Self-organization of growing and decaying particles

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Because of thermocapillary flow or other mechanisms, particles move in temperature and concentration gradients. In a system undergoing a first-order phase transition via nucleation and growth, such gradients are caused by particles themselves. This leads to a long-range interaction in which particles will attract or repel, depending on their growth rates. For the case of attraction, particles organize into clusters, while repelling particles form more uniform particle distributions where fluctuations are leveled out. The implications of this effect for materials processing are discussed. [S1063-651X(97)06906-7]

I. INTRODUCTION

When a phase transition occurs by nucleation and growth, it is typically assumed that growing second-phase particles are uncorrelated in their spatial positions. This picture differs from that of spinodal decomposition [1], which leads to a rapid formation of second-phase clusters. It is shown below that, contrary to the standard assumption, correlations can occur in a system of nucleated particles, leading either to a formation of many-particle clusters or to a more uniform spatial distribution of particles.

Two statements underlie our argument: (i) each particle causes a temperature and/or solute concentration field whose absolute value decreases as $1/r$ with the distance r from the particle, and whose sign depends on whether the particle grows or decays, and (ii) particle motion is affected by these field gradients.

Before discussing the above statements let us point out how they lead to long-range correlations of particle positions. Suppose, first, a particle moves up the field gradient and the particle's field is positive (say, a growing crystallite in a liquid moves up in the temperature gradient and causes a positive temperature field about itself). As a result, the particle increases the field in a region where it is already relatively high. This positive feedback and corresponding instability also takes place when the particle moves down a gradient, provided its field is negative. Such an instability will result in particle clustering. If, on the other hand, a particle moves up (down) the gradient and its field is negative (positive), then the feedback will be negative and nonuniformities will level out in a system undergoing a phase transition.

Another way to arrive at the same conclusions is to note that since a particle moves in the gradient of the field caused by its neighbor, there is an effective interaction between the two, either attractive or repulsive, depending on the particle's field sign and the direction it moves in the gradient. In the case of an attractive interaction the particles will form clusters, while they will array uniformly in the case of repulsion.

Because of the long-range, $1/r$, character of a particle field, many particles will be involved in such interactions. Furthermore, supposing the interaction is linear in the gradient (at small gradients), the effective force between two particles will be proportional to $1/r^2$, much as in electrostatics. This brings in many features typical of electrostatics, including the concepts of instabilities and many-particle effects. In particular, one can anticipate screening of particle fields, analogous to Debye screening, and its possible breakdown when the fields are strong enough.

The conclusion of particle clustering has much in common with that of the theory of spinodal decomposition [1]. Note in this connection that in both cases there are attractive forces that provoke clustering. The difference is that for the case of spinodal decomposition there is an attraction between the molecules forming a new phase, while for the case under consideration here the attractive force acts not between individual molecules but between the nuclei of the new phase. Another important difference is that the attraction is assumed to be of a short-range (atomic) nature for the case of spinodal decomposition, as opposed to the long-range, Coulomb-like attraction for the case under consideration.

Our paper is organized as follows. In Sec. II we consider the fields of individual particles and their screening. In Sec. III possible mechanisms of particle motion in temperature and concentration gradients are discussed. Section IV introduces a qualitative approach to understanding particle self-organization, while a more quantitative approach based on linear stability analysis is developed in Sec. V. Discussion of the results and some concluding remarks are given in Sec. VI.

II. PARTICLE FIELDS

We turn now to a discussion of statement (i) above, that a nonequilibrium particle causes a $1/r$ change in temperature T (concentration c). Its explicit form can be obtained by solving the thermal conductivity (diffusion) equation in the quasistationary approximation [2]. For the case of temperature one finds

$$T - T_\infty = (T_a - T_\infty)\frac{a}{r}, \tag{1}$$

where a is the particle radius, T_∞ is the temperature far from

the particle, and T_a is the temperature at the particle interface. For the case of concentration, δc can be obtained from Eq. (1) by replacing

$$T \rightarrow c, \quad T_\infty \rightarrow c_\infty, \quad \text{and} \quad T_a \rightarrow c_a. \tag{2}$$

Two related questions will be discussed in connection with Eq. (1). First, the problem under consideration implies an external (with respect to the particle) temperature gradient which will modify Eq. (1). Second, in dealing with many particles one should note that the growth rate of any one of them is affected by the fields of its neighbors. Because the field generated by that particle is due to its growth, this field will be affected by the neighbors as well.

To account for an external gradient we follow the standard approach [3] based on the quasistationary thermal conductivity (diffusion) equation $\nabla^2 T = 0$ for the case of axial symmetry, with the gradient $\mathbf{A}$ fixed far from the particle. We write the solutions $T_<$ and $T_>$ inside ($r < a$) and outside ($r > a$) the particle subject to the boundary conditions

$$T_< = T_>, \quad \kappa_< \frac{\partial T_<}{\partial r} - \kappa_> \frac{\partial T_>}{\partial r} = h_s \quad \text{at} \quad r = a, \tag{3}$$

where $\kappa_<$ and $\kappa_>$ are the thermal conductivities of the two phases and h_s is the heat liberated (absorbed) per second per unit area of the interface due to the phase transformation. For simplicity we adopt in what follows $\kappa_< = \kappa_> = \kappa$. Also we note that h_s is related to the growth rate by

$$h_s = q\rho \frac{da}{dt}, \tag{4}$$

where q is the latent heat, and ρ is the material density. Because of the axial symmetry we set

$$T_< = \overline{T_a} + T_1 \mathbf{A} \cdot \mathbf{r}/(Aa),$$

$$T_> - T_\infty = \mathbf{A} \cdot \mathbf{r} \left(1 + B\frac{a^3}{r^3} \right) + (\overline{T_a} - T_\infty)\frac{a}{r}, \tag{5}$$

where $\mathbf{r}$ is the radius vector and $\overline{T_a}$, T_1, and B are three parameters to be determined from the boundary conditions in Eq. (3). Although the above equations are sufficient to determine the temperature field at all points, it is desirable to obtain the results in a form that accounts for the difference between bulk-diffusion-limited and interface-limited growth kinetics. This is achieved by introducing the linear kinetic coefficient [4–6] K, determining the particle growth rate,

$$\frac{da}{dt} = K(T_{a0} - T_a). \tag{6}$$

Equation (6) expresses the fact that the particle radius changes because its interface temperature T_a differs from the equilibrium temperature T_{a0}. In accordance with Eq. (5) the interface temperature is

$$T_a = \overline{T_a} + T_1 \mathbf{A} \cdot \mathbf{r}/(Aa) \quad \text{for} \quad |\mathbf{r}| = a. \tag{7}$$

Substituting Eqs. (7), (6), (5), and (4) into Eq. (3) gives

$$\overline{T_a} - T_\infty = \frac{(T_{a0} - T_\infty)Q}{1 + Q},$$

$$T_1 = \frac{3aA}{3 + Q}, \quad B = -\frac{Q}{3 + Q}, \tag{8}$$

where we have introduced the dimensionless parameter

$$Q \equiv K\frac{aq\rho}{\kappa}. \tag{9}$$

The parameter Q determines the efficiency of an external gradient. In particular, it follows from Eq. (8) that the temperature drop $2T_1$ across the particle poles decreases by the factor

$$e_1 = \frac{3}{3 + Q}, \tag{10}$$

while the average temperature at the interface decreases by the factor

$$e_0 = \frac{Q}{1 + Q} \tag{11}$$

as compared to the case of a stable particle. The limiting case $Q \ll 1$ corresponds to interface-limited kinetics where very slow exchange between the two phases makes it possible to establish a considerable temperature gradient across the particle ($e_1 \approx 1$), while the average temperature drop at the interface is relatively small ($e_0 \ll 1$). The opposite case $Q \gg 1$ refers to bulk-diffusion-limited kinetics in which the exchange between the phases is very fast. In that case, the temperature difference across the particle poles would affect the local growth rates at the poles and thus level out the difference. This negative feedback makes the temperature gradient in the particle lower by the factor $e_1 \ll 1$ than that of a stable particle. On the other hand, the average temperature drop across the interface is close to its maximum value $e_0 \approx 1$.

Following the recipe in Eq. (2) one can modify the results in Eqs. (8) to describe the case of a concentration gradient. The parameter Q will then change to

$$Q = \frac{Ka}{D_c}, \tag{12}$$

with D_c being the solute diffusion coefficient.

We now turn to the issue of screening in a system of many growing or decaying particles. For the sake of definiteness we again concentrate on the case of a temperature field. Screening can be then understood as resulting from the fact that the temperature near a growing particle is increased by the temperature fields of remote growing particles, so its growth will slow down and thus the temperature field caused by that particle will be decreased. The corresponding screening length can be derived from the quasistationary thermal conductivity equation

$$\chi \nabla^2 T - nI = 0, \tag{13}$$

where χ is the thermal diffusivity, n is the concentration of particles, and I is the temperature flux per center. Based on Eqs. (5) and (8), we write

$$I = -\kappa(\partial T/\partial r)4\pi r^2 = 4\pi\chi a \frac{Q}{1+Q}(T_{a0}-T_\infty). \quad (14)$$

To derive the screening length we consider smooth long-range fluctuations of temperature and particle concentration. In accordance with its physical meaning, T_∞, the temperature far from a particle, will be different in different fluctuations. Hence we identify the temperature T_∞ with a local temperature T averaged over a region (fluctuation) containing many particles and varying smoothly between such regions. To describe the fluctuations explicitly we set

$$\delta n = n - \bar{n} \quad \text{and} \quad \delta T = T - \bar{T},$$

where $\bar{T}$ and $\bar{n}$ are, respectively, the average temperature and particle concentration in the system. In the linear approximation we find

$$\chi\nabla^2\delta T - 4\pi\bar{n}\chi a \frac{Q}{1+Q}\delta T = \delta n\,\bar{I}, \quad (15)$$

where the average flux

$$\bar{I} = 4\pi\chi a \frac{Q}{1+Q}(T_{a0}-\bar{T})$$

is positive or negative for the cases of growing or decaying particles, respectively. From its solution

$$\delta T = -\frac{\bar{I}}{4\pi\chi}\int \delta n(\mathbf{r}')\frac{\exp\{-|\mathbf{r}-\mathbf{r}'|/r_s\}}{|\mathbf{r}-\mathbf{r}'|}d^3r' \quad (16)$$

we see that the temperature field screening length is

$$r_s = \sqrt{\frac{1+Q}{4\pi Q\bar{n}a}}. \quad (17)$$

Along the same lines one can consider screening of concentration fields. The result is again given by Eq. (17) with Q from Eq. (12). Note also that the above screening has much in common with the standard Debye screening in electrostatics and the formulas for screening lengths look alike. This reflects the analogy between the quasistationary diffusion and electrostatic problems, both reduced to the Laplace equation.

III. PARTICLE MOBILITY

The second of the two basic statements in Sec. I, that a particle moves in a nonuniform environment, makes sense simply because the opposite seems to be unnatural. Phenomenologically, the particle velocity

$$\mathbf{V} = \xi_f D_a \nabla f \quad (18)$$

is proportional to the field gradient ∇f and the particle diffusion coefficient D_a, with the proportionality coefficient ξ_f determined by the particular mechanism of interaction. A number of different mechanisms can be suggested. Some of them are described below in this section.

For the case of a temperature gradient such a mechanism may be thermocapillary migration [7], known since the pioneering work of Young et al. [8]. Its nature is as follows. A local increase in temperature results in a local decrease in surface free energy σ that is accompanied by a nonuniform tangential stress at the surface. In response to this stress a flow occurs from the warmer to the cooler pole of the particle. Therefore the particle will move in the direction of its warmer pole. For the case of small Reynolds number the thermocapillary migration velocity is

$$\mathbf{V} = \frac{2\sigma_T a}{\nu(2+3\alpha)(2+\beta)}\nabla T \equiv D_a\xi_T\nabla T, \quad (19)$$

where $\sigma_T = \partial\sigma/\partial T$, α is the ratio of viscosity of the particle phase to that of the continuum phase, β is a similar ratio of thermal conductivities, and ν is the dynamic viscosity. Taking into account the Stokes-Einstein relationship $D_a = T/(6\pi\nu a)$ and using the order-of-magnitude estimate $|\sigma_T|\sim\sigma/T$, one finds

$$\xi_T \sim \sigma a^2/T^2 \gg T^{-1}. \quad (20)$$

It is natural to consider a similar effect due to the concentration gradient ∇c rather than ∇T above. Reasoning along the same lines, we consider a particle in a concentration gradient and assume the surface tension to decrease as the solute concentration increases. Since a local increase in solute concentration is accompanied by a local decrease in surface energy, a nonuniform tangential stress will appear that entails a flow to the low-concentration pole of the particle. Hence the particle will move up the concentration gradient. For the case when viscosities of the two phases are comparable, $\alpha\sim 1$, its velocity has an order-of-magnitude estimate

$$\mathbf{V} = D_a\xi_c\nabla c \sim \frac{\sigma_c a}{\nu}\nabla c, \quad \sigma_c = \frac{\partial\sigma}{\partial c}. \quad (21)$$

The above assumption that σ_c is positive does not hold true in general. This derivative is related to the surface excess,

$$\Gamma \equiv -\left(\frac{\partial\sigma}{\partial\mu}\right)_T = -\sigma_c\left(\frac{\partial c}{\partial\mu}\right)_T,$$

that can be either positive or negative, depending on solute chemistry [9], where μ is the chemical potential. An estimate to serve as a rough guide of $|\xi_c|$ for this mechanism can be obtained from the Gibbs equation

$$\frac{d\sigma}{dc} = -\frac{\Gamma R_0 T}{c},$$

where R_0 is the gas constant. We note that typically $|\Gamma|\sim(1-10)\times 10^{-10}$ mol/cm^2, so that the product $|\Gamma|R_0T$ is of the order of a typical surface energy σ which varies from 10 to 100 dyn/cm between different systems. Therefore one can roughly estimate $|\sigma_c|\sim\sigma/c$, in qualitative agreement with the data [9–11]. Using the latter estimate together with the Stokes-Einstein relationship gives

$$\xi_c \sim \frac{\sigma a^2}{cT} \gg 1. \qquad (22)$$

Note that if barodiffusion is taken into account it can dramatically increase the concentration-capillary effect and thus the parameter ξ_c [12].

The above consideration of capillary migration implies the particles to be stable. If on the other hand the particles grow or shrink (as we plan in what follows) the efficiency of capillary migration will decrease, because this affects the local growth rates at the poles and thus levels out the difference. As was discussed in Sec. II, the gradient of the order parameter (temperature or concentration) decreases by the factor $e_1 = 3/(3+Q)$ as compared to the case of stable particles, $Q=0$ [see Eq. (10)]. Since this factor also appears in the equations for the capillary migration velocity, we conclude that the case of bulk-diffusion-limited kinetics ($Q \gg 1$) is unfavorable for capillary migration. On the other hand, capillary flow survives slow interface kinetics ($Q \ll 1$).

It is worth noting here that, while being favorable for capillary flow, small $Q \ll 1$ leads to correspondingly weak fields caused by individual particles, as is seen from Eq. (11). In other words, at $Q \ll 1$ particles act as ineffective sources and effective receivers of the field. Interparticle interactions depend on both these competing factors, which balance each other. This can be qualitatively understood from the fact that in the region of linear dimension r_s [with r_s from Eq. (17)] the characteristic field is proportional to the number of particles nr_s^3, their effective charges e_0, and inversely proportional to r_s. Since $e_0 r_s^2$ does not depend on Q, the characteristic fluctuation field affecting an individual particle remains finite at $Q \ll 1$. This reasoning implies, however, that the fluctuation has time to evolve over the distance r_s; the latter time becomes infinitely long as $Q \to 0$ (see Secs. IV and V below). Meanwhile, our consideration is not restricted to the case of small $Q \ll 1$.

In a recent paper [13] another mechanism of thermomigration in a multiphase system subjected to an imposed temperature gradient was suggested. This is associated with asymmetric thermodynamic properties of the underlying coexisting phases. Due to the phase asymmetry, thermodynamic forces occur at the surface of the droplet, since one phase tends to be on the colder side and the other phase on the hotter side. Such forces will not be present in the symmetric phase situation. Droplets of different phases migrate in opposite directions because this leads to a decrease in the free energy of the system. As opposed to thermocapillary migration, the latter is due to the bulk (not interface) characteristics of the phases. Although no analytical results on the migration velocity have been presented, the computer modeling in Ref. [13] shows that the velocity is linear in temperature gradient and may win out over that of the standard thermocapillary model and have a different sign. Based on that, we conclude that the phenomenological equation (18) is applicable to the situation where the latter mechanism dominates and that the parameter ξ_T above may have the opposite sign and larger absolute value than in the case of thermocapillarity.

Similar concepts of thermodynamic force related to a decrease in free energy due to particle motion were put forward

in Ref. [14] for the case of growing and decaying particles in a nonuniform solute. The result, that the force on a particle is proportional to its growth rate and local solute concentration gradient, agrees with the phenomenological description in Eq. (18). Based on the estimate in Ref. [14] we get

$$\xi_c \sim \frac{a^3}{a_0^3} \frac{c - c_a}{c} \gg 1,$$

where a_0 is the characteristic molecular dimension. However, since the approach in Ref. [14] is restricted to a purely diffusive model and does not account for possible hydrodynamic effects, the absolute value and even sign of the thermodynamic force may be different.

We mention also one more specific mechanism of mobility suggested for a living cell in a concentration gradient [15] and based on hydrodynamic effects caused by ionic currents flowing through the cell.

We end this section by presenting some general hydrodynamic arguments showing the existence of a force on a growing or decaying particle in a nonuniform environment. To eliminate all the effects that are not due to the gradient and growth we assume that for a hypothetical case of a stable particle all the forces are balanced and there are no currents in the system. Because of particle growth currents will appear both normal and tangential to its surface. Correspondingly, the force on the particle will consist of two contributions. The first one, normal to the interface, is due to direct momentum transfer associated with particle growth. The second, tangential contribution results from the viscous friction on the particle surface exerted by the fluid flow. For definiteness we consider the case of a temperaure gradient.

The first contribution, F_n, can be understood by using a local reference frame pinned at some point of the growing particle surface. Since the surface is at rest at this frame, the force per unit area on it is the momentum transferred per unit area per second. The latter is associated with the motion of surrounding fluid feeding the particle. The corresponding velocity near the interface is da/dt in the reference frame chosen. The force on a hemisphere is then $F_n \sim \delta\rho(da/dt)^2 a^2$, where $\delta\rho$ is the difference between the material densities of the two phases. Because of the gradient, the temperature difference across the particle changes by $\delta T_c \sim a\nabla T$. Hence the forces on the opposite hemispheres do not completely balance each other. With Eq. (6) taken into account the net force on the particle will be

$$F_n \sim \delta\rho \frac{da}{dt} a^3 K\nabla T.$$

The second contribution, F_τ, can be estimated by noting that the surrounding fluid velocity da/dt changes across the particle by $\delta v \sim Ka\nabla T$ and that a is the only space scale in the problem. From that we find

$$F_\tau \sim \eta Ka^2\nabla T.$$

If we express the linear kinetic coefficient K through the parameter Q [see Eqs. (9) and (12) above] and note that both the cases of interface-limited ($Q \ll 1$) and bulk-diffusion-limited ($Q \gg 1$) growth are realistic, we see that, depending on the parameters of the system (say, the sign of $\delta\rho$), both

the cases of particle migration up and down the gradient are possible. The corresponding dimensionless parameter $T\xi_T$ in Eq. (18) can be either larger or smaller than unity in absolute value.

It follows from the above analysis that many different mechanisms can contribute to an unstable particle migration in a nonuniform medium. Which of them dominates depends on the parameters of the system. Both cases of downhill and uphill migration are possible, and the dimensionless parameter $f\xi_f$ determining the absolute value of the particle velocity can be much larger than unity.

IV. PARTICLE SELF-ORGANIZATION

In this section we discuss particle self-organization on a qualitative level. We begin here with pairwise interparticle interactions that are assumed to cut off at the screening length. For the case of two identical particles, characterized by the parameters a, T_a, and ξ_T, based on Eqs. (1) and (19) and taking into account the particle mobility D_n/T, one can write a quasi-Coulomb interparticle force

$$\mathbf{F(r)} = -\frac{\mathbf{r}}{r^3} a\xi_T T(T_a - T_\infty).$$ (23)

For the case of the standard thermocapillary mechanism, $\xi_T > 0$, two growing particles attract, while two decaying particles repel. However, if other mechanisms dominate there may be $\xi_T < 0$, so that the situation reverses.

As described in Sec. I, for the case of attracting particles we expect clustering to develop, such that each cluster contains many particles. We estimate the characteristic minimum cluster dimension r_c by equating the diffusion current

$$J_D \sim D_n \frac{\delta n}{r_c}$$

out of the region and the inward drift current

$$J_F \sim \frac{D_n}{T} F(r_c)(\delta n r_c^3)\bar{n}$$

caused by $\delta n r_c^3$ excess particles, each of them producing the force $F(r_c)$ given in Eq. (23). Here D_n/T is the nucleus mobility. From that we find

$$r_c \sim \sqrt{\frac{1}{4\pi\bar{n}\xi_T a(T_a - \bar{T})}},$$ (24)

where we have replaced the temperature T_∞, smoothly varying in space, by the average temperature $\bar{T}$. We recall that, in accordance with the considerations in Sec. II, the interface temperature is determined by the type of growth kinetics via the parameter Q. With Eq. (8) taken into account we express

$$r_c \sim \sqrt{\frac{1+Q}{4\pi Q\bar{n}\xi_T a(T_{a0} - \bar{T})}}.$$ (25)

Note that above we have neglected the effects of screening that oppose clustering. The screening length r_s must be

larger than r_c in order that clustering not be suppressed. Equating r_s from Eq. (17) and r_c from Eq. (25) introduces the critical undercooling

$$T_{a0} - T = \frac{1}{\xi_T},$$ (26)

such that at $T_{a0} - T > \xi_T^{-1}$ the clustering wins out over the screening, while in the opposite case the clustering is suppressed. As long as the dimensionless product $\xi_T T \gg 1$ (in accordance with estimates in Sec. III) the critical undercooling is relatively small, $T_{a0} - T \ll T$. That screening cannot prevent clustering at large undercooling can be interpreted as a breakdown of the electrostatic analogy mentioned above. We shall see in Sec. V below that the crossover between the two regimes at the critical undercooling occurs as a critical phenomenon.

One other point to note is that the critical undercooling does not depend on the kinetic parameter Q for the case of small $Q \ll 1$. Physically this means that a small thermocapillary effect corresponding to $Q \ll 1$ is compensated by a large number of particles involved in the region of linear dimension r_s that increases as Q decreases, as discussed after Eq. (22) above. The parameter Q will, however, determine the characteristic time scale r_c^2/D_n over which particle self-organization evolves. In the limiting case of $Q \rightarrow 0$ this characteristic time becomes infinitely long, making fluctuations unobservable. In the alternative limiting case of large $Q \gg 1$ the interaction parameter ξ_T becomes small since it is proportional to the factor e_1 [Eq. (10)] as discussed in Sec. III. This may cause the critical undercooling in Eq. (26) to increase beyond the region where the phase transformation occurs by nucleation and growth. The alternative region of spinodal decomposition is not described by the present theory.

It follows from the above derivation that the drift current J_F will increase as the radius r of the fluctuation increases. Therefore fluctuations of $r > r_c$ will increase spontaneously with characteristic times that are decreasing functions of r. This reasoning is, however, restricted to the assumption of established temperature fields ($\delta T \propto 1/r$) underlying the force in Eq. (23). This implies that the heat must diffuse fast enough. If we equate the characteristic time r^2/χ to establish thermal equilibrium in a region of linear dimension r and the characteristic time r/v_n of particle drift with velocity $v_n \sim J_F/\bar{n}$, then we get a new characteristic dimension

$$r_{max} \sim r_c \sqrt{\frac{\chi}{D_n}}.$$ (27)

Fluctuations of $r > r_{max}$ will not grow. From that we conclude that there exist fastest-growing modes of some linear dimension R such that $r_c < R < r_{max}$. In the approximation neglecting the growth of all modes except those of the fastest ones, the fluctuations will exhibit a set of clusters of characteristic dimension R. We again observe the similarity of the phenomena under consideration to spinodal decomposition.

V. LINEAR STABILITY ANALYSIS

To make the analysis of Sec. IV more quantitative we write the kinetic equations and employ linear stability analysis. We consider a system of a fixed number of particles, thus neglecting the possibility of their creation or annihilation, and suppose for simplicity that they all have the same radius a. For instance, such a system may serve as a model for the growth stage of second-phase nucleation, at which new nuclei are unlikely to appear while coarsening has not yet begun. With Eq. (18) taken into account the kinetic equation for the particle concentration becomes

$$\frac{\partial \delta n}{\partial t} = D_n \xi_T \overline{n} \nabla^2 \delta T + D_n \nabla^2 \delta n, \tag{28}$$

Eq. (28) is linearized in δn and δT. The temperature kinetics beyond the quasistationary approximation can be described by adding the corresponding time derivative to Eq. (15):

$$\frac{\partial \delta T}{\partial t} = \chi \nabla^2 \delta T - \delta n \, \overline{I} - 4\pi \overline{n} \chi \frac{Q}{1+Q} a \, \delta T. \tag{29}$$

Letting $\widetilde{T}(\mathbf{k}, \omega)$ and $\widetilde{n}(\mathbf{k}, \omega)$ be the Fourier transforms of the temperature $\delta T(\mathbf{r}, t)$ and nucleus concentration $\delta n(\mathbf{r}, t)$, respectively, corresponding to wave vector $\mathbf{k}$ and frequency ω, Eqs. (28) and (29) give

$$(-i\omega + D_n k^2)\widetilde{n} + \xi_T \overline{n} D_n k^2 \widetilde{T} = 0,$$

$$\overline{I}\widetilde{n} + \left(-i\omega + 4\pi \frac{Q}{1+Q}\overline{n}\chi a + \chi k^2\right)\widetilde{T} = 0.$$

The condition that these equations be compatible has the form of a dispersion equation

$$\omega(\mathbf{k}) = i\left(-\frac{A}{2} \pm \sqrt{\frac{A^2}{4} + B}\right) \equiv i\gamma, \tag{30}$$

where

$$A = k_0^2 \chi + k^2(D_n + \chi), \quad k_0 = \sqrt{4\pi \frac{Q}{1+Q}\overline{n}a},$$

$$B = D_n \chi k^2 \{k_0^2[(T_{a0} - \overline{T})\xi_T - 1] - k^2\}.$$

Note that the characteristic wave vector k_0 is exactly the reciprocal of the screening radius r_s in Eq. (17). The fluctuation is unstable provided that the frequency ω has a positive imaginary part, that is, $\gamma > 0$. The latter is achieved for the case of attracting particles, $T_a > \overline{T}$, provided that $B > 0$. On the other hand, for the case of repelling particles, the fluctuations decay since the inequality $T_a - \overline{T} < 0$ leads to $B < 0$ and the real part of γ is negative. These conclusions agree with those derived above on qualitative grounds.

For the case of attracting particles the fluctuations that are unstable possess wave numbers

$$k < k_c \equiv k_0 \sqrt{(T_{a0} - \overline{T})\xi_T - 1} \tag{31}$$

or (what is the same) space scales larger than $r_c = k_c^{-1}$. In the linear approximation their amplitudes increase exponentially with time,

$$\delta T(t), \quad \delta n(t) \propto \exp(\gamma t).$$

It follows from Eq. (30) that the amplification factor $\gamma(k)$ reaches its maximum

$$\gamma_m = k_c^2 D_n \quad \text{at} \quad k = k_m \approx k_0[\sqrt{\xi_T(T_{a0} - \overline{T})} - 1]. \tag{32}$$

Because $\gamma(k)$ has a maximum and it occurs in an exponential, it is convenient in the first approximation to ignore the growth of all modes but those near the fastest-growing ones. In this approximation we return to the prediction [after Eq. (27) above] of a set of clusters characterized by linear dimension $R_m = k_m^{-1}$ that falls in the interval $(r_c, r_{\max})$.

One other point is that, in accordance with Eq. (31), clustering will develop only if the critical undercooling given in Eq. (26) is exceeded, again in agreement with the qualitative analysis in Sec. IV above. Equation (31) predicts crossover between the regimes of screening and clustering to have the character of a critical phenomenon.

Generalization of the above results to the case of other mechanisms of particle mobility is straightforward. For the case of the concentration-capillary effect it is achieved by replacing $\xi_T \to \xi_c$, $\overline{T} \to \overline{c}$, $T_a \to c_a$, $\chi \to D_c$.

Note that the kinetic equations above neglect the time dependence $a(t)$. This implies the function $a(t)$ to be slow in the sense $|da/dt| \ll a\gamma_m$. For the case of the concentration-capillary effect this reduces to the inequality $na^3|\xi_c|cD_n/D_c \gg 1$ which seems to be realistic with the estimate $|\xi_c c| \sim \sigma a^2/T \gg 1$ taken into account. For the thermocapillary effect in dense gases the corresponding inequality $na^3|\xi_T|TD_n/\chi \gg 1$ may hold true as well, while it is unlikely for the case of condensed matter because of the inequality $D_n \ll \chi$. We emphasize in this connection that the restriction $a(t) = \text{const}$ and others imposed in the course of the above linear stability analysis have been chosen for the sake of simplicity only. From our qualitative reasoning, self-organization of particles will take place in any system undergoing a first-order phase transition.

VI. DISCUSSION OF THE RESULTS

We now estimate the characteristic cluster dimension r_c using typical material parameters corresponding to alloying materials [16]. We take $n \sim 10^{18}$ cm^{-3}, $a \sim 10$ Å, $\xi_c(c - c_{a0}) \sim 1$ [close to the critical supersaturation determining the crossover between the clustering and screening, cf. Eq. (26)]. Also, rather arbitrarily, we set $Q \sim 10^{-4}$ (values of Q less than 0.01 are realistic [7,17]). Then, from Eq. (25) we obtain $r_c \sim 3$ μm with $\sim 10^8$ particles per cluster. Since small Q corresponds to an interface barrier, it depends on temperature exponentially as does r_c.

It follows from the above estimate that second-phase concentration can fluctuate considerably on a long-range (mesoscopic) space scale. Although we do not see from the theoretical point of view how one can eliminate the fluctuations predicted, we have to admit that we are not aware of experi-

mental evidence in favor of such fluctuations. The only conclusion we can draw to reconcile this fact with our predictions is that the issue of mesoscopic correlations has not been adequately addressed in the experimental study of phase transformation kinetics. Average numbers of second-phase particles per volume depending on time, composition, and annealing schedules are typically measured; much less attention is paid to the question of their possible space correlation. We hope that the present work will stimulate new experimental activity in studying first-order phase transformations on mesoscopic scale.

Although there is no direct experimental evidence for the clustering predicted, two supporting pieces of evidence can be pointed out. First, a vigorous thermocapillary flow in a droplet undergoing evaporation was observed recently [18]. This shows that the phenomena of phase transformations and capillary flow are compatible, in agreement with the results of our analysis in Sec. II above. Second, Tanaka [19] observed an attraction between growing droplets in a binary fluid which he qualitatively attributed to a direct coupling of diffusion fields around droplets.

Associated with the fluctuations in second-phase concentration will be fluctuations in material parameters, such as rigidity, elasticity, reflectivity, and so forth. Since such fluctuations are important (and normally undesirable) from the technological standpoint [20], we also hope that the above findings may have implications for technology. As an example we note that adding a very slight amount of some impurity is known to suppress capillary flow by contaminating the particle interface and thus supporting tangential stress without steady-state flow. With that in mind, we suggest the possibility of improving multiphase material uniformity by means of properly chosen doping. Another possibility is to use a thermal treatment (say, a short-time anneal) that, while having no time to destroy second-phase particles, changes their interactions from attractive to repulsive and thus levels out the fluctuations.

In conclusion, we have shown that in a system undergoing a first-order phase transition, self-organization of nucleated particles can take place, leading either to formation of clusters or to a space-uniform distribution, depending on the thermal treatment schedule and material chemistry.

[1] J. W. Cahn, Trans. Metall. Soc. AIME **242**, 166 (1968).
[2] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, London, 1981).
[3] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, New York, 1987).
[4] P. G. Shewman, Trans. Metall. Soc. AIME **233**, 736 (1965).
[5] J. W. Cahn, in *Crystal Growth*, edited by H. S. Peiser, Suppl. J. Phys. Chem. Solids (Pergamon Press, Oxford, 1967), p. 681.
[6] R. L. Parker, in *Solid State Physics: Advances in Research and Applications*, edited by H. S. Peiser (Academic Press, New York, 1970), Vol. 26.
[7] R. Balasubramaniam, C. E. Lacy, G. Woniak, and R. S. Subramanian, Phys. Fluids **8**, 872 (1996).
[8] N. O. Young, J. S. Goldstein, and M. J. Block, J. Fluid. Mech. **6**, 350 (1959).
[9] A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1976).
[10] M. J. Rosen, *Surfactant and Interfacial Phenomena* (Wiley, New York, 1985).
[11] *Structure/Performance Relationships in Surfactants*, edited by M. J. Rosen, ACS Symposium Series Vol. 253 (American Chemical Society, Washington, DC, 1984).
[12] V. G. Karpov, A. Yu, and D. W. Oxtoby, Phys. Fluids (to be published).
[13] R. Bhagavatula and D. Jasnow, J. Chem. Phys. **105**, 337 (1996).
[14] V. G. Karpov, Phys. Rev. Lett. **74**, 3185 (1995); **75**, 2702 (1995).
[15] M. Leonetti, Europhys. Lett. **32**, 561 (1995).
[16] H. I. Aaronson and F. K. LeGoues, Metall. Trans. A **23**, 1915 (1992).
[17] J. Zhang, D. B. Williams, and J. I. Goldstein, Metall. Mater. Trans. A **25**, 1639 (1994).
[18] J. J. Hegseth, N. Rashidnia, and A. Chai, Phys. Rev. E **54**, 1640 (1996).
[19] H. Tanaka, J. Chem. Phys. **105**, 10 099 (1996).
[20] J. J. Lewandowski, C. Liu, and W. H. Hunt, Jr., Mater. Sci. Eng. A **107**, 241 (1989); D. L. Davidson, Composites **24**, 248 (1993); D. J. Lloid, Acta Metall. Mater. **39**, 59 (1991).