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On the theory of Ostwald ripening in the presence of different mass transfer mechanisms

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ABSTRACT

A theoretical description of the concluding stage of Ostwald ripening based on the Slezov theory (Slezov, 1978) and recently developed approach (Alexandrov, 2015) is formulated. The present analysis focuses on the formation and relaxation of the particle size distribution function from the intermediate stage of ripening process to its final state, which is described by the universal distribution. The boundaries of the transition layer in the vicinity of a blocking point are found. The time-dependent corrections to the growth rates of crystals and the distribution functions are determined for different mass transfer mechanisms. The obtained analytical distributions are in good agreement with experimental data. All analytical results are presented in a form directly suitable for their use in applications.

1. Introduction

The first analytical description of Ostwald ripening processes begins from the classical theories developed by Lifshitz and Slyozov [1,2] in the case of diffusion-limited crystal growth and by Wagner [3] in the case of interface-limited growth. As in many real processes different mass transfer mechanisms can be involved simultaneously (when the mass transfer occurs along the dislocation lines and grain boundaries concurrently with volume diffusion), shortly thereafter Slezov et al. [4] explained these scenaria of Ostwald ripening. Note that the corresponding solutions obtained in this way describe a great variety of problems met in materials science, condensed matter and applied physics, ranging from applications to the condensation and freezing of liquids to life science and chemical industry [5–9]. All these theories describe the concluding stage (asymptotic state) of ripening process when larger particles grow at the expense of smaller ones. The analytical solutions independent of initial conditions (obtained in [1–4] in zeroth approximation) demonstrate that crystals whose dimension exceeds the blocking points u_{0k} do not contribute to the distribution functions $P_k(u)$ at sufficiently large times (here u is the dimensionless crystal size and subscript k designates the mass transfer mechanism). The growth rates of crystals therewith vanish at the blocking points u_{0k}. Note that the universal distribution functions describing this asymptotic state vanish in the region $u > u_{0k}$.

However, there are a large number of experimental data and numerical simulations showing that the particle-radius distribution functions are more broad and squat than the aforementioned asymptotic solutions (see, among others, [10–13] and 20 year experiments presented in [14]). These discrepancies between the asymptotic theory and experimental data are connected with the fact that the real distribution function evolves with time and smoothly decreases in the region $u > u_{0k}$. In order to describe this dynamic behavior, the time-dependent functions ε_k responsible for blurring of the blocking points u_{0k} and the initial times τ_{0k}, at which the asymptotic description of the Ostwald ripening can be used with a proper accuracy, should be determined. With this object in view, in the present study, a new analytical theory based on the method of time-asymptotic solutions [15] as well as on the recently developed approach of formation of the universal distribution [16] is developed for different mass transfer mechanisms.

2. Fundamental equations and their asymptotic solutions

The growth rates of macrodefects for different mass transfer mechanisms can be written in terms of the general expression as follows [4]:

$$\frac{da}{dt} = \frac{D_k \mu^{k-3}}{a^{k-2}}\left(\Delta(t) - \frac{\sigma}{a}\right), \quad k \geq 2, \tag{1}$$

where a is the particle radius, t is the time, $\Delta(t)$ is the supersaturation, $\sigma = 2\alpha v' c_{0\infty}/(k_B T)$, α is the interface surface tension, v' is the volume per atom of the dissolved component, $c_{0\infty}$ is the equilibrium concentration at the plane boundary, k_B is the Boltzmann constant, and T is the absolute temperature. Here $D_k \mu^{k-3}$

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determines the mass transfer mechanism. In the case of interface-limited growth, when $k=2$, the growth rate takes the form [17] $da/dt = a^{-1}(a/a_{av} - 1)D_2\sigma/\mu$, where $a_{av} = \sigma/\Delta$. In the case of diffusion-limited growth of grains due to mass transfer through the volume, when $k=3$, we get $D_k\mu^{k-3} = D$, where D is the diffusion coefficient of the dissolved component. If diffusion goes in the bulk of the material and spreads to the boundaries crossing the inclusions (grain-boundary diffusion), we have [4] ($n=4$): $D_4\mu \propto ND_s l$, where N is the number of surfaces crossing the inclusions, D_s is the diffusion coefficient along the surface, and l is the lattice constant. If the mass transfer occurs either as a result of a two-stage diffusion or predominantly along the dislocation lines (connecting the neighboring inclusions) the growth rate (1) should be calculated at $k=5$ or $k=6$, respectively (see for details [4]).

Let us introduce the following relative dimensions of the crystals $u = a/a_*$ and the times $\tau_k = k \ln x$ and $x = a_*(t)/a_*(0)$ (a_* is the critical radius of crystals). In this case, Eq. (1) can be rewritten in the form

$$\frac{du}{d\tau_k} = \frac{\gamma_k(\tau_k)(u-1) - u^k}{ku^{k-1}}, \tag{2}$$

where

$$\gamma_k(\tau_k) = D_k\sigma k\mu^{k-3}\frac{dt}{da_*^k}. \tag{3}$$

The classical theory of Ostwald ripening [2,4,18,19,21] demonstrates that asymptotically ($\Delta \to 0$, $\tau_k \to \infty$) the growth rate (2) vanishes at the k-dependent blocking point $u_{0k} = k/(k-1)$, and

$$\gamma_k(\tau_k) = \gamma_{0k}\left(1 - \varepsilon_k^2(\tau_k)\right) \to \gamma_{0k} = k^k/(k-1)^{k-1}. \tag{4}$$

Substituting the growth rate $v_{uk} = du/d\tau_k$ from expression (2) into the dimensionless continuity and mass balance [4,21]

$$\frac{\partial\varphi_k}{\partial\tau_k} + \frac{\partial}{\partial u}(v_{uk}\varphi_k) = 0, \quad \kappa_1 e^{-\tau_k/k} + \kappa e^{3\tau_k/k}\int_0^\infty \tilde{u}^3\varphi(\tau_k, \tilde{u})\,d\tilde{u} = 1,$$
$$\kappa = \frac{4\pi a_*^3(0)\omega_p}{3Q\omega}, \quad \kappa_1 = \frac{\sigma}{a_*(0)Q} \tag{5}$$

and neglecting the first term in the second equation (5) in the limit $\tau_k \to \infty$, one can obtain the size distribution function $\varphi_k = a_* f = A_k e^{-3\tau_k/k}P_k(u)$. Here Q is the total initial quantity of the material, f is the dimensional distribution function, ω_p is the volume per atom of pure solvent, ω is the volume of a single atom in the precipitate, and $\Delta(0) = \sigma/a_*(0)$.

The distribution functions $P_k(u)$ and the values of the system parameters u_{0k}, γ_{0k}, A_k, and the average size $\bar{u}_k$

$$\bar{u}_k = \int_0^{u_{0k}} uP_k(u)\,du, \quad \int_0^{u_{0k}} P_k(u)\,du = 1$$

for different mass transfer mechanisms are given in Table 1. Note that the average radius $\bar{a}_k = a_*\bar{u}_k$ coincides with a_* for $k=3$.

The asymptotic distribution functions $P_k(u)$ and growth velocities $du/d\tau$ for different mass transfer mechanisms (different k) are illustrated in Fig. 1. As is easy to see, the distribution function becomes more broad and flat whereas the blocking point moves to the right with decreasing k. Note that crystals of sizes exceeding the blocking points u_{0k} (for different k) have no influence on the asymptotic distributions $P_k(u)$. In other words, $P_k(u) = 0$ at $u > u_{0k}$. By virtue of the fact that these solutions describe the limiting (asymptotic) state at infinitely large time $t \to \infty$ ($\tau_k \to \infty$) they do not allow us to study the formation of the universal distributions when the distribution functions contain the tails on the right of blocking points u_{0k}. In order to describe this ripening process from its early to its final stage the initial distribution function should be taken into account.

3. Formation of the universal distribution

Expanding $du^k/d\tau_k$ from Eq. (2) in a Taylor series in the vicinity of the blocking point u_{0k}, we obtain

$$\frac{du}{d\tau_k} = \frac{1}{ku^{k-1}}[\gamma_k(u-1) + U_k(u)],\ U_k(u)$$
$$= u_{0k}^{k-1}(k(u_{0k}-u) - u_{0k}) - \frac{k(k-1)u_{0k}^{k-2}(u-u_{0k})^2}{2}$$
$$\times\left(1 + \frac{(k-2)(u-u_{0k})}{3u_{0k}} + \frac{(k-2)(k-3)(u-u_{0k})^2}{12u_{0k}^2}\right), \tag{6}$$

where $k = 2, 3, 4$ and $\gamma_k(\tau_k) = \gamma_{0k}(1 - \varepsilon_k^2(\tau_k))$. Since the growth velocity $du/d\tau_k < 0$ (Fig. 1), the leakage rate of particles through the transition layer $u_{2k} < u_{0k} < u_{1k}$ (which is responsible for the

Table 1
Functions and parameters describing the asymptotic solutions for different mass transfer mechanisms.

k	u_{0k}	γ_{0k}	$\bar{u}_k$	$A_k^{-1}\kappa^{-1}$	$P_k(u)$
2	2	4	$\frac{8}{9}$	0.957	$P_2(u) = \begin{cases} \dfrac{24u\exp\left(3 - \dfrac{6}{2-u}\right)}{(2-u)^5}, & u \le u_{02} \\ 0, & u > u_{02} \end{cases}$
3	$\frac{3}{2}$	$\frac{27}{4}$	1	1.13	$P_3(u) = \begin{cases} \dfrac{81u^2\exp\left(1 - \dfrac{1}{1-2u/3}\right)}{2^{5/3}(u+3)^{7/3}(3/2-u)^{11/3}}, & u \le u_{03} \\ 0, & u > u_{03} \end{cases}$
4	$\frac{4}{3}$	$\frac{256}{27}$	1.034	1.176	$P_4(u) = \begin{cases} \dfrac{34.51u^3\exp\left(\dfrac{2}{3u-4} - \dfrac{1}{6\sqrt{2}}\arctan\dfrac{u+4/3}{4\sqrt{2}/3}\right)}{(4/3-u)^{19/6}(u^2+8u/3+16/3)^{23/12}}, & u \le u_{04} \\ 0, & u > u_{04} \end{cases}$