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Influence of stochastic effects on Ostwald ripening

F.-P. LUDWIG, J. SCHMELZER
Fachbereich Physik der Universität Rostock, Universitätsplatz, D-18051 Rostock, Germany
J. BARTELS
Institut für Athmosphärenphysik, Schloßstr. 4–6, D-18225 Kühlungsborn, Germany

According to the Lifshitz–Slezov theory of Ostwald ripening and its generalizations in the asymptotic stage of the competitive growth of an ensemble of clusters, a time-independent cluster size distribution in reduced coordinates is established. The shape of this distribution deviates, however, from the experimentally observed curves, which are in general broader and more symmetric. A number of different proposals have been developed in the literature for an explanation of this discrepancy. Here it is shown that the influence of stochastic effects on coarsening due to thermal noise, which has not been considered so far, may significantly diminish the gap between experiment and theory.

1. Introduction

The late stages of first-order phase transformations in solid or liquid solutions are often characterized by a growth of the larger (supercritical) clusters at the expense of the smaller (subcritical) ones, connected with a decrease of the number of clusters and an increase of their average size. This process of competitive coarsening is usually denoted as Ostwald ripening [1–5].

Though this phenomenon was well known from experiments, at least since the investigations of Ostwald [1] carried out at the beginning of our century, the first adequate theoretical description was developed only in 1958 by Lifshitz and Slezov [6–8]. The Lifshitz–Slezov theory is based on the solution of a set of three coupled equations: the growth equation for a single cluster, the continuity equation for the cluster size distribution function, and an expression for the conservation of the number of particles of the segregating component. Their work was extended by Wagner [9] and others to account for different mechanisms of growth and a number of additional factors which may influence the process of Ostwald ripening [10–16] (for an overview see e.g. [5, 10]).

Independent of the particular mechanism of growth, the basic results of the theory turn out to be the same: the asymptotic stage of Ostwald ripening is characterized by power laws for the time-dependence of the average cluster radius $\langle R \rangle$ and the number of clusters N in the system, and a universal time-independent cluster size distribution is reduced coordinates. Qualitatively, these theoretical results are confirmed by experiments. However, the observed experimental particle size distributions are broader and more symmetric as compared with the predictions of the Lifshitz–Slezov theory.

A number of attempts have been made to resolve these difficulties. Proposals in this direction include qualitative modifications of the growth equations to account for non-steady-state effects in cluster growth [17], diffusional interaction of the growing or dissolving clusters, coalescence, elastic strains, particular diffusion mechanisms, non-ideality of the system, multi-phase precipitation (for an overview see [18, 19] and the references cited therein). Marder [19] stressed in particular the influence of the diffusional interaction of the growing or dissolving clusters for the observed deviations of the Lifshitz–Slezov results from the experimental curves.

Here we want to show that already in the framework of the mean-field theory of Lifshitz and Slezov the gap between experimental and theoretical results can be diminished if stochastic influences on the evolution of the cluster size distribution are taken into account, resulting from the intrinsically random character of processes of transport, incorporation and evaporation of monomers to and from the growing or dissolving clusters. Such stochastic effects are incorporated into the theory in the present study by description of the evolution of the cluster size distribution function in terms of a Fokker–Planck equation [20]. Generalizations are, of course, possible.

2. Basic equations

By the introduction of a dimensionless time scale t' given by

$$t' = \frac{2\sigma D c}{c_\alpha^2 k_B T R_{co}^3} t \qquad (1)$$

where σ is the specific surface energy, D the bulk diffusion coefficient, c the equilibrium solubility of the

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segregating particles in the matrix, c_α their volume concentration in the cluster phase, k_B the Boltzmann constant, T the absolute temperature and R_{co} the critical cluster radius at $t = 0$, the commonly used growth equation for diffusion-limited growth of a cluster of radius R, namely

$$\frac{dR}{dt} = \frac{2\sigma Dc}{c_\alpha^2 k_B T}\left(\frac{1}{R}\right)\left(\frac{1}{R_c} - \frac{1}{R}\right) \qquad (2)$$

may be written in the form

$$\frac{dR}{dt'} = \frac{R_{co}^3}{R}\left(\frac{1}{R_c} - \frac{1}{R}\right) \qquad (3)$$

where R_c is the actual critical cluster radius. It is determined by the difference between the chemical potentials per particle in the cluster phase (μ_α) and in the matrix (μ_β) via

$$R_c = \frac{2\sigma}{c_\alpha \Delta\mu} \qquad \Delta\mu = \mu_\beta - \mu_\alpha \qquad (4)$$

R_{co} is its value for $t = 0$, the initial state of Ostwald ripening.

For perfect solutions which we deal with in the following discussion, the critical cluster radius is determined through the ratio of the actual (c_β) and the equilibrium concentration (c) of the segregating particles in the matrix via

$$R_c = \frac{2\sigma}{c_\alpha k_B T \ln(c_\beta/c)} \qquad (5)$$

As already mentioned, the Lifshitz–Slezov theory is based on Equation 3, the continuity equation for the cluster size distribution function $f(R, t')$ given by

$$\frac{\partial f(R,t')}{\partial t'} + \frac{\partial}{\partial R}\left[f(R,t')\frac{\partial R}{\partial t'}\right] = 0 \qquad (6)$$

and the mass balance equation for the segregating particles. With the introduction of the reduced radius u and a new time scale τ given by

$$u = \frac{R}{R_c} \qquad \tau = 3\ln\left(\frac{R_c(t')}{R_{co}}\right) \qquad (7)$$

a size distribution in reduced variables $\Phi(u, \tau)$ also enters the theory. Taking into account that the number of clusters dN at any moment of time in an interval R to $R + dR$, and u to $u + du$ can be expressed in two ways as shown by the equation

$$dN = f(R,t')dR = f(R,t')R_c d(R/R_c) = \Phi(u,\tau)\,du \qquad (8)$$

it becomes evident that the connection between $f(R, t')$ and $\Phi(u, \tau)$ is of the form

$$f(R,t')R_c = \Phi(u,\tau) \qquad (9)$$

In the asymptotic stage of Ostwald ripening $\Phi(u, \tau)$ is shown by Lifshitz and Slezov [6–8] to become

$$\Phi(u,\tau) = N(0)e^{-\tau}P(u) \qquad (10)$$

where $P(u)$ is a universal time-independent cluster size distribution and $N(0)$ the number of clusters at the beginning of the coarsening process.

For diffusion-limited growth $P(u)$ has a shape as described [6–8] by

$$P(u) = \frac{3^4 e u^2 \exp[-3/(3-2u)]}{2^{5/3}(u+3)^{7/3}(3/2-u)^{11/3}} \qquad u \leqslant 3/2$$
$$P(u) = 0 \qquad u > 3/2 \qquad (11)$$

$P(u)$ fulfils the normalization condition

$$\int_0^\infty P(u)\,du = 1 \qquad (12)$$

Both Equations 3 and 6, underlying the original Lifshitz–Slezov theory, are purely deterministic equations and, consequently, stochastic effects are not incorporated in the theoretical description outlined so far.

3. Introduction of stochastic effects into the theoretical description of Ostwald ripening

In reality, deviations from the purely deterministic behaviour are always to be expected, connected with the intrinsically random character of the processes of transport of monomers to the cluster and of aggregation and evaporation of monomers to and from the cluster surface. Such stochastic effects can be introduced into the theory in the following way.

Applying the basic assumptions of classical nucleation theory, the evolution of the cluster size distribution can be described by a system of rate equations of the form [21–23]

$$\frac{\partial N(j,t)}{\partial t} = J(j-1,t) - J(j,t) \qquad (13)$$

$$J(j,t) = w^+(j)N(j,t) - w^-(j+1)N(j+1,t) \qquad (14)$$

where $N(j, t)$ is the number of clusters consisting at time t of j monomers. The coefficients of attachment $w^+(j)$ and detachment $w^-(j + 1)$ of single particles (monomers) reflect the specific mechanism of cluster growth and decay. For diffusion-limited growth in three spatial dimensions $w^+(j)$ can be determined on the basis of the stationary solution of the diffusion equation. As the result one obtains for perfect solutions (see e.g. [24–26] for details)

$$w^+(j) = 4\pi DcR(j) \qquad (15)$$

while w^- is usually determined via the condition of detailed balancing. D is the diffusion coefficient of the segregating particles in the matrix.

The condition of detailed balancing allows us to determine $w^-(j + 1)$ via Equation 16 as

$$w^-(j+1) = 4\pi DR(j)\exp\left[\frac{2\sigma}{c_\alpha k_B T}\left(\frac{1}{R(j)}\right)\right] \qquad (16)$$

where $R(j)$ is the radius of a spherical cluster consisting of j monomers. The relation between R and the monomer number j of a spherical cluster follows from simple geometrical considerations as

$$R(j) = \left(\frac{3}{4\pi c_\alpha}\right)^{1/3} j^{1/3} \qquad (17)$$

For the sufficiently large cluster sizes which we deal with in Ostwald ripening, the set of kinetic equations can be transformed into a Fokker–Planck equation [20, 27, 28] by a Taylor expansion of the terms $w^+(j)N(j,t)$ and $w^-(j+1)N(j+1,t)$, including second-order terms, to give

$$\frac{\partial N(j,t)}{\partial t} = -\frac{\partial}{\partial j}[v(j,t)N(j,t)] + \frac{1}{2}\left(\frac{\partial^2}{\partial j^2}[a(j,t)\,N(j,t)]\right) \quad (18)$$

Here the notations

$$\begin{aligned} v(j,t) &= w^+(j,t) - w^-(j,t) \\ a(j,t) &= w^+(j,t) + w^-(j,t) \end{aligned} \quad (19)$$

are used.

While the first term in Equation 18 describes the deterministically determined flow (the average growth rate) the second term reflects stochastic diffusion in cluster size space.

To allow a direct comparison of solutions of the set of Equations 18 and 19 with the results of the Lifshitz–Slezov theory, formulated in terms of the cluster radii and the respective distribution functions, Equations 18 and 19 may be rewritten in the following equivalent form:

$$\frac{\partial f(R,t)}{\partial t} = -\frac{\partial}{\partial R}[v_R(R,t)f(R,t)] + \frac{1}{2}\left\{\frac{\partial^2}{\partial R^2}\left[a_R(R,t)f(R,t) \times \left(\frac{d^2R}{dj^2}\right)^2\right]\right\} \quad (20)$$

with

$$v_R(R,t) = v(R,t)\frac{dR}{dj} + \frac{1}{2}a(R,t)\frac{d^2R}{dj^2} \quad (21)$$

$$a_R(R,t) = a(R,t)\left(\frac{dR}{dj}\right)^2 \quad (22)$$

In Equations 21 and 22 the monomer number j has to be replaced in the expressions for $v(j,t)$ and $a(j,t)$ by R according to Equation 17. For a solution of Equation 20 the boundary and initial conditions have to be specified. They can be expressed in the usual way as

$$\begin{aligned} N(j, t=0) &= 0 \quad \text{for } j \geqslant 2 \\ N(j > g, t) &= 0 \end{aligned} \quad (23)$$

Further parameters used in the calculations are summarized in the caption to Fig. 1.

In the figures are plotted not the distribution functions $f(R,t)$, but the distribution functions $P(u,\tau)$ normalized to unity. The connection between $f(R,t)$ and $P(u,\tau)$ is given by Equations 5, 7, 9 and 24. We have

$$P(u,\tau) = \frac{\Phi(u,\tau)}{N(\tau)} \quad (24)$$

where $P(u,\tau)$ is determined in such a way that for a purely deterministic description for $t \to \infty$ the Lifshitz–Slezov result, given in an analytic form by Equation 11, should be obtained.

4. Results and discussion

$\Phi(u,\tau)$-curves normalized to unity resulting from the numerical solution of Equations 20–24 for diffusion-limited growth are presented in Figs 1 and 3. In Fig. 1

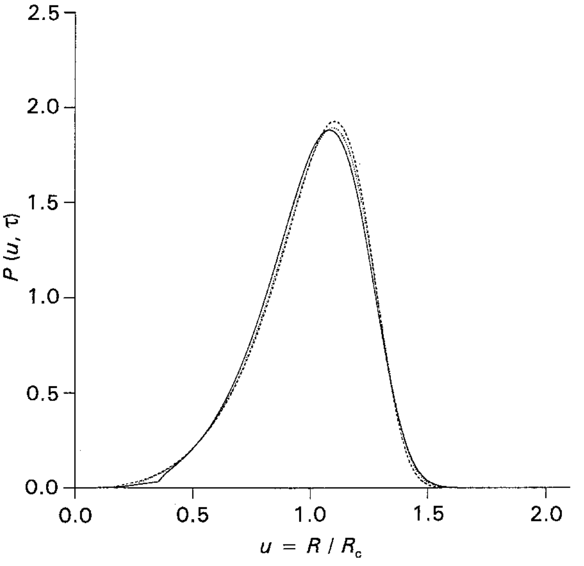

Figure 1. Different stages in the time evolution of the cluster size distribution as obtained from a numerical solution of the Fokker–Planck Equation 20. The initial distribution consists of monomers only. The different curves correspond to the following values of the reduced time: (——) $t' = 14$, (· · ·) $t' = 63$, (- - -) $t' = 260$. As can be seen, for large values of time a stationary distribution is approached. The following values are assigned to the parameters used in the calculations: $c_\alpha = 0.23 \times 10^{29}\ \text{m}^{-3}$, $D = 0.17 \times 10^{-17}\ \text{m}^2\,\text{s}^{-1}$, $\sigma = 0.08\ \text{N m}^{-2}$, $c = 0.86 \times 10^{26}\ \text{m}^{-3}$, c_β $(t = 0) = 0.86 \times 10^{28}\ \text{m}^{-3}$, $T = 730$ K. They are related to a segregation process of silver chloride particles in a sodium borate melt (for details of the experimental situation see e.g. [25]).

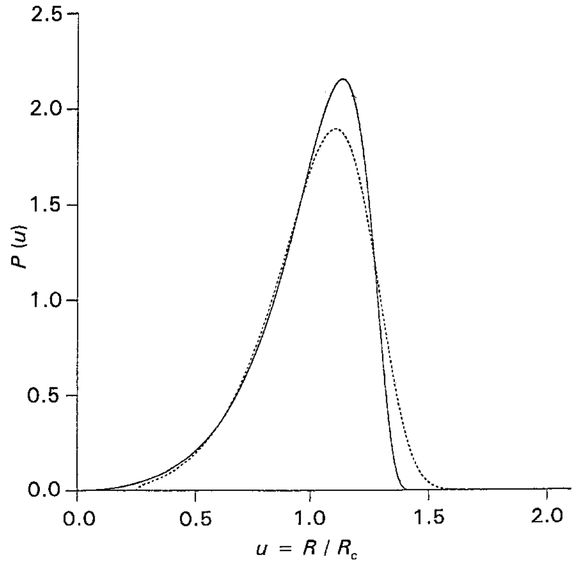

Figure 2. Comparison of (——) the Lifshitz–Slezov asymptotic distribution with (- - -) the stationary distribution obtained from the solution of the Fokker–Planck Equation 20 for large times. The incorporation of stochastic effects (thermal fluctuations) into the theory results in a broadening and a more symmetric shape of the curve as compared with the theoretical result given by Equation 11.

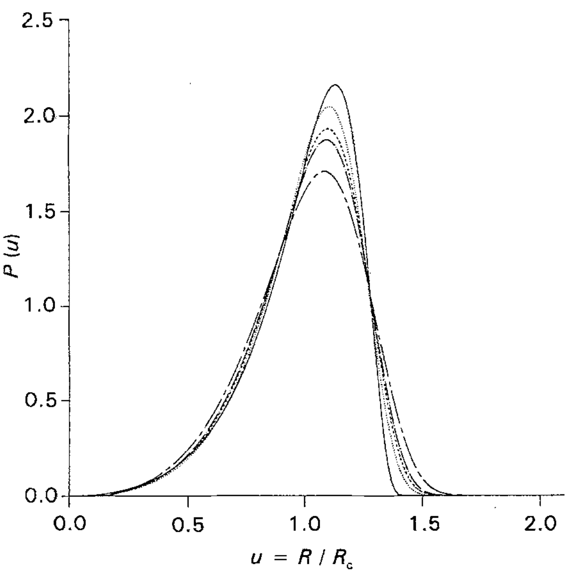

Figure 3. Asymptotic distributions obtained from the solution of the Fokker–Planck Equation 20 with a modified a_R-term ($a_R \rightarrow \alpha a_R$) in comparison with (——) the Lifshitz–Slezov analytical result given by Equation 11. The different curves correspond to the following values of the parameter α: (- - -) α = 1, (· · ·) α = 0.1, (—·—) α = 2, (— — —) α = 10. The curves shown correspond to a value of the reduced time $t' = 260$. For values of the other parameters see the caption to Fig. 1.

the distribution function is shown for different moments of time. It can be seen that for large values of time a time-independent cluster size distribution is approached. However, the shape of the distribution deviates from the form predicted by the Lifshitz–Slezov theory. This is illustrated in Fig. 2, where the curve numerically obtained for large times is compared with the analytic solution given by Equation 11.

Fig. 3 shows the results of similar numerical calculations but this time with a modified stochastic term, resulting from the original expression by a multiplication of a_R with a numerical factor α. Different values of α were chosen to demonstrate that the intensity of stochastic fluctuations is indeed responsible for the broadening of the distribution function observed in the numerical calculations.

Again, time-independent distributions are established in the course of the evolution. The degree of broadening of the shape of the distribution increases with an increase of the intensity of the thermal noise (increase of the value of α) and vice versa. Consequently, stochastic fluctuations in cluster size space lead, indeed, to a decrease of the gap between experimental results and theoretical description. A summary of experimental results which in this respect verify the statement made above can be found, for example, in the paper by Marder [19] (see also [10, 18]).

To avoid a misunderstanding we would like to underline, finally, that it is not the aim of the present contribution to distinguish stochastic on coarsening as the only possible mechanism for a broadening of the cluster size distribution. However, as shown, it has a significant influence on the shape of the distribution, at least, for intermediate time scales and has to be taken into account, consequently, if the relation between experimental and theoretical results is discussed. Moreover, this effect is always present independent of any other of the above-mentioned mechanisms which may or may not have an additional influence on coarsening. It will have a similar effect also for other mechanisms of cluster growth.

The significance of this effect and the shape of the asymptotic distribution may depend on the actual values of the thermodynamic parameters employed in the calculations for the system considered and, as shown, on the intensity of the thermal (or possibly also external) noise.

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