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Ostwald Ripening of precipitates and self similarity of size distributions in reaction controlled growth

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Abstract We present a mathematical model to describe competitive growth of spherical precipitates in reaction-controlled systems. In this model the flux of solute atoms through the interface depends on the interface migration velocity and on the differences of chemical potential at the interface. The growth-rate obtained is dependent on the precipitate radius, much like in the diffusion-controlled case. Numerical simulations were performed using a modified finite-difference approach where the time-step increase changes during evolution to avoid dissolution of more than one precipitate each step. By using the continuity equation we obtained an analytical function that represents the self-similar shape of the precipitate-size distribution dependent of the growth-parameter v. The effect of v on the coarsening evolution was investigated. Our results show that the precipitate size distribution obtained from the numerical simulations agrees well with the analytical solution. As predicted by the theory, we obtained the growth parameter ($v = 4$) and the temporal dependence of the mean-radius ($t^{1/2}$) different of the diffusion case, $v = 6.75$ and $t^{1/3}$. We also show that the self-similarity of the PSD is independent of the initial PSD.

Introduction

The competitive growth of second-phase particles, named Ostwald Ripening, is a common phenomenon that occurs in a variety of situations, as for example phase separation, solidification and ageing. Probably one of the best known examples is the growth of a finely dispersed distribution of metastable precipitates in solid state alloys. The knowledge and control of such phenomena are of great technological importance for applications like photoluminescence [1], properties of nanostructured materials [2], and in interconnection lines in microelectronic devices [3, 4], among others.

The process of Ostwald Ripening consists in the growth of large particles at the expense of the dissolution of small particles, and its driving force is the reduction in the total interfacial energy. The well-known classical quantitative description is due to Lifshitz and Slyozov [5] and Wagner [6], and is called the ''LSW'' theory (see Ref. [7] for a review). According to the LSW theory, the average length of particles increases linearly with time elevated to 1/3. For systems achieving long-time coarsening evolution, the precipitate size distribution (PSD) exhibits a self-similar behavior for a specific value of the growth parameter, $v = 6.75$. This theory presented for the first time the important characteristics of power-law evolution and dynamics scaling, that are nowadays considered as universally valid for first-order phase transitions.

The LSW is a ''mean-field'' theory, in which the precipitate evolution occurs via diffusive interaction with a mean solute concentration field. Assuming spherical precipitates, the solute concentration at the precipitate–matrix interface is given by the Gibbs–Thomson equation. The evolution of a given precipitate is a result of the balance between the Gibbs–Thomson concentration and

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the mean field concentration. There is always a particular radius, named critical radius, in which those concentrations have exactly the same values, resulting that precipitates with this length do not growth or dissolve. Precipitates larger than the critical radius will grow, while the smaller ones will dissolve. The theory is known to be valid for conservative and disperse systems. There were many efforts to improve the theory in order to best fit with experimental results [7, 8] considering diffusion-controlled growth.

The case of reaction-controlled growth has been much less investigated, since the introductory work of Wagner [6]. In a recent paper [3] we presented a collection of experimental results on the growth of Al–Cu metastable precipitates in the presence of a distribution of He bubbles in the matrix. We observed that there are many effects of the bubble system on the evolution of the precipitate system, some of them being expected to occur at the precipitate–matrix interface, where we observed a concentration of large gas cavities.

In his seminal work [6], Wagner presented an analytical function $f(r,t)$ for the description of the shape of the precipitate size distribution (PSD) for diffusion controlled-growth and reaction controlled-growth. Starting from the Gibbs–Thomson equation and from considerations of the continuity equation for $f(r,t)$, he obtained a general function for the description of both processes. Taking into account comparison between the parameters characteristic of diffusion (the diffusion coefficient D) and interface reaction (the reaction coefficient k) he was able to deduce a specific PSD for each process.

In this contribution we present a model for the description of Ostwald Ripening of precipitates in systems where the diffusion occurs faster than the reaction at the precipitate–matrix interface, i.e., reaction-controlled growth. Our model is based on fundamental physical concepts well established in the field of materials science, like interface mobility, chemical potential, and flux of atoms. Our model considers that the flux of atoms through the interface is proportional to the interface mobility and dependent on the difference of chemical potential, instead of concentration gradients. From these assumptions we obtained directly the equation of the precipitate growth-rate. We also obtained the function for the PSD, that is dependent of the growth parameter v. We studied the effect of this growth-parameter on the coarsening evolution and showed that the self-similarity occurs for a value of $v = 4$, while in the diffusion case it is well known that $v = 6.75$. On the other hand we showed that, independent of the shape of the initial PSD, self-similarity is always achieved after a transient regimen.

In the next section we present a derivation of the equation of growth-rate. Next we obtain the self-similar form of the PSD and compare it with Wagner's PSD. The following sections are devoted to numerical methods, discussions and conclusions.

Precipitate growth-rate

We consider a dispersion of spherical precipitates in an infinite matrix. The growth of a given precipitate is related to the velocity of the precipitate–matrix interface migration, given by [9]:

$$v = M\frac{\Delta\mu_{\mathrm{B}}}{\Omega_\beta} \tag{1}$$

where M is the mobility of the interface, $\Delta\mu_{\mathrm{B}}$ is the difference of chemical potential at the interface, and Ω_β is the atomic volume of β. The flux of atoms through the interface is:

$$j_{\mathrm{B}} = -M\frac{\Delta\mu_{\mathrm{B}}}{\Omega_\beta^2} \tag{2}$$

and the total flux across a spherical interface of radius r, that involves a precipitate of radius R is:

$$\vec{J} = \oint \vec{j}\cdot \mathrm{d}\vec{A} = -4\pi r^2 j_{\mathrm{B}} \tag{3}$$

The volume increase of a precipitate of radius R during a time interval dt is:

$$4\pi R^2\,\mathrm{d}R = 4\pi\Omega_\beta j_{\mathrm{B}} r^2\,\mathrm{d}t \tag{4}$$

Now, considering that the reaction occurs only at the interface, we can assume that $r = R$. Using Eq. 2 we obtain:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = -\frac{M\Delta\mu_{\mathrm{B}}}{\Omega_\beta} \tag{5}$$

The difference in chemical potential at the interface is given by the relation [9]:

$$\Delta\mu_{\mathrm{B}} = R_{\mathrm{g}}T\,\ln\left(\frac{C_i}{C_{\mathrm{e}}}\right) \approx \frac{R_{\mathrm{g}}T}{C_{\mathrm{e}}}(C_i - C_{\mathrm{e}}) \tag{6}$$

where R_{g} is the universal constant of gases, T is temperature, C_i is the solubility at the interface of the ith precipitate and C_{e} is the solute concentration in equilibrium with a flat interface. The solubility C_i depends on the interface curvature and is obtained directly from the linear approximation of the Gibbs–Thomson equation:

$$C(R) \cong C_\alpha^{\mathrm{e}}\left(1+\frac{2\gamma V_\beta}{R_{\mathrm{g}}TR}\right) \tag{7}$$

where γ is the surface free-energy and V_β is the atomic volume of β.

By substitution of Eq. 7 in Eq. 5 we obtain the growth-rate of the ith precipitate in terms of its radius:

$$\frac{\mathrm{d}R_i}{\mathrm{d}t} = 2M\gamma\left(\frac{1}{R_{\mathrm{e}}}-\frac{1}{R_i}\right) \tag{8}$$

A fundamental aspect of Ostwald Ripening theories is that there always exist precipitates that are in a steady state, i.e., not growing and not dissolving. This particular precipitate can be named ‘‘critical’’, in a sense similar to that of nucleation theory. Precipitates larger than the critical will grow, while the smaller ones will dissolve. This suggests that we can replace R_{e} in Eq. 8 by the critical radius R^*. Thus, our equation for the growth-rate becomes:

$$\frac{\mathrm{d}R_i}{\mathrm{d}t} = 2M\gamma\left(\frac{1}{R^*}-\frac{1}{R_i}\right) \tag{9}$$

Introducing the nondimensional quantities:

$$r_i = \frac{R_i}{R_0^*};\quad r^* = \frac{R^*}{R_0^*};\quad \mathrm{d}t' = \frac{2M\gamma\,\mathrm{d}t}{R_0^*}; \tag{10}$$

we obtain:

$$\frac{\mathrm{d}r_i}{\mathrm{d}t'} = \frac{1}{r^*}-\frac{1}{r_i} \tag{11}$$

Self-similar distribution function

One characteristic of competitive growth processes is the self-similar behavior of the PSD. In this section we present a derivation of an analytical equation that represents the shape of the self-similar PSD. The procedure we follow is very similar to the classical one applied by other authors [8, 10] for diffusion-controlled growth.

Defining a reduced-radius and a reduced-time:

$$\rho = \frac{r^*}{r_i};\quad \tau = \ln\left(\frac{r^*}{r_0^*}\right) \tag{12}$$

and using Eq. 11 we obtain

$$\mathrm{d}\rho = \frac{\rho-1}{\rho r^* \mathrm{d}r^*}\mathrm{d}\tau - \rho\mathrm{d}\tau \tag{13}$$

If we introduce a new quantity v, defined as:

$$v = \frac{2\mathrm{d}t'}{(r_0^*)^2} \tag{14}$$

we get:

$$\frac{\mathrm{d}\rho}{\mathrm{d}\tau} = \frac{1}{\rho}\left[v(\rho-1)-\rho^2\right] \tag{15}$$

If we assume that the total solute volume of the system is a conservative quantity, Eq. 15 should be zero. It is possible to show that conservation is satisfied if $\frac{\mathrm{d}\rho^3}{\mathrm{d}\tau}=0$ and $\frac{\mathrm{d}^2\rho^3}{\mathrm{d}\tau^2}=0$, from whish we obtain:

$v = 4.$

Integration of Eq. 14 gives:

$$\left(r_i^*\right)^2 - \left(r_0^*\right)^2 = 2\frac{t}{v} \tag{16}$$

That is, the variation of the square of the critical radius is linearly dependent of time. This result is very similar to that of the diffusion-controlled case, as discussed in the introduction. From Eq. 16, the introduced quantity v can be named ‘‘growth-parameter’’.

It is common to describe the Ostwald Ripening in terms of a distribution function $f(R,t)$, defined in such manner that $f(R,t)\mathrm{d}R$ represents the number of precipitates with radius between R and $R + \mathrm{d}R$ at time t. This function has to satisfy the following continuity equation in parameter space [6]:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial R}\left[f\frac{\partial R}{\partial t}\right] \tag{17}$$

The function $f(R,t)$ can be separated in two parts, one depending only on time, $T(t)$, and one depending only on particle size $F(\rho)$. The last one is the function we are interested. It satisfies a normalization condition:

$$\int_0^\infty F(\rho)\mathrm{d}\rho = 1 \tag{18}$$

During the coarsening evolution, solute supersaturation in the matrix tends to zero, which means that almost the total quantity of solute atoms are contained within the precipitates. Taking this in account and considering the reduced time defined in (12), Eq. 17 takes the form:

$$\frac{\partial(e^{-3\tau}F(\rho))}{\partial\tau} = -\frac{\partial}{\partial\rho}\left[\left(e^{-3\tau}F(\rho)\right)\frac{\partial\rho}{\partial\tau}\right] \tag{19}$$

Using Eqs. 15 and 18 we obtain:

$$F(\rho) = \frac{3\rho}{v(\rho-1)-\rho^2}\exp\left[\int_0^\rho \frac{3\rho}{v(\rho-1)-\rho^2}\mathrm{d}\rho\right] \tag{20}$$

This equation represents the shape of the self-similar PSD. Figure 1 presents the shape of this equation for various values of the growth-parameter v.

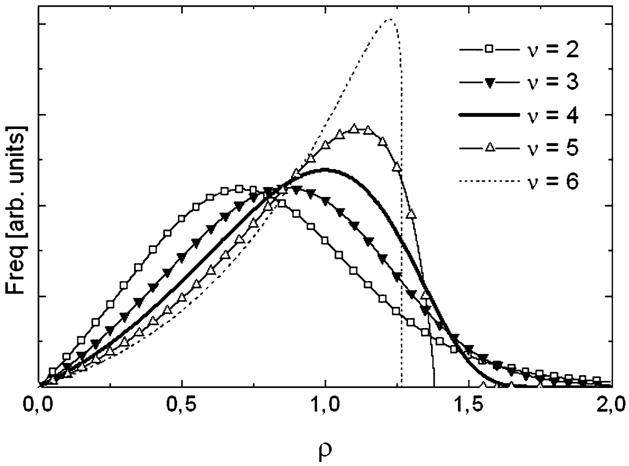

Fig. 1 Shape of the analytical distribution function—Eq. 20—for different values of the growth-parameter *ν*

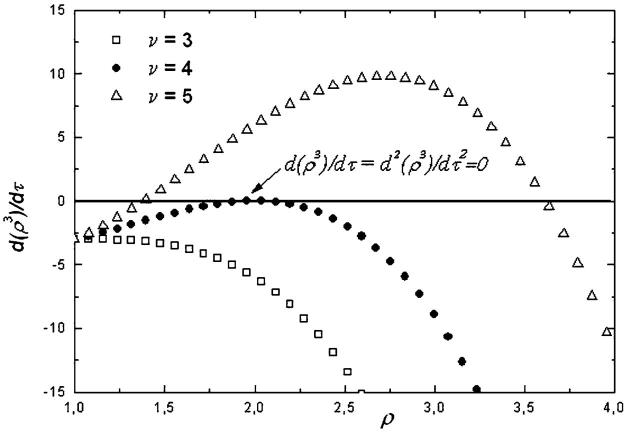

Fig. 2 Behavior of the derivatives of Eq. 15 for various values of *ν*

In Fig. 2 we present the behavior of the derivatives of Eq. 15 for various values of *ν*. It is possible to see that, as discussed above, solute conservation only is satisfied for $\nu = 4$.

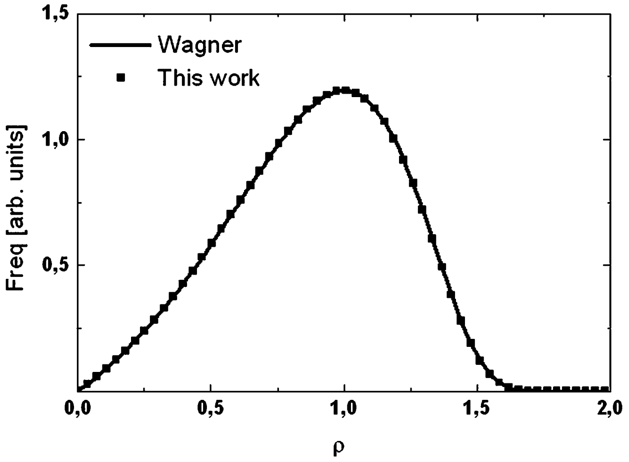

Fig. 3 Comparison of our PSD with Wagner's [6] PSD

In Fig. 3 we present a comparison of our PSD with that presented by Wagner [6]:

$$F(\rho,t) = \frac{K}{\left(1+\frac{t}{\tau_R'}\right)^2}\rho\frac{2^5}{(2-\rho)^5}e^{-\left(\frac{3\rho}{2-\rho}\right)} \tag{21}$$

where $\rho = r/r^* \leq 2$ and K is a integration constant defined to ensure normalization: $\int F(\rho,t)\mathrm{d}\rho = 1$. From Fig. 3, it is obvious that both PSD looks very similar. This indicates that it may be possible to obtain some physical relation between the two sets of parameters used. We live this question for a future contribution. Here we simply use Fig. 3 as a validation of our PSD and, consequently, of our model.

Numerical methods

In our simulations we used a modified finite-difference approach with a variable time-step. The radius of the *i*th precipitate is obtained from the scheme:

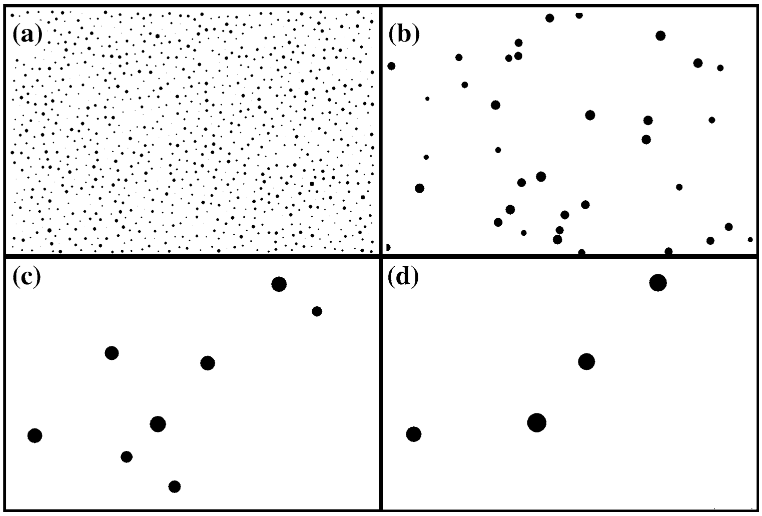

Fig. 4 Successive snapshots of our simulation showing the coarsening evolution

$$r_i(t' + \Delta t') = r_i(t') + \frac{dr_i}{dt'}\Delta t' \tag{22}$$

where the time-step $\Delta t'$ is calculated to avoid the dissolution of more than one precipitate each step, reducing numerical oscillations during simulation. Thus, if $r_{\min}$ is the radius of the smaller precipitate at time t':

$$0 = r_{\min}(t') + \frac{dr_{\min}}{dt'}\Delta t' \Rightarrow \Delta t' = -\frac{r_{\min}}{dr_{\min}/dt'} \tag{23}$$

Our simulation procedure follows the steps:

1. Generation of the initial PSD;
2. Calculation of the mean radius, smaller radius and critical radius;
3. Calculation of the time-step;
4. Calculation of the growth-rate for each precipitate;
5. Generation of the new PSD from step 4;
6. Back to step 2.

In addition, we performed a repopulation procedure each time the number of precipitates falls bellow statistical significance. This procedure is made in such a way to maintain the instantaneous shape of the PSD. Simulation goes on until the desired evolution time $t = \Sigma\ \Delta t'$ is achieved.

In the simulations, each precipitate of the initial PSD was distributed randomly in a two dimensional grid and its central position was fixed until it dissolves into the matrix. This may simulate a spatial dependence of the precipitate evolution, but we have to remember the mean-field character of the theory. That is, this is an artificial effect we introduced to guide the eyes during simulation.

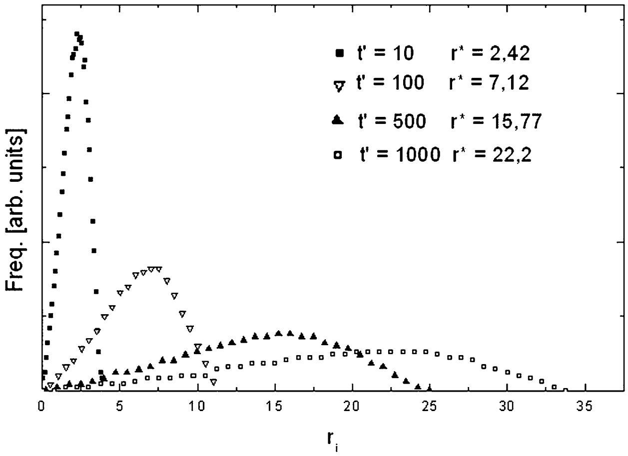

Fig. 5 Successive size histograms of the distribution for different values of the nondimensional variables t' and r^*

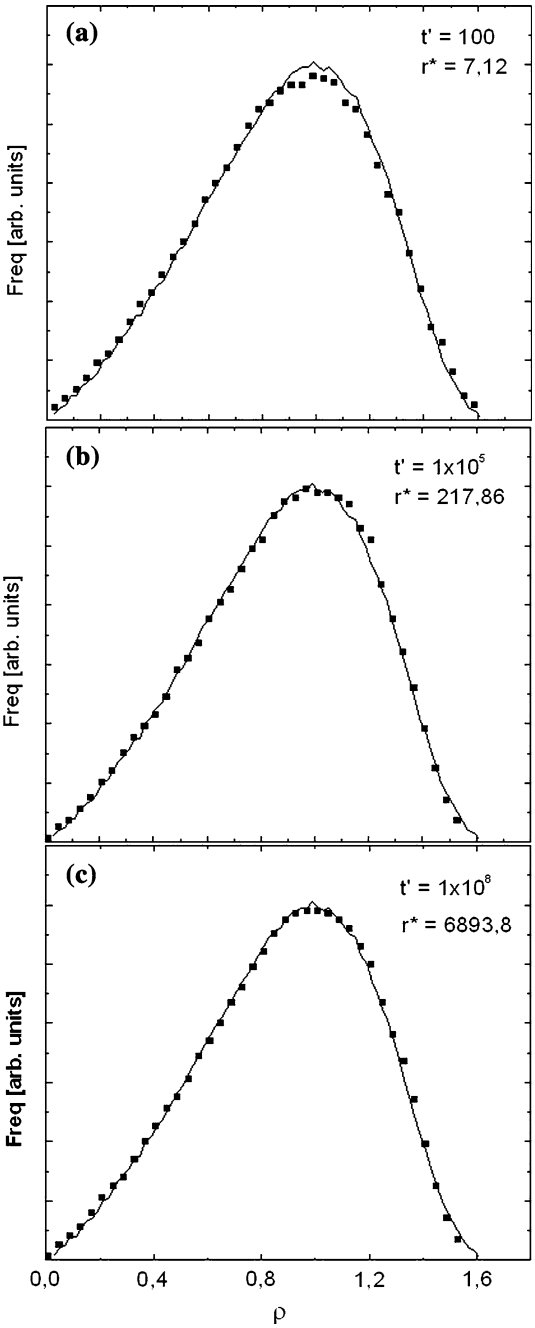

Fig. 6 Comparison between our numerical PSD with the analytical prediction for three different simulation times

Results and discussion

Figure 4 presents successive snapshots of our simulation. The initial distribution appears at $t' = 0$. It is possible to observe that the system evolves from an initial disperse system to a system with few larger precipitates. This is just a well known characteristic of Ostwald Ripening processes. It is possible to observe a very fast evolution of the system, which is expected due to Eq. 16, that is, the evolution of reaction-controlled growth is faster than in the diffusion case.

In Fig. 5 we show the successive size histograms of the distribution. We observe that the mean radius of the distribution grows together with the standard-deviation, which is also a characteristic of the OR evolution.

The self-similarity of PSD becomes apparent when we plot the same as in Fig. 5, but in terms of the reduced radius ρ. We used Eq. 20 to compare the PSD obtained from our numerical results with the predicted distribution. Figure 6 presents these results for three evolution times. It is possible to see that the numerical PSD quickly reaches the theoretical form and from this time on remains with the same shape.

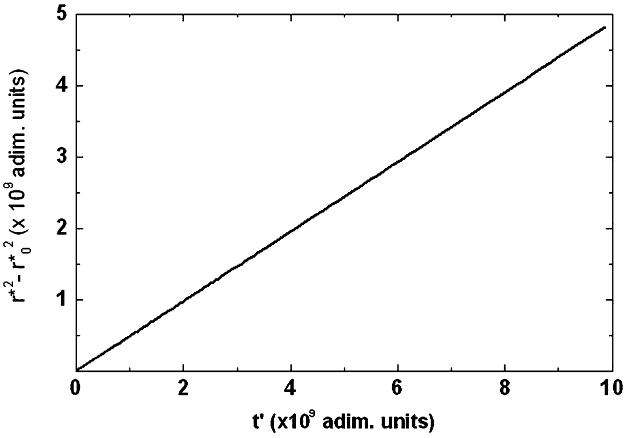

Fig. 7 Linear dependence of the square of the critical radius with time

In Fig. 7 we present a plot of the variation in the square of the critical radius as a function of time, showing that there is a linear dependence, in agreement with Eq. 16.

From Eqs. 10 and 14 it is possible to argue about the physical meaning of the growth parameter v, as a parameter that relates the critical radius with the interface mobility and the interface free energy. In this sense, $v = 4$ can be interpreted as the condition between interface mobility and interface free energy that has to be satisfied to reach self-similarity.

In the simulations, we used a initial PSD of the same shape of that predicted by Eq. 20. However, we also investigated the influence of different shapes for the initial PSD on the evolution. Figure 8(a–c) shows the evolution for an initial PSD with $v = 2$ compared to the self-similar PSD of $v = 4$. Figure 8(d–f) shows the same for $v = 6$. We observed that, no matter the form of the initial PSD, the numerical simulation always reaches the predicted shape after a sufficient evolution time.

Conclusions

Summarizing, we presented a model for the description of Ostwald Ripening of precipitates in reaction-controlled growth. Our formulation starts from the interface-migration velocity and from the consideration that the flux of solute atoms across the interface is dependent of the differences of chemical potential at the interface.

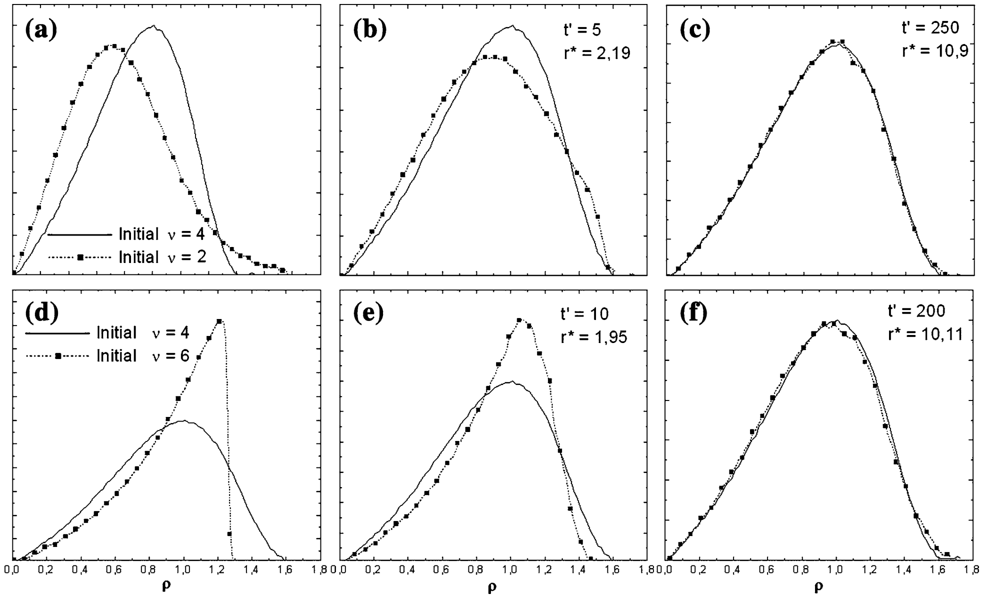

Fig. 8 Convergence of our numerical PSD for different shapes of the initial PSD. (**a**) Initial PSD with $v = 2$; (**d**) initial PSD with $v = 6$

We obtained the equation of precipitate growth-rate and the analytical form of the self-similar distribution function, dependent of the growth-parameter v. In our derivation we obtained the dependence of the critical radius with time as $t^{1/2}$ and the value of the growth-parameter of $v = 4$. The results of our numerical simulations agree well with the theoretical predictions. We investigated the effect of v on the coarsening evolution and showed that the self-similarity of the PSD does not depends on the initial PSD.

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