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Processes of microstructure coarsening at liquid phase sintering

L. Anestiev and L. Froyen
Fakulteit Toegepaste Wetenschappen, Departement MTM, Metaalkunde en Toegepaste Materiaalkunde de Croylaan 2, B-3001 Heverlee, Belgium

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A different approach to the theoretical description of the classical theory of Ostwald ripening at liquid phase sintering has been proposed. The model developed in the present approach is based on an equation describing the growth kinetics of the particles, which is different from those used until now. The model developed here accounts automatically for the influence of the initial volume fraction and predicts correctly: the time dependence of $\overline{\rho}$ at $t\to\infty - \overline{\rho}^3(t)-\overline{\rho}^3(0)=Kt$; the form of the distribution function after considerable coarsening time; the experimentally observed values for the relation $\rho_{\max}/\overline{\rho}$; and the phenomena of ''abnormal growth'' at liquid phase sintering.

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I. INTRODUCTION

Ostwald ripening, or coarsening, is a common phenomenon occurring during the last stage of the liquid phase sintering (LPS) [1–6,8–19] and at the microstructure formation of the new phase during bulk crystallization [1–6,8–14]. This process usually involves the flow of solute atoms from the small particles to the larger ones, although more generally the flow may be a flux of enthalpy, or solvent atoms at solid-liquid systems, or vacancies (void coarsening) [8,13]. The fundamental driving force for the interparticle diffusion is well understood and is caused by the chemical potential differences, due to the curvature of the particles surface.

The first major progress in the theoretical description of the coarsening behavior of a system of spherical particles dispersed in a solution with close chemical composition, was made by Lifshitz and Slyozov [1,2], and separately by Wagner [3], referred to as LSW theory. These authors were the first who formulated mathematically the fundamental equations governing the coarsening process:

$$\frac{d\rho}{dt}=\nu_\rho=2\,\frac{\Gamma D}{\rho}\left(\frac{1}{\rho^*}-\frac{1}{\rho}\right), \tag{1}$$

$$\frac{\partial f}{\partial t}=-\frac{\partial(f\nu_\rho)}{\partial\rho}, \tag{2}$$

and

$$Q_0=\Delta+\frac{4}{3}\pi\int_0^\infty f\rho^3 d\rho\,. \tag{3}$$

Here, ρ is the radius of the particles, ν_ρ is its growth velocity, ρ^* is the so-called critical radius [1–4], Γ is a constant equal to $\Gamma=\sigma V_m/RT$, σ is the surface tension, T is the temperature, V_m is the molar volume, R is the universal gas constant, D is the diffusion coefficient, $f=f(\rho,t)$ is the distribution function of the particles radii ρ into the ρ-dimension space, Δ is the current super-saturation, Q_0 is the initial super-saturation plus the initial volume fraction of the solid phase, and t is the time.

In the above system Eq. (1) describes the growth (or shrinkage) kinetics of an isolated particle [20]. Equations (2) and (3) describe respectively, the movement of the particles radii of the whole ensemble through the ρ-dimension space and the mass conservation law.

Although the LSW theory successfully predicted that asymptotically the mean particles radii $\overline{\rho}$ of the coarsening system should obey the dependence

$$\overline{\rho}^3(t)=\overline{\rho}^3(0)+Kt\,,$$

it failed to explain the following experimentally observed evidences:

1. The experimentally observed distribution functions $f=f(\rho,t)$ are much broader than the ones predicted by the LSW theory.
2. According to LSW, the relation between the particle, with the maximal radius $\rho_{\max}$ and the mean particles radius $\overline{\rho}$ is equal to $\rho_{\max}/\overline{\rho}\approx 1.5$; the experimentally observed values for $\rho_{\max}/\overline{\rho}$ vary between 1.7 and 2.1 [10,14].
3. In the case where the initial powder compact contains a small cluster of large particles, it has been noticed that during the coarsening process these particles grow preferably leading as a consequence to a dramatic shift in the particle size distribution. This phenomenon is in contradiction with the results of the LSW theory, and for this reason it was termed ''abnormal'' grain growth [14,19].

The disagreements listed above between the theory and the experiment prompted several authors to explain it from various points of view. A thorough discussion of these attempts and the models that arose can be found in [12,14,18,21–29]. A short discussion over the attempts in question is given in Appendix A.

Concluding this section, it should be noted that during the last decade several theoretical approaches have been attempted to improve the classical theory of LSW [12,14,18,21–29]. Beyond any doubt significant progress was achieved in the understanding of the coarsening kinetics since the publication of the classical works of Lifshitz, Slyozov, and Wagner. Nevertheless, there still exist problems which cannot be successfully explained by the existing theoretical models [10,14,15]. The aim of the present paper is to develop an equation describing the growth kinetics of the particles involved in the coarsening process, which consequently will be applied to study of the coarsening behavior of an ensemble of particles in general and at LPS in particular.

II. THEORETICAL APPROACH

A. Formulation of the problem

As mentioned in the Introduction the problem of Ostwald ripening includes two separate problems. The first one is the particle growth (decay), immersed in media with changing chemical composition (in our case, this is the melt). The second is the movement of the particle radii of the whole ensemble through the ρ-dimension space.

Two mechanisms of the growth (shrinkage) kinetics can be distinguished: diffusion and reaction controlled growth (shrinkage). By the first mechanism the slowest process is the diffusion and the rate of the ripening process is determined by the mass transfer inside the system. For the second mechanism the limiting process is the crystallization (dissolution) taking place at the particle surfaces. Therefore, one needs a criterion in order to distinguish which of the two mechanisms is operative in the ripening system at a given moment.

Let us consider a system of solid particles with a mean radius $\overline{\rho}$ dispersed into a melt. It can easily be shown that between whole volume V_0 of the system and the mean distance between the particles d, the following dependence is valid:

$$\frac{4}{3}\pi N\left(\overline{\rho}+\frac{d}{2}\right)^3=V_0 .$$

Here, N denotes the number of the particles in the system. Taking into account that the initial volume fraction of the solid phase is $p=4\pi N\overline{\rho}^3/3V_0$, for the mean distance d between the particles the following is obtained:

$$d=2\overline{\rho}\left(\frac{1}{p^{1/3}}-1\right) .$$

On the other hand, the distance at which the changes of the solute concentration are equalized after a time period Δt due to the diffusion is described by the expression $\delta\approx\sqrt{D\Delta t}$. Actually, Δt is not an independent parameter. It is connected with the growth (dissolution) velocity through the following expression $\Delta t=\Delta\overline{\rho}/\nu_\rho$. Here $\Delta\overline{\rho}$ is the change of the mean particle radius due to the growth (dissolution) process. Thus dividing d by δ and substituting Δt with its equal gives us the criterion that we are looking for,

$$\frac{d}{\delta}=2\overline{\rho}\sqrt{\frac{\nu_\rho}{D\Delta\rho}}\left(\frac{1}{p^{1/3}}-1\right) . \tag{4}$$

It is obvious that at $d/\delta\gg1$ the growth mechanism is diffusion controlled and at $d/\delta\ll1$, it is reaction controlled. Introducing some reasonable values for the involved parameters ($D=10^{-9}$ m^2/s, $\Delta\overline{\rho}/\nu_\rho=0.5$ s, and $\overline{\rho}=3\times10^{-5}$ m) it can be readily shown that below $p=0.3$ the coarsening mechanism is diffusion controlled and that above $p=0.7$ it is reaction controlled.

1. Diffusion controlled growth (dissolution)

The mathematical description of the diffusion problem for a spherical particle is given by the second Fick's equation, which in spherical coordinates reads

$$\frac{\partial C}{\partial t}=D\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r^2}\right) . \tag{5}$$

The initial and the boundary conditions are

$$t=0{:}C(r,t)=C_0(0),\ \rho=\rho_0 ,$$

$$r=\rho{:}C(r,t)=C(\rho,t)=C^L,\qquad -D\left.\frac{\partial C}{\partial r}\right|_{r=\rho}=\nu_\rho(C^L-C^S);$$

$$r\to\infty{:}C(r,t)=C_0(t) .$$

Here C^L and C^S are the solute concentration of the liquid and solid phase on the particle's interface, ρ_0 is the initial radius of the studied particle, r is the polar coordinate measured from the center of the particle and $C_0(t)$ is the solute concentration of the liquid phase at distances bigger than the particles dimensions, i.e., at $r\gg\rho$. Note that C^L, C^S, and ν_ρ are unknown and therefore additional equations are needed in order to account for these quantities.

In the present approach the solute redistribution at the particles interface is described with the aid of a recently developed theory of solute redistribution at crystal growth [30]:

$$\frac{\partial\Delta G^S}{\partial C^S}=\frac{\partial\Delta G^L}{\partial C^L}\left(1-\frac{\nu_\rho}{\nu_0}\right) , \tag{6}$$

$$\Delta G^L-\Delta G^S+RT\ln\left(1-\frac{\nu_\rho}{\nu_0}\right)+\frac{\partial\Delta G^L}{\partial C^L}(C^S-C^L)=\frac{2\sigma V_m}{\rho} . \tag{7}$$

Actually, ν_0 is not a constant, but a complex function of the temperature T and C^S: $\nu_0=\nu_0^T\exp[-(Q/RT)]\exp[-(\Delta G^S/RT)]$. Here ν_0^T is a constant which depends only on the microscale characteristics of the considered material, Q is the potential barrier, which also varies with the studied materials [31,32], and ΔG^S and ΔG^L are the Gibbs free energies of the solid and the liquid phases. A brief discussion of the assumptions, the way of deriving Eqs. (6) and (7) and the physical meaning of ν_0 are given in Appendix B.

Generally the free energy ΔG^S depends on T and C^S and so does also ν_0. Since in the present case the supersaturation $\Delta=C_e^L-C_0(t)$ is very small and the temperature T is constant, it can be assumed as a good approximation that $\nu_0=\text{const}$. Equations (5)–(7) thus determine explicitly the growth phenomena of a spherical particle at fixed T and C_0.

2. Reaction controlled growth (dissolution)

At the reaction controlled mechanism the limiting process is the crystallization (dissolution), taking place on the particles surfaces. Therefore, the ripening kinetics is determined only from Eqs. (6) and (7).

A second set of equations describes the dynamics of the whole ensemble of particles. The first equation is Eq. (2), which gives the change of the particles distribution function $f(\rho,t)$ over time,

$$\frac{\partial f}{\partial t}=-\frac{\partial(f\nu_\rho)}{\partial\rho}. \tag{8}$$

At $t=0$ the distribution function $f(\rho,t)$ and the particles radii ρ should obey the following conditions:

$$t=0:\rho=\rho_0;\quad f(\rho,t)=f(\rho_0,0).$$

The second equation is the mass balance equation in the coarsening system,

$$\frac{d\Delta}{dt}=-\frac{4\pi}{V_0}\int_0^\infty C^S f(\rho,t)\nu_\rho(\rho,t)\rho^2 d\rho. \tag{9}$$

The initial conditions for this equation are

$$t=0:\rho=\rho_0;\quad f(\rho,t)=f(\rho_0,0);\quad \Delta(t)=\Delta(0).$$

In Eqs. (8) and (9) $f_0(\rho_0,0)$ is the initial distribution of the particles radii in the ρ-dimension space. The set of Eqs. (5)–(9) gives the mathematical description of the coarsening process.

B. Solution of the problem

In order to make the problem easily tractable the following assumptions are made:

A. The growth velocities ν_ρ of all particles in the ensemble are much smaller than ν_0, i.e., $\nu_\rho/\nu_0\ll 1$.

B. At the diffusion controlled mechanism, the solute concentration of the liquid phase-$C_0(t)$ changes much slower than $C^L(t)$ and $C^S(t)$.

C. For the sake of simplicity in the present analysis, the case that the solid and the liquid phases are ideal solutions is discussed. It should be noted that the obtained results are valid also for real solutions. In case that real solutions are considered in Eqs. (6) and (7) the Gibbs energies ΔG^S and ΔG^L should be expressed as a functions of the thermodynamic activities instead of the concentrations C^S and C^L [33,34].

D. For the sake of simplicity it is assumed that C^S in Eq. (7) is equal to the equilibrium solidus concentration C_e^S [1–6].

1. Diffusion controlled growth (dissociation)

The first of the system of equations, Eq. (5), can be solved using the Laplace variable: $u=r/2\sqrt{Dt}$ instead r and t. This reduces Eq. (5) to an ordinary differential equation,

$$\frac{d^2C}{du^2}+\frac{2(u^2+1)}{u}\frac{dC}{du}=0$$

and also the boundary conditions to

$$u=z=\frac{\rho}{2\sqrt{Dt}}:\ \left.\frac{dC}{du}\right|_{u=z}=-\nu_\rho\sqrt{\frac{t}{D}}(C^L-C^S),\quad C=C^L,$$

$$u\to\infty:\ C=C_0,\quad z=z_0=\frac{\rho_0}{2\sqrt{Dt}}.$$

The solution of this equation, taking into account the listed above boundary conditions is [35]

$$\frac{C^L-C_0(t)}{C^L-C^S}=\frac{\nu_\rho\rho}{2D}[1-\sqrt{\pi}z\exp(z^2)\mathrm{erfc}(z)]. \tag{10}$$

Here $\mathrm{erfc}(z)=1-\mathrm{erf}(z)$, $\mathrm{erf}(z)$ is the error function and $z=\rho/2\sqrt{Dt}$.

The Gibbs free energy ΔG of an ideal solution is given by the following equation [33,34]:

$$\Delta G=(1-C)\Delta G_A^0+C\Delta G_B^0 \\ +RT[C\ln C+(1-C)\ln(1-C)].$$

Here ΔG_A^0 and ΔG_B^0 denote the Gibbs free energies of the pure components.

Substituting this expression into Eqs. (6) and (7), after uncomplicated transformations, one obtains

$$\frac{C^S}{C^L}=\left(1-\frac{\nu_\rho}{\nu_0}\right)\exp\left(\frac{\Delta G_B^{0L}-\Delta G_B^{0S}}{RT}\right)\exp\left(-\frac{2\Gamma}{\rho}\right), \tag{11}$$

$$\frac{1-C^S}{1-C^L}=\left(1-\frac{\nu_\rho}{\nu_0}\right)\exp\left(\frac{\Delta G_A^{0L}-\Delta G_A^{0S}}{RT}\right)\exp\left(-\frac{2\Gamma}{\rho}\right). \tag{12}$$

At a fixed temperature T_e and at $\nu_\rho\to 0$ and $\rho\to\infty$, the above equations are simplified to

$$\frac{C_e^S}{C_e^L}=\exp\left(\frac{\Delta G_B^{0L}-\Delta G_B^{0S}}{RT_e}\right)=k_B$$

and

$$\frac{1-C_e^S}{1-C_e^L}=\exp\left(\frac{\Delta G_A^{0L}-\Delta G_A^{0S}}{RT_e}\right)=k_A,$$

i.e., to expressions which determine the equilibrium concentrations of the solidus C_e^S and the liquidus C_e^L at T_e and the equilibrium partition coefficients k_B and k_A for this temperature [10,35].

Since in the discussed case $\Delta\ll 1$ and $\nu_\rho/\nu_0\ll 1$, it can be assumed that $T\approx T_e$ for the temperature T on the particle surface. This allows us to rewrite the set of Eqs. (11) and (12) in a more compact form, using the equilibrium partition coefficients k_A and k_B (these are easily obtained by the equilibrium phase diagram),

$$C^S=C^L k_B\left(1-\frac{\nu_\rho}{\nu_0}\right)\exp\left(-\frac{2\Gamma}{\rho}\right), \tag{11$'$}$$

$$1-C^S=(1-C^L)k_A\left(1-\frac{\nu_\rho}{\nu_0}\right)\exp\left(-\frac{2\Gamma}{\rho}\right). \tag{12'}$$

Solving Eqs. (11′) and (12′) with respect to C^S and substituting the obtained result for C^L into Eq. (10), one obtains for the growth velocity of a spherical particle with radius ρ

$$\left[\frac{\nu_\rho}{\nu_0}-\left(\frac{\nu_\rho}{\nu_0}\right)^2\right]\left[\exp\left(\frac{2\Gamma}{\rho}\right)-k_B-k_A\right]\frac{\nu_0\rho}{2D}[1-\sqrt{\pi}z\exp(z^2)\mathrm{erfc}(z)]-\frac{\nu_\rho}{\nu_0}\beta=\exp\left(\frac{2\Gamma}{\rho}\right)-\beta,$$

with $\beta=k_A+(k_B-k_A)(C_e^L-\Delta)$. Taking into account that $\nu_\rho/\nu_0\ll 1$, after uncomplicated transformations, the above equation is rewritten in a more simple form,

$$\nu_\rho=\frac{d\rho}{dt}=\nu_0\frac{\exp\left(\frac{2\Gamma}{\rho}\right)-\beta}{\frac{\nu_0\rho}{2D}[1-\sqrt{\pi}z\exp(z^2)\mathrm{erfc}(z)]\left[\exp\left(\frac{2\Gamma}{\rho}\right)-k_B-k_A+k_Bk_A\exp\left(-\frac{2\Gamma}{\rho}\right)\right]-\beta}. \tag{13}$$

2. Reaction controlled growth (dissolution)

The equation governing the reaction growth (dissolution) process can be obtained from Eq. (13) taking into account that the influence of the diffusion is negligible. This is similar to the case when the diffusion coefficient in Eq. (13) tends to infinity. Taking into account that at $D\to\infty$ $\nu_0\rho/2D[1-\sqrt{\pi}z\exp(z^2)\mathrm{erfc}(z)]\to 0$, the following reaction controlled growth (dissolution) equation is obtained:

$$\nu_\rho=\frac{d\rho}{dt}=\nu_0\frac{\beta-\exp\left(\frac{2\Gamma}{\rho}\right)}{\beta}. \tag{14}$$

Note the difference between the results obtained by substitution of $D\to\infty$ into Eqs. (1) and (13).

We remind one that Eqs. (13) and (14) are valid only for small undercoolings, small supersaturations, and ideal solutions. In cases where these conditions are not fulfilled, one should solve directly Eqs. (6), (7), and (10) or rework Eqs. (6) and (7) using the thermodynamic activity formalism.

The equations so obtained differ considerably from these used until now [1–6,8–14,20,21–29]. Compared to Eq. (1), it can be seen that at $\rho\to\infty$, the growth velocity does not tend to zero, as it does in the some of the cited cases, but tends, as should be expected, to the growth velocity of a plane front of solidification: $\nu_\rho|_{\rho\to\infty}\to\nu_0(\beta-1/\beta)$. According to Eqs. (13) and (14) the growth velocity tends to zero $v\to 0$, only at $\Delta\to 0$ and $\rho\to\infty$.

From Eqs. (13) and (14) it follows that the particle radius varies with time via $\Delta(t)$ and $\rho(t)$. These quantities determine also the sign of the $d\rho/dt$ derivative and therefore the growth status of every particle at a fixed moment. At $d\rho/dt>0$ the particle grows and at $d\rho/dt<0$ it dissolves. The situation at which $d\rho/dt$ is equal to zero $d\rho/dt=0$, determines the value of the critical radius $\rho^*(t)$. Substituting $d\rho/dt=0$ in Eqs. (13) and (14) and solving the obtained equation with respect to ρ one obtains for the critical radius

$$\rho^*(t)=\frac{2\Gamma}{\ln(\beta)}.$$

It is interesting to note that Kampmann and Kahlweit [5], using a different approach to this problem from the one described here, obtained a quite similar result for the critical radius in a two component system

$$\rho^*(t)=\frac{2\Gamma}{\ln(\Pi)},$$

with $\Pi=C^L/C_0$ [5].

Equation (15) allows us to exclude β from Eqs. (13) and (14) and to rewrite it in a more compact form,

$$\nu_\rho=\frac{d\rho}{dt}=\nu_0\frac{1-\exp\left(\frac{2\Gamma}{\rho}-\frac{2\Gamma}{\rho^*}\right)}{1-\frac{\nu_0\rho}{2D}\exp\left(-\frac{2\Gamma}{\rho^*}\right)[1-\sqrt{\pi}z\exp(z^2)\mathrm{erfc}(z)]\left[\exp\left(\frac{2\Gamma}{\rho}\right)-k_B-k_A+k_Bk_A\exp\left(-\frac{2\Gamma}{\rho}\right)\right]}, \tag{13'}$$

$$\nu_\rho=\frac{d\rho}{dt}=\nu_0\left[1-\exp\left(\frac{2\Gamma}{\rho}-\frac{2\Gamma}{\rho^*}\right)\right]. \tag{14'}$$

It is worth noting that Eq. (14′) reduces at $2\Gamma[(1/\rho)-(1/\rho^*)]\ll 1$ to

$$\nu_\rho = \frac{d\rho}{dt} = 2\Gamma \nu_0 \left(\frac{1}{\rho^*} - \frac{1}{\rho} \right),$$

which is identical with the kinetic equation used by Marquesee and Ross to account for the reaction controlled growth (decay) in their analysis [see Eq. (2.11) in [21]].

The solution of Eq. (8) is of crucial importance to the description of the coarsening process, since the latter provides the value of $f(\rho,t)$, which on its side, determines the change of the $\Delta(t)$ quantity, respectively $\rho^*(t)$ with the time. Regretfully, this first order partial differential equation cannot be solved with the method developed by Lifshitz and Slyozov for obvious reasons namely the differences between Eq. (1) and Eqs. (13) and (14). In the present paper Eq. (8) is solved using the classical procedure developed for solution of such equations, known as the method of characteristics [36].

Following the ideas of the characteristics method, the continuity equation

$$\frac{\partial f}{\partial t} + \nu_\rho \frac{\partial f}{\partial \rho} = -f \frac{\partial \nu_\rho}{\partial \rho}$$

is reduced to a system of two ordinary differential equations,

$$dt = \frac{d\rho}{\nu_\rho} = -\frac{df}{f\,(\partial \nu_\rho / \partial \rho)}.$$

Rearranging the members in the above expression one obtains

$$\frac{d\rho}{dt} = \nu_\rho \quad \text{and} \quad \frac{df}{dt} = -f \frac{\partial \nu_\rho}{\partial \rho}.$$

The first of these ordinary differential equations is actually Eq. (13) [or Eq. (14)], which have been worked out above. The second equation can be solved via separation of the variables, yielding as result

$$f(\rho,t) = f_0(\rho_0,0) \exp\left(-\int_0^t \frac{\partial \nu_\rho}{\partial \rho} d\tau \right). \tag{15}$$

Analyzing Eq. (15), the following conclusions may be drawn:

(i) In the case when the growth velocity as function of ρ and t is known, Eq. (15) provides analytical solution of the coarsening problem. Unfortunately, this is not the case with Eqs. (13) and (14).

(ii) In the case when the particles growth velocity ν_ρ is a function only of the time $\nu_\rho = \nu_\rho(t)$ then from Eq. (15) it follows that $f_0(\rho_0,0)$ does not change as a function of the time, i.e., $f(\rho,t) \equiv f_0(\rho_0,0)$. This result is a particular case of one of the basic concepts of the statistical physics, the Liouville theorem [37].

The fourth assumption, listed in the beginning of the present section, allows us to rewrite Eq. (9) in a more simple form,

$$\frac{d\Delta}{dt} = -\frac{4\pi C_e^S}{V_0} \int_0^\infty f(\rho,t)\nu_\rho(\rho,t)\rho^2 d\rho.$$

The integral at the right hand side of this equation can be rewritten as

$$\frac{d\Delta}{dt} = -\frac{4\pi C_e^S}{3V_0} \left[\rho^3 f \nu_\rho \Big|_0^\infty - \int_0^\infty \frac{\partial f \nu_\rho}{\partial \rho} \rho^3 d\rho \right].$$

Taking into account that $f(0,t)=0$ and $f(\infty,t)=0$, and that $\partial(f\nu_\rho)/\partial\rho = -\partial f/\partial t$ [see Eq. (8)], after application of the Leibnitz rule to the integral at the right-hand side of the above equation one obtains

$$\frac{d}{dt}\left[\Delta + \frac{4\pi C_e^S}{3V_0} \int_0^\infty f \rho^3 d\rho \right] = 0.$$

The integration of this differential equation yields

$$\Delta(t) + \frac{4\pi C_e^S}{3V_0} \int_0^\infty f(\rho,t)\rho^3 d\rho = \Delta(0) + \frac{4\pi C_e^S}{3V_0} \int_0^\infty f_0(\rho_0,0)\rho_0^3 d\rho_0.$$

Rearranging the members of the above equation and taking into account that the initial volume fraction of the solid phase ρ is defined as $p = 4\pi/3V_0 \int_0^\infty f_0(\rho_0,0)\rho_0^3 d\rho_0$, one finally obtains

$$\Delta(t) = \Delta(0) + pC_e^S \left[1 - \frac{\int_0^\infty f(\rho,t)\rho^3 d\rho}{\int_0^\infty f_0(\rho_0,0)\rho_0^3 d\rho_0} \right]. \tag{16}$$

Equations (13) [or (14)], (15) and (16) form a set of equations which explicitly solve the problem formulated in the present paper.

III. RESULTS AND DISCUSSION

The theory developed here can be verified on the Cu-Ni alloy system, which forms ideal solutions both in the solid and the liquid phases [16,19,38]. The used thermodynamical data for the Cu-Ni ($T_e = 1673$ K, $D = 10^{-9}$ m^2/s, $\Gamma = 1.43 \times 10^{-10}$ m) alloy system are taken from [38].

A self-consistent theory of the coarsening process at LPS should solve the problems outlined in the Introduction section, namely,

1. It should predict the cube law for the mean particles radii versus the time.
2. It should predict the form of the distribution function obtained by the experiment and the correct value for the relation $\rho_{\max}/\overline{\rho}$, or at least it should give values closer to the experimental one.
3. It should explain the ''abnormal'' growth phenomenon.

Regretfully, the system of Eqs. (13)–(16) worked here cannot be solved analytically and the results listed below have been obtained by its numerical solution. Although the numerical experiments have been carried for coarsening in liquid phase, i.e., solid particles dispersed into the liquid phase, it should be noted that the results are also applicable for the processes of coarsening in supersaturated solid solutions. In this case it can readily be shown that the ripening time τ_{sol} is proportional to $\tau_{\text{sol}} \approx \tau_{\text{liq}}(D_{\text{liq}}/D_{\text{sol}})$. Here τ_{liq} is

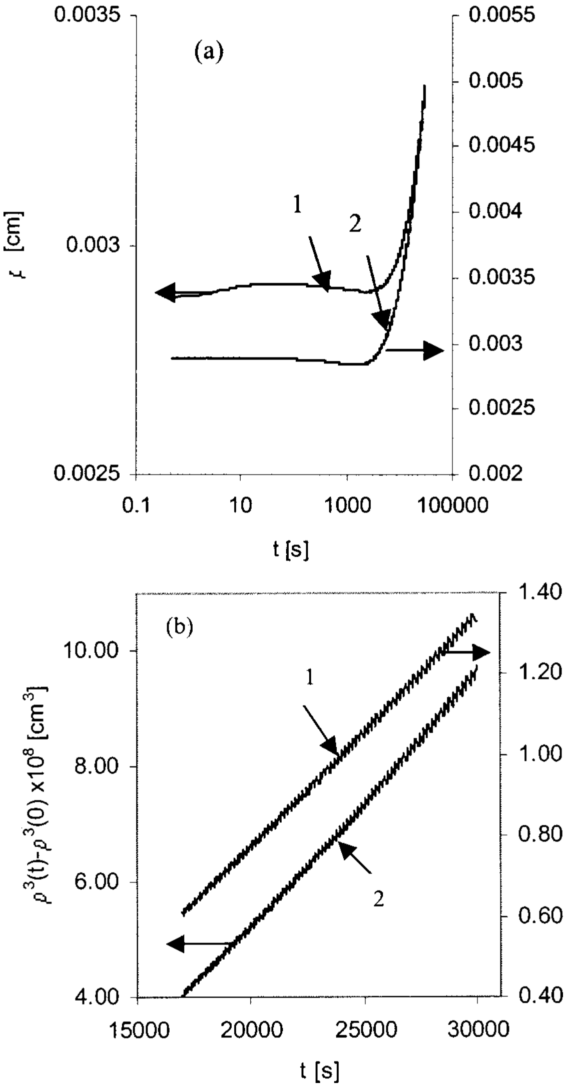

FIG. 1. (a) Plots of $\overline{\rho}(t)$ vs t for two ensembles [$p=0.2$ (1) and $p=0.9$ (2)] of particles with initial Gaussian distribution ($t_{\text{coars.}}=3\times10^4$ s, $\Delta(0)=10^{-3}$, $\varepsilon=0.33$). For the value of v_0 ($v_0=5\times10^{-4}$ m/s) used in the calculations the experimentally observed cubic law is reached after considerable coarsening time $t>10^4$ s. (b) Plots of $\overline{\rho}^3(t)-\overline{\rho}^3(0)$ vs coarsening time t, for the diffusion [$p=0.2$, (1)] and the reaction [$p=0.9$ (2)] controlled coarsening. The reaction constants K, which are obtained from these plots, are compared with the available experimental data in Table I.

the ripening time in the liquid phase and D_{sol} and D_{liq} are the diffusion coefficients of the solute in the solid and the liquid phases. In the numerical simulations performed below, a Gauss function was used as the initial distribution function, e.g.,

$$f_0(\rho_0,0)=\exp\left[-\frac{1}{2}\left(\frac{\rho_0-\overline{\rho_0}}{\varepsilon\overline{\rho_0}}\right)^2\right],$$

because it is assumed that the initial radii of the particles in the experiments, with which our results are compared, are Gaussian ones. Here ε is a parameter, which determines the width of the Gauss curve (e.g., the dispersion).

The following objectives have been pursued in the numerical simulations carried below:

TABLE I. Comparison of the calculated in the present paper and the experimentally measured values of the coarsening rate constant K for different alloy systems.

Alloy system	p	K [μm^3/s]	Reference
Ni-Cu	0.2	0.57	This work
Co-Cu	0.2	1.5	Bender and Ratke [15]
Co-Cu	0.2	0.17	Bender and Ratke [15]
Co-Cu	0.34	0.29	Kang and Yoon [17]
Ni-Cu	0.9	4.32	This work
Co-Cu	0.71	2.5	Bender and Ratke [15]
Co-Cu	0.95	2.75	Kang and Yoon [42]
Co-Sn	0.86	3.9	Hardy and Voorhees [16]
Co-Sn	0.93	6.8	Hardy and Voorhees [16]
Fe-Cu	0.9	1.32	Kang and Yoon [42]

A. Determination of the growth rate of the mean particles radii $\overline{\rho(t)}$ for both, diffusion and reaction controlled growth.

B. Determination of the distribution functions $f=f(\rho,t)$ for different coarsening regimes.

C. Modeling of the ''abnormal'' particle growth.

D. Comparison of the results obtained in points 1–3 with the available experimental data.

Typical time dependencies of the mean radius $\overline{\rho}=\overline{\rho(t)}$ for both diffusion ($p=0.2$) and reaction ($p=0.9$) controlled coarsening processes are shown in Fig. 1(a). It is seen that for the system Ni-Cu studied here, a steady growth pattern $\overline{\rho}^3\approx t$ is established after a considerable coarsening time $t_0>10^4$ s. It is obvious that t_0 is a function of ν_0 used in the calculations. We want to remind one that ν_0 depends on the energetic barrier Q, which varies with the studied material. The plots of $\overline{\rho}^3(t)-\overline{\rho}^3(0)$ versus coarsening time t, for the diffusion and the reaction controlled coarsening are shown in Fig. 1(b). Unfortunately, the alloy system Ni-Cu modelled by us has not been a subject of experimental interest so far. That is why the values obtained from the plots in Fig. 1(a) of the coarsening rate constant K are compared with the available in the literature experimental data (see Table I). The values for K as predicted by us lay within or are close to the ones obtained experimentally.

As mentioned above, a successful theory should predict the form of the distribution function $f=f(\rho,t)$. In Figs. 2(a) and 2(b) distribution functions $f(\rho,t)$ as calculated in the present paper are compared with two experimentally obtained ones [13,39]. It is seen that the theoretical and the experimental results correlate favorably with each other and that the model proposed by us predicts correctly the experimentally observed values for the relation $\rho_{\max}/\overline{\rho}$ and the place of the maximum of the distribution function $f(\rho,t)$ on the $\rho/\overline{\rho}$ axis. The differences in the scales of both y axes of the calculated and the experimental results in Figs. 2(a) and 2(b), are due to the different way of normalization of these distribution functions in the present and in the cited experimental works. It should be noted that in Figs. 2(a) and 2(b) the observed correlation between the theory and the experiment is only a qualitative one. In order to model the ripening process for a definite alloy it is necessary to solve Eqs. (4), (5), (8), (12), and (13) for a certain initial distribution $f_0(\rho_0,0)$, temperature T_e, supersaturation $\Delta(0)$ and particles volume fraction ρ.

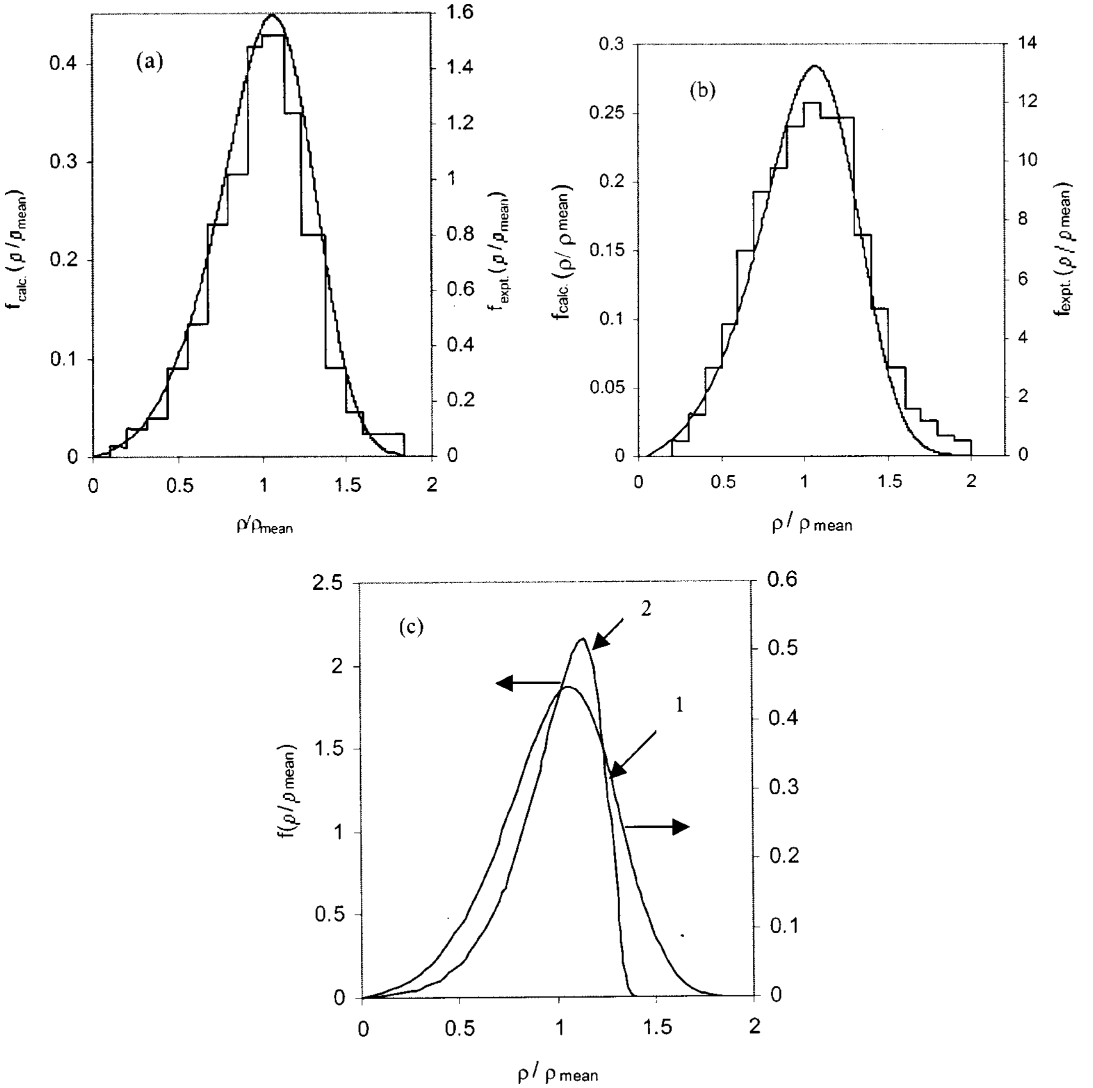

FIG. 2. (a) Comparison of the calculated distribution function $f_{calc.}(\rho/\overline{\rho})$ (the solid line) $[\Delta(0)=10^{-3}$, $p=0.32$, $\varepsilon=0.33$, $t_{coars.}=3\times10^4$ s)], with an experimentally obtained distribution function $f_{exp}(\rho/\overline{\rho})$ (histogram) for Ni_3Al precipitates in an alloy of Ni with 22 at% Co and 13 at% Al ($p=0.32$) [13]. (b) Comparison of the calculated distribution function $f_{calc}(\rho/\overline{\rho})$ (the solid line) $[\Delta(0)=10^{-3}$, $p=0.05$, $\varepsilon=0.4$, $t_{coars}=3\times10^4$ s)], with an experimentally obtained distribution function $f_{exp}(\rho/\overline{\rho})$ (histogram) for FeSi precipitates in pure Fe at 973 °K [$t_{coars}=312$ h (1.1232×10^6 s), $p\rightarrow0$] [39]. (c) Comparison between the calculated distribution function with the aid of the present model distribution function $f_{calc}(\rho/\overline{\rho})$ (1) $[\Delta(0)=10^{-3}$, $p=0.32$, $\varepsilon=0.33$, $t_{coars}=3\times10^4$ s)], and the LSW distribution function (2) [1–3]. Note that the resultant distribution obtained with the present model is sensitive to the used initial distribution $f_0(\rho_0,0)$.

As mentioned in the Introduction the ''abnormal growth'' behavior at the coarsening has not been explained so far. Here we used the developed model to study this interesting phenomena. For this purpose a complex function composed from two Gauss functions, i.e.,

$$f_0(\rho_0,0)=\exp\left[-\frac{1}{2}\left(\frac{\rho_0-\overline{\rho_0}}{\varepsilon\overline{\rho_0}}\right)^2\right]+0.18\exp\left[-\frac{1}{2}\left(\frac{\rho_0-\overline{\rho_1}}{\varepsilon_1\overline{\rho_1}}\right)^2\right]$$

[see Fig. 3(a)], was used as the initial distribution. The evolution of this distribution function with time is shown in Figs. 3(b)–3(d). It can be seen that the results obtained here confirm the ones obtained experimentally, i.e., that a small cluster of big particles should grow preferably at the expense of the smaller ones. These results therefore show that the problem of ''abnormal growth'' is merely due to the kinetic equations used up to now for the description of the growth (decay) of the particles.

As the volume of the solid fraction increases it is generally agreed that the distribution function should grow broader [14]. In order to test the substantiality of this assumption and the validity of our model, in Fig. 4 we compared the resultant distribution functions of two systems with a different solid fraction $p=0.2$ and $p=0.9$ after 3×10^4 s coarsening time. It can be seen that the distribution function for $p=0.9$ is much broader than the $p=0.2$ are, as is expected. Taking these results into account, one may conclude that the model presented here accurately describes the experimental evidence.

IV. CONCLUSIONS

An investigation of the way in which in a supersaturated solution an ensemble of particles with different radii grows (or dissolves) as a result of the diffusion and kinetic processes, has been made. Comparing the model presented here

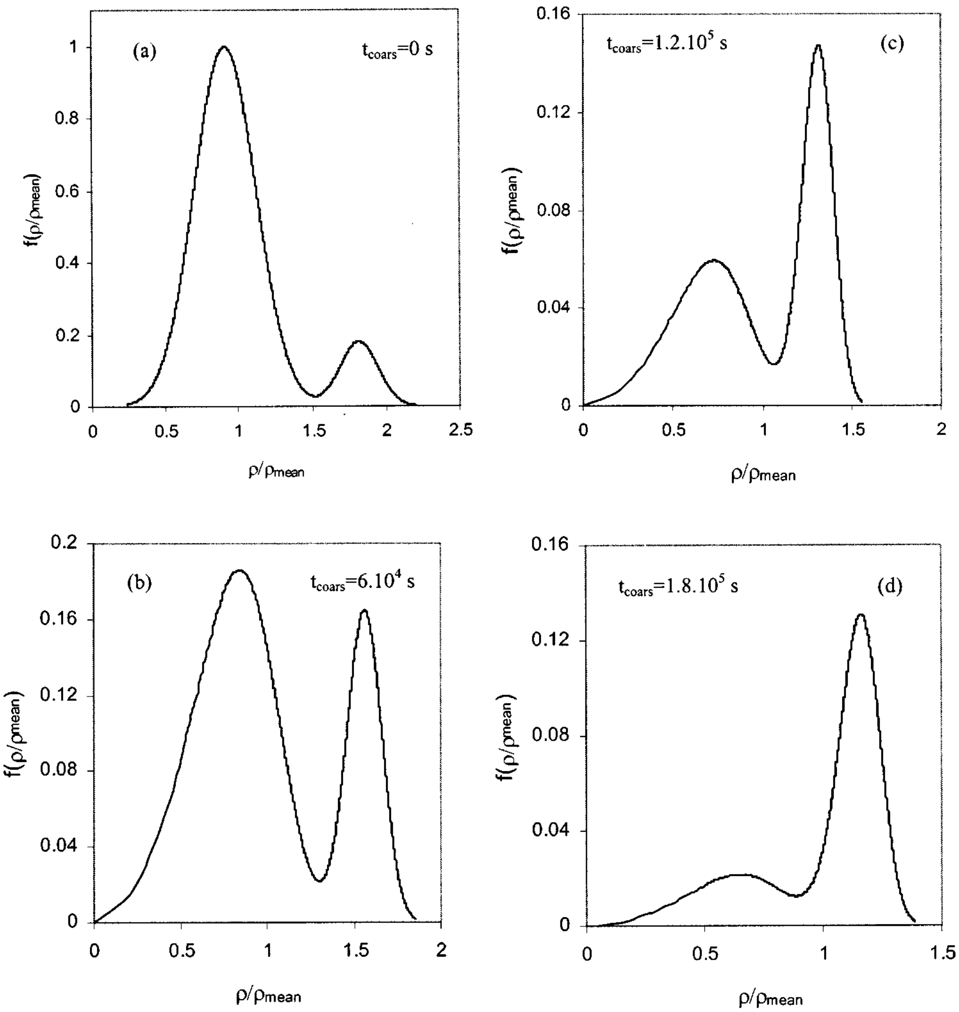

FIG. 3. Evolution with time of an ensemble of particles with a small cluster of big particles (the right-hand side of the distribution function). As seen from (b)–(d) the existence of this cluster leads to dramatic shift of the particles distribution as the coarsening proceeds with the time.

with those published previously [1–6,8–14,18,21–29] allows us to distinguish the following considerable differences:

(i) The present model is based on an equation describing the growth kinetics of a spherical particle different from the ones used up until now (Eq. (1), Ref. [20] and its variations [1–6,8–14,18,21,22,24]). A criterion is worked out that determines which process is controlling the coarsening kinetics at a certain moment. On the basis of this criterion, two main kinetic mechanisms of coarsening are distinguished as a function of the solid fraction *p*, namely, diffusion or reaction controlled coarsening. The equations obtained here, governing these two mechanisms [Eqs. (13) and (14)], are based on the exact solution of the diffusion problem and a recently developed theory of solute redistribution at crystal growth [30]. This allows one to account for the solute redistribution as a function of the growth (dissolution) velocity of the particles and to eliminate the main disadvantage following from the application of Eq. (1) [20] (see Figs. 1–3).

(ii) The set of equations which is obtained here accounts for the influence of the solid fraction *p* automatically.

(iii) In contrast with most theoretical investigations carried out until now [1–6,8–14,18,21], in the present approach the ripening process can be followed from its beginning. This feature of the present model is very useful for the modeling of short time processes taking place simultaneously with the microstructure coarsening. As for example pore coalescence at liquid phase sintering and especially the basic component dissolution and microstructure development during the selective laser sintering.

(iv) The developed model allows the study of the coarsening process in multicomponent systems [30]. This is a very useful feature, from practical point of view, since the sintered systems are rarely composed only of two chemical components.

(v) The proposed equations allow to model the ''abnormal growth'' phenomena and to explain it successfully.

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APPENDIX A

In summarizing the attempts to explain the discrepancy between theory and experiment, it should be noted that the major part of them are restricted to proposing different additions to Eq. (1) [18]. Analysis of Eqs. (1)–(3), however, leads to the conclusion, that probably the discrepancy between the theory and the experiment is mainly due to the following: the Eq. (1) describing the growth kinetics of the

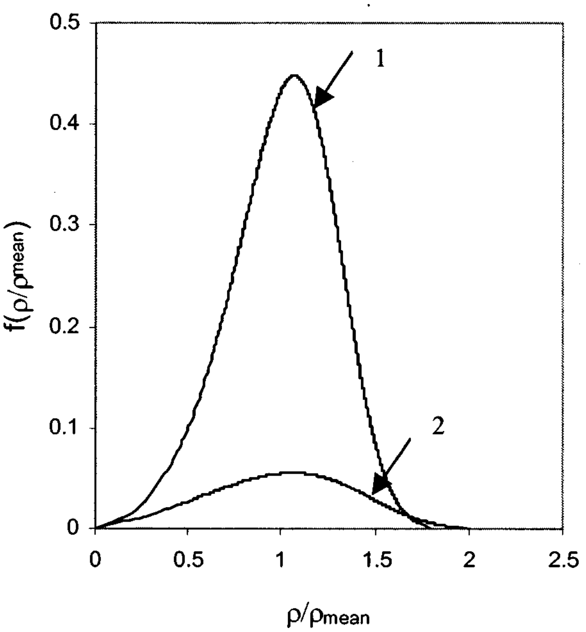

FIG. 4. Comparison between the distribution functions of two ensembles of particles after 3×10^4 s coarsening time. The initial distribution functions and the initial conditions were equal for the both ensembles [Gaussian distribution, $\varepsilon=0.33$, $\Delta(0)=10^{-3}$], but the solid fractions and the coarsening mechanisms have been different: (1) diffusion controlled; (2) reaction controlled.

particles, used until now, does not describe correctly the real kinetics of the growth process. For example, according to Eq. (1) it follows that at $\rho\to\infty$, $v_\rho\to 0$, i.e., the growth velocity of the particles with relatively large radius, should tend to zero. This automatically excludes the bigger particles from the coarsening process and explains the steep front of the distribution function $f=f(\rho,t)$ at $t\to\infty$, as predicted by the LSW theory. On the other hand, it should be expected that at $\rho\to\infty$, $v_\rho\to v_{\text{plane}}$ (here with v_{plane} is denoted the growth velocity of a plane solidification front), whereas according to Eq. (1) it tends to $v_\rho\to 0$ [compare this behavior with the predictions of the present model, e.g., Eqs. (13′) and (14′)]. According to Eq. (1) this ($v_\rho\to 0$ at $\rho\to\infty$) is valid even at considerable undercooling below the solidus temperature imposed on the coarsening system. Another confusing moment is that at $D\to\infty$ the growth velocity v_ρ of the particles independently of their radii should tend to $v_\rho\to\infty$. Therefore, from Eq. (1) follows that the crystal growth process is governed by the solute transport. This is most unlikely since it is well known that the solute transport arises as a consequence of the changes on the particle surface and not vice versa. In other words the transport processes can be a limiting, but not governing factor of the coarsening process. In order to avoid these difficulties several authors [12,21–29] developed a new approach to the problem, known as finite volume fraction analysis. The main idea of this approach is to reduce the diffusion equation (i.e., the second Fick equation) to a more simple equation, which can be easily handled from mathematical point of view. Thus, they assumed that the solute distribution around the particles changes very slowly with time that the problem may be considered as a quasistationary one (see the cited above papers for details). Unfortunately, this assumption narrows the application of the finite volume fraction analysis considerably. It can be easily checked that the coarsening system can be considered quasistationary one only in the case when the solute diffusion coefficient is a very large quantity. This condition is rarely fulfilled at liquid-solid and never at solid-solid coarsening systems.

APPENDIX B

A detailed derivation of Eqs. (6) and (7) is given in [30]. In the following, the basic concepts and the main results are outlined.

Let us consider a metastable phase β and phase α growing into the β matrix. We assume that the both phases are composed of k components. At phase transition, a part of the accumulated in the β phase free energy, $\Delta G^{\beta\alpha}$, is used for the formation of the new phase α (phase volume, solute redistribution, etc.), $\Delta G_E^{\beta\alpha}$, and the rest of it, $\Delta G_\nu^{\beta\alpha}$, as driving force of the growth process,

$$\Delta G^{\beta\alpha}=\Delta G_\nu^{\beta\alpha}+\Delta G_E^{\beta\alpha}. \tag{B1}$$

The accumulated free energy $\Delta G^{\beta\alpha}$ is easily obtained $\Delta G^{\beta\alpha}=\Delta G^{\beta}-\Delta G^{\alpha}$, e.g., this is the difference between the Gibbs energies at a certain temperature and chemical composition of the α and the β phases. The growth velocity ν can also be evaluated using some of the kinetic equations, combining together the free energy and ν. In our case the classic Turnbull equation is used for this purpose [7,40–42],

$$\Delta G_\nu^{\beta\alpha}=-RT\ln\left[1-\frac{\nu}{\nu_0}\right], \tag{B2}$$

with

$$\nu_0=\nu_0^T\exp\left(-\frac{Q}{RT}\right)\exp\left(-\frac{\Delta G^{\alpha}}{RT}\right).$$

Thus, the problem is to work out a criterion which will determine how the accumulated free energy $\Delta G^{\beta\alpha}$ is distributed between $\Delta G_E^{\beta\alpha}$ and $\Delta G_\nu^{\beta\alpha}$ and consequently to determine the growth velocity via Eq. (B2).

Let us consider a small volume including fractions of the growing phase, the matrix, and the phase boundary. For the total energy φ used for the formation of the new phase, solute redistribution, etc., one can write

$$\varphi=f\Delta G_E^{\alpha}+(1-f)\Delta G_E^{\beta}+\sigma V_m S. \tag{B3}$$

For the conservation of mass inside the volume one can put forward

$$f x_i^{\alpha}+(1-f)x_i^{\beta}=x_i^{0}\quad (i=1\dots k). \tag{B4}$$

Here S is the phase boundary surface, V_m is the molar volume, σ is the surface tension, f is the transformed part of the volume, x_i^α and x_i^β are the molar parts of the ith component in the α and β phases, x_i^0 is the molar part of the ith component in the whole volume, and ΔG_E^α and ΔG_E^β are the parts of the free energy used for the formation new phase volume, boundary, solute redistribution, etc.

In order to determine the distribution of the accumulated energy between $\Delta G_E^{\beta\alpha}$ and $\Delta G_\nu^{\beta\alpha}$ the following assumption is used: the part of the total free energy φ utilized by the system for the formation of the new phase volume and boundary, solute redistribution, etc. is minimal during the whole time of the phase transition. In other words, for the metastable system it is most important to transform into a more stable phase rather to spend energy for formation of excess boundaries and solute redistribution. The problem, thus, is reduced to determination of a conditional extremum of the φ function. A detailed description of this procedure is given in [30]. The final result is

$$\frac{\partial \Delta G^\alpha}{\partial x_i^\alpha} = \frac{\partial \Delta G^\beta}{\partial x_i^\beta}\left(1 - \frac{\nu}{\nu_0}\right) \quad (i = 1 \ldots k), \tag{B5}$$

$$\Delta G^{\beta\alpha} + RT \ln\left(1 - \frac{\nu}{\nu_0}\right) + \sum_{i=1}^{k} \frac{\partial \Delta G^\beta}{\partial x_i^\beta}(x_i^\alpha - x_i^\beta) = \sigma V_m C, \tag{B6}$$

with C as curvature of the phase boundary.

It can be easily shown that in some special cases the above equations reduce to what is well known in the physics expressions. For example,

1. At $C=0$ and $\nu/\nu_0=0$, these equations reduce to the Gibbs equations, describing the phase equilibrium between the β and α phases.

2. At $\nu/\nu_0=0$, $x_i^\alpha=0$, and $x_i^\beta=0$, they reduce to the Gibbs-Thomson equation.

3. At $x_i^\alpha=0$ and $x_i^\beta=0$, they reduce to the Machlin equation, which was obtained with the aid of the irreversible thermodynamics [40].

4. At $\nu/\nu_0=0$, they reduce to the Thomson-Freundlich equation.

The physical meaning of ν_0 (remember that $\nu_0 = \nu_0^T \exp[-(Q/RT)]\exp[-(\Delta G^\alpha/RT)]$ can be derived from Eqs. (B5) and (B6). Indeed substituting ν with ν_0 in these equations, one obtains $\partial\Delta G^\alpha/\partial x_i^\alpha = 0$ and $\Delta G^{\beta\alpha}=0$, e.g., this is the velocity at which no energy is spent for solute redistribution between the α and the β phases. In other words, it is the maximal growth velocity possible for a certain temperature and phase composition. As seen from the expression $\nu_0 = \nu_0^T \exp[-(Q/RT)]\exp[-(\Delta G^\alpha/RT)]$, ν_0 is complex function of different physico-chemical parameters of the transforming system. Therefore, one should expect that this quantity vary with the different substances.

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