

Dynamics of phase separations of a dissipative system and a fluid mixture

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The temporal evolutions of structure functions $S_k(t)$ of quenched binary mixtures are studied theoretically. With the aid of a Langevin-type equation, basic nonlinear kinetic equations for the composition fluctuation are derived for a purely dissipative system and for a fluid mixture. Predicting that the free energy is expanded on the basis of a cluster gas picture, the equations of motion for structure functions are derived. The inverse nonhydrodynamic susceptibility χ_k^{-1} , which is the first-derivative coefficient of the free energy, and $S_k(t)$ are assumed to have the form $R^{-d}\tilde{\chi}(kR)^{-1}$ and $R^d\tilde{S}(kR)$ in d dimensions. Here R is the average cluster diameter, which behaves as $t^{-a'}$ [$a' = (d+2)^{-1}$ or $(d+3)^{-1}$ for a purely dissipative system and $a' = 1/d$ for a fluid mixture]. If χ_k^{-1} has a gap of the order R^{-d} , then our calculation of $S_k(t)$ yields good agreements with experiments (for $d = 3$). The renormalizations both of the mobility and of susceptibility due to long-range hydrodynamic interactions are treated with the use of the mode-coupling technique.

I. INTRODUCTION

The early stage of the phase separation of a quenched binary mixture in the unstable region is called the spinodal decomposition.¹⁻⁵ The separation of the composition is accomplished in a short time interval, generating small clusters whose compositions are almost equivalent to the compositions at the coexistence state. Ending such an initial stage the system undergoes the cluster coarsening.⁶⁻¹⁰

When a system of a binary mixture is brought suddenly into a two-phase region (below T_c) from a single-phase region (above T_c), the system becomes thermodynamically unstable and then exhibits a phase separation. In the classical theory of Cahn-Hilliard for the alloy,¹ the equation of motion for the local composition fluctuation $\eta_{\mathbf{k}}(t, \mathbf{r})$ (difference in the densities of composite species) or its Fourier component $\eta_{\mathbf{k}}(t)$ is investigated. It is assumed that the free-energy Φ of an alloy quenched into two-phase region has an unstable point at $\eta_{\mathbf{k}} = 0$:

$$\Phi = \frac{1}{2} \sum_{\mathbf{k}} (ak^2 - b) |\eta_{\mathbf{k}}|^2 + O(\eta^3), \quad (1.1)$$

where a and b are positive constants, respectively. Here the free-energy Φ must be distinguished from the free-energy of a completely phase-separated state. The latter would not have a maximum at $\eta = 0$. Equation (1.1) is a coarse-grained free-energy with small coarse-grained cells.³ Following the theory of the irreversible thermodynamics, $\eta_{\mathbf{k}}(t)$ obeys the equation of motion:

$$\begin{aligned} \frac{d}{dt} \eta_{\mathbf{k}} &= -k_B TM^0 k^2 \frac{\partial \Phi}{\partial \eta_{-\mathbf{k}}} \\ &= -k_B TM^0 k^2 (ak^2 - b) \eta_{\mathbf{k}} + O(\eta^2), \end{aligned} \quad (1.2)$$

where M^0 is the kinetic coefficient (mobility) and

k^2 on the second side comes from the particle number conservation; namely, (1.2) must be a diffusion equation. If $\eta_{\mathbf{k}}$ at initial time ($t=0$) has a nonvanishing value $\eta_{\mathbf{k}}^0(0)$, then we obtain

$$\eta_{\mathbf{k}}(t)/\eta_{\mathbf{k}}^0(0) = \exp[-k_B TM^0 k^2 (ak^2 - b)t]. \quad (1.3)$$

There is a wave number k_m at which (1.3) has a maximum. The quantity k_m^{-1} may be regarded as a diameter of the precipitates generated after the quench.

There are several insufficiencies in the above treatment of the phase separation, and many theoretical investigations have been made on this problem. Firstly, there is no term in (1.2) representing thermal fluctuations, i.e., there is no Langevin's fluctuating force. If $\eta_{\mathbf{k}}$ in (1.2) is interpreted as the mean value, then Langevin's fluctuating force is not necessary. However, $\eta_{\mathbf{k}}$ always vanishes for the initial condition $\eta_{\mathbf{k}}(0) = 0$. Therefore $\eta_{\mathbf{k}}$ interpreted as a mean value is not a convenient variable to describe the phase separation. Cook then interpreted $\eta_{\mathbf{k}}$ as a microscopic variable (though it may be coarse grained).² This means that a fluctuating force $f_{\mathbf{k}}^0$ should be added to (1.2):

$$\begin{aligned} \frac{d}{dt} \eta_{\mathbf{k}}(t) &= -k_B TM^0 k^2 (ak^2 - b) \eta_{\mathbf{k}} + f_{\mathbf{k}}^0(t), \\ \langle f_{\mathbf{k}}^0(t) f_{-\mathbf{k}}^0 \rangle_0 &= 2k_B TM^0 k^2 \delta(t), \end{aligned} \quad (1.4)$$

where $\langle \rangle_0$ means an appropriate ensemble average. Then Cook obtained the equation of motion for the structure function $S_{\mathbf{k}}(t) = \langle |\eta_{\mathbf{k}}(t)|^2 \rangle_0$:

$$\frac{d}{dt} S_{\mathbf{k}}(t) = 2k_B TM^0 k^2 [1 - (ak^2 - b) S_{\mathbf{k}}]. \quad (1.5)$$

Even if $S_{\mathbf{k}}(0) = 0$, $S_{\mathbf{k}}(t)$ for $t > 0$ has a nonvanishing value. Cook's theory as well as the theory of Cahn-Hilliard is, however, capable of explaining only very early stages of the phase separation.

Equation (1.5) exhibits an exponential growth for $S_k(t)$. This violates the validity of the approximation which neglects the higher-order terms in (1.2) and (1.4).

Assuming that the nonlinearity is responsible for the renormalization only of the constant b in (1.1)–(1.5), Langer, Bar-on, and Miller⁴ found that the constant b is a decreasing function of time t . They found also that both the peak height of $S_k(t)$ and peak position k_m show slow temporal changes like t^x , where x is a suitable constant in each case. They obtained good quantitative agreement with computer simulation of the spin-exchange kinetic Ising model near the critical point in three dimensions.¹¹ The decay of k_m represents the growth of the cluster diameter. In their theory, the constant b is still positive, and therefore the coefficient of η_k in (1.4) can be negative. This means that fluctuations are still enhanced unstably.

When the average cluster diameter R exceeds a thermal correlation length ξ , the usefulness of the coarse-grained free-energy with maximum at $\eta_k = 0$ becomes obscure. The composition of a cluster is almost the same as that on the coexistence curve. Thus the system is in a local equilibrium state almost everywhere in space.

A physical interpretation of the late stage of the phase separation was done by Binder and Stauffer.⁷ They proposed the cluster diffusion-reaction mechanism of the late stage of the phase separation. In this model a cluster is treated as a free Brownian particle. Clusters grow not because of the instability which took place in the early stage of the phase separation where clusters are not well developed, but because of the thermal noise acting on clusters. In this mechanism there is no need to have the maximum of the free-energy at $\eta = 0$. This may be interpreted as follows. In the cluster-gas picture, any internal degrees of freedom of clusters are averaged out. Thus the free-energy appropriate to the cluster-gas picture is not the coarse-grained free-energy mentioned above, but a partially renormalized free-energy which should become identical to the free-energy of a completely phase-separated state in the limit of large cluster diameter. The renormalized free-energy Φ_{re} is written as

$$\Phi_{re} = \frac{1}{2} \sum \chi_k^{-1} |\eta_k|^2 + O(\eta_k^3), \quad (1.6)$$

which should be reduced from the coarse-grained free-energy, and must be identical to the coarse-grained free-energy if the diameter of the coarse-grained cell is equal to R . For the sake of simplicity, we shall call χ_k the susceptibility. In fact χ_k corresponds to the susceptibility of a cluster

gas. χ_k should be determined by the cluster shape and the cluster configuration. If the diameter of the coarse-grained cell is of the order ξ , then the renormalized free-energy (1.6) may be constructed from the coarse-grained free-energy by taking only the effect of the cluster formation (the amount of the local composition may be the same for both free-energies).

When the correlation among clusters is not strong, the formation of well-developed clusters is allowed if the first derivative of the coarse-grained free-energy for $\eta_k \neq 0$.³ The same effect is obtained if the inverse susceptibility χ_k^{-1} for small wave number is vanishingly small. The gapless susceptibility was already examined and was found to possibly be consistent with experiment.^{8,9}

This does not, however, mean to deny the existence of a small positive or negative gap of the order R^{-d} . Such a small gap of the susceptibility must be recognized in the cluster-gas picture.

We have calculated the structure function both for purely dissipative systems and a three-dimensional fluid mixture at low temperatures. We have then compared them with experimental data¹¹⁻¹⁴ and have found at least in three dimensions there is no need of the negative part of χ_k^{-1} for the cluster growth. Therefore, the diffusion of the clusters has been found to be essential to the cluster growth.

Besides the renormalization of the susceptibility mentioned above, there should arise the renormalization of the mobility due to the formation of clusters. This is the reason why a cluster may be regarded as a free-particle, even though the basic kinetic equation is a nonlinear equation. A cluster is treated as a free-particle with a renormalized mobility similar to the usual many-body problem. In the cluster diffusion-reaction model of Binder and Stauffer,⁷ the renormalization of the mobility may be regarded as the problem in calculating the cluster diffusivity. Particularly, for a fluid mixture the cluster-gas picture might be strongly modified. This is because the hydrodynamic interaction is not only nonlinear but also of long range. It yields further renormalizations of the mobility and the susceptibility, changing the growth rate of the cluster diameter.⁷ The growth rate of the cluster diameter R for fluid in the case where clusters are connected was considered phenomenologically by Siggia.¹⁰ Clusters in such a case grow by means of the internal flow caused by the pressure difference due to the surface tension.

In this paper we shall consider the case where clusters in a fluid mixture are well separated from each other, and therefore the clusters in the fluid grow by the diffusion-reaction-like mechanism.⁷ For the quench of a fluid mixture near the critical

point, Kawasaki and Ohta⁵ obtained the equation of motion for the structure function, adding to the equation of Langer, Bar-on, and Miller, a term arising from long-range hydrodynamic interactions. The troublesome-to-treat short-range hydrodynamic interaction may be avoided as follows. The structure function S_k with large wave numbers is readily reduced to the value in the local equilibrium state and has an asymptotic solution $S_k \approx \chi_k$. This would be valid also for a fluid mixture. Thus, S_k for a large wave number is assumed to be independent of the details of hydrodynamic interactions. Therefore, we may treat only long-range hydrodynamic interactions. This enables us to use the mode-coupling method used by Kawasaki and Ohta.⁵

In Sec. II the nonlinear Langevin-type equation for the composition fluctuation will be derived. In Sec. III the equation of motion for the structure function $S_k(t)$ will be derived. A brief review of the cluster diffusion-reaction mechanism of Binder and Stauffer⁷ will be made in order to obtain the mobility. In Sec. IV, the composition with the experimental data both for the three-dimensional-spin-exchange kinetic Ising model and the three-dimensional fluid mixture, at low temperatures, will be made. The gaps of the inverse susceptibilities will be examined. Section V is devoted to the discussions.

II. KINETIC EQUATIONS

We shall use a Langevin-type equation to obtain the kinetic equations for the composition fluctuation. The original Mori equation¹⁵ is a linear Langevin-type equation. This can be extended to include nonlinear terms.¹⁶ These equations are valid only in a stationary state, i.e., the time correlation functions appearing in these equations satisfy the time translation symmetry. The introduction of a two-time fluctuating force is capable of extending the linear Langevin-type equation to be valid in the nonstationary domain.¹⁷ The equation thus obtained will be useful for the present purpose. A further formal extension of the Langevin-type equation valid in the nonlinear-nonstationary domain is easy as will be seen below.

Let A_t be a set of dynamical variables and let H_t be another set of dynamical variables, which may be a functional of A_t . We shall introduce a time-dependent projection operator $P_s(t)$:

$$P_s(t)G = \langle GH_s^* \rangle \langle H_t H_s^* \rangle^{-1} H_t, \quad (2.1)$$

where t and s are the time arguments. Here, the asterisk means the Hermitian conjugate and $\langle \rangle$ means an ensemble average performed on the initial ensemble. Here it is assumed that H is the quantity which has the inverse $\langle H_t H_s^* \rangle^{-1}$. Let us

introduce a two-time fluctuating force $R(t, s)$ which satisfies the equation

$$\frac{d}{ds} R(t, s) = -P_s \Lambda'_s R(t, s), \quad (t \geq s) \quad (2.2)$$

$$R(t, t) = (1 - P_t) \dot{A}_t, \quad (2.3)$$

where the dot stands for the time derivative $P_t \equiv P_t(t)$ and $\Lambda'_s \equiv dP_s(t)/ds|_{t=s}$. Then it can be shown that (2.2) and (2.3) are equivalent to the Langevin-type equation

$$\dot{A}_t = P_t \dot{A}_t - \int_s^t \langle R(t, \tau) \dot{H}_\tau^* \rangle \langle H_\tau H_\tau^* \rangle^{-1} H_\tau d\tau + R(t, s), \quad (2.4)$$

$$\langle R(t, s) H_s^* \rangle = 0. \quad (2.5)$$

The same method provides us with a linear Langevin-type equation¹⁷ for H , if we replace A by H in (2.3):

$$\dot{H}_t = P_t \dot{H}_t - \int_s^t \langle \tilde{R}(t, s) \tilde{R}^*(\tau, \tau) \rangle \langle H_\tau H_\tau^* \rangle^{-1} H_\tau d\tau + \tilde{R}(t, s), \quad (2.6)$$

$$\langle \tilde{R}(t, s) H_s^* \rangle = 0, \quad (2.7)$$

which is related to the original Mori equation. The difference between the Mori equation and (2.6) is that (2.6) is valid also in nonstationary states. In the integration of (2.4) one may find that

$$\langle R(t, \tau) \dot{H}_\tau^* \rangle = \langle R(t, \tau) \tilde{R}^*(\tau, \tau) \rangle. \quad (2.8)$$

The fluctuating force R should be obtained by solving (2.2) for the final condition (2.3). For the present purpose, however, we shall assume the existence of well-separated time scales, i.e., the Markov approximation can be used. The characteristic time scale of A or H is much larger than the time scale of R , τ_R . We can then put

$$\langle R(t, \tau) \dot{H}_\tau^* \rangle \approx \begin{cases} \langle \dot{A}_t \dot{H}_\tau^* \rangle, & 0 \leq t - \tau \leq \tau_R \\ 0, & t - \tau > \tau_R. \end{cases} \quad (2.9a)$$

$$(2.9b)$$

Smooth functions such as $\langle A_t \dot{H}_\tau^* \rangle$ contribute only the correction of the order τ_R to the short time integration and therefore can be neglected.

A. Nonlinear equation for composition fluctuation I

We here derive the first basic equation for the composition fluctuation

$$\eta_k(t) = \frac{1}{\sqrt{N}} \int \eta(t, \tilde{r}) e^{-i \cdot \tilde{r}} d\tilde{r}, \quad (2.10)$$

$$\eta(t, \tilde{r}) = \frac{1}{\bar{n}_A + \bar{n}_B} [n_A(t, \tilde{r}) - n_B(t, \tilde{r})], \quad (2.11)$$

where N is the total particle number, $n_{A,B}$ are the

local number density of A, B species, respectively, and the bar denotes the mean values. It is assumed that the coarsening is slow enough. Thus the coarsening proceeds isothermally. Therefore, the basic equation which we shall derive needs only a thermal equilibrium ensemble $\rho_0(T < T_c)$, which describes a coexistence state. The time-evolution operator (or Hamiltonian) commutes with $\rho_0(T < T_c)$. In such a case (2.4) reduces to the equation in the thermal equilibrium state.¹⁶

The first nonlinear equation for $\eta_{\mathbf{k}}$ is derived by extracting all nonlinear terms of slow modes, i.e., of $\eta_{\mathbf{k}}$ and of transverse velocity $\tilde{u}_{\mathbf{k}}^{\perp}$. This can be done by putting

$$H_t = \prod_{\mathbf{k} \leq \xi^{-1}} \delta(\eta_{\mathbf{k}} - \hat{\eta}_{\mathbf{k}}(t)) \delta(\tilde{u}_{\mathbf{k}}^{\perp} - \hat{\tilde{u}}_{\mathbf{k}}^{\perp}(t)), \quad (2.12)$$

$$A_t = \hat{\eta}_{\mathbf{k}}(t), \quad (2.13)$$

where ξ is the thermal correlation length and the carat denotes phase-space functions. The streaming term $P_t \hat{A}_t$, which is odd with respect to time inversion, may be assumed as

$$\begin{aligned} P_t \hat{A}_t &\equiv \int \left\langle \frac{d\hat{\eta}_{\mathbf{k}}(t)}{dt} H_t^* \right\rangle \omega(\eta, \tilde{u}_{\mathbf{k}}^{\perp})^{-1} H_t \prod_{\mathbf{k}'} d\eta_{\mathbf{k}'} d\tilde{u}_{\mathbf{k}'}^{\perp} \\ &= i\vec{k} \sum_{\mathbf{q}} \hat{\tilde{u}}_{\mathbf{k}-\mathbf{q}}^{\perp}(t) \hat{\eta}_{\mathbf{q}}(t), \end{aligned} \quad (2.14)$$

where $\langle \dots \rangle = \text{Tr} \rho_0(T < T_c) \dots$, and

$$\omega(\eta, \tilde{u}^{\perp}) \equiv \prod_{\mathbf{k} \leq \xi^{-1}} \langle \delta(\eta_{\mathbf{k}} - \hat{\eta}_{\mathbf{k}}) \delta(\tilde{u}_{\mathbf{k}}^{\perp} - \hat{\tilde{u}}_{\mathbf{k}}^{\perp}) \rangle \quad (2.15)$$

is a time-independent distribution function for the thermal equilibrium state below T_c (the coexistence state). The following relations are also used:

$$\langle \delta(a - A) \delta(a' - A) \rangle = \delta(a - a') \omega(a), \quad (2.16)$$

$$\langle \delta(a - A) \delta(a' - A) \rangle^{-1} = \delta(a - a') \omega(a)^{-1}. \quad (2.17)$$

Let us assume that there is no slow mode other than $\hat{\eta}$ and $\hat{\tilde{u}}^{\perp}$. Then the correlation time τ_R of the fluctuating force is assumed to be vanishingly small. Thus the second term on the right-hand side of (2.4) is written as

$$\begin{aligned} - \sum_{\mathbf{k}'} \int_{t=0}^t d\tau \left\langle \frac{d\hat{\eta}_{\mathbf{k}}(t)}{dt} \frac{d\hat{\eta}_{\mathbf{k}'}(\tau)}{dt} \frac{\partial H_{\tau}}{\partial \hat{\eta}_{\mathbf{k}'}(\tau)} \right\rangle \omega(\eta)^{-1} H_{\tau} \\ \times \prod_{\mathbf{k}''} d\eta_{\mathbf{k}''} d\tilde{u}_{\mathbf{k}''}^{\perp}, \end{aligned} \quad (2.18)$$

where we have assumed that $\omega(\eta, \tilde{u}^{\perp}) = \omega(\eta) \omega(\tilde{u}^{\perp})$. Here we have neglected the correlation between $\hat{\eta}$ and $\hat{\tilde{u}}^{\perp}$ because of the time inversion symmetry. Equation (2.18) is transformed into

$$\begin{aligned} \sum_{\mathbf{k}'} \left(\frac{\partial}{\partial \eta_{\mathbf{k}'}'} \int_{t=0}^t d\tau \langle f_{\mathbf{k}}^{\perp}(t) f_{\mathbf{k}'}^{\perp}(\tau) H_{\tau} \rangle \right) \omega^{-1} H_t \prod_{\mathbf{k}''} d\eta_{\mathbf{k}''} d\tilde{u}_{\mathbf{k}''}^{\perp} \\ = M^0 k_B T k^2 \frac{\partial \ln \omega(\hat{\eta}(t))}{\partial \hat{\eta}_{-\mathbf{k}}(t)}, \end{aligned} \quad (2.19)$$

where we have rewritten the fluctuating force R as f^{\perp} and assumed that f^{\perp} is statistically independent both of $\hat{\eta}$ and $\hat{\tilde{u}}^{\perp}$. The bare mobility M^0 is given by

$$\langle f_{\mathbf{k}}^{\perp}(t) f_{\mathbf{k}'}^{\perp}(\tau) \rangle = 2k_B T k^2 M^0 \delta_{\mathbf{k}, -\mathbf{k}'} \delta(t - \tau). \quad (2.20)$$

The nonlinear Langevin equation of the first kind is written as

$$\begin{aligned} \frac{d}{dt} \hat{\eta}_{\mathbf{k}}(t) &= i\vec{k} \sum_{\mathbf{q}} \hat{\tilde{u}}_{\mathbf{k}-\mathbf{q}}^{\perp}(t) \hat{\eta}_{\mathbf{q}}(t) + k_B T M^0 k^2 \frac{\partial \ln \omega(\hat{\eta}(t))}{\partial \hat{\eta}_{-\mathbf{k}}(t)} \\ &+ f_{\mathbf{k}}^{\perp}(t) \quad (k\xi < 1), \end{aligned} \quad (2.21)$$

In $\omega(\eta)$ corresponds to the coarse-grained free-energy Φ and must have two local minima corresponding to two stable phases. Equation (2.21) is basically the (nonlinear) Cahn-Hilliard equation, amended by a hydrodynamic term and the fluctuating force.

B. Nonlinear equation for composition fluctuation II

The next step is to eliminate the transverse velocity \tilde{u}^{\perp} . H_t is now chosen as

$$H_t = H_t' \equiv \prod_{\mathbf{k} \leq \xi^{-1}} \delta(\eta_{\mathbf{k}} - \hat{\eta}_{\mathbf{k}}(t)). \quad (2.22)$$

The streaming term $P_t \hat{A}_t$ in this case vanishes due to the time translation symmetry. Here we shall assume that the characteristic time τ_1 of $\hat{\eta}_{\mathbf{k}}$ is much larger than the time of \tilde{u}^{\perp} . The second term on the right-hand side of (2.4) is written as

$$\begin{aligned} - \int_{t=\tau_0}^t d\tau \left\langle \frac{d\hat{\eta}_{\mathbf{k}}(t)}{dt} \frac{d\hat{\eta}_{\mathbf{k}'}(\tau)}{dt} \frac{\partial H_{\tau}}{\partial \hat{\eta}_{\mathbf{k}'}(\tau)} \right\rangle \omega(\eta)^{-1} H_{\tau}' \prod_{\mathbf{k}''} d\eta_{\mathbf{k}''} \\ (2.23) \end{aligned}$$

Since smooth functions such as $\langle \hat{\eta}_{\mathbf{k}}(t) \hat{\eta}_{\mathbf{k}'}(\tau) \rangle$ give only a small contribution of the order τ_0 , (2.23) can be transformed, with the aid of (2.21), into

$$\begin{aligned} k_B T k^2 M^0 \frac{\partial \ln \omega(\hat{\eta}(t))}{\partial \hat{\eta}_{-\mathbf{k}}(t)} \\ - \sum_{\mathbf{q} \neq \mathbf{k}'} \int_{t=\tau_0}^t d\tau \langle [\vec{k} \hat{\tilde{u}}_{\mathbf{k}-\mathbf{q}}^{\perp}(t)] [\vec{k}' \hat{\tilde{u}}_{\mathbf{k}'-\mathbf{q}}^{\perp}(\tau)] \rangle \\ \times \omega(\hat{\eta}(t))^{-1} \frac{\partial \hat{\eta}_{\mathbf{q}}(t) \eta_{\mathbf{q}}(t) \omega(\hat{\eta}(t))}{\partial \eta_{\mathbf{k}}(t)}. \end{aligned}$$

By extending the lower bound of the integration to $-\infty$, we obtain

$$\begin{aligned} \frac{d}{dt} \hat{\eta}_{\mathbf{k}}(t) &= k_B T k^2 M^0 \frac{\partial \ln \omega(\hat{\eta}(t))}{\partial \hat{\eta}_{-\mathbf{k}}(t)} \\ &- \sum_{\mathbf{q}, \mathbf{k}'} \int_{-\infty}^t d\tau \langle [\hat{\mathbf{k}} \hat{\mathbf{u}}_{\mathbf{k}-\mathbf{q}}(t)] [\hat{\mathbf{k}}' \hat{\mathbf{u}}_{\mathbf{k}'-\mathbf{q}}(\tau)] \rangle \\ &\times \omega(\hat{\eta}(t))^{-1} \frac{\partial \hat{\eta}_{\mathbf{q}}(t) \hat{\eta}_{\mathbf{q}}(t) \omega(\hat{\eta}(t))}{\partial \hat{\eta}_{\mathbf{k}}(t)} + f_{\mathbf{k}}'(t), \end{aligned} \quad (2.24)$$

where we have rewritten R as f' .

III. QUENCH FROM A SINGLE-PHASE REGION

The quench of a binary mixture is done by suddenly bringing the system to a coexistence region from a single-phase region. At an initial time the system is in a thermal equilibrium state described by the phase distribution function $\rho_0(T > T_c)$ of a single-phase region. The initial ensemble $\rho_0(T > T_c)$, does not commute with the time-evolution operator in a coexistence state. Thus the Langevin-type equation (2.4) describing a quenched mixture is nonstationary. We shall consider the linear Langevin-type equation for $A = H = \hat{\eta}$. Then the streaming term is given by

$$P_t \dot{A}_t = K_{\mathbf{k}}(t, t) \hat{\eta}_{\mathbf{k}}(t), \quad (3.1)$$

where

$$K_{\mathbf{k}}(t, t) \equiv \left\langle \frac{d\hat{\eta}_{\mathbf{k}}(t)}{dt} \hat{\eta}_{-\mathbf{k}}(t) \right\rangle \langle \hat{\eta}_{\mathbf{k}}(t) \hat{\eta}_{-\mathbf{k}}(t) \rangle_0^{-1} \quad (3.2)$$

and where

$$\langle \dots \rangle_0 = \text{Tr} \rho_0(T > T_c).$$

Since the time-evolution operator of $\hat{\eta}_{\mathbf{k}}$ does not commute with $\rho_0(T > T_c)$, (3.2) does not vanish. The second term on the right-hand side of (2.4) is written as

$$-k_B T k^2 M_{\mathbf{k}} S_{\mathbf{k}}(t)^{-1} \hat{\eta}_{\mathbf{k}}(t), \quad (3.3)$$

where

$$\int_{t-\tau_0}^t \left\langle \frac{d\hat{\eta}_{\mathbf{k}}(t)}{dt} \frac{d\hat{\eta}_{-\mathbf{k}}(\tau)}{dt} \right\rangle_0 d\tau = k_B T k^2 M_{\mathbf{k}}(t). \quad (3.4)$$

Here τ_0' is the correlation time of the fluctuating force, which can be equal to τ_0 if the nonlinearity of $\omega(\hat{\eta})$ does not contribute to the renormalization of the fluctuating force or the mobility. We then obtain a nonstationary linear Langevin-type equation¹⁷

$$\frac{d}{dt} \hat{\eta}_{\mathbf{k}}(t) = K_{\mathbf{k}}(t, s) \hat{\eta}_{\mathbf{k}}(t) + f_{\mathbf{k}}'(t, s), \quad (3.5)$$

$$\begin{aligned} K_{\mathbf{k}}(t, s) &\equiv \left\langle \frac{d\hat{\eta}_{\mathbf{k}}(t)}{dt} \hat{\eta}_{-\mathbf{k}}(s) \right\rangle_0 \langle \hat{\eta}_{\mathbf{k}}(t) \hat{\eta}_{-\mathbf{k}}(s) \rangle_0^{-1} \\ &= K_{\mathbf{k}}(t, t) - k_B T k^2 M_{\mathbf{k}}(t) S_{\mathbf{k}}(t)^{-1} \\ &\equiv K_{\mathbf{k}}(t), \quad t - s > \tau_0'. \end{aligned} \quad (3.6)$$

Equation (3.6), which can be regarded as the fluctuation-dissipation theorem in nonequilibrium state can be rewritten into the equation of motion for the structure function $S_{\mathbf{k}} \equiv \langle \hat{\eta}_{\mathbf{k}}(t) \hat{\eta}_{-\mathbf{k}}(t) \rangle_0$:

$$\begin{aligned} \frac{d}{dt} S_{\mathbf{k}}(t) &= K_{\mathbf{k}}(t, t) S_{\mathbf{k}}(t) + K_{-\mathbf{k}}(t, t) S_{\mathbf{k}}(t) \\ &= [K_{\mathbf{k}}(t) + K_{-\mathbf{k}}(t)] S_{\mathbf{k}}(t) + 2k_B T k^2 M_{\mathbf{k}}(t). \end{aligned} \quad (3.7)$$

$K_{\mathbf{k}}(t)$ and $M_{\mathbf{k}}(t)$ will be calculated by the use of the nonlinear equation (2.21) or (2.24).

Before proceeding further, we shall review the phenomenological theory of Binder and Stauffer,⁷ which will help us to reduce (3.7). Binder and Stauffer considered the cluster growth by a reaction of clusters. They assumed that a cluster behaves like a Brownian particle, which collides once in a mean time Δt . If the cluster diffusivity D_{c1} , which is the diffusion coefficient of the center of the gravity of a cluster is known, then Δt is given by

$$\Delta t \simeq R^2 D_{c1}^{-1}, \quad (3.8)$$

where R is the average cluster diameter and the intercluster distance is roughly given by R . In each collision, a cluster diameter is lengthened by the amount of the order R . Thus the average cluster diameter R obeys the equation

$$\frac{d}{dt} R \simeq \frac{R}{\Delta t} \simeq \frac{D_{c1}}{R}. \quad (3.9)$$

If D_{c1} is of the form

$$D_{c1} = D_0 R^{-\theta}, \quad (3.10)$$

then we find that

$$R \propto 1/t^{(\theta+2)}. \quad (3.11)$$

Binder and Stauffer⁷ evaluated θ for various systems. For a purely dissipative system (kinetic Ising spin) at low temperatures, the composition of the cluster is almost pure. Thus the Brownian movement of a cluster is caused only by the random movement of atoms at the cluster surface. Then Binder and Stauffer obtained $\theta = d + 1$ for the purely dissipative system. On the other hand they obtained $\theta = d - 2$ for the fluid mixture because of the Stokes law.

Here we shall use their estimation. By putting $K_{\mathbf{k}}(t) \simeq D_{c1} k^2$ and using a simple dimensional analysis we find that

$$M_{\mathbf{k}} = \frac{1}{k_B T k^2} \left(\frac{d\hat{\eta}_{\mathbf{k}}}{dt} \hat{\eta}_{-\mathbf{k}} \right) = \frac{D_{c1}}{k_B T} \langle \hat{\eta}_{\mathbf{k}} \hat{\eta}_{-\mathbf{k}} \rangle = \frac{1}{k_B T} D_{c1} R^d. \quad (3.12)$$

Let M^1 be the correction to the bare mobility M^0 due to the cluster formation,

$$M_k = M^0 + M^1. \quad (3.13)$$

Then M^1 may be given by

$$M_k^1 = D_{cl} R^d / k_B T, \quad (3.14)$$

which is proportional to R^{-1} for a purely dissipative system and R^2 for the fluid mixture.¹⁸ Thus for large R the renormalization of the mobility may be neglected for the purely dissipative system, while the renormalization of the mobility is essential to the fluid mixture.

We have examined the validity of the above estimation of the mobility. In the three-dimensional case, $a' = (d+2)^{-1}$ for a purely dissipative system is supported by computer simulations of kinetic Ising model at low temperatures.¹¹ However, if the computation time is extended, a' increases for the composition near the coexistence curve.^{19,20} This might be the symptom of the evaporation-condensation mechanism.⁶ For the stage where $a' = (d+2)^{-1} = 0.2$, we have ascertained that the prediction $M = M^0$ holds. Here in the unit of computer simulation M^0 is given by

$$k_B T M^0 = 1 / (4d) \quad (3.15)$$

for a square lattice or simple cubic lattice structure.⁴ We have ascertained the validity of the mobility:

$$M_k = M^0, \quad (3.16)$$

with the use of the asymptotic solution of $S_k(t)$ at small t , which will be given later. There is the region where $a' \neq (d+2)^{-1}$ but $a' = (d+3)^{-1}$ according to Binder and Stauffer,⁷ holds in two-dimensional kinetic Ising model at low temperatures.¹² In this region we found that (3.16) is really invalid. Instead of (3.16), the following is suitable:

$$M_k = k_m M^0, \quad (3.17)$$

where k_m is the position at which $S_k(t)$ has its maximum. Here the lattice constant a is always unity. This suggests that there is no effect of the bare mobility in this region. The mobility (3.17) is that of the cluster diffusivity by Binder and Stauffer. This can be found as follows. Since the cluster diffusivity is caused by the random movement of atoms on the cluster surface, the mobility of the Binder and Stauffer process is given by

$$M \approx M^0 S / V, \quad (3.18)$$

where S and V are the cluster surface area and the cluster volume, respectively. For two dimensions $S/V \approx 4R^{-1} \approx \pi R^{-1} \approx k_m$. Thus (3.18) is consistent with (3.17). The growth rates of the average cluster diameter R are consistent with the mobility for two and three dimensions. However, strictly speaking, (3.17) must be replaced by the

k -dependent mobility, in general. We could not obtain the k -dependent mobility. Thus in the present paper we shall not discuss the two-dimensional case.

For a purely dissipative system in three dimensions, the hydrodynamic interaction vanishes, i.e., $\tau_0 = 0$. Then (2.24) is written as

$$\frac{d}{dt} \hat{\eta}_k = k_B T k^2 M^0 \frac{\partial \ln \omega(\hat{\eta})}{\partial \hat{\eta}_{-\mathbf{k}}} + f_k^0. \quad (3.19)$$

Next, we must obtain an exactly renormalized linear Langevin equation corresponding to (3.5). This may be given by regarding a cluster as a free-particle, since the diffusion equation of the ideal gas may be a linear equation. The linearization of the nonlinear Langevin equation (3.19) generally gives rise to the renormalizations of the fluctuating force, the mobility, and the susceptibility. However, as was seen above, the renormalization of the mobility is of the order R^{-1} and therefore may be neglected. Thus we may simply replace the coarse-grained free-energy $\ln \omega(\hat{\eta})$ by the renormalized free-energy (1.5):

$$\frac{\partial}{\partial \hat{\eta}_{-\mathbf{k}}} \ln \omega(\hat{\eta}) \rightarrow -\chi_k^{-1} \hat{\eta}_k, \quad (3.20)$$

where χ_k is the renormalized susceptibility of a purely dissipative system and may be called the nonhydrodynamic susceptibility. If the cluster-gas picture is appropriate, one may expect that

$$\chi_k^{-1} \approx \begin{cases} 0 \sim R^{-d}, & k \leq k_m \approx \pi/R \\ \infty, & k > k_m \approx \pi/R. \end{cases} \quad (3.21a)$$

$$\chi_k^{-1} \approx \begin{cases} 0 \sim R^{-d}, & k \leq k_m \approx \pi/R \\ \infty, & k > k_m \approx \pi/R. \end{cases} \quad (3.21b)$$

It is worthwhile to note that such an assumption as (3.21) is possible only for a coexistence region, in which $\delta \ln \omega(\eta) / \delta \eta_k = 0$ for nonvanishing composition fluctuation η_k . Equations (2.21) and (2.24) are replaced by

$$\begin{aligned} \frac{d}{dt} \hat{\eta}_k(t) &= -k_B T k^2 M^0 \chi_k^{-1} \hat{\eta}_k(t) + i\mathbf{k} \sum_{\mathbf{q}} \hat{\mathbf{u}}_{\mathbf{k}-\mathbf{q}}^{\dagger}(t) \hat{\eta}_{\mathbf{q}}(t) + f_k^0(t), \\ \frac{d}{dt} \hat{\eta}_k(t) &= -k_B T k^2 M^0 \chi_k^{-1} \hat{\eta}_k(t) \\ &\quad - \sum_{\mathbf{q}, \mathbf{k}'} \int_{-\infty}^t d\tau \langle [\mathbf{k}' \hat{\mathbf{u}}_{\mathbf{k}-\mathbf{q}}^{\dagger}(t)] [\mathbf{k} \hat{\mathbf{u}}_{\mathbf{k}-\mathbf{q}}^{\dagger}(\tau)] \rangle \\ &\quad \times \omega(\hat{\eta}(t))^{-1} \frac{\partial \hat{\eta}_{\mathbf{q}}(t) \hat{\eta}_{\mathbf{q}}(t) \omega(\hat{\eta}(t))}{\partial \hat{\eta}_{\mathbf{k}}(t)} + f_k^{\dagger}(t). \end{aligned} \quad (2.21')$$

$$(2.24')$$

The mobility for the fluid mixture is calculated from (3.4) and (2.21'). By putting $\tau_0' = \tau_0$, we obtain

$$M_k = M^0 + M_k^1, \quad (3.22)$$

where M_k^1 is the mobility correction and given for

three dimensions by

$$M_k^1 = A \int_0^\infty \left(\frac{q}{k}\right)^2 \left(\frac{k^2 + q^2}{qk} \ln \left| \frac{k+q}{k-q} \right| - 2\right) S_q(t) dq, \quad (3.23)$$

and where

$$A = \lim_{k \rightarrow 0} \pi \tau_0 \langle |\hat{u}_k|^2 \rangle / (3k_B T).$$

Here we have put

$$\begin{aligned} \langle \hat{u}_k^\dagger(t) \hat{u}_k^\dagger(t') \rangle_0 &= \langle \hat{u}_k^\dagger(t) \hat{u}_k^\dagger(t') \rangle \\ &= \langle |\hat{u}_k|^2 \rangle \exp[-(k^2/\tau_0)|t-t'|], \end{aligned}$$

i.e., we have assumed that the velocity correlation is independent of the initial condition. The method of obtaining (3.23) is the same as that for the long-time tail in the normal fluid.²¹ We have used the fact that the time scale τ_1 of η_k is much longer than τ_0 .

Since in the late stage the relevant scale length is the average cluster diameter R only, one may assume that the structure function $S_k(t)$ must be scaled as

$$S_k(t) = R^d \tilde{S}(kR). \quad (3.24)$$

Then we can find that M^1 is the quantity of the order R^2 . Thus the equation of motion for $S_k(t)$ in a late stage of phase separation of a purely dissipative system is given from (3.7) by

$$\frac{d}{dt} S_k(t) = 2k_B T M^0 k^2 (1 - \chi_k^{-1} S_k), \quad (3.25)$$

where from (3.19) and (3.20) we observed that

$$K_k(t) = -k_B T M^0 k^2 \chi_k^{-1}. \quad (3.26)$$

For a fluid mixture we obtain

$$\frac{d}{dt} S_k(t) = 2k_B T M^1 k^2 (1 - \chi_k'^{-1} S_k), \quad (3.27)$$

where we have put

$$K_k(t) \equiv -k_B T M^1 k^2 \chi_k'^{-1}, \quad (3.28)$$

and the renormalized susceptibility χ_k' will be calculated later. In order that (3.24) is the solution of (3.25) or (3.27), χ_k or χ_k' must be also scaled as $R^d \tilde{\chi}_k(kR)$ or $R^d \tilde{\chi}_k'(kR)$. Then R satisfy the equation

$$R = R_0 t^{a'}. \quad (3.29)$$

Here, for the purely dissipative system²²

$$a' = (d+2)^{-1}. \quad (3.30)$$

Of course, we obtain $a' = (d+3)^{-1}$ as did Binder and Stauffer,⁷ if M is given by (3.17). For a fluid mixture we obtain²²

$$a' = 1/d. \quad (3.31)$$

At the present there are a few cases where (3.30) and (3.31) are consistent with experiments.

For a purely dissipative system $a' = (d+2)^{-1}$ is consistent with computer simulation of the three-dimensional-spin-exchange kinetic Ising model with one-to-one composition²³ and also with one-to-four composition,²⁴ at a low temperature. In these cases $M_k = M^0$ has been ascertained. Other computer simulations, i.e., the quench near the critical point and the quench at a later time for the composition near the coexistence curve at low temperature,^{19,20} in three dimensions exhibit growth rates faster than that determined by (3.30). Near the critical point, the cluster diffusivity D_{cl} takes different values.⁷ The change of the growth rate of cluster diameter in later time would be the symptom of the evaporation-condensation process of Lifshitz and Slyozov.⁶

IV. SUSCEPTIBILITIES

A simple mean-field calculation showed that $\chi_k^{-1} = 0(R^{-d})$ for $k < k_m \approx \pi/R$ and $\chi_k^{-1} = \infty$ for $k > k_m$ for a purely dissipative system at low temperatures.²⁵ We shall here expect the susceptibility similar to this. Namely, we expect the following form for χ_k :

$$\chi_k^{-1} = \alpha k_m^d [(k/k_m)^\gamma + \beta], \quad k_m \approx \pi R^{-1}. \quad (4.1)$$

Here, k_m is the wave number for which S_k has its maximum. We may predict that

$$\alpha \approx \pi^{-d}, \quad \beta \approx 1. \quad (4.2)$$

At intermediate wave numbers near k_m , the exponent γ may depend on the surface conditions of clusters.

We shall present a simple estimation of γ . Let us consider a cluster with a typical size and let Ω be the total volume of the area of other clusters with the opposite composition, which can exist within the distance r from some point within the former cluster. Here r is assumed to be smaller than R . The pair correlation function may roughly be estimated as $\langle \eta(t, \vec{r}) \eta(t, 0) \rangle_0 \approx \text{const} + R^{-d} \Omega$. Here the cluster volume is regarded as R^d . Let r be smaller than R but of the order of R . When cluster surfaces are smoothly curved,⁸ then $\Omega \approx \gamma R^{d-1}$. When, however, cluster surfaces are extremely tangled, then $\Omega = r^d$. Therefore, the asymptotic solution $S_k \approx \chi_k$ for $k \geq k_m$ gives $\gamma = d+1$ for smoothly curved surfaces and $\gamma = 2d$ for extremely tangled surfaces. The surface condition depends not only on the surface tension but also on the average composition $\bar{\eta}$. As the surface tension increases and as the average composition $\bar{\eta}$ approaches its pure one, the cluster surfaces become smoothly curved. For instance one may predict that $\gamma = d+1$ for the composition near the coexistence curve and $\gamma = 2d$ for the composition

near the center of the miscibility gap.

If we introduce the following set of reduced parameters:

$$\tilde{\alpha} \equiv R_0^{-d} \alpha, \quad \tilde{\beta} \equiv R_0^{-d} b, \quad \tilde{A} \equiv R_0^2 A, \quad (4.3)$$

then R_0 does not appear explicitly. Equation (4.2) and also $d+1 \leq \gamma \leq 2d$ give approximate estimations. These constants are more sensitive to the details of the properties of system than the exponent a' . Therefore, we have determined $\tilde{\alpha}$ and M^0 or A by comparing them with experimental data. Namely, for small t , (3.25) and (3.27) have asymptotic solutions:

$$S_k(t) \approx 2k_B T M^0 k^2 t, \quad (4.4)$$

$$S_k(t) \approx 2k_B T k^2 \int_0^t M_k^1(t) dt \propto t^{5/3}, \quad (4.5)$$

respectively, and for large t , where $dS_k/dt \approx 0$:

$$S_k(t) \approx \chi_k, \quad \chi_k' \approx \alpha^{-1} k_m^{-d+\gamma} k^{-\gamma}. \quad (4.6)$$

In order to compare the theoretical structure function $S_k(t)$ with experimental data, we have rewritten (4.1) into the form

$$\chi_k^{-1} = \alpha' t^{-a'd} (t^{a'\gamma} k^\gamma + \beta'). \quad (4.1')$$

Since k_m is observable, we can determine $k_m^0 \equiv t^{a'} k_m$. Thus we have

$$\chi_k^{-1} = \alpha' (k_m^0)^{-d+\gamma} k_m^d [(k/k_m)^\gamma + \beta' (k_m^0)^{-\gamma}]. \quad (4.1'')$$

Here, α' and β' can be determined using experimental data and k_m^0 is determined from the theoretical calculation of $S_k(t)$. For the spin-exchange kinetic Ising model at low temperatures, the best agreement of the theoretical $S_k(t)$ with experimental ones was found for $\gamma=6$. In the unit of the computer simulation the susceptibility thus determined is given by

$$\chi_k^{-1} = \frac{1}{37} k_m^3 [(k/k_m)^6 + 0.86], \quad (4.7)$$

for the one-to-one composition at $T=0.59T_c$ (Ref. 23) [see Figs. 1(a) and 1(b)] and

$$\chi_k^{-1} = \frac{1}{27} k_m^3 [(k/k_m)^6 + 0.94], \quad (4.8)$$

for the one-to-four composition at $T=0.59T_c$.²⁴

The above two susceptibilities are consistent with the prediction (4.2).

For the water-rich binary fluid mixture far from the critical point²⁶ we observed that

$$\chi_k'^{-1} \propto [(k/k_m)^4 + 2.8], \quad (4.9)$$

if we assume that the susceptibility χ_k is not renormalized by the hydrodynamic interactions, i.e., $\chi_k = \chi_k'$. Here the constant α can not be determined, since the data are not those for the structure function but those for the scattering intensity. The gap β is about three times as larger as those of

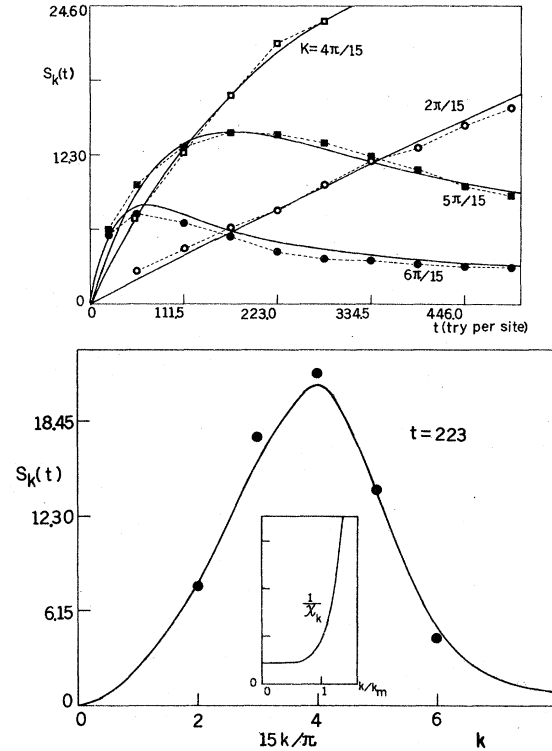


FIG. 1. (a) and (b). $S_k(t)$ of the three-dimensional-spin-exchange kinetic Ising model with one-to-one composition quenched at $T=0.59T_c$ (Ref. 23). The solid curves are calculated using (3.25) with the susceptibility (4.7).

the purely dissipative systems. Let us consider the renormalization of the susceptibility due to hydrodynamic interaction. We shall assume that the hydrodynamic interactions essential to the cluster diffusivity are those with small wave number $k < k_m$. Since χ_k' is an asymptotic solution of $S_k(t)$ for large k ($> k_m$) and is a static characteristic determined by the cluster configuration or cluster surface condition, we shall also assume that χ_k' for $k > k_m$ is not renormalized by hydrodynamic interactions. To treat remaining long-range hydrodynamic interactions, we shall assume that long-range hydrodynamic interactions are not responsible for the nonhydrodynamic properties of the system, i.e., for the cluster configuration. Therefore, the free-energy or the probability distribution function $\omega(\eta)$ should be the same as that of a purely dissipative system. Thus (3.20) with (4.1) is applicable. Then we have used a usual decoupling approximation to treat long-wavelength modes. Then, using (2.24') and the first identity of (3.6) we have obtained $K_k(t)$ or χ_k' defined by (3.28):

$$\chi_k'^{-1} = \begin{cases} \chi_k^{-1} + \frac{A}{M^0} \int_0^\infty \left(\frac{q}{k}\right)^2 \left(\frac{k^2+q^2}{qk}\right) \ln \left| \frac{k+q}{k-q} \right| - 2 \Big) (1 - S_q \chi_q^{-1}) dq, & k \leq pk_m \\ \chi_k^{-1}, & k > pk_m \end{cases} \quad (4.10a)$$

$$(4.10b)$$

where the bare mobility M^0 is neglected. Here p is a constant of the order unit and is chosen so that $S_k(t)$ may be stationary with respect to p . The second term on the right-hand side of (4.10a) vanishes in thermal equilibrium states ($\chi_k = S_k$); χ_k is not renormalized by the hydrodynamic interaction in thermal equilibrium states. Thus it is natural to put $\chi_k' \simeq \chi_k$ for $k > k_m$, where all modes are already in a local equilibrium state.

It is easy to find that the second term on the right-hand side of (4.10a) is scaled as $R^{-d}F(kR)$. Thus $(\chi_k')^{-1}$ is also scaled as the same. Equation (4.10a) is also found from the equation of motion for I_k by Kawasaki and Ohta,⁵ if we replace $\chi_k \propto (k^2 - \mu)^{-1}$ by χ_k given by (4.1). The overall contribution from the second term on the right-hand side of (4.10a) is positive as it is examined numerically. The cut-off parameter p was chosen so that the second term on the right-hand side of (4.10a), which is a function of p through $S_k(t)$, takes a stationary value as a function of p . p thus determined, is slightly larger than unity. When (4.1) is taken for the nonhydrodynamic susceptibility χ_k , the renormalized susceptibility χ_k' is no more of the same form as (4.1). $\chi_k'^{-1}$ thus given, has a minimum near $k = k_m$. The most appropriate nonhydrodynamic susceptibility for the water-rich binary fluid mixture²⁶ is given by [Figs. 2(a) and 2(b)]:

$$\chi_k^{-1} \propto k_m^3 \left[\left(\frac{k}{k_m} \right)^4 + 0.91 \right]. \quad (4.11)$$

The gap of β for the fluid mixture is consistent with those of (4.7) and (4.8). The difference in γ is due to the surface conditions of clusters.

In the later stage of the phase separation of a purely dissipative system, the Lifshitz and Slyozov process or the evaporation-condensation process⁶ will become dominant. Then the present analysis cannot be applied. Using computer simulation, Penrose *et al.*¹⁹ found in the later stage of the phase separation of kinetic Ising model the same growth rate as (4.18) for the composition near the coexistence curve. However, for the same system, Marro *et al.*²⁰ found that $S_k(t)$ is scaled as $R^3 \tilde{S}(kR)$ with $R \propto t^{0.28}$ (in three dimensions). One may find for this system the $k^{-3.3}$ tail of $S_k(t)$, which is nearly consistent with the k^{-d-1} tail.

V. DISCUSSIONS

We have studied the structure function $S_k(t)$ of quenched binary mixtures at low temperatures in

three dimensions. At least from the present study, the inverse susceptibility χ_k^{-1} in three dimensions seems to have a positive gap rather than a negative gap. Since χ_k for k small enough gives only a little contribution to S_k [see (4.4) and (4.5)] the present work might not yet give the firm evidence of the positive gap of χ_k^{-1} . In actuality, however, this is not an essential problem. No negative part of χ_k is responsible for the cluster growths. The diffusion of clusters^{7,10} or free atoms seems to be responsible for the cluster growth at temperatures far from a critical point.

Nevertheless, the positive gap of χ_k^{-1} is plausible by two reasons. One is as follows. Infinitely large number of configurations of clusters is possible under the condition that the first derivative of the

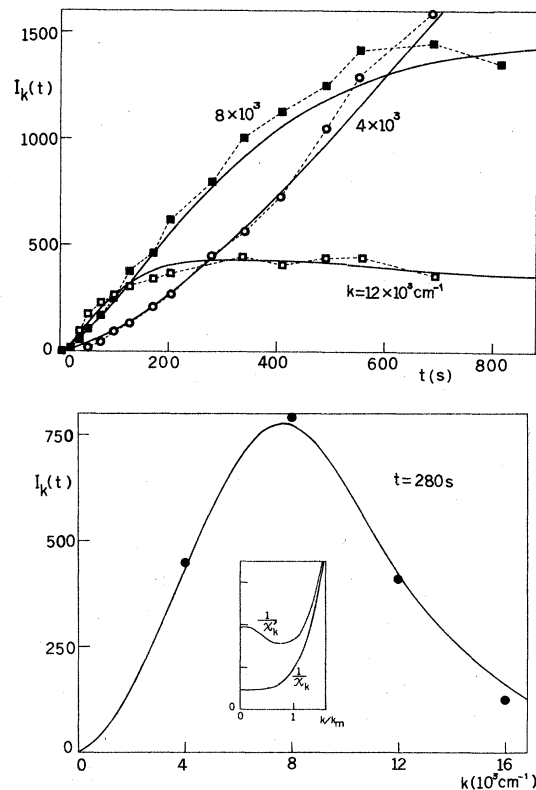


FIG. 2. (a) and (b). The scattering intensity $I_k(t)$ for the off-critical quenching of isobutyric acid + water mixture (Ref. 26). The solid curves are $S_k(t)$ calculated with the use of (3.27) with (3.23), (4.10), and (4.11). The constant A which determines $S_k(t)$ for small k or small t , and α which determines $S_k(t)$ for large k or large t are suitably chosen.

free-energy vanishes. Thus there exists an ambiguity in the cluster configurations. In order to remove such an ambiguity, one may introduce a statistical averaging procedure. The simplest way of performing the averaging procedure is to regard the assembly of clusters as the assembly of free-particles. One thus assumes that the free-energy can be reexpanded on the basis of the cluster-gas picture. Therefore, one speculated the existence of a small gap of the order of R^{-d} in χ_k^{-1} . The other reason to believe the existence of the small gap in the inverse susceptibility is as follows. Consider well separated clusters; how do attractive interactions among clusters influence the susceptibility χ_k ? It takes a long time for two or more than two clusters to meet. When each cluster moves freely, the system may be regarded as the assembly of free-particles. After a certain time interval the average size of clusters becomes larger because of the coalescence of clusters due to attractive interactions. Then the system is rescaled by the new scale length $R(t)$. The system is similar to itself before the coalescence occurred. The grown clusters are again treated as free-particles. The rescaling procedure or the time-dependent scale length $R(t)$ masks the attractive interactions among clusters. In fact, since the inverse susceptibility χ_k^{-1} for a small k is a decreasing function of t , the free-energy $\frac{1}{2}\chi_k^{-1}|\eta_k|^2$ for a fixed value of $|\eta_k|$ is a decreasing function of t . This means that the free-energy may decrease even if $|\eta_k|$ increases. Thus the scaled susceptibility χ_k may yield the same effect as that of a negative susceptibility.

The above speculation is, however, marginal when the correlation among clusters cannot be neglected. Two cases may be considered. In the one case the correlation among clusters acts to reduce the gap of the susceptibility. In this case the gap may be negative. Namely, the distinction between the early stage and the late stage is not clear. In the other case the correlation among clusters gives rise to a drastic change in the properties of clusters. The growth rate of the cluster diameter may be different for different fluid mixtures. Also the cluster shape may be changed drastically. For instance, there arises the transition between the free cluster gas and the infinitely connected clusters,²⁷ such as in the case of percolation problem.²⁸ In this case it might be possible to restore a positive gap of the susceptibility because of the existence of infinitely large number of metastable configurations, although this depends on how strong the remaining correlation among *new* clusters is.

At least in three dimensions at temperatures far from critical points, there is no evidence of the

need of the negative part of the susceptibility for the growth of clusters. At small k , S_k increases not because of the negative curvature of the free-energy but because of the reduction of the positive curvature of the free-energy. Then the composition fluctuations of phase-separating binary mixtures may have properties similar to those fluctuations in a thermal equilibrium state. For instance, the fluctuating force is important for the $S_k(t)$ to grow; also the volumes of clusters do not always monotonically increase, but often decrease, as is observed by the computer simulation.¹⁹ It is the average size which increases with time.

For two-dimensional kinetic Ising model at low temperatures¹² we observed rather a negative gap $\chi_k < 0$, using (3.17) for the mobility. This situation was not changed even if we put $M_k = M' = \text{const}$. Correlations among clusters due to the fluctuations characteristic to low dimensions would be effective in two dimensions. In fact, in one dimension there is no phase separation due to large fluctuations and thus the cluster-gas picture is essentially invalid in one dimension. We consider that two-dimensional system is a marginal case of the free-cluster-gas picture of the phase separation. Therefore, in two dimensions, there would be no definite distinction between the early stage and the late stage of the phase separation.

Recently Horner and Jüngling²⁹ discussed the phase separation of a purely dissipative system and found that the exponent a' approach $\frac{1}{4}$ in three dimensions for large t . This behavior of the exponent a' was first noted by Binder regarding the theory of Langer, Bar-on, and Miller.⁴ Such a behavior of a' results from the k^2 term in the free-energy³⁰ (kinetic energy term of the Ginzburg and Landau free-energy). If this term remains, then the structure function S_k must have the k^{-2} tail. However, experimentally, no such tail has been found at least in the late stage of the phase separation. Therefore, it seems that the k^2 term in the free-energy must be canceled out in order to form well-developed clusters.⁸ As can be seen from the relation between the mobility and a' , a' is always an increasing function of time t or a cluster diameter R .⁹ Therefore, our exponent $a' = (d+2)^{-1}$ for the purely dissipative system will fail in the later stage where the bare mobility is not dominant. However, we consider that this is not due to the neglect of the k^2 term in the free-energy but due to the neglect of the Lifshitz and Slyozov process.⁶

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- ²²When $M^1 \propto R^{-\zeta}$, we get $R \propto t^{a'}$, where $a' = (d+2+\zeta)^{-1}$. In the present mode-coupling method we obtain $M^1 \propto R^2$ which is consistent with that of Binder and Stauffer, e.g., Ref. 18.
- ²³The experimental data are taken from Fig. 8 of the first reference of Ref. 11.
- ²⁴The experimental data are taken from Fig. 4(a) of the second reference of Ref. 11.
- ²⁵H. Furukawa, *Phys. Lett.* **62A**, 377 (1977).
- ²⁶The experimental data are taken from Fig. 10 of Ref. 13.
- ²⁷K. Binder, *Solid State Commun.* **34**, 191 (1980).
- ²⁸See, for instance, D. Stauffer, *Phys. Rep.* **54**, 1 (1979).
- ²⁹H. Horner and K. Jüngling, *Z. Phys. B* **36**, 97 (1979).
- ³⁰See the second reference of Ref. 7. In our approach the k^2 term of the free-energy gives the damping coefficient $K_k \propto -k^4$ and therefore $M_k \propto k^4 \chi_k'' k^{-2} \propto R^{-(2-d)}$. Thus $a' = (d+2-d)^{-1} = \frac{1}{4}$, independently of d .