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Theory for the dynamics of "clusters." II. Critical diffusion in binary systems and the kinetics of phase separation

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A semiphenomenological cluster theory is developed for the dynamics of systems with a conserved (one component) order parameter, which is not limited to small deviations from equilibrium. Concentration fluctuations of the binary system are parametrized in terms of clusters of various "sizes" l; these fluctuations decay by cluster reactions and cluster diffusion. The cluster diffusivity D_l is estimated using the master equation for atomic exchange processes, and is confirmed by recent computer simulations of Rao *et al.* Close to equilibrium the nonlinear set of kinetic equations is reduced to a Fokker-Planck equation for the concentration of large clusters, which contains an effective chemical potential produced by the small clusters. Due to the conservation law this potential slowly varies with time. From this equation, we obtain as special cases the critical behavior of the diffusion constant both in solid and liquid binary systems close to T_c, and the Lifshitz-Slyozov theory of grain growth (below T_c). Additional terms describing the coagulation of large clusters have to be included in the latter case, however. At intermediate times the Lifshitz-Slyozov mechanism may even be neglected. A dynamic scaling solution of the coagulation equation predicts that the typical linear dimension should increase $\propto t^{1/(3+d)}$ in d dimensions, in agreement with our previous heuristic arguments. The results are compared to computer simulations and to experiments on real systems. For the nonlinear relaxation above T_c, both scaling analysis and cluster dynamics give identical predictions. We also compare our approach to other theories of spinodal decomposition, deriving them in a unified way by factorization approximations of a rigorous kinetic equation, and thus elucidate their validity.

I. INTRODUCTION

The nonequilibrium behavior of two-phase systems, such as gas-liquid systems, liquid binary mixtures, solid metallic alloys, etc., has been investigated in some detail both experimentally[1-6] and theoretically,[7-25] concentrating upon critical phenomena[1,2,7-11] and the phase-separation kinetics.[1,3-6,12-25] By now the critical dynamics treated in linear response seem quite well understood for these systems, and several alternative mechanisms have been proposed to account for the (nonlinear) relaxation processes associated with phase separation: spinodal decomposition,[12-16] growth of zones by condensation and evaporation,[17,18] nucleation,[19,20] and coagulation,[20-22] while computer simulations[15,23-25]—which present the most clear-cut "experimental data" on these processes—do not allow us to draw such clear distinctions between these various mechanisms. As a consequence, these approaches have various shortcomings (cf. Refs. 20 and 26 for a discussion), and a more-general treatment is needed.

In the present paper we attempt to give such a treatment, reformulating the dynamics in terms of "clusters" which represent order-parameter fluctuations. This concept has been described in detail in Refs. 27 and 28, where it was applied to stochastic models without any conservation laws (Glauber model[29]). Here we generalize this approach[27] including the conservation law for the order parameter, which is appropriate for the systems under consideration. We thus obtain a unified theory for the nonequilibrium behavior of binary systems, which contains critical relaxation, nucleation, the Lifshitz-Slyozov mechanism,[17] coagulation, etc., as special cases. Therefore, the conditions of validity of these various mechanisms are elucidated. Moreover, new explicit predictions for the time evolution of the cluster size distribution, structure function $S(\vec{k},t)$, etc., are obtained, which will be compared both to experiment[1,3,6] and computer simulations.[23-25]

In Sec. II we formulate our basic microscopic stochastic model (Kawasaki's[7] "spin-exchange" model with a conserved order parameter), derive the exact kinetic equation for $S(\vec{k},t)$, and briefly rederive various approximations proposed by the current theories of spinodal decomposition.[12-16] We also present a scaling analysis of $S(\vec{k},t)$ for temperatures T above the critical temperature T_c. In Sec. III we formulate our cluster-dynamics approach, and obtain (i) the critical relaxation in linear response, (ii) the nonlinear relaxation above (T_c), (iii) the Lifshitz-Slyozov mechanism below T_c for general dimensionality d, and (iv) the coagulation terms and their consequences. Section IV contains our conclusions, while the size dependence of the cluster diffusivity D_l is derived in the Appendix. A brief preliminary account of some of our results was already given in Ref. 22.

II. STOCHASTIC MODEL OF BINARY SYSTEMS AND ITS PROPERTIES

A. Exact kinetic equation for $S(\vec{k},t)$ in the Kawasaki spin-exchange model

As usual, we approximate a binary solid mixture by a pseudospin (Ising) model. Thus for the moment we neglect all elastic strain effects due to the lattice misfit of the atoms, and disregard inhomogeneities.

In the Kawasaki[7] spin-exchange model, a spin $\mu_i=+1$ is associated with a lattice site occupied by an A atom, while $\mu_i=-1$ is associated with a lattice site occupied by a B atom. In this model if one assumes an ideal crystal lattice, the relaxation then proceeds by direct interchange of neighboring atoms.[15] Here we consider it as a model of solid mixtures, being well aware that in real systems the direct interchange is rather unimportant in comparison with the indirect interchange via vacancies, etc. We emphasize the point that most of our cluster treatment applies to this more-general situation as well, and can even be used for liquid mixtures, since the details of the lattice structure nowhere enter our calculations.

In this model the distribution $P(\mu_1, \ldots, \mu_N, t)$ describes the probability that at time t the first spin has the value μ_1, etc., and the Nth spin the value μ_N. P evolves according to a master equation

$$\frac{d}{dt}P(\mu_1, \ldots, \mu_N, t) = -\sum_i \sum_{l_i} W(i \to l_i) P(\mu_1, \ldots, \mu_N, t) + \sum_i \sum_{l_i} W(l_i \to i) P^{(il_i)}(\mu_1, \ldots, \mu_N, t) \; . \tag{2.1}$$

In this equation the first sum (i) runs over all N lattice sites, while the second sum (l_i) runs over the z nearest neighbors of i, with which an interchange of atom i may take place. $W(i \to l_i)$ describes the transition probability that an interchange occurs per unit time. $P^{(il_i)}$ is the probability for a state where atoms at sites i and l_i are interchanged. The transition probability W must satisfy a detailed balance condition with the thermal equilibrium distribution

$$P_0(\mu_1, \ldots, \mu_N) \propto \exp(-\mathcal{H}/k_B T),$$

where the Hamiltonian $\mathcal{H}$ may be represented by an Ising model

$$\mathcal{H} = -\sum_{j(\neq i)} J_{ij}\mu_i\mu_j - \sum_i H_i \mu_i + \mathcal{H}_0 \; . \tag{2.2}$$

The "exchange constants" J_{ij}, the "fields" H_i, and the background term $\mathcal{H}_0$ can be related to pair potentials $\phi_{AA}(\vec{r}_i - \vec{r}_j)$, $\phi_{AB}(\vec{r}_i - \vec{r}_j)$, and $\phi_{BB}(\vec{r}_i - \vec{r}_j)$ between the various atoms in a well-known fashion.[15] Our choice of transition probability is

$$W(i \to l_i) = (\tfrac{1}{2}\tau_s)[1 - \tanh(\delta\mathcal{H}/2k_B T)] \; , \tag{2.3}$$

where τ_s is a parameter which sets the time scale (it will depend on the activation energy of the atomic difusion process), and $\delta\mathcal{H}$ is the change in energy produced by the interchange. Equations (2.1)–(2.3) specify the model completely (including conservation of order parameter). Averages of any quantities $A(\{\mu_m\})$ are then calculated from

$$\langle A(\{\mu_m(t)\})\rangle = \sum_{\{\mu_m\}} A(\{\mu_m\}) P(\mu_1, \ldots, \mu_N, t) \; . \tag{2.4}$$

A quantity of particular interest is the Fourier transform $S(\vec{k}, t)$ of the spatial pair-correlation function

$$S(\vec{k}, t) = \sum \exp[i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)] \times [\langle \mu_i(t)\mu_j(t)\rangle - \langle \mu_i(t)\rangle\langle \mu_j(t)\rangle] \; . \tag{2.5}$$

Note that Eq. (2.5) refers to an equal-time correlation but it nevertheless depends on time t if we consider a relaxation process far from thermal equilibrium. The various theories of spinodal decomposition[12–16] are concerned with the time evolution of $S(\vec{k}, t)$. In order to obtain an exact kinetic equation for $S(\vec{k}, t)$ in our model, one simply puts $A(\{\mu_m\}) = \mu_i\mu_j$ in Eq. (2.4), takes a time derivative, and inserts Eq. (2.1). A tedious but straightforward calculation then yields the exact result

$$\begin{aligned}\tau_s \frac{d}{dt}\langle \mu_i\mu_j\rangle = &-\sum_{l_i}\langle(\mu_i - \mu_{l_i})\mu_j\rangle - \sum_{l_j}\langle \mu_i(\mu_j - \mu_{l_j})\rangle \\ &+\sum_{l_i}\left\langle(1 - \mu_i\mu_{l_i})\mu_j \tanh\frac{1}{k_B T}\left(\sum_{m(\neq i)} J_{im}\mu_m - \sum_{m(\neq l_i)} J_{ml_i}\mu_m + H_i - H_{l_i}\right)\right\rangle \\ &+\sum_{l_j}\left\langle(1 - \mu_j\mu_{l_j})\mu_i \tanh\frac{1}{k_B T}\left(\sum_{m(\neq j)} J_{jm}\mu_m - \sum_{m(\neq l_j)} J_{ml_j}\mu_m + H_j - H_{l_j}\right)\right\rangle \; .\end{aligned} \tag{2.6}$$

In the derivation of Eq. (2.6) we have made use of Eqs. (2.2) and (2.3) and the symmetry relation

$$\langle \mu_i \mu_j \rangle = \sum_{\{\mu_m\}} \mu_i \mu_j P(\mu_1, \ldots, \mu_N, t)$$

$$= \sum_{\{\mu_m\}} \mu_{l_i} \mu_j P^{(i l_i)}(\mu_1, \ldots, \mu_N, t) . \qquad (2.7)$$

As expected, Eq. (2.6) is not a "closed" equation but contains higher-order correlation functions. In order to get a tractable kinetic equation for $S(\vec{k}, t)$ one has to approximate these higher-order correlations in some way.

B. Derivation of various approximations from the exact hierarchy of equations for the correlations functions

In this subsection we show that the various theories of spinodal decomposition[12–16] are obtained from the exact Eq. (2.6) by various factorization assumptions.

1. Cahn-Hilliard theory

The simplest approximation is obtained if we put

$$1 - \mu_i \mu_{l_i} \approx 1 - \langle \mu \rangle^2, \quad \tanh x \approx x , \qquad (2.8)$$

and also consider spatially homogeneous interactions (which lead[15] to $H_i = H_{l_i}$, etc.). Then we find an equation which contains pair-correlation functions only

$$\tau_s \frac{d}{dt} \langle \mu_i \mu_j \rangle = -\Big(z \langle \mu_i \mu_j \rangle - \sum_{l_i} \langle \mu_{l_i} \mu_j \rangle \Big) - \Big(z \langle \mu_i \mu_j \rangle - \sum_{l_j} \langle \mu_i \mu_{l_j} \rangle \Big) + \frac{1 - \langle \mu \rangle^2}{k_B T}$$
$$\times \Big[\sum_{l_i} \Big(\sum_{m(\neq i)} J_{im} \langle \mu_m \mu_j \rangle - \sum_{m(\neq l_i)} J_{l_i m} \langle \mu_m \mu_j \rangle \Big) + \sum_{l_j} \Big(\sum_{m(\neq j)} J_{mj} \langle \mu_i \mu_m \rangle - \sum_{m(\neq l_j)} J_{m l_j} \langle \mu_i \mu_m \rangle \Big) \Big] . \qquad (2.9)$$

Considering a hypercubic lattice in d dimensions with lattice spacing a_0 for simplicity, we may expand as follows:

$$\sum_{l_i} \langle \mu_{l_i} \mu_j \rangle = z \langle \mu_i \mu_j \rangle + a_0^2 \nabla^2 \langle \mu_i \mu_j \rangle + \cdots , \quad \nabla = \frac{\partial}{\partial \vec{r}_i} , \qquad (2.10)$$

$$\sum_{m(\neq i)} J_{im} \langle \mu_m \mu_j \rangle = J(0) \big(\langle \mu_i \mu_j \rangle + R^2 \nabla^2 \langle \mu_i \mu_j \rangle + \cdots \big) , \qquad (2.11)$$

where we have introduced the Fourier transform of the exchange $J(\vec{k})$,

$$J(\vec{k}) = \sum_{i} J_{ij} \exp[i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)] , \qquad (2.12)$$

as well as the range of the interaction R,

$$R^2 = [J(0)]^{-1} \sum_{j(\neq i)} \frac{J_{ij} (\vec{r}_i - \vec{r}_j)^2}{2d} . \qquad (2.13)$$

Then Eq. (9) reduces to an equation of the Cahn-Hilliard-type[12]

$$\tau_s \frac{d}{dt} \langle \mu_i \mu_j \rangle = 2 a_0^2 \nabla^2 \Big(1 - (1 - \langle \mu \rangle^2) \times \frac{J(0)}{k_B T} - (1 - \langle \mu \rangle^2) \frac{J(0)}{k_B T} R^2 \nabla^2 \Big) \langle \mu_i \mu_j \rangle , \qquad (2.14)$$

which is solved by Fourier transformation to yield the desired kinetic equation for $S(\vec{k}, t)$ [Eq. (2.5)], i.e.,

$$\tau_s \frac{d}{dt} S(\vec{k}, t) = -2 a_0^2 k^2 \Big(1 - (1 - \langle \mu \rangle^2) \frac{T_c}{T} + (1 - \langle \mu \rangle^2) \frac{T_c}{T} R^2 k^2 \Big) S(\vec{k}, t) . \qquad (2.15)$$

This is precisely the result of Cahn and Hilliard,[12] since in the molecular field approximation [which is equivalent to Eq. (2.8)], the critical temperature is given by $k_B T_c = J(0)$ and the equation of the spinodal curve in this case[30] is

$$\langle \mu \rangle^2 = 1 - T/T_c . \qquad (2.16)$$

Equation (2.15) therefore predicts (exponential) enhancement of fluctuations with $k \to 0$ for concentrations of B atoms $c_B \equiv \frac{1}{2}(1 - \langle \mu \rangle)$ within the spinodal curve.

2. Cook's theory

Equation (2.15) does not even allow for a nonzero $S_{\mathrm{eq}}(\vec{k})$ in thermal equilibrium (which is the steady-state solution of the kinetic equation). The reason for this failure is that Eq. (2.14) does not make any sense for $i = j$, of course ($\langle \mu_i^2 \rangle \equiv 1$). Therefore, a term $\propto \delta_{ij}$ has to be added on the right-hand side of Eq. (2.14). It turns out that a treatment of fluctuations consistent within this approximation is obtained if Eq. (2.14) is replaced by

$$\tau_s \frac{d}{dt}\langle\mu_i\mu_j\rangle = 2a_0^2\nabla^2\left[\left(1-(1-\langle\mu\rangle^2)\frac{J(0)}{k_BT} - (1-\langle\mu\rangle^2)\frac{J(0)}{k_BT}R^2\nabla^2\right)\langle\mu_i\mu_j\rangle - k_BT\delta_{ij}\right] . \qquad (2.17)$$

Fourier transformation of Eq. (2.17) yields the result of Cook[16]

$$\tau_s \frac{d}{dt}S(\vec{k},t) = -2a_0^2k^2\left[\left(1-(1-\langle\mu\rangle^2)\frac{T_c}{T} + (1-\langle\mu\rangle^2)\frac{T_c}{T}R^2k^2\right)S(\vec{k},t) - k_BT\right] , \qquad (2.18)$$

which has the familiar Ornstein-Zernike expression as equilibrium solution

$$S_T(k) = \frac{k_BT}{1-(1-\langle\mu\rangle^2)T_c/T + (1-\langle\mu\rangle^2)(T_c/T)R^2k^2} . \qquad (2.19)$$

3. Theory of Langer et al.

A better approximation is obtained avoiding Eq. (2.8) but using the Taylor expansion equation (2.10) in Eq. (2.6). This yields

$$\tau_s \frac{d}{dt}\langle\mu_i\mu_j\rangle = 2a_0^2\nabla_j^2\left(\langle\mu_i\mu_j\rangle - \sum_{m(\neq i)}\frac{J_{im}}{k_BT}\langle\mu_m\mu_j\rangle + \sum_{m(\neq i)}\frac{J_{im}}{k_BT}\langle\mu_i\mu_{l_i}\mu_m\mu_j\rangle + \cdots\right) , \qquad (2.20)$$

where ∇_j means a gradient with respect to $\vec{r}_j$, and the dots represent higher-order terms in the expansion of the tanh function. Expanding then also the second term of Eq. (2.20) with the help of Eq. (2.11) gives

$$\tau_s \frac{d}{dt}\langle\mu_i\mu_j\rangle = 2a_0^2\nabla_j^2\left[\frac{J(0)}{k_BT}R^2\nabla_j^2\langle\mu_i\mu_j\rangle + \left(1-\frac{J(0)}{k_BT}\right)\langle\mu_i\mu_j\rangle + \sum_{m(\neq i)}\frac{J_{im}}{k_BT}\langle\mu_i\mu_{l_i}\mu_m\mu_j\rangle\cdots\right] . \qquad (2.21)$$

Equation (2.21) is still exact in the limit $|\vec{r}_i - \vec{r}_j| \rightarrow \infty$, but it contains higher-order correlation functions. An assumption which generalized Eq. (2.17) is due to Langer *et al.*,[14]

$$\left(1-\frac{J(0)}{k_BT}\right)\langle\mu_i\mu_j\rangle + \sum_{m(\neq i)}\frac{J_{im}}{k_BT}\langle\mu_i\mu_{l_i}\mu_m\mu_j\rangle + \cdots \approx \langle\mu_i\mu_j\rangle A(t) - k_BT\delta_{ij} , \qquad (2.22)$$

where $A(t)$ is a function which depends on time, while in Eq. (2.17) it was a constant. If one wants to determine $A(t)$ in a sort of "self-consistent" manner, one has to supply Eq. (2.22) with further assumptions on the probability distribution $P(\mu_1, \ldots, \mu_N, t)$, as discussed by Langer *et al.*[14] If we accept Eq. (2.22), Eq. (2.21) is solved again by Fourier transformation

$$\tau_s \frac{d}{dt}S(\vec{k},t) = -2a_0^2k^2 \times\left[\left(\frac{T_c}{T}R^2k^2 + A(t)\right)S(\vec{k},t) - k_BT\right] . \qquad (2.23)$$

It is seen that the factor in front of the k^4 term depends on the type of approximation made [cf. Eqs. (2.18) and (2.23)]; therefore, one is on the safe side if one replaces it by an adjustable constant. Then Eq. (2.23) becomes precisely the equation proposed by Langer *et al.*[14] The important point is, however, that our derivation of Eq. (2.23) is quite different from that of Langer *et al.*[14] The latter is based on the assumption of a coarse-grained free energy, which is defined in terms of a coarse-grained smoothly varying order parameter. Since the coarse-graining length must be much larger than the lattice spacing but smaller than the correlation length ξ of thermal fluctuations,[14] the original derivation[14] is valid only for temperatures close to T_c, and even the quantitative choice of the coarse-graining length is ambiguous. Our derivation does not suffer from this drawback: this fact may explain why Eq. (2.23) gives a quite good account of data[24] at temperatures as low as $T \approx 0.6T_c$. The crucial point is to provide a physical justification for Eq. (2.22), of course: Firstly, one may argue the correlation $\langle\mu_i\mu_{l_i}\mu_m\mu_j\rangle$ which is a function of *three* distances $\vec{r}_j - \vec{r}_i$, $\vec{r}_j - \vec{r}_{l_i}$, $\vec{r}_j - \vec{r}_m$ becomes a function of one distance only as the limit $|\vec{r}_j - \vec{r}_i| \rightarrow \infty$ is taken, since the lattice points $\vec{r}_i$, $\vec{r}_{l_i}$, and $\vec{r}_m$ are all close together. Secondly, since the spins μ_i, μ_{l_i}, and μ_m are highly correlated, and both $\langle(\mu_i\mu_{l_i}\mu_m)\mu_j\rangle$ and $\langle\mu_i\mu_j\rangle$ contain μ_j linearly, it is plausible that the $\vec{r}_j$ dependence of both quantities is the same. Then Eq. (2.22) results. Clearly, these arguments are not completely convincing: but this fact will be not too surprising, as we find that Eqs. (2.22) and (2.23) are, in general, not correct, although they accurately describe the early stages of the process. Thus we derived various previous approximations in a unified way, which allows us to see more clearly the limitations of these approaches.

C. Behavior of $S(\vec{k},t)$ for large times

Here we consider the asymptotic behavior of $S(\vec{k},t)$ as $t\to\infty$ for the various approximations derived above. The approximations (2.14) and (2.17) are not useful in this case, since they imply unlimited exponential increase of fluctuations within the spinodal curve, Eq. (2.16). This increase is limited due to the neglected nonlinear terms, however. A nonlinear version of the Cahn-Hillard equation[12,13] can be obtained for the local order parameter $\langle\mu_i(t)\rangle$ by a derivation[15] from the master equation [Eq. (2.1)] similar to the one presented above, however. This equation reads[12,13,15,31]

$$\tau_s \frac{\partial}{\partial t}\langle\mu_i(t)\rangle = a_0^2\nabla^2 \times\left\{\left[1-\left(\frac{J(O)}{k_BT}\right)+\frac{1}{3}\left(\frac{J(O)}{k_BT}\right)^3\langle\mu_i(t)\rangle^2\right] - \frac{J(O)}{k_BT}R^2\nabla^2\right\}\langle\mu_i(t)\rangle. \qquad (2.24)$$

No exact solution of Eq. (2.23) can be obtained because of the nonlinear term. But the asymptotic behavior of Eq. (2.23) can be understood extending[32] an argument of Langer.[13] It is assumed that in the late stages of the process the state of the system is described by spherical grains of B-rich phase on the background of A phase. One then uses Eq. (2.24) to study the time evolution of one single grain. One uses polar coordinates, putting the coordinate origin in the center of the grain. Then stationary inhomogeneous solutions of Eq. (2.24) are found, which describe the "concentration profile" of the grain. Now linearizing $\langle\mu_i(t)\rangle$ around this concentration profile, the smallest eigenvalue of the resulting linear equation can be estimated.[32] On the basis of such a treatment one finds that the volume V of the grain increases with time as[32]

$$V\propto t^{d/3},\quad d\geq 2, \qquad (2.25)$$

neglecting logarithmic corrections which come into play for $d=2$.

Next we discuss the asymptotic behavior of the equation due to Langer, Bar-on, and Miller,[14] Eq. (2.23). We assume that for $t\to\infty$ the behavior of $A(t)$ can be represented as a power law, $A(t)\to A_\infty t^{a_1}+A(\infty)$ for $t\to\infty$. Now we attempt a scaling solution [a_1, a_2, a_3 are scaling powers to be determined below; A_∞ is a constant and $\tilde{S}(x)$ is a scaling function]

$$S(k,t)\underset{\substack{t\to\infty\\ k\to 0}}{\sim} k^{a_2}\tilde{S}(tk^{a_3})+S(k,\infty). \qquad (2.26)$$

Equations (2.23) and (2.26) yield [$\tilde{S}'=d\tilde{S}(x)/dx$]

$$\tau_s k^{a_2+a_3-2}\tilde{S}'(x) = -2a_0^2(T_c/T)R^2k^{2+a_2}\tilde{S}(x) -2a_0^2Ak^{a_2-a_3a_1}x^{a_1}\tilde{S}(x). \qquad (2.27)$$

Equation (2.26) solves Eq. (2.27), if

$$a_2+a_3-2=2+a_2=a_2-a_3a_1<0,$$

since then the extra k factors cancel. From Eq. (2.27) we conclude that $a_3=4, a_1=-\frac{1}{2}$. The exponent a_2 can be determined from the sum rule

$$\frac{1}{N}\sum_{\vec{k}} S(\vec{k},t)=1-\langle\mu\rangle^2, \qquad (2.28)$$

which gives $a_2=-d$. Hence we have shown that Eq. (2.26) may be a solution of Eq. (2.23) [it is *not* proven, of course, that Eq. (2.26) is actually the asymptotic solution]. Accepting Eq. (2.27) would imply a growth law for the volume different from Eq. (2.25), however:

$$V\propto t^{d/4},\quad d\geq 2. \qquad (2.29)$$

We shall see later that Eq. (2.25) also results from the Lifshitz-Slyozov theory and its extensions. Thus the resulting Eq. (2.23) is presumably inaccurate, since it leads to the questionable Eq. (2.29)

D. Scaling theory of $S(\vec{k},t)$ for $T_f \geq T_c$

While Sec. II C was concerned with the behavior of $S(\vec{k},t)$ at temperature quenches ΔT which led from a temperature T_i in the one-phase region to a temperature $T_f=T_i-\Delta T$ in the two-phase region [Fig. 1(a)], we now consider quenches were both T_i and T_f are in the one-phase region [Fig. 1(b)].

First we introduce a formal solution of the master equation (2.1) in terms of a "Liouville operator" $L^{(T_f)}$,

$$\begin{aligned}\frac{d}{dt}P(\{\mu_m\},t)&=-L^{(T_f)}P(\{\mu_m,t\}),\\ P(\{\mu_m,t\})&=\exp(-L^{(T_f)}t)P_{T_i}(\{\mu_m\}),\end{aligned} \qquad (2.30)$$

where $P_T(\{\mu_m\})$ is the distribution which is the equilibrium solution of the respective master equation [$L^{(T)}P_T(\{\mu_m\})=0$], and we have made use of the initial condition $T=T_i$. Defining $\mu(\vec{k})=N^{-1/2}\sum_i e^{i\vec{k}\cdot\vec{r}_i}\mu_i$, Eq. (2.5) may then be cast in the following form:

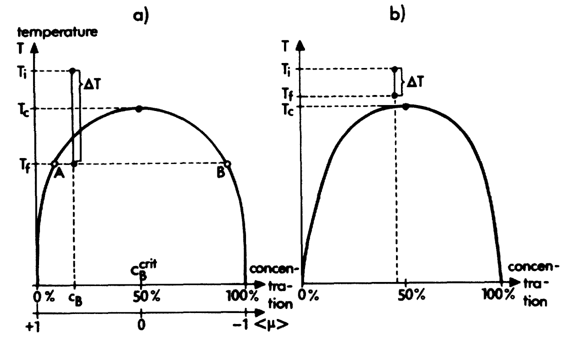

FIG. 1. Concentration-temperature phase diagram of a mixture showing temperature quenches ΔT of a sample with concentration C_B which lead to phase separation (a) and which lead to critical relaxation (b). Phase separation ends up with coexistence of two macroscopic phases which have the concentrations of the points A, B.

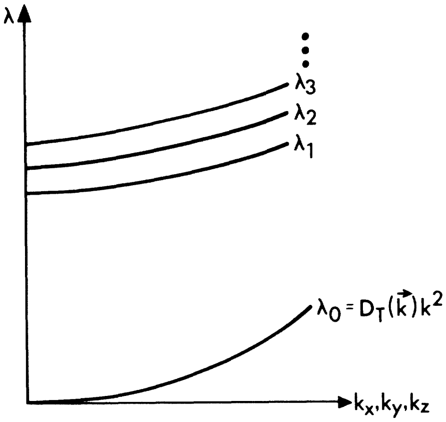

FIG. 2. Qualitative behavior of the eigenvalue spectrum $\{\lambda_i(\vec{k})\}$ of the time evolution operator $\hat{L}$ for a binary mixture.

$$S(\vec{k},t) - S_{T_f}(\vec{k}) = \sum_{\{\mu(\vec{k})\}} e^{-L^{(T_f)}t} \times [P_{T_i}(\{\mu(\vec{k})\}) - P_{T_f}(\{\mu(\vec{k})\})] \times [\mu(-\vec{k}) - \langle\mu\rangle][\mu(\vec{k}) - \langle\mu\rangle], \tag{2.31}$$

where we have subtracted the final thermal equilibrium $[\lim_{t\to\infty} S(\vec{k},t) = S_{T_f}(\vec{k})]$.

Instead of keeping the variables $\mu(\vec{k})$ fixed and let the probability develop in time, one can consider the equivalent situation where the probability is kept fixed and one lets the variables $\mu(\vec{k})$ develop in time.[33] Then Eq. (2.31) may be written

$$S(\vec{k},t) = \sum_{\{\mu(\vec{k})\}} [P_{T_i}(\{\mu(\vec{k})\}) - P_{T_f}(\{\mu(\vec{k})\})] \times \exp(-L^{(T_f)}t)[\mu(-\vec{k}) - \langle\mu\rangle][\mu(\vec{k}) - \langle\mu\rangle] + S_{T_f}(\vec{k}). \tag{2.32}$$

In order to proceed further we make use of the eigenvalue spectrum of $L^{(T)}$,

$$L^{(T)}\psi = \lambda\psi, \tag{2.33}$$

which behaves qualitatively as shown in Fig. 2, following Kawasaki.[7] There is one hydrodynamic branch $\lambda_0 = D_T(\vec{k})k^2$, where $D_T(0)$ is the diffusion constant of the system, while the rest of the spectrum (which we have drawn as several discrete branches rather than a continuous band for simplicity) is separated from the origin by a gap. As a consequence, in the hydrodynamic regime $k\to 0, t\to\infty$ the relaxation due to all higher eigenvalues λ_i will have died out, and the relaxation due to the lowest eigenvalue λ_0 dominates. We thus find the asymptotic behavior of $S(\vec{k},t)$ in Eq. (2.32) for $t\to\infty$ by taking only λ_0 into account. In this case the eigenfunction ψ is nothing else but $\mu(\vec{k}) - \langle\mu\rangle$, however.[7] This statement can be verified considering the equilibrium relaxation function $S^{eq}(\vec{k},t)$, which is the Fourier transform of a time-displaced correlation function

$$\begin{aligned} S^{eq}(\vec{k},t) \equiv \langle\mu(-\vec{k},0)\mu(\vec{k},t)\rangle - \langle\mu\rangle^2 &= \sum_{\{\mu(\vec{k})\}} P_T(\{\mu(\vec{k})\})[\mu(-\vec{k}) - \langle\mu\rangle]e^{-L^{(T)}t}[\mu(\vec{k}) - \langle\mu\rangle] \\ &= \sum_{\{\mu(\vec{k})\}} P_T(\{(\vec{k})\})[\mu(-\vec{k}) - \langle\mu\rangle][\mu(\vec{k}) - \langle\mu\rangle]e^{-D_T(\vec{k})k^2t} \\ &= [\langle\mu(-\vec{k})\mu(\vec{k})\rangle - \langle\mu\rangle^2]e^{-D_T(\vec{k})k^2t} = S_T(\vec{k})e^{-D_T(\vec{k})k^2t}, \quad k\to 0. \end{aligned} \tag{2.34}$$

Similarly, Eq. (2.32) leads to

$$\begin{aligned} S(\vec{k},t) &= \sum_{\{\mu(\vec{k})\}} [P_{T_i}(\{\mu(\vec{k})\}) - P_{T_f}(\{\mu(\vec{k})\})][\mu(-\vec{k}) - \langle\mu\rangle][\mu(\vec{k}) - \langle\mu\rangle]e^{-D_{T_f}(\vec{k})k^2t} + S_{T_f}(\vec{k}) \\ &= S_{T_i}(\vec{k})e^{-D_{T_f}(\vec{k})k^2t} + (1 - e^{-D_{T_f}(\vec{k})k^2t})S_{T_f}(\vec{k}), \quad \begin{cases} k\to 0, \\ t\to\infty. \end{cases} \end{aligned} \tag{2.35}$$

Equation (2.35) holds throughout the region outside of the coexistence curve in Fig. 1. We now assume that T_F is close to T_c and $\langle\mu\rangle$ is close to zero. Then we can make static and dynamic scaling assumptions[34] $[\epsilon = |(T_f - T_c)/T_c|]$

$$S_{T_f}(\vec{k}) = \epsilon^{-\gamma}\tilde{S}(k\xi), \quad \xi = \epsilon^{-\nu}\tilde{\xi}(\epsilon^{-\beta}\langle\mu\rangle), \tag{2.36}$$

$$D_{T_f}(\vec{k}) = \epsilon^{\gamma}\tilde{D}(k\xi). \tag{2.37}$$

Here $\tilde{S}(x)$, $\tilde{\xi}(x)$, and $\tilde{D}(x)$ are scaling functions, which reduce to critical amplitudes[34] for $x=0$, and have the asymptotic behavior for large x,

$$\tilde{S}(x) \approx \hat{S}x^{-2+\eta}, \quad \tilde{\xi} \approx \hat{\xi}x^{-\nu/\beta}, \quad \tilde{D} \approx \hat{D}x^{2-\eta}, \tag{2.38}$$

where we have made use of the scaling relation[34] between the exponents γ, η, and ν $[\gamma = \nu(2-\eta)]$. We now use Eqs. (2.36)–(2.39) to make specific predictions on $S(\vec{k}, t)$ [Eq. (2.35)]. For $k \to 0$ we find

$$S(\vec{k}, t) = S_{T_i}(\vec{k}) + [\epsilon^{\gamma}\tilde{D}(0)S_{T_i}(\vec{k}) + \tilde{S}(0)\tilde{D}(0)]k^2 t, \quad k\xi \ll 1, \tag{2.39a}$$

$$S(\vec{k}, t) = S_{T_i}(\vec{k}) + k^{2-\eta}\hat{D}\tilde{S}_{T_i}(0) + \hat{S}\hat{D}k^2 t, \quad k\xi \gg 1. \tag{2.39b}$$

Hence we predict that the initial curvature is always proportional $k^2 t$ and does not depend on temperature in a critical manner. In general, $S(\vec{k}, t)$ at fixed t will have a maximum at some value $k_m(t)$. Equation (2.35) always yields a maximum for $D_{T_f}(\vec{k})k^2 t$ being of order unity. This condition yields

$$k_m(t) \propto (\epsilon^{\gamma} t)^{-1/2}, \quad k_m(t)\xi \ll 1, \tag{2.40a}$$

$$k_m(t) \propto t^{-1/(4-\eta)}, \quad k_m(t)\xi \gg 1. \tag{2.40b}$$

The crossover from Eq. (2.40a) to (2.40b) occurs for times $t_c \propto \epsilon^{-\nu(4-\eta)}$. In practice, it may be impossible to identify both growth laws separately and one may rather observe effective values for the exponent a in the $k_m(t) \propto t^a$ law which depends on ϵ and lies in between Eqs. (2.40a) and (2.40b), $-\frac{1}{2} \leqslant a \lesssim -\frac{1}{4}$.

Next we obtain the behavior of the energy

$$E_T = \sum_j J_{ij}\langle\mu_i\mu_j\rangle = \sum_k \sum_j J_{ij} e^{i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)}\langle\mu(-\vec{k})\mu(\vec{k})\rangle, \tag{2.41}$$

which is again time dependent in a quenching experiment:

$$E(t) = E_{T_f} + \sum_k J(\vec{k})[S(\vec{k}, t) - S_{T_f}(\vec{k})]. \tag{2.42}$$

The time dependence of $E(t)$ is thus obtained inserting Eq. (2.35) and carrying out the k summation in Eqs. (2.41) and (2.42). It must be noted, however, that the dominant contribution to Eq. (2.41) does not come from regime $k\xi \ll 1$ but from regime $k\xi \gg 1$. Hence we use the expansion of

$$\tilde{S}(x) = \hat{S}x^{-2+\eta} + \hat{S}_1 x^{-(\gamma+1-\alpha)/\nu} + \cdots,$$

which is valid[35] for large x, and replace $\sum_k J(\vec{k})$ by const × $\int dx$, where the integration is extended up to some cutoff of order a_0^{-1}. This yields

$$E_{T_f} \propto \int_0^{a_0^{-1}} dk\, k^{d-1}\hat{S}k^{-2+\eta} + \epsilon^{1-\alpha} \times \int_0^{a_0^{-1}} dk\, k^{d-1}\hat{S}_1 k^{-(\gamma+1-\alpha)/\nu}, \tag{2.43}$$

$$E(t) - E_{T_f} \propto \epsilon^{-\gamma}\int_0^{a_0^{-1}} dk\, k^{d-1}\,\tilde{S}(0)e^{-\epsilon\gamma\tilde{D}(0)k^2 t}, \quad t \to \infty, \quad k_m(t)\xi \ll 1, \tag{2.44a}$$

and

$$E(t) - E_{T_f} \propto \int_0^{a_0^{-1}} dk\, k^{d-1}\hat{S}k^{-2+\eta}e^{-\hat{D}k^{4-\eta}t}, \quad t \to \infty, \quad k_m(t)\xi \gg 1. \tag{2.44b}$$

From Eq. (2.43) one finds that $E_{T_f} = E_{T_c}$ + const $\times \epsilon^{1-\alpha}$, which is correct. The constant depends on the cutoff, and thus cannot be obtained reliably. In Eq. (2.44), on the other hand, the cutoff becomes unimportant as $t \to \infty$ and one hence finds, assuming $|T_i - T_f|/T_c \gg \epsilon$,

$$E(t) - E_{T_f} \propto \epsilon^{-\gamma(1+d/2)}t^{-d/2}, \quad k_m(t)\xi \ll 1, \tag{2.45a}$$

$$E(t) - E_{T_f} \propto t^{-(d-2+\eta)/(4-\eta)}, \quad k_m(t)\xi \gg 1. \tag{2.45b}$$

In linear response $(|T_i - T_f|/T_c \ll \epsilon)$, Eq. (2.35) yields a factor $|T_i - T_f|\epsilon$ in Eq. (2.45a).

The crossover from Eq. (2.45a) to (2.45b) again occurs for times $t_c \propto \epsilon^{-\nu(4-\eta)}$. If we have $T_f = T_c$, a single law [Eqs. (2.40b) and (2.45b)] would, however, be observed.

We now compare Eq. (2.45) to the computer experiments.[23,24] For $d=2$ and $T_f = 1.1\ T_c$ they gave a law $E(t) - E_{T_f} \propto t^{-b}$ with $b \approx \frac{7}{12}$, while for $d=3$ this result was $b \approx 0.79$. We interpret these values in terms of a crossover from b_c $[=(d-2+\eta)/(4-\eta)] = \frac{1}{15}$ to b $(=\frac{1}{2}d) = 1$ for $d=2$ and $b_c \cong 0.266$ to $b = 1.5$ for $d=3$, using $\eta = \frac{1}{4}$ for $d=2$ and[34] $\eta = 0.05$ for $d=3$. Indeed, we estimate $t_c \propto 5600$ at $d=2$ and $t_c \propto 350$ at $d=3$, if we put the prefactor in the relation $t_c \propto \epsilon^{-\nu(4-\eta)}$ equal to unity, which should give at least a rough order-of-magnitude estimate. The resulting values t_c are indeed comparable to the periods of observation in Refs. 23 and 24. In the experiment on real substances $E(t)$ is hard to measure. It has been shown,[36] however, that for $t \to \infty$ the energy has the same behavior as the electrical resistivity: $\rho(t)-\rho_{T_f}\propto E(t)-E_{T_f}$. Measurements of the electrical-resistivity changes are thus suggested. Of course, the annealing of lattice defects created by the quench may obscure the behavior of an ideal system to which we restrict ourselves here.

We emphasize the point that due to the use of Eq. (2.37) the above analysis is restricted to *solid* binary mixtures. If we write, more generally, $D_{T_f}(\vec{k})=\epsilon^{(z-2)\nu}\tilde{D}(k\xi)$, other systems can be treated in an analogous manner: while we have $z=4-\eta$ in the above case,[37] we have $z=\frac{1}{2}(5-\eta)$ in an isotropic ferromagnet,[37] and $z\cong d+\frac{1}{19}(4-d)$ in a *liquid* binary mixture.[38] In the case a ferromagnet Eqs. (2.40a) and (2.40b) are replaced by

$$k_m(t)\propto\epsilon^{-\nu(1-\eta)/2}t^{-1/2},\quad k_m(t)\xi\ll 1, \tag{2.46a}$$

$$k_m(t)\propto t^{-2/(5-\nu)},\quad k_m(t)\xi\gg 1, \tag{2.46b}$$

the crossover occuring at $t_c\propto\epsilon^{-\nu(5-\eta)}$. In the liquid mixture we find instead

$$k_m(t)\propto\epsilon^{-\nu[d-2+(4-d)/19]/2}t^{-1/2},\quad k_m(t)\xi\ll 1, \tag{2.47a}$$

$$k_m(t)\propto t^{-1/[d+(4-d)/19]},\quad k_m(t)\xi\gg 1, \tag{2.47b}$$

and the crossover occurs for $t_c\propto\epsilon^{-\nu[d+(4-d)/19]}$. For the energy, we obtain, in the case of the isotropic magnet,

$$E(t)-E_{T_f}\propto\epsilon^{-\gamma}\epsilon^{-(d\nu/2)(1-\eta)/2}t^{-d/2},\quad k_m(t)\xi\ll 1, \tag{2.48a}$$

$$E(t)-E_{T_f}\propto t^{-2(d-2+\eta)/(5-\eta)},\quad k_m(t)\xi\gg 1. \tag{2.48b}$$

In the case of the liquid mixture we finally obtain

$$E(t)-E_{T_f}\propto\epsilon^{-\gamma}\epsilon^{-(d\nu/2)[d-2+(d-4)/19]}t^{-d/2},\quad k_m(t)\xi\ll 1, \tag{2.49a}$$

$$E(t)-E_{T_f}\propto t^{-(d-2+\eta)/[d+(4-d)/19]},\quad k_m(t)\xi\gg 1. \tag{2.49b}$$

We are not aware of any measurements in isotropic ferromagnets by which Eqs. (2.46) and (2.48) would be tested.

III. TIME EVOLUTION OF THE CLUSTER CONCENTRATIONS

A. Clusters and their reactions

In this section we reformulate the dynamics of the system in terms of a kinetic evolution of the *cluster pattern*, as done in Paper I. A "cluster" labeled by coordinates $\{l,\vec{x},s,\ldots\}$ is defined as a group of l B atoms, such that each atom is a nearest neighbor of at least one other atom of the cluster. By $\vec{x}$ we denote the center of gravity of the cluster, by s the surface area of its outer contour, etc. [Fig. 3(A)]. If only enough cluster coordinates are specified, each state of the system is described by any desired degree of accuracy. By this coordinate transformation in phase space (from the set of coordinates $\{\mu_i\}$ considered in Sec. II to a set of clusters coordinates) we thus keep the full information on the system.[20,27] We are not interested in this full information, of course, but will be interested rather in the concentration of clusters with coordinates $\{l,x\}$ at time t, which is denoted as $\bar{n}_l(\vec{x},t)$, where the bar means that an average over all other cluster coordinates is taken, and in $\bar{n}_l(t)=\int d\vec{x}\,\bar{n}_l(\vec{x},t)$, where the integration is extended over the total volume of the system.

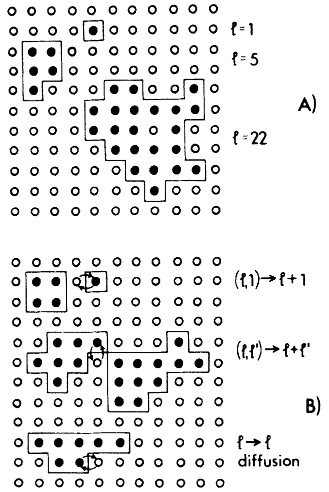

FIG. 3. (A) Clusters of l B atoms (full dots) on a background of A atoms (open dots). The drawn contours measure the sizes of the surface area of the clusters. (B) Stochastic interchange of atoms leads to cluster reactions and cluster diffusion.

If atomic exchange processes are now taking place, the cluster pattern evolves in time [see the examples shown in Fig. 3(B)]. Some exchanges will lead to "cluster reactions" (where the coordinate l associated with the cluster is changing), others lead to "cluster diffusion" only (where coordinates of the cluster other than l are changing). The cluster reactions are also accompanied by cluster diffusion [the center of gravities of the l and $l+1$ cluster in the example shown in Fig. 3(B) are a bit different]. Since it is assumed that the atomic exchanges occur at random [governed only by some transition probability, e.g., Eq. (2.3)], it is clear that the displacements of the cluster centers of gravity produced in this way will be random in direction. Hence these movements of the clusters will add up to a diffusion and not to an inertial propagation.[39]

From the master equation describing the atomic exchange processes [e.g., Eq. (2.1)] one may derive a master equation describing the time evolution of the cluster pattern. Similarly as in Sec. II it was attempted to derive a *closed* kinetic equation for moments of the atomic distribution function like $S(\vec{k}, t)$, one may attempt to derive a *closed* kinetic equation for suitable moments of the cluster distribution function, as e.g., $\bar{n}_l(t)$. The derivation of such an equation is completely analogous to the case, where the order parameter is not conserved (see Paper I). The result is, for $l>1$,

$$\begin{aligned}\frac{d}{dt}\bar{n}_l(t) = {} & \sum_{l'=1}^{\infty} \frac{\bar{n}_{l+l'}(t)}{n_{l+l'}} W(l, l') \\ & - \frac{1}{2}\sum_{l'=1}^{l-1} \frac{\bar{n}_l(t)}{n_l} W(l-l', l') \\ & + \frac{1}{2}\sum_{l'=1}^{l-1} \frac{\bar{n}_{l'}(t)}{n_{l'}} \frac{\bar{n}_{l-l'}(t)}{n_{l-l'}} W(l-l', l') \\ & - \sum_{l'=1}^{\infty} \frac{\bar{n}_l(t)}{n_l} \frac{\bar{n}_{l'}(t)}{n_{l'}} W(l, l') \ . \end{aligned} \tag{3.1}$$

For $l=1$, a similar equation holds, only the terms containing sums over l' running up to $l-1$ have to be omitted. We now discuss the physical meaning of the terms on the right-hand side of Eq. (3.1), explaining also the notation.

(i) The first term accounts for the gain of l clusters due to all splitting reactions $l+l' \rightarrow (l, l')$ [i.e., the inverse reaction to Fig. 3(B), middle part]. The cluster reaction matrix $W(l, l')$ is the number of such reactions per unit time in thermal equilibrium, while $n_{l+l'}$ is the value of $\bar{n}_{l+l'}(t)$ in thermal equilibrium, if we consider a state in the one-phase region. It is inherent in the derivation of Eq. (3.1) (see Paper I) that both quantities can be extended into the two-phase region, also (for instance, by analytic continuation of n_l), since the cluster reactions depend on local conditions of atomic arrangement only, and *not* on the global state of the system. The physical properties of both quantities will be considered later. Note that the evaporation of single atoms is included by the $l'=1$ term.

(ii) The next term describes the loss of l clusters due to all splitting reactions $l \rightarrow (l-l', l')$. The factor $\frac{1}{2}$ accounts for overcounting pairs of $(l', l-l')$ in the summation.

(iii) The third term describes the gain of l clusters due to all coalescence reactions $(l', l-l')$. A detailed balance condition has been invoked to relate the rate of these processes to the inverse ones, considered under (ii). Note that the condensation of single atoms is included by the $l'=1$ term.

(iv) The last term describes the loss of l clusters due to all coalescence reactions $(l, l') \rightarrow l+l'$ [cf. Fig. 3(B)]. It is obvious that the rate of all coalescence processes is proportional to the actual concentrations $\bar{n}_l(t), \bar{n}_{l'}(t)$ of the clusters involved in these processes, and hence Eq. (3.1) is a nonlinear set of coupled differential equations for the $\bar{n}_l(t)$.

It should be noted that the cluster diffusion does not show up explicitly in Eq. (3.1). If one generalizes the above treatment to $\bar{n}_l(\vec{x}, t)$ which yields

$$\frac{\partial}{\partial t}\bar{n}_l(\vec{x}, t) = D_l \nabla^2 \bar{n}_l(\vec{x}, t) + \cdots \ , \tag{3.2}$$

then in addition to cluster reaction terms of similar structure as in Eq. (3.1) [represented by the dots in Eq. (3.2)] one has a diffusive term accounting for the processes of Fig. 3(B), lower part. The cluster diffusion constant D_l depends on cluster size l and will be estimated in the appendix. Integrating Eq. (3.1) over the total volume and omitting unimportant surface terms leads back to Eq. (3.1), of course.

Reactions involving three or more clusters at the same time are neglected in Eq. (3.1). Both Eqs. (3.1) and (3.2) are based on the assumption that the use of only one cluster coordinate (l) provides a sufficiently accurate description. An extension of the treatment to the case of many coordinates is possible,[20,28] but will not be considered here. Also, it was invoked that the atomic exchange processes (and hence the cluster reactions) satisfy detailed balance conditions, even if the state of the system is far from thermal equilibrium. We do not think that this assumption is a serious one, however: (i) in the considered systems all other degrees of freedom (like lattice vibrations, etc.) come much quicker into thermal equilibrium after the quench than the local concentration variables. (ii) The rate of atomic exchanges depends on local atomic configurations only, and not on the global state of the system. The various geometrically possible local atomic configurations occur both in equilibrium states and in situations far from equilibrium (their probabilities of occurrence are somewhat different, of course).

Finally, we have assumed that the concentration of the minority phase (the B atoms) is low enough, such that no clusters of infinite size appear on the lattice. If one wants to treat the region close to the critical point, where the concentration is higher, one may avoid the occurrence of clusters of infinite size ("percolation problem"[40]) by using a definition of clusters different from the one given above (see Paper I and Refs. 28 and 41).

Concluding this subsection we emphasize that Eqs. (3.1) and (3.2) are not restricted to models where atoms on a lattice are directly interchanged. Adjusting the reaction matrices $W(l, l')$

and diffusivity D_l suitably, a description of liquid mixtures or of solids with indirect interchange via vacancies may as well be obtained.

B. Nucleation-coagulation equation

In this subsection we derive an approximate equation, which is somewhat easier to handle than Eq. (3.1) and which serves as a basis for our subsequent discussion of the Lifshitz-Slyozov theory.[17] Considering any approximations it is very important not to violate the conservation law for the total concentration c_B. Since[42] we have

$$c_B = \sum_{l=1}^{\infty} l \bar{n}_l(t) \ , \tag{3.3}$$

the conservation law $dc_B/dt = 0$ implies

$$\sum_{l=1}^{\infty} l \frac{d\bar{n}_l(t)}{dt} = 0 . \tag{3.4}$$

Inserting Eq. (3.1) into Eq. (3.4) and using the symmetry relation

$$W(l, l') = W(l', l), \tag{3.5}$$

it is a matter of nearly straightforward algebra to show that Eq. (3.4) is fulfilled as an identity. This result is nontrivial, since Eq. (3.1) is already approximate, as discussed above.

We now proceed to consider approximations valid for large $l \gg 1$. Standard nucleation theory[20] is obtained by making the following approximations: (i) one makes Taylor expansions around l,

$$\frac{\bar{n}_{l\pm l'}(t)}{n_{l\pm l'}} = \frac{\bar{n}_l(t)}{n_l} \pm l' \frac{\partial}{\partial l} \frac{\bar{n}_l(t)}{n_l} + \tfrac{1}{2} l'^2 \frac{\partial^2}{\partial l^2} \frac{\bar{n}_l(t)}{n_l} \ , \tag{3.6a}$$

$$W(l - l', l') = W(l, l') - l' \frac{\partial W}{\partial l} \ . \tag{3.6b}$$

(ii) The deviation from equilibrium of $\bar{n}_{l'}(t)/n_{l'}$ is neglected in the nonlinear terms, i.e., one puts there $\bar{n}_{l'}(t)/n_{l'} = 1$. This leads to the well-known results (see Paper I and Ref. 20) of the Fokker-Planck-type:

$$\frac{\partial \bar{n}_l(t)}{\partial t} = \frac{\partial}{\partial l}\left(R_l n_l \frac{\partial}{\partial l} \frac{\bar{n}_l(t)}{n_l}\right), \tag{3.7a}$$

$$R_l = \frac{1}{n_l} \sum_{l'=1}^{[l/2]} l'^2 W(l, l'). \tag{3.7b}$$

Contributions to the reaction rate which come from the regime $[l/2] < l' < \infty$ have been neglected. It is easy to see that this standard nucleation equation does not satisfy the conservation law, Eq. (3.4). This failure has a simple physical interpretation: it has been assumed above that the concentration of the small clusters $\{\bar{n}_{l'}(t)\}$, with which one considered large cluster interacts, are that of the supersaturated metastable one-phase equilibrium $\{n_{l'}\}$. What actually happens is that due to the buildup of large clusters the supersaturation of the environment decreases during the course of time. Hence the ratios $\bar{n}_{l'}(t)/n_{l'}$ are smaller than unity and time dependent.

It is intuitively appealing to speculate that the small clusters $\{\bar{n}_{l'}(t)\}$ correspond to some *equilibrium* $\{n_{l'}(\Delta h)\}$, where the parameter Δh characterizing the supersaturation is now a function of time t. This conjecture would also be consistent with the computer simulations.[25] Then one expects that the concentration of the large clusters $\bar{n}_l(t)$ obeys a Fokker-Planck equation such as Eq. (3.7a): However, now not the concentrations of the original supersaturated state $\{n_{l'}\}$ at $t = 0$ enter, but rather the concentrations of the actual supersaturated state $\{n_{l'}(\Delta h(t))\}$:

$$\frac{\partial \bar{n}_l(t)}{\partial t} = \frac{\partial}{\partial l} R_l(\Delta h) n_l(\Delta h) \frac{\partial}{\partial l} \frac{\bar{n}_l(t)}{n_l(\Delta h)} \ . \tag{3.7c}$$

The time dependence of Δh is then obtained in this picture by imposing the conservation law, Eq. (3.4), as additional condition.

Next we put this idea on a more quantitative basis, using Eq. (3.1). First we note that the dependence of $n_l(\Delta h)$ on h should be exponential. Thus we may *define* Δh by requiring

$$n_l(\Delta h) = n_l \exp(-l \Delta h), \tag{3.8}$$

since detailed balance is then fulfilled for arbitrary reactions $l + l' \rightleftarrows (l, l')$:

$$W(l, l') \frac{n_{l+l'}(\Delta h)}{n_{l+l'}} - \frac{n_l(\Delta h)}{n_l} \frac{n_{l'}(\Delta h)}{n_{l'}} = 0, \tag{3.9}$$

irrespective of the time dependence of Δh. Equation (3.9) should hold in any *equilibrium* state. We now assume that $\bar{n}_{l'}(t)$ may be approximated by $n_{l'}(\Delta h)$ in the nonlinear terms of Eq. (3.1), which yields a quasilinear set of equations in the $\bar{n}_l(t)$, namely,

$$\begin{aligned} \frac{d}{dt} \bar{n}_l(t) = & \sum_{l'=1}^{\infty} \frac{\bar{n}_{l+l'}(t)}{n_{l+l'}(\Delta h)} W_{\Delta h}(l, l') \\ & - \sum_{l'=1}^{[l/2]} \frac{\bar{n}_l(t)}{n_l(\Delta h)} W_{\Delta h}(l - l', l') \\ & + \sum_{l'=1}^{[l/2]} \frac{\bar{n}_{l-l'}(t)}{n_{l-l'}(\Delta h)} W_{\Delta h}(l - l', l') \\ & - \sum_{l'=1}^{\infty} \frac{\bar{n}_l(t)}{n_l(\Delta h)} W_{\Delta h}(l, l'), \end{aligned} \tag{3.10}$$

where

$$W_{\Delta h}(l, l') = \exp[-(l + l')\Delta h] W(l, l'). \tag{3.11}$$

Using now an expansion similar to Eqs. (3.6) in Eq. (3.10) one immediately obtains Eq. (3.7c) instead of Eq. (3.7a), with

$$R_l(\Delta h)=\frac{1}{n_l(\Delta h)}\sum_{l'=1}^{[l/2]} l'^2 W_{\Delta h}(l,l'). \tag{3.12}$$

It remains to determine Δh. Use of Eq. (3.10) in (3.4) yields the condition

$$\sum_{l=1}^{\infty}\frac{\bar{n}_l(t)}{n_l}\sum_{l'=1}^{\infty}e^{-l'\Delta h}l'W(l,l')$$
$$=\sum_{l=1}^{\infty}\sum_{l'=1}^{\infty}l'W(l,l')\frac{\bar{n}_{l+l'}(t)}{n_{l+l'}}\,. \tag{3.13}$$

If we normalize $\Delta h=0$ such that the $\{n_l\}$ in Eq. (3.8) are those of the one-phase state at the coexistence curve [point A in Fig. 1(a)], then $\Delta h\to 0$ for late times and it is legitimate to use $e^{-l'\Delta h}\approx 1-l'\Delta h$. Expanding also the terms $\bar{n}_{l+l'}(t)/n_{l+l'}$ with Eq. (3.6a), one obtains an explicit formula for Δh,

$$\Delta h(t)=-\left(\sum_{l=1}^{\infty}R_l n_l\right)^{-1}\sum_{l=1}^{\infty}R_l n_l\frac{\partial g_l(t)}{\partial l}, \tag{3.14}$$

where we have introduced the relative derivation from equilibrium

$$g_l(t)=\bar{n}_l(t)/n_l-1. \tag{3.15}$$

The interpretation of the result Eq. (3.14) is as follows: in the final thermal equilibrium we would have coexistence of a background of the A-rich phase [with B concentration according to point A in Fig. 1(a)] and infinitely large domains of B-rich phase [with B concentration according to point B in Fig. 1(a)], Then the concentrations of all cluster sizes in the A-rich phase would be in equilibrium. At finite times, the domains of the B-rich phase have finite size (l) and must thus be considered as l clusters, producing strong deviations of $\bar{n}_l(t)$ from equilibrium. This deviation from equilibrium produces in a "self-consistent" manner a supersaturation $\Delta h(t)$ [Eq. (3.14)], with which the small clusters are in equilibrium.

The treatment presented so far still suffers from an inconsistency, however: in Eq. (3.10) we have replaced *all* $\bar{n}_{l'}(t)$ by $n_{l'}(\Delta h)$ in the nonlinear terms, although we have assumed that the very large clusters (l) are *not* described by this "equilibrium" [otherwise there would not be any evolution, due to Eq. (3.9)]. A better approximation is obtained if we allow for this replacement of $\bar{n}_{l'}(t)$ by $n_{l'}(\Delta h)$ only for $1\leq l'\leq l_c$, where the cutoff l_c satisfies the condition $1\ll l_c\ll l$. The reactions involving clusters with $l'>l_c$ can be approximated differently: splitting away of such large clusters is a very improbable event, and hence can be safely neglected. In addition, sums may be replaced by integrals in the regime $l'>l_c$. Thus for $l>l_c$ we obtain

$$\frac{\partial\bar{n}_l}{\partial t}=\frac{\partial}{\partial l}\left(R_l(\Delta h)n_l(\Delta h)\frac{\partial}{\partial l}\frac{\bar{n}_l(t)}{n_l(\Delta h)}\right)$$
$$+\frac{1}{2}\int_{l_c}^{l}dl'\,W(l-l',l')$$
$$\times\frac{\bar{n}_{l'}(t)}{n_{l'}}\frac{\bar{n}_{l-l'}(t)}{n_{l-l'}}-\frac{\bar{n}_l(t)}{n_l}$$
$$\times\int_{l_c}^{\infty}dl'\,W(l,l')\frac{\bar{n}_{l'}(t)}{n_{l'}}, \tag{3.16}$$

while Eq. (3.7c) remains valid for $l\leq l_c$. Now $R_l(\Delta h)$ is defined by

$$R_l(\Delta h)=\frac{1}{n_l(\Delta h)}\sum_{l'=1}^{l_c}l'^2W_{\Delta h}(l,l'). \tag{3.17}$$

The field Δh is again determined implicitly in terms of the $\bar{n}_l(t)$ by the conservation law (3.4). Equation (3.16) is the central result of this subsection, and will constitute a basis for our further discussions.

C. Diffusion and relaxation close to thermal equilibrium

In this subsection we investigate the decay of small fluctuations in thermal equilibrium states by using our results for the cluster dynamics, Eqs. (3.14), (3.7c), and (3.16). Our goal is to show that this treatment reproduces the behavior of $S^{\mathrm{eq}}(\vec{k},t)$ known from other methods.[7,8,10] Thereby it is shown that the approximations of the previous sections are not too serious, and a connection between $S^{\mathrm{eq}}(\vec{k},t)$ and the dynamics far from equilibrium is established.

In thermal equilibrium states the cluster distribution n_l and all moments ln_l, l^2n_l, etc., are strongly decreasing functions of l for $l\gtrsim l_\xi$, where l_ξ corresponds to clusters with linear dimensions of the correlation length ξ of concentration fluctuations.[43] If we choose a cutoff l_c somewhat larger than l_ξ, the coagulation events in Eq. (3.16) are clearly rather unimportant and may be neglected [i.e., we may use Eq. (3.7c) for all cluster sizes]. In addition, we may put in linear response, using Eq. (3.15) and $n_l(\Delta h)\equiv n_l[1+g_l^0(t)]$,

$$\frac{\bar{n}_l(t)}{n_l(\Delta h)}=\frac{1+g_l(t)}{1+g_l^0(t)}\approx g_l(t)-g_l^0(t)\ , \tag{3.18}$$

and also invoking Eq. (3.8), we find

$$g_l^0(t)=\exp[-\Delta h(t)l]-1\approx-\Delta h(t)l\ . \tag{3.19}$$

Combining Eqs. (3.7c), (3.18), (3.19), and (3.14) we get the desired linear equation for $g_l(t)$,

$$\frac{\partial}{\partial t}g_l(t)=\frac{1}{n_l}\frac{\partial}{\partial l}\left\{R_ln_l\left[\frac{\partial g_l(t)}{\partial l}-\left(\sum_{l'=1}^{\infty}R_{l'}n_{l'}\right)^{-1}\right.\right.$$
$$\left.\left.\times\sum_{l'=1}^{\infty}R_{l'}n_{l'}\frac{\partial g_{l'}(t)}{\partial l'}\right]\right\}. \tag{3.20}$$

It is convenient to introduce a vector notation defining a scalar product

$$\langle f|g\rangle = \langle g|f\rangle \equiv \sum_{l=1}^{\infty} f(l)g(l)n_l \;, \tag{3.21}$$

where $f(l)$ and $g(l)$ are functions which vanish for $l \to \infty$. Then Eq. (3.22) can be rewritten in terms of an effective "Liouville operator" $\hat{L}$,

$$\frac{\partial}{\partial t}\,|g(t)\rangle = -\hat{L}\,|g(t)\rangle \;, \tag{3.22a}$$

with the matrix elements of $\hat{L}$ in the l representation being given by

$$L_{ll'} = -\frac{1}{n_l}\frac{\partial}{\partial l} R_{l'} n_{l'} \times \left(\delta_{ll'} - R_l n_l \Big/ \sum_{l''=1}^{\infty} R_{l''} n_{l''}\right) \frac{\partial}{\partial l'} \;. \tag{3.22b}$$

It is easily proven that $\hat{L}$ is a Hermitian operator (i.e., $\langle f|\hat{L}g\rangle = \langle g|\hat{L}f\rangle$), replacing the l summation in Eq. (3.21) by an integral and integrating by parts.[44] Therefore, $\hat{L}$ has real and nonnegative eigenvalues $\{\lambda_i\}$. Denoting the normalized eigenfunction by $|\psi_k\rangle$, we have

$$\hat{L}|\psi_i\rangle = \lambda_i|\psi_i\rangle, \quad \langle\psi_i|\psi_{i'}\rangle = \delta_{ii'} \;, \qquad \lambda_i \geq 0, \quad i = 0, 1, 2, \ldots \;. \tag{3.23}$$

Now we consider the spatially inhomogeneous case, where the diffusive term [Eq. (3.2)] must be included. Introducing the Fourier transforms

$$g_l(\vec{k}, t) = \int d\vec{x}\, e^{i\vec{k}\cdot\vec{x}}\, \frac{\bar{n}_l(\vec{x}, t) - n_l}{n_l}$$

and the associate vector $|g(\vec{k}, t)\rangle$, one immediately finds that Eq. (3.22a) has to be replaced by

$$\frac{\partial}{\partial t}\,|g(\vec{k}, t)\rangle = (-\hat{L} - D_l k^2)\,|g(\vec{k}, t)\rangle \;. \tag{3.24}$$

For $k \to 0$ the operator $D_l k^2$ may be considered a small perturbation, and hence one finds from perturbation theory that the eigenvalues of $-\hat{L} - D_l k^2$ are

$$\lambda_i(k) = \lambda_i + \langle\psi_i|D_l k^2 \psi_i\rangle \;, \tag{3.25}$$

and the solution of Eq. (3.24) is expanded formally as

$$|g(\vec{k}, t)\rangle = \sum_i |\psi_i\rangle\langle\psi_i|g(\vec{k}, t)\rangle = \sum_i e^{-\lambda_i t}\,|\psi_i\rangle\langle\psi_i|g(\vec{k}, 0)\rangle \;. \tag{3.26}$$

A general solution of the above eigenvalue problem has not been found. But the lowest eigenvalue λ_0 and its eigenfunction $\psi_0(l)$ can be found: putting $\psi_0(l) \propto g_l^0 \propto l$ [$\Delta h(t)$ in Eq. (3.19) cancels out if $\psi_0(l)$ is normalized, cf. Eq. (3.23)], it is seen that this is a solution of Eq. (3.20) with $\lambda_0 = 0$. From Eq. (3.25) one then finds

$$\lambda_0(k) = k^2\langle\psi_0|D_l\psi_0\rangle = k^2 \sum_{l=1}^{\infty} l^2 D_l n_l \Big/ \sum_{l=1}^{\infty} l^2 n_l \;. \tag{3.27}$$

Hence we have found an eigenvalue spectrum of the type shown in Fig. 2. Equation (3.27) is exact if $D_l = D$ (independent of l), while it otherwise holds in first-order perturbation theory only. Note that the solution

$$g_l(\vec{k}, t) = -\Delta h(\vec{k}) l \exp(-D_T k^2 t) = g_l(\vec{k}) \exp(-D_T k^2 t) \;, \tag{3.28a}$$

with

$$D_T = \sum_{l=1}^{\infty} l^2 D_l n_l \Big/ \sum_{l=1}^{\infty} l^2 n_l \;, \tag{3.28b}$$

satisfies the initial condition that for $t \to 0$ there was thermal equilibrium in a "field" (proportional to the supersaturation) $\Delta h(\vec{k})$. Using Eq. (3.28a) in Eq. (3.4) immediately yields $\Delta h(\vec{k}, t) = \Delta h(\vec{k}) \times \exp(-D_T k^2 t)$. Clearly, for large enough times the relaxation due to the higher branches λ_i, $i = 1, 2, \ldots 3, \ldots$ (Fig. 2) has died out, and the behavior of the relaxation function is then $S^{\text{eq}}(\vec{k}, t) = S_T(\vec{k}) \exp(-D_T k^2 t)$, i.e., Eq. (2.34).

Recently, Ackerson *et al.*[45] interpreted the Rayleigh linewidth in light scattering of fluids in terms of a cluster model. These authors used Eq. (3.2) but erroneously omitted all cluster reaction terms [i.e., they put $\hat{L} = 0$ in Eq. (3.24)]. Since then the various cluster sizes may decay uncoupled from each other, and the decay constants $D_l q^2$ depend on cluster size, they obtain a nonhydrodynamic structure function

$$S^{\text{eq}}(\vec{k}, t) = S_T(\vec{k}) \exp(-D' k^{4/3} t^{2/3})$$

by averaging over the cluster size spectrum. This result which contradicts hydrodynamics is incorrect, of course, and does not agree with experimental observation.[46] In our treatment it is seen that the cluster reactions provide a coupling between the various hydrodynamic decay modes $D_l q^2$ of the clusters, and therefore the asymptotic decay is dominated by the typical cluster size l_ξ, $D_T \approx D_{l_\xi}$. Such a behavior was already suggested in Ref. 22.

We now discuss the critical behavior of the diffusion constant D_T. Close to the critical point (T_c, c_B^{crit}) (Ref. 47) the cluster concentration n_l satisfies a scaling assumption (see Paper I)[48]

$$n_l = l^{-2-1/\delta}\,\tilde{n}(\epsilon l^{1/\beta\delta}, \langle\mu\rangle l^{1/\delta}) \;, \tag{3.29}$$

where β, δ are the critical exponents[34] associated with the order parameter $\langle\mu\rangle \equiv (c_B - c_B^{\text{crit}})/c_B^{\text{crit}}$ and

$\tilde{n}$ is the "scaling function" associated with n_l. It will be shown in the Appendix that the behavior of D_l for a solid mixture close to the critical point can be approximated by[22]

$$D_l = D' l^{-(1-1/\delta)}, \quad l \to \infty \ . \tag{3.30a}$$

From Eqs. (3.29) and (3.30a) it is seen that for $\epsilon \to 0, \langle \mu \rangle \to 0$ the main contribution to the summations in Eq. (3.28b) comes from $l \to \infty$. Thus, one may replace the summation by an integration

$$\begin{aligned} D_T &= \int_0^\infty dl\, l^2 D_l n_l \bigg/ \int_0^\infty dl\, l^2 n_l \\ &= \epsilon^\gamma \tilde{D}\left(\frac{\langle \mu \rangle}{\epsilon^\beta}\right) \ , \end{aligned} \tag{3.31a}$$

with $\tilde{D}(x)$ the appropriate scaling function. Equation (3.31a) is equilvalent to the dynamic scaling result equations (2.36) and (2.37), as expected. Next we consider the behavior of the interaction energy E after a small quench (δT) of the temperature. In thermal equilibrium, E_T is represented with the help of Eq. (2.41) in terms of cluster concentrations

$$\begin{aligned} E_T &= \sum_{\vec{k}} J(\vec{k}) \langle \mu(-\vec{k}) \mu(\vec{k}) \rangle \\ &= \sum_{\vec{k}} J(\vec{k}) \sum_{l=1}^{\infty} l n_l g_l(\vec{k}) \ , \end{aligned} \tag{3.32}$$

where $g_l(\vec{k})$ describes the response of the cluster concentration to a field $h(\vec{k})$ varying with wave vector $\vec{k}$ (see Paper I). Equation (3.32) can be cast in a form analogous to Eq. (3.3) rearranging the double sum

$$\begin{aligned} E_T &= \sum_{l=1}^{\infty} l^{1/\beta\delta} n_l^E \ , \\ n_l^E &\equiv n_l l^{1-1/\beta\delta} \sum_{\vec{k}} J(\vec{k}) g_l(\vec{k}) \ . \end{aligned} \tag{3.33}$$

In Eq. (3.33) a factor $l^{1/\beta\delta}$ was taken out arbitrarily, in order that n_l^E has the same scaling structure as n_l [Eq. (3.29)] in the critical region (cf. Paper I, where Eq. (3.33) was suggested on a more tentative basis). From Eqs. (3.32) and (3.33), we find

$$\begin{aligned} E_{T_i} &= E_{T_f} + \delta T \sum_{l=1}^{\infty} l^{1/\delta\beta} \frac{\partial n_l^E}{\partial T} \\ &= E_{T_f} + \delta T \sum_{l=1}^{\infty} l \frac{\partial n_l}{\partial T} \sum_{\vec{k}} J(\vec{k}) g_l(\vec{k}) \ , \end{aligned} \tag{3.34}$$

and using now Eq. (3.28a) we further find

$$E(t) = E_{T_f} + \delta T \sum_{l=1}^{\infty} l \frac{\partial n_l}{\partial T} \sum_{\vec{k}} J(\vec{k}) g_l(\vec{k}) e^{-D_T k^2 t} \ . \tag{3.35}$$

For $t \to \infty$ only contributions $\vec{k} \to 0$ matter; then

$$\begin{aligned} \sum_{\vec{k}} J(\vec{k}) e^{-D_T k^2 t} &\propto J(0) g_l(0) \\ &\quad \times \int_0^\infty e^{-D_T k^2 t} k^{d-1} dk \propto l (D_T t)^{-d/2} \ , \end{aligned} \tag{3.36}$$

and hence

$$E(t) - E_{T_f} \propto \delta T \sum_{l=1}^{\infty} l^2 \frac{\partial n_l}{\partial T} (D_T t)^{-d/2} \ , \tag{3.37}$$

which corroborates Eq. (2.45a). [Note that in the critical region, we have

$$\sum_{l=1}^{\infty} l^2 \frac{\partial n_l}{\partial T} \approx \int_0^\infty l^2 \frac{\partial n_l}{\partial T}\, dl \propto \epsilon^{-(\gamma+1)} \ ,$$

as can be seen from Eq. (3.29).]

In a fluid or liquid binary mixture, Eq. (3.30a) is replaced by Stokes' law

$$D_l \propto (V_l)^{-(1-2/d)} / \eta_v \ , \tag{3.30b}$$

where V_l is the cluster volume and η_v is the viscosity. Using $V_l \propto l^{1+1/\delta}$ (see Paper I) yields

$$\begin{aligned} D_T &\approx \int_0^\infty dl\, l^2 D_l n_l \bigg/ \int_0^\infty dl\, l^2 n_l \\ &= \epsilon^{(d-2)\nu} \tilde{D}\left(\frac{\langle \mu \rangle}{\epsilon^\beta}\right) \ , \end{aligned} \tag{3.31b}$$

neglecting the weak singularity of the viscosity.[49] Equation (3.31b) agrees then with Eq. (2.47a), as expected.

D. Lifshitz-Slyozov theory and the asymptotic time dependence of the cluster size distribution

Having established that Eq. (3.16) provides a useful description of the dynamics of fluctuations in thermal equilibrium states, we now apply it to the nonequilibrium situation of Fig. 1(a).

First we make several approximations, by which Eq. (3.16) is reduced to the Lifshitz-Slyozov theory,[17] which we generalize to arbitrary dimensionality. We assume that the coagulation terms are unimportant in the late stages of the process and neglect the Δh dependence of $R_l(\Delta h)$, replacing $R_l(\Delta h)$ by $R_l(0)$. We assume that the Δh dependence of $n_l(\Delta h)$ is that of the classical-nucleation theory[20]

$$n_l(\Delta h) = n_0 \exp(\Delta h l - f_0 l^{1-1/d}) \ , \tag{3.38}$$

where n_0 and f_0 are constants (f_0 is proportional to the surface tension). Then we obtain

$$\frac{\partial \bar{n}_l}{\partial t} + \frac{\partial}{\partial l}\left\{\bar{n}_l(t) R_l(0)\left[\Delta h(t) - f_0\left(1 - \frac{1}{d}\right) l^{-1/d}\right]\right\} = 0 \ , \tag{3.39}$$

where we have neglected the "diffusive term" $\partial^2 \bar{n}_l / \partial l^2$ in comparison with the "drift term" of the nucleation equation. This neglect is legitimate if one wants to describe the growth (or shrinking) of supercritical (subcritical) clusters with sizes l differing from the critical size[20] l^* sufficiently, i.e., $(l-l^*)^2Z^2 \gg 1$, where the "Zeldovich factor"[20] Z behaves as $Z \propto l^{*-1}$. For $l, l^* \to \infty$ this condition becomes valid for the whole size distribution. Again the time dependence of $\Delta h(t)$ is found from the conservation law, Eq. (3.4). We now estimate $R_l(0)$ similarly as done in Ref. 17 for $d=3$. We assume that in the final stages of the process the clusters are simply spherical domains of volume V_l, i.e., measuring lengths in units of the lattice spacing

$$V_l = l/\Delta c_B = U_d r_l^d/d \ , \tag{3.40}$$

where Δc_B is the concentration difference between points A, B in Fig. 1(a); U_d is the surface of a d-dimensional unit sphere; and r_l is the cluster radius. The current of B atoms which impinge on the cluster surface per unit area is then

$$j = D_T \left. \frac{\partial c_B(r)}{\partial r} \right|_{r=r_l} \propto D_T \frac{\Delta c_B}{r_l} \ . \tag{3.41}$$

The total current, and hence $R_l(0)$, is obtained by multiplying j with the cluster surface area, which yields $R_l(0) \propto r_l^{d-1}/r_l$ or, with Eq. (3.40),

$$R_l(0) = R' l^{1-2/d} \ , \tag{3.42}$$

where R' is a constant. We now look for a scaling solution of Eq. (39), i.e., we put

$$\bar{n}_l(t) = t^y \tilde{n}(l t^{-x}), \quad l \to \infty, \quad t \to \infty \ , \tag{3.43}$$

where x, y are exponents which we determine below, and $\tilde{n}(z)$ is the appropriate scaling function. Equation (3.4) implies $y=-2x$, since now the sums may be converted to an integral

$$\begin{aligned} 0 &= \frac{d}{dt} \int_0^\infty dl\, l\bar{n}(t) \\ &= \frac{d}{dt} t^{y+2x} \int_0^\infty z\, dz\, \tilde{n}(z) \ . \end{aligned} \tag{3.44}$$

From Eq. (3.39), we now obtain similarly for $\Delta h(t)$, using Eq. (3.44) and integrating over l by parts

$$\begin{aligned} \Delta h(t) &= f_0 \left(1-\frac{1}{d}\right) \int_0^\infty dl\, \bar{n}_l(t) R_l(0) l^{-1/d} \Big/ \int_0^\infty dl\, \bar{n}_l(t) R_l(0) \\ &= c_1 f_0 \left(1-\frac{1}{d}\right) t^{-x/d} \ , \end{aligned} \tag{3.45}$$

where c_1 is a constant. Then inserting Eq. (3.43) into (3.39), we get $(\tilde{n}' = d\tilde{n}/dz)$

$$y\tilde{n} - xz\tilde{n}' = f_0 \left(1-\frac{1}{d}\right) R' t^{1-3x/d} \frac{d}{dz} [\tilde{n} z^{1-2/d}(z^{-1/d} - c_1)] \ . \tag{3.46}$$

Hence Eq. (3.43) is indeed a solution, if

$$x = d/3 \ , \tag{3.47a}$$

the same result as Eq. (2.25) [cf. Eq. (3.40)]. Equation (3.46) then yields the scaling function $\tilde{n}(z)$ $[v(y) = 3y^{1-2/d} - y - 2y^{1-3/d}]$,

$$\tilde{n}(z) = A \exp\left(\int_0^{z/z_0} \frac{dy}{v(y)} \right) \Big/ \left| v\left(\frac{z}{z_0}\right) \right|, \quad z \le z_0 \ , \tag{3.47b}$$

$$z_0 = \left(\frac{3R' f_0 (1-1/d)}{2d} \right)^{d/3}, \quad n(z) = 0, \quad z > z_0 \ ,$$

where A is a constant determined by[50]

$$c_B = c_B^{\text{coex}} + \int_0^\infty dz\, z\tilde{n}(z) \ .$$

Figure 4 shows the resulting $\tilde{n}(z)$ for $d=2$. Equations (3.47) and (3.43) show that the linear dimensions of the clusters increase $\propto t^{1/3}$ independent of dimensionality d. Applying methods similar to that of Ref. 17, it can be shown that Eq. (3.47) is obtained from Eq. (3.39) as an asymptotic solution, irrespective of the initial condition.

A complementary approximation is obtained neglecting the nucleation-condensation term in Eq. (3.16) and taking rather the coagulation terms into account. If one makes a scaling assumption for the reaction matrix

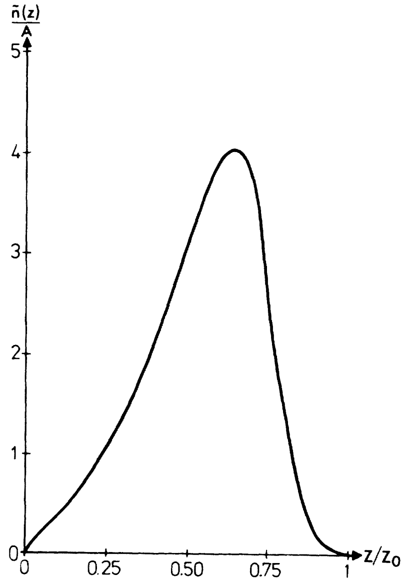

FIG. 4. Normalized scaling function $\tilde{n}(yz_0)/A = \exp\{-\frac{2}{9}[5\ln(1-\sqrt{y}) + 3\sqrt{y}/(1-\sqrt{y}) - 4\ln(1+\frac{1}{2}\sqrt{y})]\}/(y + 2/\sqrt{y} - 3)$ [cf. Eq. (3.47b)] for the cluster size distribution according to the Lifshitz-Slyozov mechanism in two dimensions.

$$W(l,l') = n_l n_{l'} l'^{v} \tilde{W}(l/l') \ , \tag{3.48}$$

where v is a new exponent and $\tilde{W}(x)$ is a scaling function, one finds that Eq. (3.16) is again solved by Eq. (3.43), with $y=-2x$, and

$$x = (1-v)^{-1} \ , \tag{3.49}$$

and the scaling function $\tilde{n}$ is now determined by the equation

$$y\tilde{n} - xz\tilde{n}' = \int_0^z dz' z'^{v} \tilde{W}\left(\frac{z-z'}{z'}\right) \tilde{n}(z')\tilde{n}(z-z')$$

$$- \tilde{n}(z) \int_0^\infty dz' z'^{v} \tilde{W}\left(\frac{z}{z'}\right) \tilde{n}(z') \ . \tag{3.50}$$

While an explicit solution of the nonlinear equation (3.50) is much more difficult than in the case of the linear equation (3.46), and hence not attempted here, we rather estimate the exponent v and hence x, using Eq. (3.49). At very low temperatures, the diffusivity of clusters is due to atoms evaporating from the cluster surface and reimpinging there again (cf. Appendix). This leads to Eq. (A11), i.e., $D_l \propto l'^{-1-1/d}$. The mass Δm which is incorporated per unit time Δt into a l cluster is then given by

$$\frac{\Delta m}{\Delta t} = l'(D_{l'}/\Delta^2)\bar{n}_{l'}(t) \ , \tag{3.51}$$

where Δ is the average distance between the l cluster and the l' clusters in the system. From the fact that the total mass fraction in the clusters is of order unity, and that l and l' have the same order of magnitude [this is implied in the scaling assumption, Eq. (3.43)], we conclude that $\Delta = Cl'^{1/d}$, where C is a constant of order unity: the average distance between the clusters is of the same order of magnitude as the linear dimension of the clusters. From the identification

$$\frac{\Delta m}{\Delta t} \bar{n}_l(t) \equiv W(l,l') \frac{\bar{n}_l(t)}{n_l} \frac{\bar{n}_{l'}(t)}{n_{l'}}$$

and Eqs. (3.48) and (3.51), we immediately predict $[\Delta m/\Delta t = l'^{v} \tilde{W}(l/l')\bar{n}_{l'}(t)]$

$$l'^{v} \propto l'^{1-2/d} D_{l'} \propto l'^{-3/d}, \quad v = -3/d \ , \tag{3.52}$$

since $\tilde{W}(l/l')$ is also of order unity for $l \approx l'$. Equations (3.49) and (3.52) then imply

$$x = d/(d+3) \ , \tag{3.53}$$

which was suggested in Ref. 22 on the basis of more-heuristic arguments. Thus the typical size of clusters increase as $l \propto t^{d/(d+3)}$.

At temperatures intermediate between the $T \to 0$ and $T \to T_c$ limits, B clusters contain a nonzero fraction of "holes" (i.e., A atoms). The center of gravity of a B cluster is then shifted more quickly by diffusion of these A atoms within the cluster than by the above surface rearrangement mechanism. This leads to Eq. (A12), i.e., $D_{l'} \propto l'^{-1}$, and Eq. (3.52) is replaced by $v=-2/d$; Eq. (3.49) then implies

$$x = d/(d+2) \ . \tag{3.54}$$

At temperatures $T \to T_c$ and concentrations near the critical concentration it is necessary to interpret our cluster coordinate l as the excess number of B molecules in the cluster, rather than the total number (or cluster volume v), in order to avoid percolation difficulties.[5-] Using[41] $V_l \propto l^{1+1/\delta}$, one has $\Delta = Cl'^{(1+1/\delta)/d}$, and [Eq. (3.30)] $D_{l'} \propto l'^{-1+1/\delta}$. Equation (3.51) then becomes

$$\frac{\Delta m}{\Delta t} = l' \frac{D_{l'}}{\Delta^2} \bar{n}_{l'}(t)$$

$$\propto l'^{1/\delta - 2(1+1/\delta)d} \bar{n}_{l'}(t) \ , \tag{3.55}$$

i.e., $v = 1/\delta - 2/d(1+1/\delta)$, and hence [Eq. (3.49)] $x = d/[d(1-1/\delta)+2(1+1/\delta)]$. Using the scaling relation[34] $\eta = 2 - d(\delta-1)/(\delta+1)$, this result can be rewritten

$$x = \frac{d}{1+1/\delta} \frac{1}{4-\eta} \ , \tag{3.56}$$

implying [Eq. (3.43)] that V_l behaves as $t^{-d/(4-\eta)}$, and the linear dimension $V_l^{1/d}$ behaves as $t^{1/(4-\eta)}$, which is the same result as obtained from the scaling analysis, Eq. (2.40b). For $d=3$, Eq. (3.56) gives $x \approx \frac{2}{3}$.

Equations (3.53)–(3.56) are restricted to solid binary mixtures. For fluids or liquid binary mixtures, on the other hand, the use of Eq. (3.30b) in Eq. (3.51) readily yields for T far below T_c $[V_l = l$, Eq. (3.40)] that $v=0$ and

$$x = 1 \ . \tag{3.57}$$

It appears that in this case for $d=3$ the diffusion-coagulation mechanism and the condensation-evaporation mechanism [Eqs. (3.38)–(3.47)] give the same value for the scaling power x, while for solid mixtures the diffusion-coagulation mechanism is much slower [Eqs. (3.53), (3.54), and (3.56)]. We also note that for $T \to T_c$ due to $V_l \propto l^{1+1/\delta}$ we get

$$x + (1+1/\delta)^{-1} \ , \tag{3.58}$$

implying that the volume V_l increases with t, and the linear dimension with $t^{1/d}$, in agreement with Eq. (2.47b).

We next turn to the asymptotic time dependence of the interaction energy. For $t \to 0$, interaction energy different from the ground-state energy is associated with the surfaces of the clusters only. Since for a compact cluster [similar to Eq. (3.40)] we have for this energy E_l,

$$E_l \propto V_l^{1-1/d} \propto l^{1-1/d} \quad , \tag{3.59}$$

the excess energy is Eq. (3.43),

$$\begin{aligned} E(t) - E(\infty) &= \int_0^\infty dl\, E_l \bar{n}_l(t) \\ &\propto t^{-x/d} \int_0^\infty dz\, z^{1-1/d} \tilde{n}(z) \quad . \end{aligned} \tag{3.60}$$

Hence according to the Lifshitz-Slyozov condensation mechanism we would obtain, from Eqs. (3.47) and (3.60),

$$E(t) - E(\infty) \propto t^{-1/3} \quad , \tag{3.61}$$

while the cluster diffusion-coagulation mechanism yields at low temperatures [Eqs. (3.53) and (3.60)]

$$E(t) - E(\infty) \propto t^{-1/(d+3)} \quad , \tag{3.62}$$

and at intermediate temperatures [Eqs. (3.54) and (3.60)]

$$E(t) - E(\infty) \propto t^{-1/(d+2)} \quad . \tag{3.63}$$

Although at intermediate temperatures the clusters contribute also a bulk term to the interaction energy, Eq. (3.60) is nevertheless valid: the total bulk interaction energy of the clusters is proportional to the total cluster volume, which is constant [Eqs. (3.40) and (3.44)]. For $T \to T_c$, Eq. (3.59) breaks down, however, and has to be replaced by

$$E_l / l \propto (l/V_l)^2 \propto l^{-2/\delta} \quad , \tag{3.64}$$

assuming that the energy/(excess atom) is proportional to the square of the excess concentration of the cluster.[28] Equations (3.64) and (3.43) yield

$$E(t) - E(\infty) \propto t^{-2d/(4-\eta)(1+\delta)} \quad . \tag{3.65}$$

Since $2d/(1+\delta) = d - 2 + \eta$, Eqs. (3.65) and (3.45b) agree.

The results, Eqs. (3.62)–(3.65), apply again to solid mixtures. For fluids and liquid binary mixtures, we find from Eqs. (3.57) and (3.60),

$$E(t) - E(\infty) \propto t^{-1/d} \quad , \tag{3.66}$$

while for $T \to T_c$, Eqs. (3.64) and (3.58) imply that

$$E(t) - E(\infty) \propto t^{-2/(\delta+1)} \propto t^{-(d-2+\eta)/d} \quad . \tag{3.67}$$

Equation (3.67) agrees with Eq. (2.49b) [note that we have disregarded the weak divergence of the viscosity here, which contributes the correction term $\frac{1}{19}(4-d)$ in Eqs. (2.47) and (2.49)]. Again we note[36] that the electrical resistivity behaves as $\rho(t) - \rho(\infty) \propto E(t) - E(\infty)$.

E. Observability of the grain growth laws: Comparison with experiments and computer simultations

In Sec. III D we have derived growth laws for the time dependence of the average grain "size" $\bar{l}(t)$, since [Eqs. (3.43) and (3.44)]

$$\bar{l}(t) \equiv \int_0^\infty dl\, l^2 \bar{n}_l(t) \Big/ \int_0^\infty dl\, l \bar{n}_l(t) \propto t^x, \quad t \to \infty \quad , \tag{3.68}$$

which are given in Eqs. (3.47), (3.53), (3.54), and (3.56) for solid mixtures; in Eqs. (3.57) and (3.58) for liquid mixtures and fluids; while Eqs. (3.61)–(3.67) give the analogous results for the energy (or electrical resistivity). We now consider the question, in which regimes of cluster size and temperature these growth laws can actually be observed.

It is obvious that the Lifshitz-Slyozov condensation-evaporation mechanism [Eqs. (3.47) and (3.61)] provides the quickest relaxation in the case of the solid mixture. Hence one expects that this mechanism must dominate, at least asymptotically for $t \to \infty$. At this point it is important to recall, however, that in our treatment we have not considered the "lattice misfit" of the two constituents. This lattice misfit clearly leads to elastic strain fields of long range. Ultimately these fields tend to destroy the host lattice ("loss of coherence"[4,5]), i.e., the surface of the grains become crystallographic grain boundaries such that the lattice points of the B-rich grain no longer correspond to lattice points of the surrounding host matrix of A-rich phase. Clearly further studies are necessary which investigate the influence of this elastic interaction on the grain growth behavior before this loss of coherence occurs. While in the literature[4,5] it is claimed that a broad evidence for the $\bar{l}(t) \propto t^{d/3}$ law [Eqs. (3.47) and (3.68)] exists, only a few examples (e.g., Ref. 52) are really convincing: most of the results are either inaccurate or restricted to too short time intervals and therefore consistent with both Eq. (3.47) and (3.53), (3.54), as demonstrated in Ref. 26 (Fig. 3) with the data of Ref. 53. Other data,[3,6] on the other hand, imply definitely smaller values of x, which are comparable with Eqs. (3.53) and (3.54). In the case of fluids or binary mixtures, there is no difference between Eq. (3.47) and (3.57) for $d=3$. Nevertheless a consideration of the *prefactors*, which were not considered explicitly in Eqs. (3.47), (3.57) showed[1] that in the case of the 2-6 lutidine-water mixture it is the coagulation mechanism (3.57) and not the condensation mechanism (3.47) which is dominant. Figure 9 of Ref. 1 demonstrates that quantitative agreement between the experimental data and Eq. (3.57) is obtained. In addition, the coagulation mechanism[21] has a well-known application in the formation of clouds of water drops in a supersaturated atmosphere.[54] But in this case, as well as in the case of droplet growth by condensation[55] the situation is clearly more complicated, since the acceleration of droplets due to gravity and their interaction due to electric charges has to be taken into account, as well as large-scale hydrodynamic flows. It is possible that the latter are responsible also for some unexplained puzzling features occuring in the intermediate stages of the phase separation experiment described in Ref. 1. In neither solids nor liquids we are aware of any measurements of the energy or electrical resistivity which are suitable for a check of Eqs. (3.61)–(3.67).[56]

It is possible to obtain a more meaningful check on our results comparing them to recent computer simulations.[23–25,57,58] For $d=2$ these authors obtained[58] for $T/T_c \cong 0.6$, $c_B = 0.2$,

$$l(t) \underset{\sim}{\propto} t^{0.36}, \quad E(t) - E(\infty) \underset{\sim}{\propto} t^{-0.18} , \tag{3.69}$$

which agrees well with Eqs. (3.53) and (3.62). The agreement with Eqs. (3.54) and (3.63) would not be as good, although a direct determination[58] of $D_{l'}$ suggests that the data should belong to the regime described by these formulas. In some runs[25] extending to longer times at $T/T_c \cong 0.6$, but $c_B = 0.5$, it was found that Eq. (3.69) holds for the energy up to about $t = 7000$ Monte Carlo steps/atom, while afterwards we have $E(t) - E(\infty) \underset{\sim}{\propto} t^{-0.45}$. This result may be taken as an indication that actually for large times Eq. (3.61) becomes valid, although the inaccuracy of the determination of $E(\infty)$ due to finite size effects precludes any definitive statements. The results[25] for the position of the peak $k_m(t)$ in the structure function $S(\vec{k}, t)$ are also consistent with Eq. (3.53), if one puts[22] $k_m^d(t)\overline{V}_l(t) = k_m^d(t)\overline{l}(t) = \text{const}$, which gives [Eq. (3.68)] $k_m(t) \propto t^{-x/d}$. The three-dimensional computer results[25] for $c_B = 0.5$ are

$$\begin{aligned} k_m(t) &\propto t^{-0.21} \quad (T/T_c \cong 0.6) , \\ k_m(t) &\propto t^{-0.25} \quad (T/T_c \cong 0.8, 0.9) , \end{aligned} \tag{3.70}$$

while the energy behaves as $E(t) - E(\infty) \propto t^{-0.2}$ up to $t \approx 200$ Monte Carlo steps/spin, and then a crossover to $E(t) - E(\infty) \propto t^{-0.24}$ occurs.[26] These results are consistent with Eqs. (3.54) and (3.63), and again a crossover to Eq. (3.61) seems plausible. For $c_B = 0.2, T/T_c \cong 0.6$ it was found that $\overline{l}(t) \propto t^{0.5}$, in agreement with Eq. (3.53).[26,59]

In order to improve our understanding of these results it is necessary to consider the interplay of the various mechanisms: cluster growth by condensation [Eq. (3.47)] or by cluster diffusion and coagulation [Eqs. (3.53) and (3.54)]. Including both the diffusion via surface rearrangement and via diffusion of "holes," one has (cf. Appendix)

$$D_l = [S_l(T) + c_H(T)l](a/l)^2 , \tag{3.71}$$

where a is a constant of order unity, $S_l(T)$ is the surface area of a cluster, and $c_H(T) = 1 - \langle\mu\rangle$ is the concentration of "holes" in the cluster. As $l \to \infty$, we have $S_l(T) \propto l^{1-1/d}$, but for small l, $S_l(T) \approx S' l^{\sigma'}$ with $\sigma' > 1 - 1/d$, as has been shown by computer simulations.[60] Due to this enhancement of the surface area of small clusters, and the admixture of the $c_H(T)l$ term [note that always $c_H(T) \ll S'$] the effective behavior will always be in between Eqs. (3.53) and (3.54); the deviation from Eq. (3.53) will be the stronger the higher the temperature. This result is consistent both with Eq. (3.70) and with the experiment on $CuMn_3$-Al alloys, where for the exponent x/d the "effective values" 0.127, 0.172, and 0.216 at $T = 200$, 240, and 300 °C, respectively, have been quoted.[6]

We now consider the crossover between Eqs. (3.47) and (3.53). For that purpose the prefactors in the $\overline{l}(t) \propto t^x$ law have to be estimated. This is done rederiving Eqs. (3.47) and (3.53) in a simplified fashion. In the coagulation-dominated regime, we assume the particle radius to grow as

$$r_l^2 = tD_l , \tag{3.72}$$

neglecting a factor of order unity. From $D_l \cong D_T l^{-1-/d}$ [cf. Eq. (A11)] and $l \approx \pi r_l^d \Delta c_B$ for $d = 2, 3$ [cf. Eq. (3.40)] one gets

$$D_l \cong D_T(\Delta c_B \pi)^{-1-1/d} r_l^{-d-1} ,$$

and hence

$$r_l = [D_T/(\pi\Delta c_B)^{1+1/d}]^{1/(d+3)} t^{1/(d+3)} . \tag{3.73}$$

In the condensation-dominated regime, one may argue as follows: a grain of size l which is well separated from other grains would be in equilibrium with a "field" $\Delta h = f_0(1 - 1/d)/l^{1/d}$ [from Eq. (3.39)]. We introduce the susceptibility χ by $\chi = \partial\langle\mu\rangle/\partial h = (\langle\mu\rangle_{\text{coex}} - \langle\mu\rangle)/\Delta h$; since $\Delta h = 0$ at the coexistence curve $\langle\mu\rangle_{\text{coex}}$, one gets $\langle\mu\rangle = \langle\mu\rangle_{\text{coex}} - \chi f_0(1 - 1/d)\pi^{-1/d}/r_l$. Thus the grain would be in equilibrium with a concentration

$$c_B(r_l) = c_B^{\text{coex}} + \tfrac{1}{2}\chi f_0(1 - 1/d)\pi^{-1/d}/r_l . \tag{3.74}$$

Assuming as in Eq. (3.73) that the mean distance between grains is r_l, and that the radius of a neighboring grain is $r_l + \Delta r$, we get a concentration gradient

$$\begin{aligned} \frac{\partial c_B}{\partial r} &= \frac{c_B(r_l) - c_B(r_l + \Delta r)}{r_l} \\ &\approx \tfrac{1}{2}\chi f_0\left(1 - \frac{1}{d}\right)\pi^{-1/d} \frac{\Delta r}{r_l^2(r_l + \Delta r)} \\ &\approx \frac{\tfrac{1}{2}\chi f_0(1 - 1/d)\pi^{-1/d}}{r_l^2} , \end{aligned} \tag{3.75}$$

where furthermore $\Delta r \cong r_l$ was assumed. The current is then $j=D_T(\partial c_B/\partial r)$, and hence the change of mass is

$$\frac{d}{dt}\left(\frac{U_d}{d}r_l^d\right)=U_d r_l^{d-1}j$$

$$=D_T U_d \frac{\chi f_0}{2}\left(1-\frac{1}{d}\right)\pi^{-1/d}r_l^{d-3}, \quad (3.76)$$

and thus

$$r_l=\left[\frac{3}{2}\frac{D_T\chi f_0}{\pi^{1/d}}\left(1-\frac{1}{d}\right)\right]^{1/3}t^{1/3}. \quad (3.77)$$

Equating Eqs. (3.73) and (2.77) gives an estimate for the time t where the crossover from Eq. (3.73) to (3.77) occurs

$$t_{\mathrm{cr}}\cong\left[\left(\frac{D_T}{(\pi\Delta c_B)^{1+1/d}}\right)^3\Big/\left(\frac{3D_T\chi f_0(1-1/d)}{2\pi^{1/d}}\right)^{d+3}\right]^{1/d}$$

$$=\frac{1}{D_T}\left[\pi^2\times\frac{3}{2}\chi f_0\left(1-\frac{1}{d}\right)^{d+3}\right]^{-1/d}(\Delta c_B)^{-(3/d)(1+1/d)}. \quad (3.78)$$

From the Ising-model susceptibility in two dimensions[61] $\chi=0.025\,54(1-T/T_c)^{-1.75}$, one finds $\chi(T=0.59T_c)=0.0155$, and for the surface tension f_0 in our units, one finds[62] $f_0=3.68$. From Fig. 11 of Ref. 25 one estimates $D_T\approx 0.05$, and hence one finds $t_{\mathrm{cr}}\approx 5.10^3$ Monte Carlo steps/atom as an order of magnitude estimate, while the experimental value quoted above was $t_{\mathrm{cr}}\approx 7\times 10^3$. In three dimensions and $T/T_c=0.6$, χ is distinctly larger than in two dimensions, and the crossover time correspondingly smaller.

Hence we have found that the behavior of $\bar{l}(t)$ is rather given by $\bar{l}(t)\propto t^{x_{\mathrm{eff}}}$, with x_{eff} starting out with a value somewhere in between $d/(d+3)$ and $d/(d+2)$, which then gradually crosses over to $x_{\mathrm{eff}}=\frac{1}{3}d$ at large times. Therefore, it is not surprising that the theory of Langer *et al.*[14] [note $x=\frac{1}{4}d$, Eq. (2.29)] is in reasonably accurate agreement with the computer experiments at intermediate times, although it fails to describe correctly the late time behavior.

It is also interesting to apply these estimates to real materials. Suppose that at $T=0.6T_c$ the diffusion constant is $D_T=10^{-10}$ cm²/sec, or, if lengths are measured in units of the lattice spacing as done here, $D_T\cong 10^5$/sec. Then Eq. (3.77) yields, very roughly, $r_l\propto(10^4 t)^{1/3}$, and the crossover is at $t_{\mathrm{cr}}\cong 10^{-2}$ sec, i.e., the crossover should occur at $r_l\approx 5$ lattice spacings (grains containing 500 atoms). In this case the cluster coagulation would hardly be observable in most experiments. In the experiment on CuMn$_3$-Al alloys $T_c=360$ °C and at 200 °C a wavelength of about 50 Å was observed after 600 sec. Supposing a diffusion constant of $D_T=10^{-1}$ cm²/sec, one would get $r_l\propto(10^{0}t)^{1/3}$, and crossover at $t_{\mathrm{cr}}\cong 10^2$ sec. While this latter choice yields values of r_l in rough agreement with the experiment, one would conclude that one is probably in the Lifshitz-Slyozov regime, in contrast to the observation. This numerical discrepancy indicates that Eqs. (3.73), (3.77), and (3.78) may be too crude.

How are these predictions changed due to the fact, that interchanges occur indirectly via impurities or vacancies rather than directly? If the distribution of the vacancies stays unaffected by the phase separation, then only the time scale will be affected, and our arguments still hold. The situation is different, however, if the vacancies diffuse to the grain boundaries and then stay preferentially there. Since the total number of vacancies stays constant, their density $c_v(t)$ at the grain boundaries cannot stay constant: the total grain boundary area decreases proportional to the excess energy, and thus $c_v(t)$ increases: $c_v(t)\propto t^{x/d}$. Instead of Eqs. (3.48)–(3.53) we then have $\Delta m/\Delta t=t^{x/d}l'D_{l'}/\Delta^2\bar{n}_{l'}(t)$, i.e., $W(l,l')$ contains a factor $t^{x/d}$, and (3.49) changes to $x=(1-v-1/d)^{-1}$, and Eq. (3.52) then implies that Eq. (3.54) holds also in this case.

IV. CONCLUSIONS

In this paper we attempted to give a detailed theory of both the critical dynamics and the phase separation kinetics of binary mixtures, where the average concentration is conserved. In the following we list our main results:

(i) The dynamics of both solid and liquid binary mixtures can be described in a unique way in terms of the concentrations of clusters $\bar{n}_l(t)$, where l measures the amount of order parameter associated with the cluster [Eq. (3.1)], even far from thermal equilibrium. Both for critical dynamics and the late stages of phase separation only very large clusters matter. Then the rate of change $\partial\bar{n}_l/\partial t$ can be decomposed into two parts: a nucleation-condensation term and a coagulation term [Eq. (3.16)].

(ii) Close to thermal equilibrium, coagulation may be neglected. In linear response the nucleation-condensation term then gives rise to a hydrodynamic relaxation in the structure function $S^{\mathrm{eq}}(\vec{k},t)=S_T(\vec{k})\exp(-D_T k^2 t)$ [cf. Eq. (3.28)]. The diffusion constant D_T can be expressed in terms of the cluster diffusivity D_l and the equilibrium cluster concentration n_l. Errors are pointed out in related other theories which predicted a nonhydrodynamic structure function.

(iii) Below T_c and within the coexistence curve, coagulation of clusters dominates during the earlier stages of the phase separation. Later on the nucleation-condensation term dominates again. The

TABLE I. Exponents x_V, x_E describing the asymptotic time dependence of the typical grain volume $\bar{V}_l(t)$ and the internal energy $E(t)$, respectively: $\bar{V}_l(t) \propto t^{x_V}, E(t) - E(\infty) \propto t^{-x_E}$. The position $k_m(t)$ of the maximum of the structure function varies as $k_m(t) \propto t^{-x_V/d}$ for d-dimensional systems. Droplet model predictions are shown for various regimes. Note that the correlation length ξ diverges at T_c ($\xi \propto |T - T_c|^{-\nu}$) and that the exponent $\eta = \frac{1}{4}$ for $d = 2$ and $\eta \approx 0.05$ for $d = 3$.

Temperature regime			Solid mixture		Liquid mixture	
			x_V	x_E	x_V	x_E
$T \gtrsim T_c$	$V(t)/\xi^d \gg 1$		$\frac{1}{2}d$	$\frac{1}{2}d$	$\frac{1}{2}d$	$\frac{1}{2}d$
	$V(t)/\xi^d \ll 1$		$1/(4-\eta)$	$(d-2+\eta)/(4-\eta)$	1^{a}	$(d-2+\eta)/d^{a}$
$T < T_c$	$V(t)/\xi^d \ll 1$		$1/(4-\eta)$	$(d-2+\eta)/(4-\eta)$	1^{a}	$(d-2+\eta)/d^{a}$
	$V(t)/\xi^d \gg 1$	$t < t_{cr}$	$d/(d+2)$	$1/(d+2)$	1	$1/d$
		$t > t_{cr}$	$\frac{1}{3}d$	$\frac{1}{3}$		
$T \to 0$		$t < t_{cr}$	$d/(d+3)$	$1/(d+3)$	1	$1/d$
		$t > t_{cr}$	$\frac{1}{3}d$	$\frac{1}{3}$		

[a] The weak divergence of the viscosity modifies these results, cf. Eqs. (2.47b) and (2.49b).

Lifshitz-Slyozov theory is recovered as a special case of this term, and a solution is given for general dimensionality d. We find that both in the coagulation theory (C) and in the Lifshitz-Slyozov (LS) theory the late-time behavior of $\bar{n}_l(t)$ can be represented by scaling solutions, $\bar{n}_l(t) = t^{-2x}\tilde{n}(lt^{-x})$ [Eq. (3.43)]. From this result we find that both the average grain size $\bar{V}_l(t)$ and the excess energy $E(t) - E(\infty)$ [or resistivity $\rho(t) - \rho(\infty)$, respectively] can be represented as power laws $= \bar{V}_l(t) \propto t^{x_V}, E(t) - E(\infty) \propto t^{-x_E}$. The exponents x_V, x_E are universal within the same dynamic universality class, but different cases ($T \to 0, T < T_c, T = T_c, T > T_c$) must be distinguished. Our corresponding estimates for these exponents are summarized in Table I. These results are compared to experiment and computer simulations (Secs. II D and III E) whereever available, and good agreement is found. We also attempt to estimate the cluster size where the crossover between the coagulation mechanism and LS mechanism occurs, and obtain at least an order of magnitude agreement.

(iv) Near T_c a static scaling assumption for n_l leads to dynamic scaling for $S^{eq}(\vec{k}, t)$. In particular, we obtain $D_T \propto \epsilon^{\gamma}$ for the solid mixture, and $D_T \propto \epsilon^{(d-2)\gamma}$ for the liquid mixture, when we neglect the weak singularity of the viscosity. These results are identical to those obtained by a direct dynamic scaling analysis of the structure function (Sec. II D). The latter analysis also confirms the exponents quoted in Table I for $T \gtrsim T_c$.

(v) A kinetic Ising-model formulation which is appropriate to the computer simulations to which we compare our predictions is also presented, and various previous approximations are rederived: Cahn-Hilliard theory, Cook's theory, and the theory of Langer *et al.* Our simple unified derivation elucidates the shortcomings of the various approaches. While the nonlinear Cahn-Hilliard equation leads to a coarsening law which is consistent with the LS theory, the theory of Langer *et al.* does not: we argue that is leads to a $\bar{V}_l(t) \propto t^{d/4}$ behavior.

(vi) The present treatment is still incomplete in several respects: (a) While we tentatively put $k_m(t) \propto [\bar{V}_l(t)]^{-1/d}$ to relate the structure function $S(\vec{k}, t)$ crudely to the evolution of the cluster pattern, a detailed decomposition of $S(\vec{k}, t)$ into the contributions of the individual $\bar{n}_l(t)$ remains to be given. Also, Eq. (3.1) must be solved numerically if one wants to study the initial stages of the relaxation within the cluster dynamics description. During these initial stages small clusters dominate and hence Eqs. (3.6) and (3.16) are not valid. (b) The elastic interaction due to a "lattice misfit" of the two constituents of the (solid) mixture is disregarded throughout, as done in most of the literature.[13-18,22-25] An inclusion of elastic interaction has been performed within the framework of linearized Cahn-Hilliard theory only.[12] Since the latter has convincingly be demonstrated to be incorrect in the case without elastic interactions,[22-25,14] there is no reason to assume that it becomes correct when elastic distortions are added. Therefore experiments on systems with very small lattice misfit are desirable. (c) It is assumed that the atomic exchange processes can be described by Markovian master equations, neglecting any "memory effects." More microscopic studies of the atomic hopping processes revealed a non-Markovian behavior, however, at least for the diffusion of hydrogen in metals.[63] It is unclear how this will affect the behavior of the cluster diffusivity D_l, which is estimated on the basis of random-walk considerations in the Appendix.

In conclusion, we nevertheless feel that the present approach, which unifies previous theoretical treatments and yields many detailed predictions which have been verified by computer simulations, is versatile enough to be generalized to these more complicated situations as well. In any case it would be invaluable if detailed measurements would be performed on alloys with small lattice misfit: there the equation of state, diffusivity, structure function, grain size distribution and electrical resistivity should be obtained at the *same sample.* It is to be expected that such a comparative study could improve our understanding of the phase separation kinetics considerably.

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APPENDIX: DERIVATION OF CLUSTER DIFFUSION CONSTANTS IN SOLID MIXTURES

Here we are concerned with the derivation of the cluster diffusivity D_l, assuming that the basic atomic processes are interchanges of A and B atoms. We consider a rather isolated B cluster in the A matrix [Fig. 3(A)], and estimate the number of B atoms N_{ev} which evaporate per unit time

$$N_{\mathrm{ev}} = \nu \sum_i \exp\left(-\frac{2J}{k_B T}\Delta z_i\right), \tag{A1}$$

where ν is an "attempt frequency" for the exchange (in the computer simulations[15,23-26] $\nu = 1/q$ Monte Carlo steps/atom, q being the coordination number of the lattice), the sum extends over surface sites of the lattice, $2J$ is the binding energy associated with a $B-B$ bond and Δz_i the number of "broken bonds" which would be produced by the exchange. For very large clusters and $T \to 0$, Eq. (A1) may be replaced by

$$N_{\mathrm{ev}} = \nu \exp[-(2J/k_B T)\langle\Delta z\rangle](dV_l)^{1-1/d} U_d^{1/d}, \tag{A2}$$

where $\langle\Delta z\rangle$ is an effective average of Δz_i over the cluster surface. Next we prove that nearly all evaporated B atoms reimpinge at the cluster again, and calculate the shift in the center of gravity of the cluster produced by this process. Since the probability of reimpingement on an irregular surface is hard to calculate, we only consider a flat infinite surface; both probabilities should have the same order of magnitude. We introduce the probability $p_n(\rho)$ that an evaporated B atom, whose first step leads from the first layer adjacent to the surface to the second one, is after n steps in the ρth layer without reimpinging again (i.e., without moving into the layer $\rho = 1$). If interactions of the B atoms with other clusters are neglected, one has the rigorous recursion relation (for square or simple cubic lattices)

$$\begin{aligned} p_n(\rho) = (1/q)[p_{n-1}(\rho-1) + p_{n-1}(\rho+1) \\ + (q-2)p_{n-1}(\rho)], \quad n \geqslant 2, \end{aligned} \tag{A3}$$

with the initial condition $p_1 + (2) = 1$, $p_1(\rho = 2) = 0$, and the boundary condition describing impinging: $p_n(1) = 0$, all $n \geqslant 2$. The probability that the particle walks n steps without impinging is obviously

$$P(n) = \sum_{\rho=2}^{n} p_n(\rho). \tag{A4}$$

In the limit $\rho \to \infty$, $n \to \infty$, Eq. (A3) is equivalent to a diffusion equation

$$\frac{\partial p_n(\rho)}{\partial n} = \frac{1}{q}\frac{\partial^2 p_n(\rho)}{\partial \rho^2}, \tag{A5}$$

and a solution of Eq. (A5) which satisfies the initial condition $p_1(\rho) = \delta(\rho - 2)$ and the boundary condition $p_n(1) = 0$ is

$$\begin{aligned} p_n(\rho) = \Bigg[\exp\left(\frac{-(\rho-2)^2}{4q(n-1)}\right) \\ - \exp\left(\frac{-\rho^2}{4q(n-1)}\right) \Bigg] \Big/ 2[\pi q(n-1)]^{1/2}. \end{aligned} \tag{A6}$$

and hence one obtains

$$P(n) \propto n^{-1/2}, \quad n \to \infty, \tag{A7}$$

replacing the sum in Eq. (A4) by an integral, and putting the upper limit of integration equal to infinity, since the main contribution comes from the vicinity of $\rho = [4q(n-1)]^{1/2}$. Equation (A7) shows that nearly all atoms which evaporate from a lange cluster (with linear dimension $V_l^{1/d} \gg 1$) will reimpinge: in order that they get away a distance of order $V_l^{1/d}$ from the cluster, a number $n \propto V_l^{2/d}$ of steps would be necessary, which occurs with very small probability only: $p(V_l^{2/d}) \propto V_l^{-1/d} \ll 1$. The net effect of nearly all evaporation and condensation events is thus a shift of the center of gravity $\vec{x}$ of the cluster. We define $\vec{x}$ by (m_A, m_B are the masses of A and B atoms)

$$\vec{x}=\sum_i (m_B-m_A)\vec{x}_i\Big/\sum_i (m_B-m_A)=\frac{1}{l}\sum_i \vec{x}_i, \qquad (A8)$$

where the sums are extended over all lattice sites $\vec{x}_1$ of B atoms within the cluster. If due to evaporation of one atom and its reimpingement one $\vec{x}_i$ changes to $\vec{x}_i'=\vec{x}_i+\Delta\vec{x}_i$, the center of gravity changes by an amount of $\Delta\vec{x}=\Delta\vec{x}_i/l$. Adding up these random displacements $\Delta\vec{x}$ will yield us the cluster diffusivity D_l. In order to do this we have to estimate the average displacement $\langle(\Delta\vec{x}_i)^2\rangle$ per exchange. For that purpose we introduce the probability $p_n(\rho, x_{\parallel})$, that an evaporated atom is after n steps in the ρth layer and in the distance $x_{\parallel}$ parallel to the surface, without hitting the surface on its random walk. Clearly we have

$$p_n(\rho)=\sum_{x_{\parallel}} p_n(\rho, x_{\parallel}). \qquad (A9)$$

The desired quantity $\langle(\Delta\vec{x}_i)^2\rangle$ is then given by

$$\langle(\Delta\vec{x}_i)^2\rangle=\frac{1}{q}\sum_{x_{\parallel}}\sum_{n}\frac{p_n(2,x_{\parallel})x_{\parallel}^2}{n}, \qquad (A10)$$

since the atoms in layer $\rho=2$ at $x_{\parallel}$ hit the surface (the point $\rho=1$, $x_{\parallel}$ is adjacent to the surface) with probability $1/q$. From random walk theory it follows that $p_n(2,x_{\parallel})$ is strongly peaked at $x_{\parallel}=\text{const}\times\sqrt{n}$ for large n, i.e.,

$$\sum_{x_{\parallel}} p_n(2,x_{\parallel})x_{\parallel}^2=\text{const}\times n\sum_{x_{\parallel}} p_n(2,x_{\parallel})$$

$$=\text{const}\times np_n(2).$$

Hence the large n give a contribution of order $n^{-1/2}$ in Eq. (A10), since $p_n(2)\propto n^{-3/2}$ [cf. Eq. (A6)]. Since the main contribution to $\langle(\Delta\vec{x}_i)^2\rangle$ comes from small n, one would have to evaluate Eq. (A10) numerically.

From random-walk theory we then conclude, combining Eqs. (A2), (A10) and using $V_l=l$,

$$\begin{aligned}D_l&=N_{\text{ev}}\langle\Delta\vec{x}^2\rangle\\&=\frac{\langle\Delta\vec{x}_i{}^2\rangle}{l^2N_{\text{ev}}}\\&=\langle\Delta\vec{x}_i{}^2\rangle\nu\exp\left(-\frac{2J}{k_BT}\langle\Delta z\rangle\right)\\&\quad\times U_d^{1/d}d^{1-1/d}l^{-1-1/d}.\end{aligned}\qquad (A11)$$

Owing to Eq. (A2) this result is valid for spherical clusters. But clearly the effect of other shapes will be to change the prefactor $\langle\Delta\vec{x}_i^2\rangle/d^{1-1/d}$ only, as long as the cluster is compact. In addition, for rather small clusters the l dependence of D_l may be different, since the surface of a small cluster is proportional[60] to $l^{\sigma'}$ with $\sigma'>1-1/d$. Then cluster shapes are rather asymmetric, and consequently a rather "asymmetric" cluster diffusion may result, and D_l is no longer simply related to the cluster surface.[64] The available computer simulation data on D_l which are taken in this range are consistent with Eq. (A11), however. Data for larger l have been obtained with a different simulation method[58] and suggest $D_l\propto l^{-1}$ instead of Eq. (A11). This result is interpreted[58] by the fact that A atoms, which exist within a B cluster with concentration $\frac{1}{2}(1-\langle\mu\rangle)$, may be interchanged without cost of activation energy. This interchange leads to a shift of the center of gravity of the cluster as above. One thus has

$$D_l=\nu V_l\frac{1-\langle\mu\rangle}{2}\langle\Delta\vec{x}^2\rangle=\nu\frac{1-\langle\mu\rangle}{2}l^{-1}, \qquad (A12)$$

noting that in this case $\Delta\vec{x}_i^2=1$. Since for $T\rightarrow 0$ we have $\langle\mu\rangle\cong 1-2l^{-q2J/k_BT}$, the prefactor in Eq. (A12) is much smaller than that of Eq. (A11), since $\langle\Delta z\rangle<q$. In the vicinity of T_c one has to use[27,28] $V_l=\hat{V}l^{1+1/\delta}$ and hence[22]

$$D_l=\tfrac{1}{2}\nu\hat{V}e^{-2qJ/k_BT_c}l^{-(1-1/\delta)} \qquad (A13)$$

from Eq. (A12). In general, we expect D_l to be the sum of the two contributions from atomic exchanges at the cluster surfaces, Eq. (A11), and in the cluster interiors, Eqs. (A12) and (A13).

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[48] Usually this expression is given in terms of the field h conjugate to the order parameter (see I). Equation (3.29) is found using $\langle\mu\rangle \propto \epsilon^{-\gamma} h$ and the scaling law (Ref. 34) $\gamma = \beta(\delta - 1)$.

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