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Ripening with noise

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The process of ripening has been considered taking into account the noise from different sources, namely the scatter of compositions (supersaturation Δ) in the vicinity of precipitates and scatter of the Gibbs–Thompson term α. The evolution of the particle size distribution (PSD) has been investigated using parameters that characterize the width, sharpness and slope of the peak. Accounting for noise in our model produces a PSD that is closer to the experimental data compared with LSW theory.

Keywords: Ripening; Noise; LSW theory; Particle size distribution

1. Introduction

LSW theory [1–4] still remains the basis of our understanding of ripening. Yet experimentally observed particle size distributions (PSDs) at the asymptotic stage of ripening are usually broader than those predicted by LSW theory. There are different possible reasons for this [5–10]. There is one more reason, however, which seems to be obvious, but, to our knowledge, has not been investigated systematically, and that is noise. The aim of the present paper is to do this by simple simulations of the growth/shrinkage equations with noise terms for a large array of independent precipitates. In this analysis we do not take the short-range order and corresponding correlations into account—that is the subject of a separate paper. Therefore, our noise is of Gaussian type consisting of many independent contributions with additive dispersions.

The growth/shrinkage of each individual precipitate under the assumption of steady-state concentrations is determined by the well-known equation, which we write here for the ripening of almost pure element B in a weak solution:

$$\left.\frac{\mathrm{d}r}{\mathrm{d}t}\right|_{\rho} = \frac{D}{r^2}\cdot(r\cdot\Delta(t,\boldsymbol{\rho})-\alpha),$$

$$\Delta(t,\boldsymbol{\rho}) = C(t,\boldsymbol{\rho}) - C^{\mathrm{eq}}, \quad \alpha = C^{\mathrm{eq}}\frac{2\gamma\Omega}{kT}, \tag{1}$$

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where C^{eq} is the equilibrium concentration (atom fraction) at the planar interface, $C(t, \boldsymbol{\rho})$ is the local concentration at the 'point' with radius vector $\boldsymbol{\rho}$, where 'point' means a 'small' volume containing at least one precipitate, σ is the isotropic surface tension, Ω is the molar volume, and T is temperature.

Supersaturation here characterizes the vicinity of the precipitate with a characteristic length not less than the particle size r.

One can distinguish at least three possible sources of noise—the scatter of diffusivities D in the vicinity of precipitates due to local structure inhomogeneities in the parent phase, the scatter of the Gibbs–Thomson term α (due to surface tensions γ or c^{eq}, or T) and scatter of compositions (supersaturations Δ) in the vicinity of particles. In the following we analyse these types independently, constructing the corresponding algorithms for numerical simulations (sections 2 and 3). We start (section 2) with scatter of compositions since this factor seems to be unavoidable even for 'pure' experiments (long-term annealed alloys with minimal structure inhomogeneities, small lattice mismatch).

2. Noise of concentrations

The growth/shrinkage rate of each particle is determined, first of all, by local supersaturation in the vicinity. In LSW theory this supersaturation is considered to be some mean-field value, the same around each particle due to the very fast diffusive composition equilibration compared with the slow dynamics of ripening. In other words, the characteristic time of composition equilibration in some region of size λ (proportional to the interparticle distance) is much slower than the characteristic time of precipitate size evolution:

$$\frac{\lambda^2}{D} \ll \frac{\langle r \rangle^3}{D\alpha}, \quad t \to \infty. \tag{2}$$

However large λ becomes, λ^2 increases with time as $t^{2/3}$, and $\langle r \rangle^3$ increases with time as t^1, therefore, eventually (at the asymptotic stage), inequality (2) will hold. Strictly speaking, this argument is not correct, since inequality (2) does not indicate the equilibration of compositions, but just the rapid attainment of the steady-state concentration field. This field is, strictly speaking, not homogeneous due to the random distribution of precipitates serving as sinks/sources. Yet, as we will see below, if the number of particles in the λ region is large, their contributions to the concentration field almost compensate each other (noise is negligible), and the mean-field approximation works well. On the other hand, we will see that, in real experimental situations, the λ region cannot be regarded as large enough, and the noise factor becomes important (as well as the short-order correlations, but this is the subject of a separate paper).

One of the most important developments in ripening theory after LSW was the discovery of the screening effect [6, 7]. Since this effect seems to be crucial for an understanding of ripening problems, let us briefly review the main idea. The concentration field around each particle is modified by the surrounding particles, serving (in coarsened space scale $\boldsymbol{\rho}$ with $d^3\rho \approx L^3$, L being the half-distance between the centres of neighbouring particles) as a medium with sinks/sources. Therefore, in

this coarsened scale the diffusion equation for the concentration field around a particle can be written as

$$\frac{\partial C(t,\boldsymbol{\rho})}{\partial t} = D\nabla^2 C - \int 4\pi r^2 \frac{\mathrm{d}r}{\mathrm{d}t}\bigg|_{\rho} \cdot f(t, r|\boldsymbol{\rho})\,\mathrm{d}r, \tag{3}$$

with $f(t, r|\boldsymbol{\rho}) = f(t, r)$ being the PSD, normalized to the density of precipitates per unit volume,

$$\int f(t, r)\,\mathrm{d}r = n \approx \frac{1}{L^3}, \tag{4}$$

and $\mathrm{d}r/\mathrm{d}t|_{\rho}$ being determined by equation (1). Substituting equations (1) and (4) into equation (3), together with the steady-state approximation, gives

$$\nabla^2 C = 4\pi\left\{\int r\Delta(\boldsymbol{\rho}) f(t, r|\boldsymbol{\rho})\,\mathrm{d}r - \alpha n\right\}.$$

Now we assume (as a first-order approximation) the local supersaturation to be uncorrelated with size. Such an approximation is common in screening theories. Then the supersaturation can be extracted from the integral on the right-hand side of the last equation, which can now be expressed in terms of the average size

$$\nabla^2 C = 4\pi n(\langle r\rangle \Delta(\boldsymbol{\rho}) - \alpha).$$

We thus obtain the screening-type equation

$$\nabla_{\rho}^2\big(\Delta(\boldsymbol{\rho}) - \bar{\Delta}\big) = \frac{1}{\lambda^2}\big(\Delta(\boldsymbol{\rho}) - \bar{\Delta}\big), \quad \lambda = (4\pi n\langle r\rangle)^{-1/2}, \tag{5}$$

where $\bar{\Delta} = \alpha/\langle r\rangle$ (in standard LSW theory this would be a mean-field supersaturation), with a typical spherically symmetrical solution

$$\big(\Delta(\boldsymbol{\rho}) - \bar{\Delta}\big) \sim \frac{\exp(-\rho/\lambda)}{\rho}. \tag{6}$$

Here, λ is the screening length, which is more convenient for us to express in terms of the interparticle half-distance length L (size of the 'Wigner cell') and volume fraction f. From equation (5) we have $\lambda = (1/4\pi n\langle r\rangle)^{1/2}$. The density of particles per unit volume is $n = N/V = 1/(4/3)\pi L^3$ ($(4/3)\pi L^3$ is the 'elementary' volume per particle (on average), which we can consider as a sphere (or a cube, L^3)).Then,

$$\lambda = \sqrt{\frac{(4/3)\pi L^3}{4\pi\langle r\rangle}} = \sqrt{\frac{L^3}{3\langle r\rangle}}.$$

We neglect factors of the order of unity, and take

$$\lambda \approx \sqrt{L^3/\langle r\rangle} \approx \langle r\rangle \cdot f^{-1/2} = L \cdot f^{-1/6}. \tag{7}$$

The existence of a screening length means that each precipitate can 'feel' the existence of other precipitates only within the λ sphere. In other words, the randomly walking atom can reach the 'central' precipitate without being trapped by other precipitates only if it starts its migration within the λ sphere. The radius of the λ sphere as well as the number Z of particles ($Z \approx \lambda^3/L^3 \approx f^{-1/2}$) inside it increase with volume fraction f tending to zero. Of course, the screening effect exists for any volume fraction, but the above equations are valid for small volume fractions

only, when the screening length is much longer than the mean interparticle distance (see below). Only in this case can one use the coarsened space scale.

2.1. *Determination of the 'noise level'*

Let us first analyse the noise effect for the case of very small volume fractions, where we can use the coarsened space scale. Let us divide the space around some 'central' particle into concentric spheres of radii l and thickness $dl \ll 1$, but containing sufficient precipitates ('physically small volumes'). The number of precipitates inside each spherical slice is $n^*4\pi l^2 dl$. Each (kth) precipitate gives the following contribution to the deviation of the supersaturation around the central particle:

$$\delta C_1[k] = \frac{r[k]\cdot\Delta[k]-\alpha}{l}\exp\left(-\frac{l}{\lambda}\right) \approx \frac{r[k]\cdot\bar{\Delta}-\alpha}{l}\exp\left(-\frac{l}{\lambda}\right). \tag{8}$$

Here we treat $r[k]$ (and the corresponding $\delta C_1[k]$) as random values, uncorrelated with the central particle size and each other. The dispersion of contributions from individual particles is then equal to

$$\left\langle(\delta C_1)^2\right\rangle \approx \frac{\left\langle r^2\right\rangle\cdot\bar{\Delta}^2-\alpha^2}{l^2}\exp\left(-\frac{2l}{\lambda}\right) = \bar{\Delta}^2\cdot\frac{\left\langle r^2\right\rangle-\langle r\rangle^2}{l^2}\exp\left(-\frac{2l}{\lambda}\right) \tag{9}$$

(here we have used the relations $\langle r\rangle = \alpha/\bar{\Delta}$ and $\left\langle\delta C_1\right\rangle = 0$).

Since the contributions of all precipitates to the composition around the central particle are regarded as independent, the total dispersion will be the sum of the dispersions of the individual contributions

$$\begin{aligned}\left\langle(\delta C)^2\right\rangle &\approx \int_0^\infty dl\cdot 4\pi l^2\cdot n\cdot\bar{\Delta}^2\cdot\frac{\left\langle r^2\right\rangle-\langle r\rangle^2}{l^2}\exp\left(-\frac{2l}{\lambda}\right)\\ &= 2\pi\lambda n\bar{\Delta}^2\cdot\left(\left\langle r^2\right\rangle-\langle r\rangle^2\right) = \bar{\Delta}^2\cdot\frac{\langle r\rangle}{2\lambda}\cdot\left(\frac{\left\langle r^2\right\rangle}{\langle r\rangle^2}-1\right).\end{aligned} \tag{10}$$

In terms of volume fractions it translates into the following 'noise level':

$$\nu \equiv \frac{1}{\bar{\Delta}}\sqrt{\left\langle(\delta C)^2\right\rangle} \approx f^{1/4}\cdot\sqrt{\frac{\left\langle r^2\right\rangle}{\langle r\rangle^2}-1}. \tag{11}$$

The term in parentheses on the RHS of equation (10) characterizes the width of the size distribution, and for the LSW distribution it is equal to 0.0463 (the square root being 0.21).

Equations (10) and (11) demonstrate why a mean-field approximation should work well in the limiting case $f \to 0$ (LSW theory). The inputs of large numbers of precipitates from the λ sphere almost compensate each other, allowing the use of the concept of the unique average concentration.

The 'noise level', even for a volume fraction as small as 1%, should be 6.8%, which is important, especially in the vicinity of the critical size. Moreover, feedback will play a role—noise will broaden the PSD, and this broadening, in turn, makes the noise value even larger. Experimentally observed PSDs have a width (standard deviation) significantly larger than the LSW value of 0.21.

The above analysis was based on using the coarsened space scale with 'elementary volume' $1/n$ much less than the volume of the λ sphere. Such a continuous

description fails when the screening length λ is of the order of or less than $2L$, the average distance between neighbouring particles. From equation (7), one can see that this occurs if $f \leq f^* = (1/2)^6 \approx 0.016$. For volume fractions roughly equal to or greater than this 2% threshold, we should consider an L sphere instead of the λ sphere: each precipitate in this case interacts diffusively only with its nearest neighbours. Then

$$\left\langle (\delta C)^2 \right\rangle \approx Z \cdot \bar{\Delta}^2 \cdot \frac{\langle r^2 \rangle - \langle r \rangle^2}{L^2} \approx Z f^{2/3} \bar{\Delta}^2 \cdot \left(\frac{\langle r^2 \rangle}{\langle r \rangle^2} - 1 \right), \quad Z \propto 10^1, \tag{12}$$

so that the noise level will be

$$\nu \equiv \frac{1}{\bar{\Delta}} \sqrt{\left\langle (\delta C)^2 \right\rangle} \approx 3 f^{1/3} \cdot \sqrt{\frac{\langle r^2 \rangle}{\langle r \rangle^2} - 1} \tag{13}$$

(if one treats the nearest neighbours number Z as independent of volume fraction). For $f = 0.05$, this gives a noise level of 24%.

Intuitively, it appears evident that such a noise level should significantly influence the shape of the PSD. Below we present a simple model to investigate this influence.

2.2. *Computer model of noise concentration*

In accordance with the above arguments, we investigated the time behaviour of an array of N_0 particles (in our simulations $N_0 = 9000$), changing their sizes according to the following modification of classical equation (1):

$$\frac{\mathrm{d}r^3[i]}{\mathrm{d}t} = 3D \cdot (r[i] \cdot \Delta \cdot (1 + \varepsilon[i]) - \alpha), \tag{14}$$

with

$$\varepsilon[i] = \nu \cdot \sin(2\pi \cdot \mathrm{random}) \cdot \sqrt{\ln(1/\mathrm{random})}. \tag{15}$$

Equation (14) was written and solved for cubic size instead of linear size to prevent zero appearing in the denominator, when the particle disappears. Applying the phase volume conservation condition (at the asymptotic stage),

$$\sum \frac{\mathrm{d}r^3[i]}{\mathrm{d}t} = 0, \tag{16}$$

one obtains

$$\Delta = \frac{N\alpha}{\sum r[i] + \sum \varepsilon[i] \cdot r[i]} = \frac{\alpha}{\langle r \rangle + \langle \varepsilon r \rangle}. \tag{17}$$

Then, instead of equation (14) we use

$$\frac{\mathrm{d}r^3[i]}{\mathrm{d}t} = 3D\alpha \cdot \left(\frac{r[i] \cdot (1 + \varepsilon[i])}{\langle r \rangle + \langle \varepsilon r \rangle} - 1 \right), \quad 1 \leq i \leq N, \tag{18}$$

with N decreasing by 1 each time a particle disappears. To obtain better statistics, each time N becomes equal to $N_0/2$, we double the particle number by creating 'copies' of the remaining particles with very small deviations of $r[i]$ and $\varepsilon[i]$. Experimentally, this translates into viewing larger and larger volumes. The main

remaining problem is how to treat the time dependence of the noise. So far we have treated $\varepsilon[i]$ as constant in time.

A characteristic PSD (histogram) for a noise level of 0.5 is shown in figure 1 and is compared with the PSD predicted by LSW theory and experimental data, summarized by Marder [7]. Moreover, the PSDs obtained were characterized by special parameters characterizing the width, the slope of the peak and the sharpness, namely,

$$\text{standard deviation,} \quad s = \left(\left\langle (u-1)^2 \right\rangle\right)^{1/2},$$
$$\text{skewness,} \quad \text{skew} = \left(\left\langle (u-1)^3 \right\rangle\right)/s^3,$$

and

$$\text{kurtosis,} \quad K = \left(\left\langle (u-1)^4 \right\rangle\right)/s^4 - 3.$$

The ripening rate $k_{\text{gr}} \equiv (\langle r \rangle^3 - \langle r_0 \rangle^3)/t$ was found to be approximately constant (after some transient stage depending on the noise level (figure 2(*a*)). For the particles size distribution in LSW theory these parameters are $s = 0.215$, skew $= -0.920$ and $K = 0.675$. In ripening with noise we investigated the behaviour with time and calculated the asymptotical average values for different levels of noise (figures 2(*b*)–(*d*)). For the case of figure 1, we have $-s = 0.305$, skew $= -0.18$ and $K = -0.276$. These parameters were calculated from experimental PDSs for different systems [11, 12]. The summarized data are shown in table 1.

Moreover, for different values of parameter ν, the time dependence of the cube of the average radius was investigated. This dependence still remains linear with growth rate, depending on the noise level (figure 2(*a*)). The growth kinetics obtained by the use of computer modelling for different noise levels are shown in figure 3.

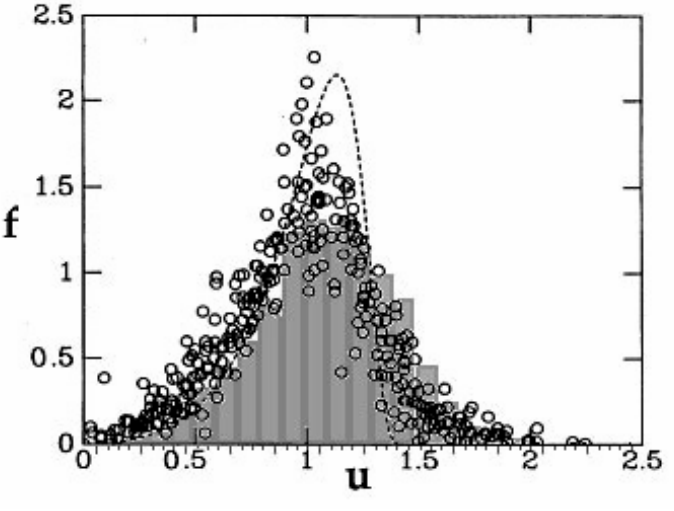

Figure 1. Particle distribution $f(u)$ versus scaled sizes $u = r/\langle r \rangle$. The ripening with noise (histogram) for the case $\nu = 0.5$ is compared with the predictions of LSW theory (dashed line) and experimental data summarized by Marder [7].

3. Noise of the Gibbs–Thomson factor α

It follows from the Gibbs–Thomson equation that the Gibbs–Thomson term may fluctuate due to the surface tension, equilibrium concentration (depending on the fluctuating temperature) and the temperature itself.

To investigate the process of the growth/shrinkage of particles we modified equation (1), giving the following form:

$$\frac{\mathrm{d}r^3[i]}{\mathrm{d}t} = 3D(\Delta \cdot r[i] - \alpha[i]), \tag{19}$$

where $\alpha[i] = \langle \alpha 0 \rangle \cdot (1 + \varepsilon[i])$.

Using the condition of volume conservation we have

$$\frac{1}{3D}\sum \frac{\mathrm{d}r^3[i]}{\mathrm{d}t} = 0 = \Delta \cdot \sum r[i] - \sum \alpha[i]. \tag{20}$$

Thus,

$$\Delta = \frac{\sum_{i=1}^{NN} \alpha[i]}{\sum_{i=1}^{NN} r[i]} = \frac{\langle \alpha 0 \rangle \cdot (1 + \langle \varepsilon \rangle)}{\langle r \rangle}. \tag{21}$$

Therefore,

$$\frac{\mathrm{d}r^3[i]}{\mathrm{d}t} = \left(\frac{r[i]}{\langle r \rangle} \cdot (1 + \langle \varepsilon \rangle) - (1 + \varepsilon[i]) \right), \quad 1 \le i \le N. \tag{22}$$

The behaviour of k_{gr}, s, skew and K for such a case is shown in figure 4.

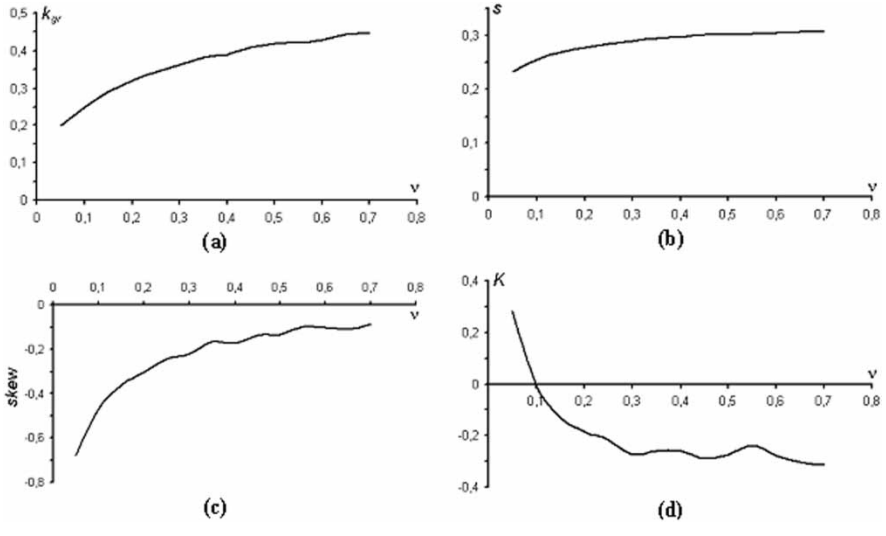

Figure 2. Rate of ripening k_{gr}, deviation s, skewness skew and kurtosis K versus noise level ν for the noise of concentration.

Table 1. Values of s, skew and K from the LSW theory, and experimental and modelling data.

	LSW theory	Ni–Ti [11]	Ni–Ge [11]	Ni–Si [12]	Noise of composition
s	0.215	0.294	0.292	0.26–0.29	0.305
skew	−0.920	0.308	−0.173	−0.6–0.5	−0.18
K	0.675	−0.216	−0.235	−1.2–0.2	−0.276

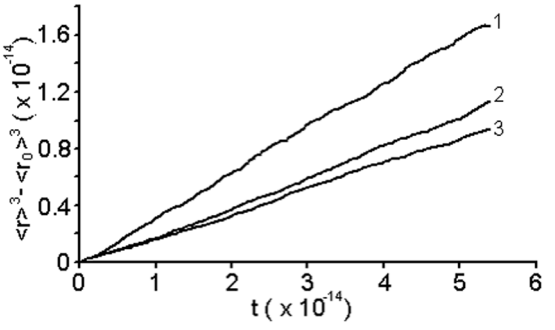

Figure 3. Time dependence of the average particle size: (1) $\nu = 0.5$; (2) $\nu = 0.1$; (3) $\nu = 0.05$.

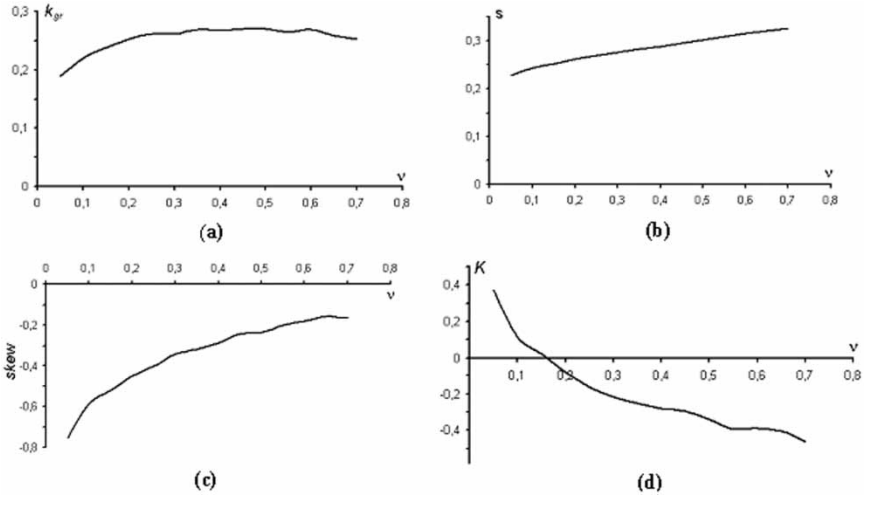

Figure 4. Rate of ripening k_{gr}, deviation s, skewness skew and kurtosis K versus noise level ν for the noise of α.

4. Conclusions

Thus, accounting for noise during ripening (with a reasonable noise level) produces PSDs that are much closer to experiment than the LSW theory. The main drawback of our model is the treatment of the noise terms as constant in time. The calculation of time correlations for noise will be considered elsewhere.

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