The coarsening rate accelerates further at a second crossover determined by the acceleration due to gravity and the density difference of the two coexisting phases.

II. THEORY

A. System parameters

We will frequently refer to the data in Table I to screen by simple scaling or dimensional arguments some of the myriad of effects possible in a multiphase nonequilibrium fluid. Whever possible, quantities measured for either the isobutyric-acid-water (I-W) system or the 2-6-lutidine-water (L-W) system with its inverted coexistence curve are cited. (We will designate the one-phase region in either system by "$T > T_c$" and the two phase region by "$T < T_c$.") Most of the tabulated properties differ by no more than a factor of 2 among binary mixtures with a room-temperature critical point.

The $T > T_c$ correlation length for L-W, tabulated in Swinney and Henry,[3] was divided by 2 when used below T_c.[17] The surface tension is close to $k_B T_c \xi^{-2}$. The actual prefactor for σ as well as for Δc was taken from measurements on the cyclohexane-methanol system with $T_c = 45$ °C.[18] The density contrast between the two coexisting phases has been tabulated separately for L-W and I-W.[19]

TABLE I. Characteristic parameters in binary fluids near T_c [cgs units, $\epsilon = (1 - T/T_c)$].

Correlation length	ξ	$1.0 \times 10^{-8}\epsilon^{-0.62}$	Kinematic viscosity	ν	0.024	
Surface tension	σ	$100\epsilon^{1.23}$	Thermal diffusivity	κ	10^{-3}	
Normalized concentration difference	$\dfrac{\Delta c}{\bar{c}}$	$2\epsilon^{1/3}$	Diffusion constant	D	$6.0 \times 10^{-6}\epsilon^{0.55}$	
Density difference	$\Delta\rho$					
I-W		$0.053\epsilon^{0.31}$				
L-W		$0.11\epsilon^{0.33}$				

The difference between the two systems stems from the different densities at T_c of 2,6-lutidine, 0.91; and isobutyric acid, 0.95. Both mixtures are ~66% water by weight. We will occasionally need other experimental numbers such as $(\partial c/\partial \mu)|_{T,P}$, in what follows. Fortunately they always occur in combinations predicted by the renormalization group to be universal. We are therefore able to exploit the well-known correspondence between the liquid-gas and binary fluid transitions and utilize the rather accurately known Xe data collected in Ref. 20.

Among the dynamic parameters, the kinematic viscosity varies by no more than 15% from $\epsilon = 10^{-3}$ to 2×10^{-5} and its temperature dependence may be safely ignored.[21] Similarly the thermal diffusivity was estimated from room-temperature measurements on pure lutidine and water.[22] The measured diffusion constant does not appear to satisfy the scaling relation $D\nu = k_B T/(5\pi\rho\xi)$ for $T > T_c$, but even at $\epsilon = 10^{-5}, \epsilon^{0.544}\xi \sim 2.$[6] The prefactor measured in Ref. 21 above T_c was multiplied by 2 to account for the smaller correlation length below T_c. We have used the measured exponent in numerical estimates except when ξ remains variable in which case the "correct" exponent is used. Note that $k_B T_c/5\pi\rho\nu\xi_0 = 1.1 \times 10^{-5}$.

B. Droplet coalescence

It is well known that the diffusion constant of a spherical drop of one fluid in another of similar viscosity is

$$D = k_B T/5\pi\rho\nu a , \qquad (2.1)$$

where a is the radius.[23] Smoluchowski was the first to calculate the recombination rate of a dilute mist of drops moving purely diffusively. Consider a drop of radius a, fixed at the origin in a uniform cloud containing n_2 drops per volume of radius a_2. Drops that just touch should be pulled together very quickly, in comparison to a diffusion time τ_D by surface tension. The fusion time τ_σ can be estimated from $\nabla p/\rho \sim \nu\nabla^2 v$, with $p \sim \sigma/l$ and $l \sim \min(a_1, a_2)$. One finds

$$\tau_\sigma \sim \rho\nu l/\sigma \sim 10^{-2} \text{ sec} \ll ,$$

$$\tau_D \sim l^2/D \sim 1 \text{ sec}$$

for $\epsilon = 10^{-5}$ and $l = 1$ μm. Further from the critical point τ_σ/τ_D will be smaller still.

For $t \gg \tau_D$ a depletion layer will be established about the drop at the origin and the radial distribution of the drops follows from a solution of $\nabla^2 n_2 = 0$ with the boundary condition $n_2 = 0$ at $r = a_1 + a_2$. The number of collisions per time I follows from an integral of the particle flux over the surface $r = a_1 + a_2$ ($D_2 = D$ for $a = a_2$),

$$I = 4\pi(a_1 + a_2)D_2 n_2 . \qquad (2.2)$$

In reality, the drop at the origin is free to move and if we imagine n_1 drops of radius a_1 and diffusion constant D_1 the number of collisions between the two populations per time per volume is

$$I_{1,2} = 4\pi(a_1 + a_2)(D_1 + D_2)n_1 n_2 . \qquad (2.3)$$

The radius of the new drops a_3 is of course $a_3^3 = a_1^3 + a_2^3$.

If one assumes that a population of drops agglutinating at a rate given by (2.3) approaches a stationary distribution when scaled by the average radius a the time dependence of a follows from

$$\frac{dn}{dt} = -16\pi Dan^2 . \qquad (2.4)$$

Now (Da) is independent of time and we find

$$a^3 = 12(Da)v(t + t_0) = 1 \times 10^{-12}v(t + t_0) \text{ cm}^3 , \qquad (2.5)$$

where $v \leqslant s/\Delta c$ (see Fig. 1), is the volume fraction occupied by the drops, and t_0 can be found from the initial drop size.

The argument just given has neglected hydrodynamic interactions between the drops. That is, in order for two drops to merge, the suspending fluid in between must be squeezed out. The relative diffusion constant will be smaller than the one used above and depend on the separation between the drops.

The motion of two hard spheres in a fluid has been thoroughly studied, and we will be able to carry over these results to the droplet problem.[24,25] The application is not a trivial one since near T_c the surface tension is small and the drops undergo some distortion upon approach. In addition, circulations inside the drops can be set up. Consideration of both effects will show that droplet coalescence can proceed no more slowly than it would for hard spheres and of course no more rapidly than if hydrodynamic interactions were neglected altogether. The correct law for drops may not correspond to any single variable diffusion process at all. The upper and lower bounds on the rate of droplet coalescence will be shown to be sufficiently tight to render a more refined theory superfluous in so far as spinodal decomposition experiments are concerned.

The relative diffusion constant or mobility for a pair of spheres is a tensor that depends on the vector R joining their centers.[25] Different motions result from forces parallel and perpendicular to R. The coalescence rate will again be calculated from the diffusive flux of a spherically symmetric gas of drops onto an adsorbing surface of radius $a_1 + a_2$ fixed at the origin. Thus only the radial diffusion constant or corresponding mobility is need-

ed. They are related by the usual Einstein rela-
tion. Although the necessary mobility is known
exactly for several values of a_1/a_2,[24,25] we prefer
to reproduce a crude version of the lubrication
theory argument first used by Rayleigh in this
context.[26] It will provide a number of useful in-
termediate results and insight on how to treat sur-
face deformations and internal circulations.

Consider two spheres of radius $a_1 < a_2$ moving
radially together with a velocity $\dot{h}$ satisfying $h\dot{h}/\nu$
$\ll 1$, where h is the minimum distance between
the surfaces. To make the trivial problem ap-
proximate the surface of the larger sphere by an
infinite plane and model the smaller sphere by a
disk of radius $b = (a_1 h)^{1/2}$ (see Fig. 2). The pa-
rameter b was chosen as the radius at which the
perpendicular separation between the sphere and
a flat surface is the $\sqrt{2}$ times the minimum separ-
ation at $r = 0$, i.e., h.

For small Reynolds numbers and $h \ll b$, the
trapped fluid is squeezed radially outward at a
rate determined by the velocity of approach and
the no slip boundary conditions at the bounding
planar surfaces

$$v_r = 6\dot{r}hz\,(h-z)/h^3\,.\qquad(2.6)$$

The pressure follows from $\nabla(p/\rho) = \nu\nabla^2 v$ and the
boundary condition that it fall to zero at the edge
of the disk

$$p = 6\nu\rho\dot{h}\,(b^2 - r^2)/h^3\,.\qquad(2.7)$$

The force on either surface is found by integrating
the pressure and substituting for b,

$$F = 3\pi\rho\nu a_1^2\dot{h}/h\,.\qquad(2.8)$$

A more careful treatment of the spherical geo-
metry yields twice F when $a_1 \ll a_2$ and one-half
F when $a_1 = a_2$.[27] The diffusion constant for the
small sphere with the other held fixed is

$$D = k_B T h/3\pi\rho\nu a^2\,.\qquad(2.9)$$

Before using (2.9) to solve the diffusion equa-
tion, two conditions must be satisfied. The first
is that the corresponding relaxation time $\tau = mD/$
$k_B T$ multiplied by the average velocity $(k_B T/m)^{1/2}$,
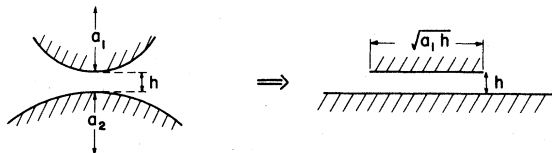where m is the droplet mass; should be $\ll h$. For

FIG. 2. Approximations made to reduce the effects
of hydrodynamic interactions on the relative motion of
two spheres to an equivalent disk and plane problem.

micron-sized drops the required ratio is $\sim 10^{-4}$.
The second condition, in addition to $h\dot{h}/\nu \ll 1$, is
necessary if lubrication theory is to apply to the
trapped fluid.

Brownian motion corresponds roughly to an er-
ratically varying velocity of magnitude $\sim(k_B T/m)^{1/2}$
and duration τ. The trapped fluid must respond
in a time $\ll\tau$ in order that the steady motion, we
assumed in deriving (2.8) and thus τ itself, be at-
tained. In response to a change in velocity, a pres-
sure gradient is established at the speed of sound
and the velocity in the layer approaches its steady
value in a diffusion time set by h and ν. Thus,

$$\tau\nu/h^2 \sim h/a \ll 1\,.\qquad(2.10)$$

Note that if the sphere were actually a disk (of
fixed radius independent of h), then D would be pro-
portional to h^3 and the inequality in (2.10) would be
reversed.

To find the coalescence rate, we again consider
only a drop of average size a and solve a time in-
dependent diffusion equation for the spatial distri-
bution of drops outside of an adsorbing surface at
$r = 2a + \delta$, $\delta/a \ll 1$:

$$\nabla\cdot(\vec{D}\cdot n) = 0$$

or

$$\frac{\partial}{\partial r}\left(r^2(r-2a)\frac{\partial n}{\partial r}\right) = 0\,.$$

The required solution for $\delta \ll a$ is

$$n(r) = n_0\left[1 - \left[\frac{2a}{r} + \ln\left(\frac{r-2a}{r}\right)\right]\Big/\ln\left(\frac{\delta e}{2a}\right)\right]\qquad(2.11)$$

and n_0 is the density of drops at infinity. The
reason for placing the adsorbing surface slightly
outside the combined radii of the spheres is ap-
parent from (2.11).

For drops, the parameter δ is the distance in-
side of which they will fuse rapidly under the action
of surface tension forces. Clearly δ can be no
smaller than the interfacial thickness $\delta \gtrsim \xi$. The
Van der Waals forces set a second, possibly more
restrictive, limit on δ.

First note that the Van der Waals potential
energy between two spheres of radius a and dielec-
tric constant e suspended in a medium of nearly
equal dielectric constant $\bar{e}$ at separations $l \gg a$ is
approximately

$$U = \tfrac{1}{3}k_B T[(e-\bar{e})^2/\bar{e}^2](a/l)^6\,;$$

in the London limit, $l \gg c\hbar/k_B T\bar{e}^{1/2} \sim 10^{-3}/\bar{e}^{1/2}$ cm,
and

$$U = (\hbar c/\bar{e}^{1/2}l)[(e-\bar{e})^2/\bar{e}^2](a/l)^6\,,$$

when $l \ll c\hbar/(k_B T\bar{e}^{1/2})$.[28] The fractional difference

in dielectric constants $(e/\bar{e}) - 1$ is of course proportional to $\Delta c/\bar{c}$ in Fig. 1. For well separated drops, the influence of the Van der Waals forces on their relative diffusion is $\sim U/k_B T$ and thus negligible.

When two planar samples with dielectric constant e are separated by $l \ll c\hbar/(k_B T \bar{e}^{1/2})$, Ref. 28 shows there is an attractive force per area of roughly

$$F \sim 10^{-2}(\hbar c/l^4 \bar{e}^{1/2})[(e - \bar{e})/\bar{e}]^2 , \qquad (2.12)$$

where $\bar{e}$ is the dielectric constant of the intervening medium and $e/\bar{e} - 1 \ll 1$. To apply this result to a pair of spheres with minimum spacing h and radius $a \gg h$ set $l = h + r^2/(2a)$ and do an integral $\pi \int_0^\infty dr^2$ on F. Convert to a potential by then integrating on h. Normalizing U by $k_B T$ and replacing $(e/\bar{e}) - 1$ by $\Delta c/\bar{c}$ yields

$$U/k_B T \sim 10^{-6}(a/h^2)(1 - T/T_c)^{0.68} ,$$

with all lengths in cm. We will show in the following paragraph that $U/k_B T \sim 1$ determines the distance at which coalescence occurs rapidly. Thus,

$$\delta/\xi \sim \max[1, 10^5 a^{1/2}(1 - T/T_c)] , \qquad (2.13)$$

and for large (~ 10 μm) drops, far ($\gtrsim 10^{-3}$) from the critical point, the Van der Waals cutoff exceeds the correlation length.

The generalization of (2.11) when a short-ranged potential U acts between the spheres is

$$n(r) = n_0 \exp(-U/k_B T)[1 - J(r)/J(2a)] ,$$

where

$$J(r) = \int_r^\infty \frac{\exp[U(r')/k_B T]}{r'^2(r' - 2a)} dr' .$$

Note that for $U/k_B T = -[\delta/(r - 2a)]^2$, J is convergent at $r = 2a$. The total flux I incident on the surface $r = 2a$ is

$$I = 4\pi D_0 a^{-1}/J(2a) ,$$

where $D_0 = k_B T/(3\pi \rho v a)$. Assuming $\delta/2a \ll 1$, $J(2a)$ can be approximated as

$$-\frac{\ln(3.63\delta/2a)}{(2a)^2} ,$$

so that

$$I = \frac{16\pi D_0 a n_0}{\ln[2a/(3.63\delta)]} , \qquad (2.14)$$

which except for the constant within the logarithm would have followed from (2.11). Equation (2.14) is the analog of (2.2). To find $a(t)$ we double I, multiply by n_0, and equate to $-dn_0/dt$. We finally have, following (2.5),

$$a^3 = \frac{4 \times 10^{-12} v(t + t_0)}{\ln(0.55a/\delta)} \ \text{cm}^3 . \qquad (2.15)$$

Note that the argument of the logarithm in (2.15) through a and possibly also through δ in (2.13) is time dependent. Equation (2.15) is only applicable when a is sufficiently large that $a(t)$ from (2.15) is less than $a(t)$ from (2.5). Hydrodynamic interaction cannot accelerate the coalescence process. We will continue to use (2.15) when δ is determined by ξ even though the fusion process is not driven by a singular potential. The error is considerably less than the uncertainty over whether to assume the interface has a thickness ξ or 2ξ for instance. The numerical factor in (2.15) could be off by a factor of 3 due to neglect of the distribution of droplet sizes. Somewhat unexpectedly, Eq. (2.15) is not terribly different numerically from (2.5). If D in (2.9) vanished as h^2 for small h, the average radius a would grow as $t^{1/4}$.

In order to use (2.15) as a lower bound on the rate of droplet coalescence near the critical point, two effects, neglected in the lubrication theory derivation of D, must be estimated. No further discussion is necessary for the short distance cutoff δ.

Firstly, as two drops are slowly squeezed together and at constant velocity the radial motion of the trapped fluid induces circulation into the drops themselves. In our effective disk against surface (or disk against disk), approximation to the two-sphere problem, we should modify (2.6) to read

$$v(r) = 6\alpha r \dot{h} z (h - z)/h^3 + \beta h r/h , \qquad (2.16)$$

where the second term is the velocity within either drop (assumed of equal radii) at the surface adjacent to the trapped fluid. To conserve the mass of the trapped fluid, $\alpha + \beta = 1$. For steady motion within the drop, we estimate the surface stress as

$$S \sim \rho v[\beta \dot{h} r/(ha)] . \qquad (2.17)$$

That is, we assume the velocity induced at the pressing surface relaxes over the drop radius a. But (2.17) must equal the stress calculated from (2.16) for $z = 0$ or h. Thus, for $h \ll a$, $\beta \approx 1$, and $\alpha = h/(6a)$. The pressure calculated from (2.16) comes only from the α term leading to a force and thus a diffusion constant independent of h in contrast to (2.9).

The second objection to (2.6)–(2.9) is peculiar to the critical point where the surface tension tends to zero. Recall that Brownian motion consists of an erratic velocity with magnitude $\sim (k_B T/m)^{1/2}$ and a lifetime τ much greater than the viscous diffusion time h^2/v. Compare the pressure at $r = 0$ for $\dot{h} = (k_B T/m)^{1/2}$ with the pressure in the drop in excess of the ambient pressure, i.e., $2\sigma/a$. One finds, assuming $a/h = 10$,

$$ap(0)/(2\sigma) = 10^{-2}a^{-1.5}\epsilon^{-1.23}, \qquad (2.18)$$

with a in μm. When (2.18) exceeds 1, the drop
will flatten, making it more difficult for the trapped
fluid to escape which then increases $p(r = 0)$ at con-
stant $\dot{h}$.

Surface deformation and internal circulation act
in opposite directions on the coalescence rate.
Both effects however are greatly overestimated if
the diffusion constant is extracted, following Ein-
stein, from the force developed in response to a
steady velocity $\dot{h}$. In particular, we will see that
the surface deformation is completely negligible
so the hard sphere result can be used with con-
fidence as a lower bound on the recombination rate
for drops.

In thermal equilibrium, the magnitude of a drop's
deformation can be gauged from the ratio $4\pi\sigma a^2/$
$k_B T \gg 1$, which is always much larger than one for
$\epsilon > 3 \times 10^{-6}$. Hence droplets remain spherical.
Similarly the kinetic energy of the internal cir-
culation implied by (2.16) and (2.17) is $k_B T a/h$
when $\dot{h}$ is a thermal velocity. In addition, the in-
terior motion attains its stationary value only
when $\dot{h}$ is constant over times $\gg a^2/\nu$.

A more explicit argument can be constructed
to rule out surface deformations and thus show the
coalescence can proceed no more slowly than
(2.15). Consider a time $\bar{\tau}$ much greater than the
persistance time of the thermal jitter $mD/k_B T$
and large enough that if (2.6) and (2.7) are aver-
aged over $\bar{\tau}$ and $\dot{h}$ replaced by $(D/\bar{\tau})^{1/2}$, the aver-
aged pressure for $r = 0$, $b = \sqrt{ah}$ is less than σ/a.
If $\bar{\tau}$ can still be chosen much less than the time
necessary for drops separated by h to merge, T,
we will have broken down the random walk into
super steps of duration $\bar{\tau}$ long enough for the
trapped fluid to be squeezed out without droplet
deformation. The complete diffusion process
can then be reconstructed from the steps of size
$\bar{\tau}$ and shown to conform to the same diffusion
constant D. In more formal language we are sug-
gesting that the path integral from 0 to T of a mul-
tivariate problem, i.e., center of mass plus sur-
face modes, may be factored into integrals over
subunits of length $\bar{\tau}$ for which the motion is de-
scribable in terms of only the center of mass. The
ratio of times becomes

$$\bar{\tau}/T = (6\nu\rho a^2 D/\sigma h^3)^2 \sim (k_B T/\sigma h^2)^2, \qquad (2.19)$$

where (2.9) was used for D. Now by (2.13), h is
always greater than ξ and from Table I, $\sigma \sim 4k_B T/$
ξ^2. Surface deformations are negligible except
near T_c and just prior to fusion. If (2.1) were used
for D, the expression for $\bar{\tau}/T$ would be increased
by $(a/h)^2$ and could considerably exceed one. Either
complete neglect of hydrodynamic effects or in-

clusion of only internal circulations for a spherical
drop may be inconsistent sufficiently near T_c since
they imply a diffusion constant that leads to sur-
face deformations which then slow the coalescence.
The hard-sphere result, (2.15), with hydrodynam-
ic effects, is consistent in this respect and there is
no reason to believe that droplet coalescence will
proceed any more slowly.

C. Evaporation-condensation mechanism

Lifshitz-Slyozov, in a well-known paper, have
constructed a mean-field theory for droplets grow-
ing from a slightly supersaturated broth.[16] Their
treatment is very complete and we will merely
summarize the necessary conditions for its ap-
plication to fluids and reproduce several formulas
with parameters appropriate to the critical point.
Of more importance, will be a check that their
solution is stable against a number of possible
hydrodynamic instabilities.

The Lifshitz-Slyozov theory will only apply in
the late stages of evolution when drops are much
larger than a correlation length and most of the
latent heat of the transition has been released. In
a binary fluid near T_c, the finite thermal diffusiv-
ity maintains a uniform temperature and only the
concentration field has to be followed. Lastly, the
supersaturation and thus the volume fraction oc-
cupied by the drops should be small. Note that a
volume fraction of 2% resulting from an off-cri-
tical mixture quenched through the nucleation point
for $\epsilon > 10^{-3}$, corresponds for a regular array of
drops, to a spacing of six radii. Clustering ef-
fects are apt to be suppressed since if two close
drops do not diffuse together their depletion layers
will overlap, slowing their growth rate, and lead-
ing to eventual reevaporation.

The rate of change of a drop's volume is a func-
tion of its radius and the current supersaturation.
A solution to the diffusion equation in the region
exterior to the drop with the correct boundary
conditions at the drop's surface yields the flux
of the minority phase onto the drop and thus $\Delta c \, da/$
dt. The fundamental equation is

$$\frac{da}{dt} = \frac{D}{a}\left(\frac{s}{\Delta c} - \frac{0.12\xi}{a}\right), \qquad (2.20)$$

where the supersaturation s (Fig. 1) is a function
of time in order to conserve the quantity of minor-
ity phase as the number and radii of the drops
changes. The numerical factor in the second term
is just

$$2\sigma\xi^{-1}\Big/\left((\Delta c)^2 \frac{d\mu}{dc}\Big|_{T,p}\right),$$

which is universal and was evaluated from the Xe
data cited in Ref. 20. The average radius then

evolves according to

$$a^3 = 0.053 D\xi t. \tag{2.21}$$

Equation (2.21) follows by comparing Eqs. (2) and (28) of Ref. 16 with (2.20). The coarsening rate depends on neither $T - T_c$ or the degree of super-saturation. Both parameters, however, enter the characteristic relaxation time T_R beyond which (2.21) will apply

$$T_R \sim 2 \times 10^{-15} \epsilon^{-1.8} (\Delta c/s)^3 \text{ sec}. \tag{2.22}$$

A somewhat larger initial relaxation time can intervene when the initial distribution of drops is both more rarified and of larger initial radius a_0 than appropriate for the initial supersaturation, i.e.,

$$a_0 \gg a_e = 0.12 \Delta c \xi /s .$$

Equation (2.22) is then multiplied by $(a_0/a_e)^3$.

We conclude our discussions of Lifshitz-Slyozov by eliminating a number of possible instabilities that small drops growing from a supersaturated broth could be liable. In solid solutions as well as liquids, the purely diffusive instability analyzed by Mullins and Sekerka can occur but the amplitude of the deformation grows no more rapidly than the radius itself and cannot lead to the disruption of the drop.[29] A drop growing according to (2.20) is stable against the "convective" and dendritic instabilities analyzed by Langer and co-workers.[30]

According to Lifshitz-Slyozov, once a drop begins to decrease in size, evaporation of material continues until it disappears. Any instability leading to fragmentation of a shrinking drop should not seriously modify the mean-field theory. In a fluid, the surface tension plus ability to flow should counteract the effects of the diffusive instabilities in an isothermal system.

Although it must not be inferred that the fluid degrees of freedom are necessarily stabilizing, we have not found any instabilities that could conceivably invalidate the Lifshitz-Slyozov mechanism in a fluid. Potential instabilities may be classified according to the force driving the velocity. One common mechanism in multiphase systems invokes a spatially varying surface tension to set the fluid into motion. The temperature variation sustained by the velocity is then responsible for the variable surface tension.[23] In spinodal decomposition one might conjecture that the latent heat release could set up a convective flow which would deliver more supersaturated solution to the surface to release more heat and thus sustain the motions.

To rule out surface-tension-driven instabilities, we construct the analog of a Reynolds number from the maximum temperature difference between the drops surface and infinity ΔT; the drop radius

a and ν and κ. If δv and δT denote small changes in velocity and temperature due to convection then

$$\delta v \Delta T/a \sim \kappa \delta T/a^2 ,$$

and from a stress balance

$$\rho \nu \delta v/a^2 \lesssim \frac{\delta T (d\sigma/dT)}{a} .$$

The dimensionless parameter is

$$B = \frac{\Delta T a (d\sigma/dT)}{\rho \nu \kappa} . \tag{2.23}$$

We believe that the critical value of B for a sphere will exceed the corresponding value for an infinite layer of fluid of depth a. Pearson has done a careful eigenvalue analysis for the later problem and finds $B \gtrsim 100.$[31] Using numbers from Table I yields,

$$\Delta T \gtrsim 0.01 \epsilon^{-0.23} \text{ cgs}.$$

Now ΔT, irrespective of source, can not exceed ΔT_f and a surface tension instability is inconceivable near the critical point for $a < 1$ mm.

D. Concentrated mixtures

Several novel growth mechanisms, unique to fluids, are possible for the 50-50 mixtures that result from a critical quench. We are unable to provide any hard theoretical criterion for what constitutes a sufficiently concentrated mixture for the results below to apply. The percolation concentration ~15% is a natural guess but the two phases are by no means arranged at random. Recall that randomly packed hard spheres of constant radius occupy 63% of their container's volume. The experiments to be discussed below and others that could be done provide useful information on this point.

The mechanisms of Secs. II B and II C will continue to operate in concentrated mixtures. Although none of our formulas are strictly valid, both mechanisms yield a similar amplitude and the same exponent $\frac{1}{3}$ that is expected to persist on dimensional grounds. New growth mechanisms are possible if the minority phase is assumed connected and surface tension forces are included.

To see the essential physics, imagine a long tube of fluid of radis a with a significant radial undulation of wavelength $l \gg a$ in a medium of uniform pressure. The undulations lead to a pressure gradient $\sim \sigma/al$ along the axis that tends to transfer fluid from the necks to the bulges. The corresponding averaged velocity follows for instance from the equation for Poiseuille flow

$$v \sim 0.1 \sigma a/l \rho \nu .$$

To apply this result to spinodal decomposition, assume there is only one length $a \sim k_m^{-1}(t)$ and a single velocity da/dt. Then

$$a \sim (0.1\sigma/\rho v)t. \qquad (2.24)$$

A similar formula, lacking perhaps the factor 0.1, follows from dimensional analysis applied to $\nabla(p/\rho) = \nu\nabla^2 v$.[32] Equation (2.24) requires that the Reynolds number

$$R \sim 2\times 10^4 a \epsilon^{1.23},$$

with a in cm, is small (in practice $\lesssim 100$), which is certainly true for $a \lesssim 100$ μm and $\epsilon \lesssim 10^{-3}$. Our Reynolds number is actually an overestimate since experiment shows that the numerical factor in (2.24) should be 10^{-3}. The connectedness assumption necessary to apply (2.24) is by no means trivial as our example above suggests. A fluid tube will fragment into a string of blobs which will not evolve further in the absence of diffusion even though the lowest energy state is a single large blob.[23] In a concentrated mixture, disconnected blobs may be picked up as the interfaces migrate during the coarsening. It should be stressed that the coefficient in (2.24) is extremely uncertain and one might suspect an overestimate, since a complicated surface, through the surface tension induced pressure gradient, will send conflicting signals into the body of the fluid as to the direction of flow necessary to coarsen the mixture.

The crossover from diffusive coarsening to the rate described by (2.24) occurs for

$$a^2\sigma \sim k_B T. \qquad (2.25)$$

Equation (2.25) was derived by equating two values of da/dt [one from (2.5) and the other from (2.24)]. It cannot be correct since it places the crossover in the "early stages" when the interfaces are not yet well defined and surface tension driven flows are a logical impossibility. Equation (2.25) does have two important implications. The first is that apart from the Kawasaki-Ohta calculation in the "early stages" which gave approximately a $t^{1/3}$ dependence, there is no distinct $t^{1/3}$ regime for a concentrated mixture in the late stages as there is for the dilute mixtures. Of course one should not use (2.5) with $v = \frac{1}{2}$ to derive (2.25) but it is "reasonably close to the predictions of Ref. 9 and experiment. Secondly, we expect the coarsening rate to go as t throughout the late stages in concentrated mixtures. Comparison with experiment will show that the numerical factor in (2.24) is $\sim 10^2$ too large so that a rederivation of (2.25) would place the crossover at $a \sim 10\xi$ where it should be on thermodynamic grounds.

A second crossover to gravity-dominated motion takes place when

$$a^2 \sim \sigma/g\Delta\rho, \qquad (2.26)$$

where $\Delta\rho$ is the density difference of the two phases. The expression corresponding to (2.26) for $a(t)$ does not follow a power law and diverges in a finite time. For any experimentally attainable value of ϵ, gravity effects will follow the linear regime (2.24).

III. COMPARISON WITH EXPERIMENT

For off-critical quenches that are not too deep [in practice $(\Delta T_f)/(\Delta T_i) < 20$], either (2.21) or (2.15) should apply throughout the late stages of coarsening; and although there may be transients that mask the $t^{1/3}$ scaling, they should be calculable. Equation (2.5) should be used in place of (2.15) whenever it would give a smaller value of the radius. The crossover from Lifshitz-Slyozov to direct recombination occurs at a volume fractions v of precipitate of $\sim 1\%$. There could be a factor of 4 error in this last figure due to the uncertainties in (2.15). Note that the Lifshitz-Slyozov rate is independent of v.

The data plotted in Fig. 6 of Ref. 13 for $k_m(\sim a^{-1})$ vs t collapse onto $t^{1/3}$ with a prefactor in accord with our expectations to within a factor of 2. The fraction of minority phase runs from 4%–20% and ΔT_f from 63 to 430 mk. There is a tendency for the deeper quenches to be somewhat more evolved at the latter times. While this is in agreement with (2.15) it could also arise from faster transients or a change in the relation between k_m^{-1} and a. The 20% mixture is of particular interest since it was at a temperature sufficiently removed from T_c, and carried out to sufficiently long times or large lengths, that it should have crossed over to the linear regime, (2.24), if it were connected. Runs L and P (not plotted), were rather shallow quenches, nearer to T_c than the others, and produced exponents decidedly less than 0.33. The onset of scattering was delayed beyond the moment of quench and the authors infer that phase separation was initiated by nucleation. Their quench depths are compatable with the limits to supercooling set by other experimenters.[33]

A nucleated transition proceeds by events rare on a microscopic scale and might well be expected to yield a rarified mist of drops with mean radius considerably larger than the equilibrium value at that supersaturation. Now if some of the condensation occurred heterogeneously either on the walls or at some impurity, or only a small fraction of the precipitate was in drops with the rest still in solution, v in (2.15) would be $\ll s/\Delta c$. Droplet coalescence would not be a factor in the early

stages. As we have seen, the initial transients implied by Lifshitz-Slyozov are considerably enhanced by a shallow quench and a replot of the data say as a^3 vs t on linear scales so as to allow for a nonzero intercept might demonstrate consistency with $a \sim t^{1/3}$ at latter times.

Similar remarks apply to recent measurements of Goldburg and co-workers.[15] Their quenches were always just through the nucleation line, the observation were in the range 0.18-0.26. Their last points at 100 sec fall about where (2.21) suggests, however. Since their measurements give a coarsening that is no faster than either Lifshitz-Slyozov or Eq. (2.15), it is difficult not to attribute their low exponents to transients unless a way can be found to suppress evaporation-condensation. Impurities that resided on the drop surfaces and modified the surface tension might have this effect but their affinity for the surface would be hard to explain since the two phases are very similar near T_c. Longer off-critical runs coupled with direct microscopic observation of the droplets at later times should permit an unambgiuous test of the theory. The distribution of drop sizes should also be checked against theory.

Our predictions for the critical quenches are also borne out by experiment, although the prefactors are far off. Figure 5 of Ref. 13 shows for separate runs at variable quench depths, a coarsening law, measured for a common range of wave numbers, varying from $t^{1/3}$ to t at the deeper quenches. The cross over length $(a \sim k_m^{-1})$ is about 3 μm at $\epsilon \sim 10^{-5}$ and the slope in the linear regime at $\epsilon \sim 2.7 \times 10^{-5}$ is $\sim 10^{-5}$ cm/sec. The corresponding numbers from Eqs. (2.25) and (2.24) are 0.2 μm for the crossover and 10^{-3} cm/sec for the slope. The Wong-Knobler results are in accord with unpublished measurements of Goldburg also on isobutyric-acid water that displayed the $\frac{1}{3}$ to 1 crossover in a single run. The prefactor in (2.24) is thus 100 times too large, an error in part due to the difficulty of associating quantitatively the scaling length with k_m^{-1}. Critical quenches at different temperatures can be collapsed onto a common curve in both the $t^{1/3}$ and linear regimes by plotting a/ξ vs t/ξ^3.

Goldburg and co-workers found for lutidine water at $\epsilon \sim 10^{-5}$ a crossover from $t^{1/3}$ for $a \sim 10$ μm to a rate faster than t.[14] We attribute this last result to gravity effects, superimposed on (2.24), that according to (2.26) should appear at $a \sim 50$ μm for $\epsilon \sim 10^{-5}$. Gravity effects are more pronounced in lutidine-water than isobutyric-acid–water (see Table I), and because Wong-Knobler never went beyond ~20 μm at $\epsilon = 2.7 \times 10^{-3}$ in the latter system, gravity played no role in their observations. A deeper quench should push the crossover length

of Eq. (2.26) into the range of scale sizes accessible to light scattering.

A calculation of the complete structure function $S(k, t)$ for concentrated mixtures is a formidable task and to deduce the scattering intensity $I(k, t)$ is yet more difficult since multiple scattering is frequently important in the experiments. For a dilute array of spheres, such as a shallow off critical quench would produce, a great deal is known in the absence of multiple scattering between spheres.[34] For simplicity, we will assume the spheres are of constant radii and nonoverlaping but otherwise arranged at random. The scattering intensity from a volume V of fluid can be factored into $i(k, t)$, the scattering from a single sphere, times

$$\langle n_k n_{-k} \rangle / V \quad \left(n_k = \sum_l e^{i\vec{k} \cdot \vec{R}_l} \right).$$

Near the critical point, it will frequently be possible to use the Rayleigh-Gans formula (or equivalently the first Born approximation) which applies when the phase shift across the drop, measured with respect to the suspending medium, is much less than one.[34] For the isobutyric acid water system, the higher terms in the Born series are negligible when

$$a \lesssim \lambda/\epsilon^{1/3}, \tag{3.1}$$

where a is the radius and λ the wavelength. The scattering intensity per drop varies as the dipole matrix element squared a^6 and is otherwise a function of ka with a maximum at $ka = 0$ and a shoulder that extends to $ka \sim 1.5$, where k is the momentum transfer. To complete $I(k, t)$, one removes a factor n_0, the number of drops per volume, from $\langle n_k n_{-k} \rangle / V$. What remains is a function of $n_d a^3$ and ka and when plotted against ka has a peak around $ka \sim 6$. A simple analytic form is given by Ashcroft.[35] Since $n_d a^3$ is independent of time, $I(k, t)$ grows as $a^3 \sim t$ for any fixed value of ka. Depending on the exact form of $\langle n_k n_{-k} \rangle$, I should have a peak around $ka \sim 2$ where $i(k, t)$ begins to fall off as $(ka)^{-4}$ while $\langle n_k n_{-k} \rangle$ is still rising.

Wong and Knobler[13] find $I(k_m, t) \sim t^{1.15}$ and a peak around k_m that is somewhat sharper than Refs. 34 and 35 would suggest. Perhaps there is some large-scale clustering. Multiple scattering, as manifest by the reduction in the transmitted beam, is clearly a problem in their experiments.

When (3.1) is violated in a dilute mixture and the transmitted beam is weakly attenuated we can still factor $I(k, t)$ into $i(k, t)$, which now scales as a^4,

times $\langle n_k n_{-k} \rangle$. Now, however, $I(k, t)$ no longer measures the concentration-concentration correlation function $S(k, t)$, since there is multiple scattering (equivalent to diffraction-refraction) within and around the drops.[34] In this regime, $I(k_m, t) \sim a(t)$. In concentrated mixtures it is more difficult to estimate $I(k, t)$, but it should be emphasized that the scattering intensity is not proportional to $S(k, t)$ if (3.1) is violated even if the reduction in the transmitted beam is small.

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