

Theory for the Slowing Down of the Relaxation and Spinodal Decomposition of Binary Mixtures

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The weak nonexponential relaxation $\propto t^{-a'}$ recently found in computer experiments on the phase separation of alloys is explained in terms of a cluster reaction and diffusion process. The nonlinear features of this process can be accounted for by a time-dependent diffusion constant. Estimates for the resulting exponents [$a' = 1/(3+d)$] are consistent with the computer simulations. The experimental observability of this slowing down is discussed.

Phase separation occurs if A - B mixtures are suddenly quenched to a sufficiently low temperature while being kept at constant concentration. The kinetics of this unmixing process has been investigated recently by computer experiments on simple model systems,¹⁻⁴ as well as theoretically^{5,6} and experimentally.^{7,8} Most striking are the slow asymptotic $t^{-a'}$, $t^{-b'}$ decays of both the structure function $S_{\Delta T}(\vec{k}, t)$ and the energy $E(t)$, where¹⁻³ $a', b' \approx \frac{1}{5} - \frac{1}{6}$. Previous theories (a "Ginzburg-Landau" approach,^{5,6} or a linearized diffusion theory⁹) predicted $a' = \frac{1}{3}$ in three dimensions. In both approaches this prediction $a' = \frac{1}{3}$ can be generalized¹⁰ to arbitrary (nonintegral) dimensionality $d > 2$. "Conventional" theories^{4,6,11} lead to even more rapid (i.e., exponential) decay.

In this paper we outline a phenomenological theory in terms of the diffusion and reactions of clusters, generalizing previous studies of single-spin-flip kinetic Ising models, where only cluster reactions are important.^{12,13} This model describes satisfactorily both the equilibrium and metastable states of a binary mixture.^{13,14} First we obtain the critical relaxation of our diffusion constant in agreement with the established results.¹⁵ Then we discuss the nonlinear case and estimate the exponents a' and b' . We show that several regimes with different behavior can be distinguished.

We denote a typical fluctuation of the local (coarse-grained) concentration $c(\vec{x})$ as a cluster of size l , if it contains l more B atoms than would correspond to the surrounding concentration. Two regimes of cluster behavior must be distinguished.¹⁶ First, at very low temperatures, the clusters contain nearly pure B phase. Hence we

find for the cluster volume, surface, and diffusivity ($l \gg 1$)

$$\begin{aligned} V_i &\propto l, & S_i &= \hat{S}l^{1-1/d}, \\ D_i &= \tilde{D}S_i(c_1/l)^2 = \hat{D}l^{-1-1/d}. \end{aligned} \quad (1)$$

The constants in Eq. (1) may be adjusted to account for nonspherical cluster shapes.^{3,16} In deriving D_i we used the fact that¹⁰ most atoms "evaporating" from a cluster because of stochastic exchanges reimpinge at the same cluster again. By such a process the "center of gravity" of a cluster, $\vec{x}_c = \sum \vec{x}_i/l$ (it is summed over the coordinates \vec{x}_i of all the atoms of the cluster), is randomly shifted by an amount c_1/l (henceforth the c_i are constants or order unity). Since the number of A - B exchanges per unit time is (at least roughly) proportional to the cluster surface, Eq. (1) results.

The second regime occurs for T near T_c and above, where the concentration difference between a typical fluctuation and its environment is rather small, and hence we have¹⁰

$$\begin{aligned} V_i &= \hat{V}l^{1+1/\delta}, \\ D_i &= \tilde{D}'V_i(c_2/l)^2 = \hat{D}'l^{-1+1/\delta}. \end{aligned} \quad (2)$$

The exponent δ enters by the requirement that the average cluster volume be $\xi^d [\propto (1 - T/T_c)^{-\beta\delta(\alpha+1/\delta)}]$, ξ being the correlation length.¹⁶ Now atoms exchanging their sites in the interior of the cluster may also shift the "center of gravity" of the cluster.

The dynamics of the system is described by a master equation, stochastic exchanges of atoms occurring according to thermal equilibrium with a "heat bath."¹⁷ Let $n_i(\vec{x}, t)$ be the local time-

dependent cluster concentration and let $g_i(\vec{x}, t) = [n_i(\vec{x}, t) - n_i]/n_i$, where n_i is the equilibrium concentration. If we disregard the details of the kinetics due to the various local geometric arrangements of the atoms, we find that the equation may be approximated by an equation describing the reactions and the diffusion of clusters.^{10,13} For generality, we do not use any explicit formula for n_i (such as the Fisher cluster model¹³). But scaling implies that the dominant contributions to the relaxation near thermal equilibrium come from the diffusive term $\partial g_i(\vec{x}, t)/\partial t = D_i \nabla^2 g_i(\vec{x}, t)$ in the vicinity of the "dominating" cluster size l_ξ ,¹⁰

$$l_\xi \propto |1 - T/T_c|^{-1/\delta}, \quad (3)$$

corresponding to clusters of volume ξ^d . It turns out that for $l \ll l_\xi$ and $l \gg l_\xi$, cluster reactions dominate, while for $l \approx l_\xi$ and $t \rightarrow \infty$ cluster diffusion dominates, for wave vector $\vec{k} \rightarrow 0$. Then $S(\vec{k}, t)$ is reasonably approximated by

$$\begin{aligned} S(\vec{k}, t) &\equiv \int d^3x e^{i\vec{k} \cdot \vec{x}} [\langle c(0, 0)c(\vec{x}, t) \rangle - \langle c \rangle^2] \\ &\approx S(\vec{k}) \exp(-c_3 D_i k^2 t). \end{aligned} \quad (4)$$

Equations (2)–(4) show that $D_i \propto |1 - T/T_c|^\gamma$, in agreement with the renormalization-group results.¹⁵ Thus our description is consistent with critical dynamics in linear response.

We now assume that the relaxation function has in the general (nonlinear) case essentially the same structure for $\vec{k} \rightarrow 0$ as in Eq. (4), but instead of D_i we must insert the diffusion constant D_m which corresponds to the typical cluster size k_m^{-1} (instead of ξ) of the actual situation.

In the unmixing (computer) experiments the system is cooled from $T_0 \gg T_c$ [where $S_{\Delta T}(\vec{k}, 0) \cong 0$] to $T < T_c$, where $S_{\Delta T}(k, \infty) \cong c_4/(k^2 + k_D^2)$ [for $k \ll \xi^{-1}(T)$] describes regions of two phases coexisting in equilibrium¹ (k_D^{-1} is the domain size).

After a complicated initial stage one observes ordered regions of typical size $k_m^{-1}(t)$, which steadily grow to infinite size $k_m(t) \propto t^{-a'}$. Hence we approximate $S_{\Delta T}(\vec{k}, t)$ asymptotically by

$$\begin{aligned} S_{\Delta T}(\vec{k}, t) &\approx \frac{c_4(t)}{k^2 + k_m^2(t)} \{1 - \exp[-c_5 D_m(t) k^2 t]\}, \\ k &\lesssim k_m(t) \ll \xi^{-1}(T). \end{aligned} \quad (5)$$

The constants $c_4(t)$ and c_5 depend on the mean concentration of B atoms in the system; in contrast to Ref. 9 our treatment is not restricted to the dilute limit. $S_{\Delta T}(\vec{k}, t)$ has its maximum at a wave vector $\propto k_m(t)$ [see, e.g., Fig. 3 of Ref. 1], and

thus

$$k_m^2(t) D_m(t) = c_6/t. \quad (6)$$

For $T < T_c$ Eq. (1) applies for the relation between $D_m(t)$ and the domain volume $V_m(t) \propto [k_m(t)]^{-d}$; thus

$$D_m(t) \propto [V_m(t)]^{-1-1/d} \propto [k_m(t)]^{d+1},$$

and

$$k_m(t) \propto t^{-a'}, \quad a' = 1/(3+d), \quad T \rightarrow 0. \quad (7)$$

From the sum rule $\sum_{\vec{k}} S_{\Delta T}(\vec{k}, t) = 1$ we then derive¹⁰ $c_4(t) \propto [k_m(t)]^{2-d}$. Our main result, Eq. (7), can be interpreted more simply directly from Eq. (1), by noting that a change $\Delta V_m \approx V_m(t)$ of the cluster volume occurs within the time Δt needed for the cluster to "travel" the mean distance between neighboring clusters, which is of the same order as $k_m(t)$. From $k_m^{-2} \propto D_m \Delta t$ and $dV_m/dt = \Delta V_m/\Delta t \propto V_m k_m^2/\Delta_m$, we get $V_m \propto t^{d/(3+d)}$, i.e., Eq. (7).

For $T \cong T_c$ Eq. (2) applies and hence $\{D_m(t) \propto V_m(t)^{-(1-1/\delta)/(1+1/\delta)} \propto [k_m(t)]^{d(\delta-1)/(\delta+1)} = [k_m(t)]^{2-\eta}\}$,

$$k_m(t) \propto t^{-a_c}, \quad a_c = 1/(4-\eta), \quad k_m(t) \xi \gg 1. \quad (8)$$

For not too large times Eq. (8) may hold for $T \lesssim T_c$ and even $T \gtrsim T_c$. For $k_m(t) \ll \xi^{-1}$ ($T > T_c$) we need D_i rather than $D_m(t)$ in Eq. (6) and hence

$$k_m(t) \propto t^{-a}, \quad a = \frac{1}{2}, \quad k_m(t) \xi \ll 1. \quad (9)$$

For $T < T_c$ and $k_m^{-1}(t) \rightarrow \infty$ the excess energy $E(t)$ is basically the total surface ("domain-wall") energy of the $N_m(t)$ regions of size $k_m^{-1}(t)$, and thus $E(t) \propto N_m(t) [k_m(t)]^{-(d-1)}$. Conservation of the total concentration gives $N_m(t) V_m(t) \propto N_m(t) [k_m(t)]^{-d} = \text{const}$, and hence

$$E(t) \propto k_m(t) \propto t^{-b'}, \quad b' = a'. \quad (10)$$

For $T > T_c$ and $k_m^{-1}(t) \gg \xi$, the excess energy $E(t)$ of a structure of size $k_m^{-1}(t)$ is basically a volume energy, since a high degree of correlation exists only over distances ξ . Asymptotically this energy should be proportional to the square of the order-parameter fluctuation $c_m(t)$ in this region,¹⁹ $c_m(t) \propto [V_m(t)]^{-1/2}$, $E(t) \propto N_m(t) V_m(t) c_m^2(t)$, and we find

$$E(t) \propto [k_m(t)]^d \propto t^{-b}, \quad b = da = d/2. \quad (11)$$

The relaxation of the energy at T_c can be obtained similarly.¹⁰ The rather crudely derived Eq. (11) follows also from a different estimate. When the excess energy $E(t)$ becomes small, its decay should correspond to the decay of the energy-energy correlation function of an equilibrium state,

and hence^{20, 21}

$$\begin{aligned} \langle \mathcal{H}(0)\mathcal{H}(t) \rangle_{\text{corr}} &\propto \int d^3x \langle c(0, 0)c(\vec{\rho}, 0)c(\vec{x}, t)c(\vec{x} + \vec{\rho}, t) \rangle_{\text{corr}} \\ &\geq \int d^3x \langle c(0, 0)c(\vec{x}, t) \rangle_{\text{corr}}^2 = \int d^3x \int d^3k \int d^3k' \exp[i(\vec{k} - \vec{k}') \cdot \vec{x}] S(\vec{k}', t) S(\vec{k}, t) \\ &= \int d^3k S^2(\vec{k}, t). \end{aligned} \quad (12)$$

Since $S(\vec{k} \rightarrow 0) \rightarrow \text{const}$ for $T > T_c$, the $\exp(-Dk^2t)$ decay gives $b = d/2$ [combining Eqs. (5) and (12)]. Note that also Eqs. (8) and (9) can be obtained from scaling assumptions without the use of any cluster picture.¹⁰

References 1 and 2 gave $a' \approx b' \approx \frac{1}{5}$ for $T = 0.58T_c$ and $d = 2$, in agreement with Eqs. (7) and (10). Far shorter computing times make the $a' = \frac{1}{5}$ of Ref. 3 less accurate. At $T = 1.1T_c$ and $d = 2$, only $b \approx \frac{7}{12}$ has been given,¹ which can be interpreted in terms of changeover from the critical behavior to $b = 1$ [Eq. (11)].

In conclusion, the estimated exponents are in satisfactory agreement with observation. Our basic physical assumption is that for a range of times the relaxation proceeds by the diffusion and coalescence of large "clusters." The diffusivity depends on cluster size, and hence on time, and therefore size and time are related by the self-consistency condition Eq. (6). Our assumption implies that more rapid processes are not dominant, at least not within a broad range of times. These other processes include the growth of the clusters by incorporation of small clusters or single atoms in their environment, or the diffusion of single atoms one after the other from one stationary cluster to the other. In order to simulate this latter process, the continuum approximation of Ref. 9 took the driving force for this diffusion to be proportional to the mean supersaturation of the solution. In our short-range interaction model, however, the atomic exchanges depend on local conditions only, and not on averages over the whole system. This fact may explain why the treatments^{5, 9} yield a decay which is too rapid.

Several measurements exist for glasses and metallic alloys.^{22, 23} However, usually the later stages of the separation process are very much affected by dislocations or other imperfections, or by elastic strain fields, preventing further growth of $k_m^{-1}(t)$. The latter effect is unimportant, however, for $k_m^{-1}(t) \ll (T_c/\Theta_B)(1/\Delta)^2$, Θ_B being the Debye temperature of the B phase, and Δ the relative difference in lattice spacing of the A - and B -rich phases.¹⁰ Also small concentration gradients, etc., affect the decomposition only in its latest stages.⁴ If A - B exchanges are pos-

sible via vacancies only, which are accumulated near the grain boundaries (i.e., the cluster surfaces), one rather observes $a' = b' = 1/(d + 2)$, however.¹⁰

Such problems do not occur in liquid mixtures. So far only one study of the early stages of phase separation in liquids is available⁷ and hence a study of larger times and of other systems is suggested. However, in a liquid the dominant contribution to the cluster diffusion for $d = 3$ is $D_i \propto 1/\eta_v V_i^{1/d}$ instead of Eqs. (1) and (2), according to Stokes's law [this term is missing in our case, the viscosity of a solid being $\eta_v = \infty$], and in analogy to Eqs. (6)–(8) we then get a decay $\propto t^{-1/3}$. Thus we predict the asymptotic decay of the decomposition in solid and liquid mixtures to be rather different, as is the case for the critical relaxation.^{15, 24}

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Longitudinal and Transverse Resonance in the *B* Phase of Superfluid He³

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I report measurements of the longitudinal resonance in the *B* phase of superfluid He³ at melting pressures over a broad temperature interval. I also present the results of a transverse NMR study in the *B* phase which is designed to test the theory of textures in the *B* phase and to provide accurate measurements of the *B*-phase susceptibility. Finally, I report the first measurements of a field-dependent frequency shift in the transverse *B*-phase NMR associated with the anisotropy energy of the rotation axis of the Balian-Werthamer state.

In the context of the spin-fluctuation theory of Brinkman, Serene, and Anderson^{1,2} the *B* phase of superfluid He³ must be identified as the Balian-Werthamer (BW) or "isotropic" state³ described by Leggett⁴ in which the spin and orbit coordinates are rotated by $\cos^{-1}(-\frac{1}{4})$ about an arbitrary axis \vec{n} . Yet to date most experimental results have not been interpreted as supporting this identification.^{5,6} Only the work of Osheroff and Brinkman⁷ (OB) seems to clearly support the Brinkman-Serene-Anderson result. As a consequence of the OB interpretation of their data as evidence for domain structure or a "texture"⁸ in the *B* phase, Brinkman, Smith, Osheroff, and Blount⁹ (BSOB) have developed a Ginzburg-Landau theory to determine the effects of surfaces and magnetic fields on the spatial orientation of the axis \vec{n} and the effects of this spatial orientation upon the transverse NMR spectrum.

In this work I present measurements of longitudinal resonance in the *B* phase at melting pressures. I also present results of a careful transverse-resonance study in the *B* phase designed to

test the BSOB theory. I finally use the BSOB theory to derive the reduced *B*-phase susceptibility $\chi(B)/\chi(F.L.)$ from present NMR absorption measurements and use these values to compare the longitudinal resonant frequencies in the *B* phase with those measured by OB in the *A* phase.

The compressional apparatus used in this work has been described by Osheroff and Anderson¹⁰ (OA) and by OB as have the NMR and thermometry techniques. This work utilized the NMR tail piece used by OA, which included a longitudinal resonance coil not mentioned by OA. This coil had a smaller diameter than the equivalent coil of OB which improved the He³ filling factor for the new coil by about a factor of 4.

Longitudinal resonance in the *B* phase was observed in a manner similar to the measurements made in the *A* phase by sweeping the cell pressure (temperature) and plotting the rf level across the tank circuit as a function of both time and pressure. The temperature of the resonance at a given frequency was obtained by averaging the apparent resonant temperature on equal numbers