

межячеечного расстояния и скорости движения границы фаз в результате ячеистого распада на основании экспериментального исследования системы Pb-Sn при различных пересыщениях.

**Ключевые слова:** диффузия, миграция границ зерен, ячеистый распад, максимальность производства энтропии.

**Summary.** *Yu.O. Lyashenko, L.I. Gladka, O.A. Shmatko. Comparison of the different approaches to solution of the cellular precipitation inverse problem. For the description of the cellular precipitation of the supersaturated binary alloys the values of the interlayer distance and interface velocity are included as some combination in the solution of the mass transport problem. The additional model assumptions, which include the principle of the maximal rate of the free energy dissipation, are used for the separate determination of these parameters. In our work we present the comparison of the two approaches for the separate calculation of the interlayer distance and interface velocity, which are made on the basis of the experimental investigation of the lead-tin system at different levels of the supersaturation.*

**Keywords:** diffusion, grain boundary migration, cellular precipitation, maximum entropy production.

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## OSTWALD RIPENING REVISITED

*Standard theory of coarsening (Ostwald ripening) assumes a very small volume fraction of the precipitated phase. Yet, most experiments have been conducted under the condition of volume fractions  $f$  of at least several %. We call volume fraction “large” if a diffusive screening length is not more than an average interparticle distance ( $f$  larger than about 1%). In this case large compositional noise and short-range diffusive interaction invalids the LSW-type approach. To circumvent this crucial problem, we first reformulate the LSW basic growth/shrinkage equation in terms of “velocity = mobility  $\times$  driving force”. Then we apply the “normalized space approach”, developed recently for grain growth, to ripening with the mobility taken to be inversely proportional to particle size.*

**Keywords:** coarsening, diffusion, precipitation, size distribution, mean field analysis

### Introduction

Last stage of decomposition – Ostwald ripening – is usually described in the frame of LSW approach, developed 55 years ago, initially by Lifshitz and Slezov [1-3], and later by Wagner [4]. It predicts the  $t^{1/3}$  – law for mean particle size and the universal asymptotic (for  $t \rightarrow \infty$ ) size distribution,  $g(u)$  against the reduced sizes  $u = \frac{r}{\langle r \rangle}$ , independent on any physical parameter. Today, LSW theory still remains the base for our understanding of diffusion controlled coarsening and is used sometimes even for interpreting phenomena without long range diffusion as in grain growth [5]. Moreover, LSW-type approach has been used recently for interpreting flux-driven ripening during reactive diffusion [6] and for flux-driven grain growth during thin film deposition [7]. Despite so wide popularity, one of the two major LSW predictions contradicts most of available experimental results; the universal size distribution of LSW does not agree with the measured experimental particle size distributions (PSDs) while an excellent fit to the  $t^{1/3}$  - law for average size dependence exists [8-10]. The following explanations for this discrepancy have been offered: finite (non-zero) volume fraction  $f$  of the precipitating phase, annealing time not long enough to reach the asymptotic regime, possibility of direct collisions (and coalescence) of particles, as well as stresses in solid state ripening. Modifications of LSW theory for non-negligible volume fractions (see, for example, [11-13] and review [9]), as a rule, contradict the experimental data for solid state ripening by predicting an increasing growth rate for increasing volume fractions, which in fact is not observed. Here we present an attempt to formulate the criterion of what means a “large” volume fraction for ripening and to obtain a reasonable PSD for “large” volume fraction ripening. This attempt is based on approaching the ripening problem by decoupling the free energy of a central precipitate from the rest (reservoir) in the normalized space [14].

Below we formulate the criterion of “large” volume fractions on the basis of the concept of diffusive screening, developed in Ref. [15, 12]. In large volume fractions each precipitate can diffusively feel only its nearest neighbors, resulting in a strong short-range interaction and correlation within the Wigner-Seitz cell around the precipitate and in turn the large local compositional fluctuations among cells. Thus, the LSW approach becomes inapplicable in principle in large volume fraction ripening. Then, we reformulate the basic growth/shrinkage equation of ripening in terms of “velocity = mobility x driving force” approach. Then in, we demonstrate that the driving force on an arbitrary precipitate can be decoupled from the rest (the reservoir), if we treat thermodynamics of ripening in the normalized space with unit length, changing with time and proportional to mean size. It enables us to formulate the “velocity = mobility x driving force” relation in the normalized space with a mobility which is inversely proportional to size. We obtain a new growth/shrinkage equation of ripening and new PSD. Finally, we make comparisons to experimental data and discuss the limitations of the theory of ripening in normalized space (RNS).

**Criterion of large volume fraction in ripening**

One of the major developments of ripening theory after LSW was the discovery of diffusive screening effect [15, 12]. This effect seems to be crucial for understanding problems in ripening, so we discuss briefly here the main idea in it. The concentration field around each precipitate is modified by the surrounding precipitates, which serve (in coarsened space scale) as a medium with sources/sinks. Let  $C(t, \vec{\rho})$  be an atomic fraction of species B in a dilute solution of B in A, averaged over volume  $L^3$ , surrounding an arbitrary point  $\vec{\rho}$ , and  $L$  be approximately an average half-distance between the centers of neighboring precipitates (see below). In this coarsened scale the diffusion equation for concentration field around a precipitate can be written as:

$$\frac{\partial C(t, \vec{\rho})}{\partial t} = D \nabla^2 C - \int 4\pi r^2 \frac{dr}{dt} \Big|_{\rho} \cdot f(t, r | \vec{\rho}) dr \quad (1)$$

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

$$\int f(t, r) dr = n \approx 1 / (4\pi L^3 / 3), \quad (2)$$

and

$$\frac{dr}{dt} \Big|_{\rho} = \frac{D}{r^2} \cdot (r \cdot \Delta(t, \vec{\rho}) - \alpha), \quad (3)$$

$$\Delta(t, \vec{\rho}) = C(t, \vec{\rho}) - C^{eq}, \alpha = C^{eq} \frac{2\gamma\Omega}{kT}$$

for precipitation of almost pure elements in a dilute solution, where  $C^{eq}$  is solubility limit of solute (dimensionless) or the equilibrium concentration on a flat surface of the precipitated phase,  $D$  is diffusivity,  $\gamma$  is the surface energy per unit area of the precipitate,  $\Omega$  is atomic volume or partial molar volume of solute in the precipitate, and  $kT$  has the usual meaning of thermal energy. We note that we have used  $f$  to represent volume fraction, but in Eq. (1) we use  $f(t, r)$  to represent size distribution function.

Combination of Eqs.(1-3) with steady-state approximation for concentration gives:

$$\nabla_{\rho}^2 (\Delta(\vec{\rho}) - \bar{\Delta}) = \frac{1}{\lambda^2} (\Delta(\vec{\rho}) - \bar{\Delta}), \quad (4)$$

where

$$\lambda = (4\pi n \langle r \rangle)^{-1/2} \approx \sqrt{L^3 / (3 \langle r \rangle)} \approx \langle r \rangle \cdot f^{-1/2} = L \cdot f^{-1/6}. \quad (5)$$

In Eq. (5),  $f$  is defined as the volume fraction of ripening and  $f = \frac{\langle r^3 \rangle}{L^3}$  is the ratio of the volume of a precipitate and the volume of its Wigner-Seitz cell (see Discussion) or the ratio of the total volume of precipitates and the volume of the sample. Eq. (4) is a typical equation for screening with a typical solution of

$$(\Delta(\vec{\rho}) - \bar{\Delta}) \propto \frac{\text{Exp}(-\rho / \lambda)}{\rho}, \quad (6)$$

and  $\lambda$  is a typical screening length.

Existence of screening length means that each precipitate can feel the existence of other precipitates only within the  $\lambda$  - sphere. In other words, a randomly walking atom can reach

the “central” precipitate without being trapped by other precipitates only if it starts its walking within the  $\lambda$ - sphere. The radius of  $\lambda$ - sphere as well as the number  $Z$  of particles ( $Z \approx \lambda^3 / L^3 \approx f^{-1/2}$ ) inside it increases with decreasing volume fraction as  $f \rightarrow 0$ . This is the main reason why a mean-field approximation should work well in the limiting case  $f \rightarrow 0$  (LSW theory).

It can be shown (see Appendix A), that the “noise level” – the amplitude of composition fluctuations in each point  $\bar{\rho}$  (in each Wigner-Seitz cell around precipitate) relative to average super-saturation - is tending to zero with  $f \rightarrow 0$  as

$$v \equiv \frac{1}{\Delta} \sqrt{\langle (\delta C)^2 \rangle} \approx f^{1/4} \cdot \sqrt{\frac{\langle r^2 \rangle}{\langle r \rangle^2} - 1} = f^{1/4} \cdot s$$

where  $s$  is the standard deviation of size distribution. It means that the stochastic inputs of a large number of precipitates from almost infinite  $\lambda$ - sphere ( $f \rightarrow 0$ ) compensate each other almost completely, allowing us to use the concept of mean-field or average concentration, which is similar to the “rigid” order parameter  $\Psi$  in the superconductivity (due to overlapping of Cooper electron pairs). In LSW case of a very small volume fraction ripening, the super-saturation is such an order parameter. Yet, it is clear that if  $\lambda$  is less than the average distance  $2L$  between neighboring precipitates, each precipitate will feel only its nearest neighbors ( $Z \approx 6$  to  $12$ ), and the use of coarsened space scale will also fail. Another analogy is plasma. Due to the long-range character of electrostatic interaction (the same as diffusive interaction), the rarefied plasma can be well described by the mean-field Vlasov equations [16]. Yet, when plasma becomes condensed liquid or solid, the mean-field concept is no longer applicable since in the condensed phases each atom feels only its nearest neighbors. In ripening the role of atoms is played by Wigner-Seitz cells with the precipitate inside being the nucleus. When the fraction of the precipitate phase inside Wigner-Seitz cells exceeds some critical value, the diffusive interaction becomes trapped in the first coordination shell. In the following, we shall find this critical value.

Since  $\lambda$  and  $L$  are related by rather slow dependence ( $\lambda \approx L / f^{1/6}$ ), it means that the mean-field approximation fails at about

$$f \geq f^* \approx 2^{-6} \text{ (less than 2\%).} \quad (7)$$

Furthermore, we will treat Eq. (7) as the criterion of “large” volume fractions, for which the ripening theory should be different from LSW. We can find at least two major reasons at large  $f$  for crucial difference from LSW:

- 1) Non-negligible noise of concentrations around precipitate, and
- 2) Very strong correlations between the sizes of neighboring precipitates.

We shall treat the ripening with noise in a separate paper. Here we shall concentrate on the correlation effect, which was first systematically investigated by Marder [12] with  $f^{1/2}$  as a small parameter.

Under the condition in Eq. (7) of large volume fraction, each precipitate is able to exchange atoms only with the nearest neighbor precipitates due to a small screening length within its Wigner-Seitz cell. In other words, while the wall of the cell is transparent for

diffusing atoms, they are nevertheless trapped inside the first coordination shell of neighbors. The nearest neighbors form a cage. Each precipitate can grow only at the expense of its nearest neighbors. In this respect the situation is similar to the grain growth (GG) case, when each grain can grow only at the expense of its neighbors. In GG case grains touch each other, and in ripening case Wigner-Seitz cells touch each other. The difference is that the mobility in GG is usually treated as constant, but the mobility in ripening is inversely proportional to the size of precipitate due to the diffusive nature of interaction (see Section III). As we know, applying LSW-type approach to grain growth (e.g., by Hillert [5]) appeared to be unsuccessful since it has predicted a PSD, which is very far from experimental data. So, LSW theory is not applicable to ripening under the condition in Eq. (7) for large volume fractions. Moreover, the abovementioned short-range interaction between neighboring Wigner-Seitz cells leads to uphill-diffusion of sizes as shown in Appendix B.

### **LSW in terms of driving force and mobility**

Thus, there exist very fundamental reasons why LSW cannot be applied to  $f$  larger than few percents. In this situation, the expanding of Marder's correlation analysis [12] to higher orders of  $f^{1/2}$  does not seem to be a good idea, because as we have just shown, at  $f > f^*$ , the coarsened space scale is not applicable anymore, moreover, the convergence of corresponding series is also questionable. In other words, most probably, it is impossible to solve the ripening problem for large volume fractions by constructing any perturbation theory, based on LSW as a zero approximation. A different approach for large  $f$  is presented below.

It has been demonstrated recently [14] that a very reasonable grain size distribution under the normal grain growth mode in polycrystals can be derived if one applies the usual thermodynamic and kinetic arguments within a normalized size space, with the length scale in the normalized space being determined by the average grain size  $R$ . If we intend to apply the same approach to ripening, i.e., ripening in a normalized size space, we should at first reformulate the main growth/shrinkage equation of ripening theory as a relation between thermodynamic driving force and growth rate. In other words, this is a different approach in considering ripening and it may be convenient because in the case of strong nearest neighbor interactions, i.e., large volume fractions, the local super-saturation becomes a rather unpredictable function, so it is difficult to use mass balance to derive the growth/shrinkage equation.

The alternative form for ripening can be obtained from the original LSW growth/shrinkage equation of the precipitated phase:

$$\frac{dr}{dt} = \frac{D\alpha}{r} \cdot \left( \frac{1}{\bar{r}} - \frac{1}{r} \right) \quad (8)$$

We shall first examine how can this equation be interpreted from the thermodynamic point of view. We consider a system of  $N$  precipitates, consisting of a "central" precipitate of size  $r$  and the rest of  $N-1$  precipitates with a mean size  $\bar{r}$  as the "reservoir." The reservoir can be regarded as a mean-field for the central precipitate. Considering all the precipitates as spheres for simplicity, we have the constraint of constant volume of all the precipitates in the form:

$$V^{new} = \frac{4}{3}\pi(r^3 + (N-1)\bar{r}^3) = const, \quad (9)$$

(The volume is almost conserved, and just redistributed in ripening, leading to decreasing total interfacial area), so that if all the precipitates in the reservoir change equally, we have

$$d\bar{r} = -dr \left( \frac{r}{\bar{r}} \right)^2 \frac{1}{N-1}. \quad (10)$$

It means that a change of size of the “central” precipitate leads to a change of others due to the constraint of almost constant volume. While this change is small for each precipitate in the reservoir, it gives a non-negligible effect on the total surface:

$$dS^{total} = 4\pi \cdot d(r^2 + (N-1)\bar{r}^2) = 8\pi \left( \frac{1}{r} - \frac{1}{\bar{r}} \right) r^2 dr. \quad (11)$$

Thus, the driving force of the growth of the “central” precipitate is

$$-\frac{\partial F}{\partial V} = -\frac{1}{4\pi r^2} \frac{\partial F}{\partial r} = -\frac{\gamma}{4\pi r^2} \frac{\partial S^{total}}{\partial r} = 2\gamma \left( \frac{1}{\bar{r}} - \frac{1}{r} \right), \quad (12)$$

where  $F = \gamma S^{total}$  is a free energy of the whole system (chemical bulk energy is much smaller than surface energy,  $\frac{F^{chem}}{F^{surface}} \ll 1$ ), so the driving force is being just the difference of Laplace pressures between mean-field and the “central” precipitate. Then the basic growth/shrinkage equation can be represented in the standard “velocity = mobility x driving force” form, as it has been applied to normal grain growth problems [16, 5]:

$$\frac{dr}{dt} = M \left( -\frac{\partial F}{\partial V} \right), \quad (13)$$

By combining Eqs. (8), (12) and (13), we obtain the mobility (for the simplest case of ripening in a dilute solution):

$$M = \frac{D\alpha}{2\gamma} \cdot \frac{1}{r} = \frac{D\Omega C^{eq}}{kT} \cdot \frac{1}{r} = \frac{B}{r}, B = \frac{C^{eq} D\Omega}{kT}. \quad (14)$$

We recall that in the case of normal grain growth, the mobility has been taken to be constant. Thus, the main difference between normal grain growth and ripening is that in the latter case the mobility depends on size, which is quite clear due to the diffusive mechanism of growth/shrinkage of the precipitate. Thus, eqs.(12-14) are just another set of basic LSW equations but, as explained above, they can be used only for the case of very small volume fractions.

### Ripening in normalized size space

The driving force in Eq. (12) contains comparable inputs from both the central precipitate and the reservoir. Such coupling leads to cross-term effects between a precipitate and its surrounding, which are difficult to account for in the cases of large volume fractions. This basic difficulty can be circumvented, by using the normalized size space. Below we will repeat partly the main arguments of normalized size space concept, introduced in Ref. [14].

Let  $R(t)$  be some average characteristics of the system, being proportional to all kinds of averages of the same dimension. The proper choice of  $R$  will be made later to satisfy the constraint of constant total volume. We introduce a non-dimensional space with  $R$  being a unit length, furthermore we shall consider ripening in this space. In the following, we shall use the sign “ $\sim$ ” above a parameter to represent it in the normalized space.

During the ripening stage, the surface energy is much larger than the bulk chemical energy of a slightly supersaturated solution. In real space, the surface energy is given as

$$F = 4\pi\gamma \sum_{i=1}^N r_i^2,$$

In real space, the dimension of free energy is  $kg \cdot m^2 / s^2$ . In the normalized space the free energy is represented by  $\tilde{F} = \frac{F}{R^2}$ , with a dimension of  $kg / s^2$ ,

$$\tilde{F} = 4\pi\gamma \sum_{i=1}^N \tilde{r}_i^2, \tilde{r}_i = \frac{r_i}{R}. \quad (15)$$

In the framework of mean-field approach, we shall consider an arbitrary precipitate 1 as the “central” precipitate, and all the others as the reservoir:

$$\tilde{F} = 4\pi\gamma \left( \tilde{r}^2 + \sum_{i=2}^N \tilde{r}_i^2 \right) = 4\pi\gamma \left( \tilde{r}^2 + (N-1) \langle \tilde{r}^2 \rangle \right) \quad (16)$$

Since  $R$  is proportional to average size, the ratio  $\frac{\langle r^2 \rangle}{R^2} = \langle \tilde{r}^2 \rangle$  is constant. The number of precipitates  $N$  can be treated as constant when the change of size is infinitesimal. (This condition is changed in LSW cases of very small volume fractions – see Discussion.) Thus, the second term in Eq. (16) is constant, and the change of free energy of the central precipitate (defined in normalized size space) is independent on reservoir:

$$-\frac{\partial \tilde{F}}{\partial \tilde{V}} = -\frac{1}{4\pi\tilde{r}^2} \frac{\partial \tilde{F}}{\partial \tilde{r}} = -\frac{2\gamma}{\tilde{r}}. \quad (17)$$

The influence of reservoir will be present only after the transition back to real space:  $dF = R^2 d\tilde{F} + \tilde{F} dR^2$ .

Thus, in the normalized size space we have a base to use the linear relationship among driving force, mobility and velocity without cross-terms:

$$\frac{d\tilde{r}}{dt} = \tilde{M} \cdot \left( -\frac{\partial \tilde{F}}{\partial \tilde{V}} \right) = -\tilde{M} \cdot \frac{2\gamma}{\tilde{r}}. \quad (18)$$

The “minus” sign means that in the normalized size space it is thermodynamically favorable to decrease the size of any precipitate. In real space it translates to mean that even if some precipitate is growing, its growth rate is less than the rate of change of the mean size.

Here  $\tilde{M}$  is mobility in the normalized size space. It can be deduced from the mobility in real space by considering the dimensions in Eq.(14) and by taking into account that  $B$  in this equation has dimension of  $m^3 s^1 kg^{-1}$  ( $\tilde{D} = \frac{D}{R^2}$ ,  $\tilde{\Omega} = \frac{\Omega}{R^3}$ ,  $\tilde{\gamma} = \gamma$ ,  $\tilde{kT} = \frac{kT}{R^2}$ ):

$$\tilde{M} = \frac{\tilde{B}}{\tilde{r}} = \frac{B}{R^3} \frac{1}{\tilde{r}}. \quad (19)$$

Thus, we obtain the main growth/shrinkage equation of ripening in the normalized space:

$$\frac{d\tilde{r}}{dt} = -\frac{A}{R^3(t)} \cdot \frac{1}{\tilde{r}^2}, \text{ or } \frac{d\tilde{r}^3}{dt} = -\frac{3A}{R^3(t)}, \text{ or } \frac{d\tilde{v}}{dt} = -\frac{4\pi A}{R^3(t)}, \quad (20)$$

where  $\tilde{v} = \frac{4}{3}\pi\tilde{r}^3$  is the precipitate volume in the normalized space, and

$$A = B \cdot 2\gamma = D\alpha. \quad (21)$$

Considering the constraint of constant volume, we obtain,

$$0 \cong \sum_{i=1}^N \frac{d(R^3 \tilde{r}_i^3)}{dt} = R^3 \cdot N \cdot \frac{-3A}{R^3(t)} + \frac{dR^3}{dt} \sum_{i=1}^N \tilde{r}_i^3 = N \cdot \left( -3A + \frac{dR^3}{dt} \langle \tilde{r}^3 \rangle \right),$$

so that (taking into account that all average sizes in normalized space are constant)

$$\frac{dR^3}{dt} = \frac{A}{\langle \tilde{r}^3 \rangle} = \text{const} \text{ and therefore } \frac{d \ln R}{dt} = \frac{A}{\langle r^3 \rangle} = \frac{1}{3t}. \quad (22)$$

(the average cubed size depends on time linearly). In the real size space, we obtain the following expression for the growth rate:

$$\frac{dr}{dt} = R \frac{d\tilde{r}}{dt} + r \frac{dR}{dt} = \frac{A}{r} \cdot \left( \frac{r^2}{\langle r^3 \rangle} - \frac{1}{r} \right). \quad (23)$$

In classical LSW theory the critical size is just an average one. In our approach, as it follows from Eq.(23),  $r_{crit} = (\langle r^3 \rangle)^{1/3}$ .

Our approach remains of mean-field type, but it is now in the normalized space. This transition to normalized space provides some account of correlations in real space. Indeed, comparing Eq. (23) with LSW Eq. (8), the effective super-saturation around a precipitate depends on its volume size:  $\Delta(r) = \frac{\alpha \cdot r^2}{\langle r^3 \rangle}$  instead of  $\Delta = \frac{\alpha}{\langle r \rangle}$  in LSW. The larger the particle when it is compared with average size, the larger the effective super-saturation around it. It correlates with the fact that a large particle, in case of short-range interactions, has more chance to be surrounded by small precipitates, serving as its feeding base and therefore having higher concentration  $C^{eq} + \alpha / r$  around it. (See “uphill diffusion” of sizes in Appendix B.)

Substituting Eq. (20) into the continuity equation in the normalized space or Eq. (23) in real space gives:

For the normalized volume distribution

$$\frac{\partial \tilde{f}(t, \tilde{v})}{\partial t} = -\frac{\partial}{\partial \tilde{v}} \left( \tilde{f} \cdot \frac{d\tilde{v}}{dt} \right) = \frac{4\pi A}{R^3} \frac{\partial \tilde{f}}{\partial \tilde{v}}. \quad (24)$$

For the size distribution in real space

$$\frac{\partial f(t, r)}{\partial t} = -\frac{\partial}{\partial r} \left( f \cdot \frac{A}{r} \left( \frac{r^2}{\langle r^3 \rangle} - \frac{1}{r} \right) \right) \quad (25)$$



The scaling solution of Eqs. (24) and (25) are following (One can use, for example, the methods presented in Appendix B in Ref.[14] and in Sections 5-6 in Ref.[6] to obtain them.) :

$$\tilde{f}(t, \tilde{v}) = \frac{const}{R^3} \cdot \exp\left(-\frac{\tilde{v}}{\langle \tilde{v} \rangle}\right), \quad (26)$$

or, in real space of volumes,

$$f(t, v) = \frac{d\tilde{v}}{dv} f(t, \tilde{v}) = \frac{const}{\langle v \rangle^2} \cdot \exp\left(-\frac{v}{\langle v \rangle}\right) = \frac{const}{t^2} \exp\left(-\frac{v}{\langle v \rangle}\right), \quad (27)$$

or, in real space of linear sizes:

$$f(t, r) = \frac{const}{t^2} \cdot r^2 \exp\left(-\frac{r^3}{\langle r^3 \rangle}\right) \quad (28)$$

Since usually experimental data for PSD are presented over the reduced size  $u = \frac{r}{\langle r \rangle}$ , we will reformulate Eq.(28) for this representation. From Eq.(28) we obtain,

$$\langle r \rangle = \langle r^3 \rangle^{1/3} \cdot \frac{\int_0^{\infty} x^3 \cdot \text{Exp}(-x^3) dx}{\int_0^{\infty} x^2 \cdot \text{Exp}(-x^3) dx} = 0.89298 \langle r^3 \rangle^{1/3}, \quad \frac{\langle r \rangle^3}{\langle r^3 \rangle} = 0.712073. \quad (29)$$

Therefore the scaling part of PSD takes the following form:

$$g(u) = 2.13622 \cdot u^2 \cdot \text{Exp}(-0.712 \cdot u^3), \quad \int g(u) du = 1 \quad (30)$$

According to Eqs. (22, 29), the kinetics for average size is determined by

$$\langle r \rangle^3 = 0.712(3At) = 2.14 \cdot D\alpha \cdot t \quad (31)$$

One can compare the scaling part of PSD  $g(u)$  as the function of reduced size  $u$ , given by LSW (dotted lines) and our RNS (dashed lines) theories, at Figs. 1-3.

Finding the time dependence for average super-saturation in RNS is not so straightforward as in LSW theory since our approach is based on “velocity = mobility x driving force” relationship without direct use of super-saturation. Yet, as we have already mentioned, we can

treat  $\frac{\alpha \cdot r^2}{\langle r^3 \rangle}$  as effective super-saturation around individual particles. Then the average super-saturation in the matrix can be found as

$$\bar{\Delta} = \frac{\alpha \cdot \langle r^2 \rangle}{\langle r^3 \rangle} = \frac{\alpha}{\langle r \rangle} \frac{\langle u^2 \rangle}{\langle u^3 \rangle} = \frac{\alpha}{(2.14D\alpha \cdot t)^{1/3}} \cdot 0.806 = 0.626 \frac{\alpha}{(D\alpha \cdot t)^{1/3}}. \quad (32)$$

## Discussion

The main feature of the obtained size distribution in RNS is the absence of a sharp cut-off of the distribution function. Actually, the cut-off is one of the main discrepancies between LSW theory and experiments. So, our distribution is better in this aspect. Moreover, our distribution is not so sharp (in comparison with LSW) in the vicinity of the average sizes, which also agrees better with experiments.

To quantify the differences between RNS and LSW, we shall calculate the standard deviation in width,  $s = (\langle (u-1)^2 \rangle)^{1/2}$ , skewness  $Skew = (\langle (u-1)^3 \rangle) / s^3$  and Kurtosis (sharpness of the peak)  $K = (\langle (u-1)^4 \rangle) / s^4 - 3$ .

In LSW,  $s = 0.215$ ,  $Skew = -0.920$ ,  $K = 0.675$ .

In RNS we obtain  $s = 0.363$ ,  $Skew = +0.168$ ,  $K = -0.271$ .

In the following, we compare these numbers with some available experimental data.

In Ref. [18] the ripening of  $Ni_3Ti$ -presipitates in binary Ni-Ti alloys was investigated. Volume fractions varied from 1.73 % to 30.7 % (They are large according to our criterion in eq. (7)). The following “average” values were obtained:  $s = 0.294$ ,  $Skew = +0.308$ ,  $K = -0.216$ .

The datum for standard deviation does not seem to agree well with the RNS value. Yet, the averaging was made over all times from 1 to 64 hours, and the data at least for standard deviation clearly show the trend of increasing “s” with time. For example, for the alloy with  $f = 1.7\%$ , the standard deviation increases with time from 0.285 at 1 hour to 0.36 at 64 hours; for the alloy with  $f = 11.7\%$ , it increases from 0.275 at 1 hour to 0.37 at 8 hours, and 0.36 at 16 hours; and for the alloy with  $f = 24\%$ , it increases from 0.25 at 1 hour to 0.325 at 16 hours (no experimental points for longer annealing and for other alloys). As we can see, for long annealing times the “s” value is close to RNS prediction. Data for skewness in Ref. [18] are much more scattered (due to relatively small number of particles measured), but definitely they correspond to positive skewness instead of a negative one in LSW. Kurtosis values are also very scattered, but the “average” value (-0.216) is close to our predicted value of (-0.271).

Analogous experiments for ripening of  $Ni_3Ge$  precipitates in Ni-Ge alloys give  $s = 0.292$ ,  $Skew = -0.173$ ,  $K = -0.235$ . Yet, the statistics in this case is poorer (about 200 particles – just enough for average growth kinetics but not enough for reliable PSD).

In Ref. [19] the ripening of  $Ni_3Si$ -precipitates in binary Ni-Si alloys was investigated, giving  $s$  from 0.26 to 0.29 and very scattered data for skewness (from -0.6 to +0.5) and Kurtosis (from -1.2 to +0.2).

For more illustration, we present the data for ripening of ice in water (by heat diffusion), and of cementite, taken from the paper of Bitti and diNunzio [10], with superimposed curves of LSW theory, of Bitti-di Nunzio (BN) theory, and of our RNS theory in Figs. 1 and 2. In Fig.3 we superimpose our RNS-plot on the experimental data, summarized by Marder [12].

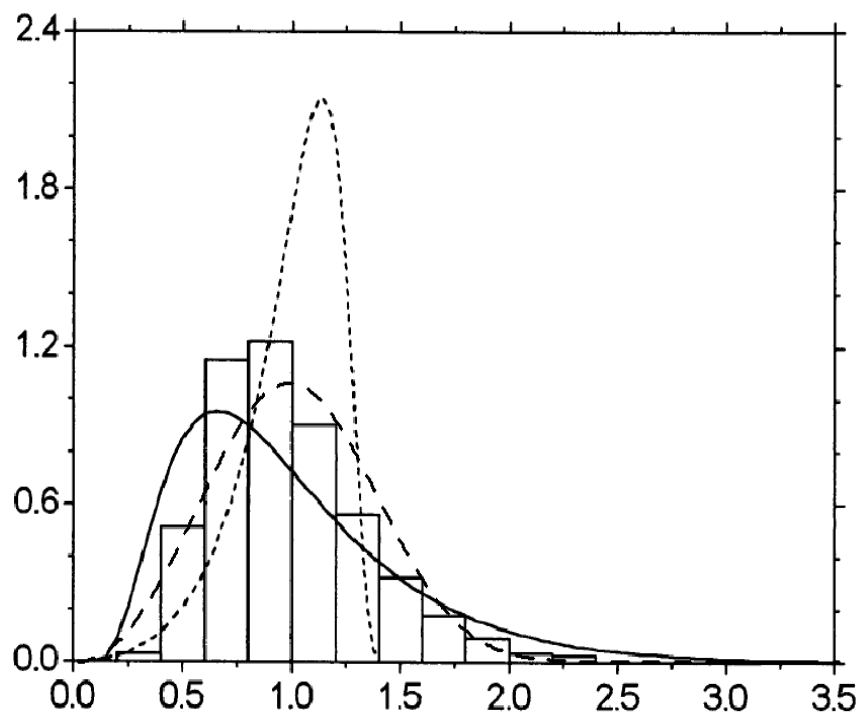


Fig. 1. Normalized PSD  $g(u)$  over reduced size  $u$  for ice ripening in water with superimposed LSW, BN and RNS-curves. Histogram – experimental data summarized by Bitti&Di Nunzio [10], dotted line – LSW theory, solid line –BN theory, dashed line - RNS theory.

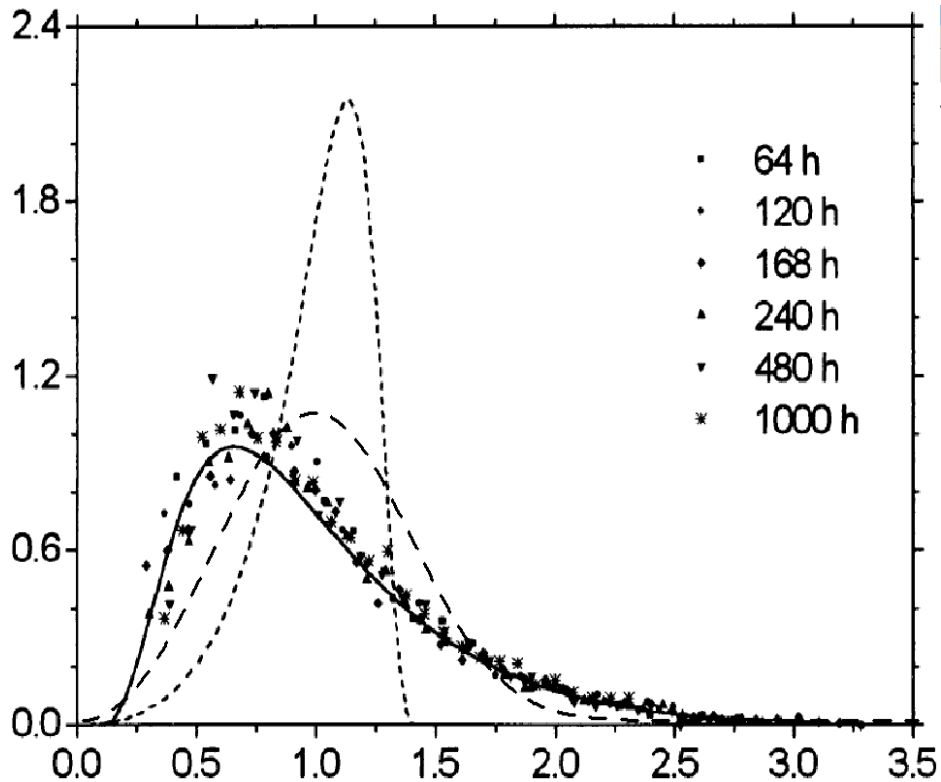


Fig. 2. PSDs for cementite ripening with superimposed LSW, BN and RNS-curves.

Scattered points –experimental data summarized by Bitti&Di Nunzio [10], dotted line – LSW theory, solid line –BN theory, dashed line - RNS theory.

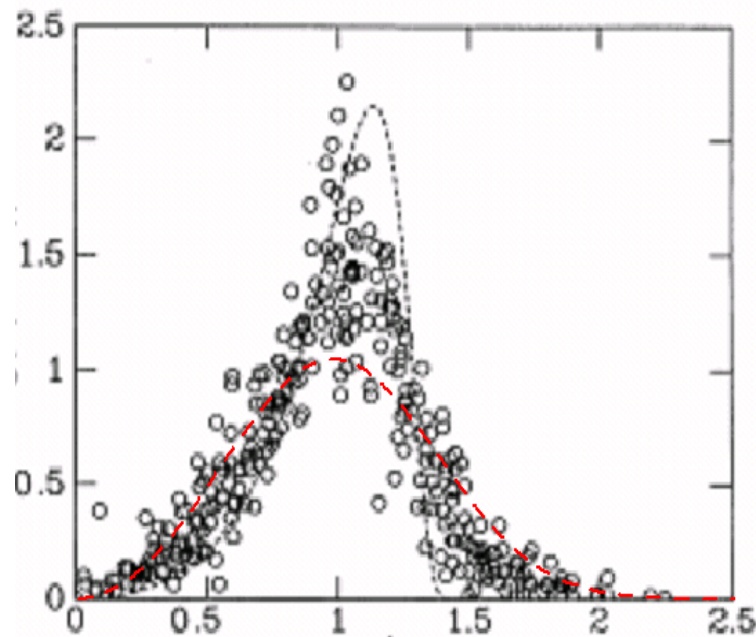


Fig.3. Experimental data, summarized by Marder [12] with superimposed LSW (dotted) and our RNS (dashed)-curves.

In the following, we shall discuss some general features and limitations of the RNS.

1. Our theory predicts the same linear time law for cubed mean size as LSW theory, differing only with pre-factor (2.14 in Eq. (31) instead of 4/9 in LSW).

2. Possible stress influence is not discussed here.

3. In our analysis the mobility as well as the driving force in normalized space do not depend on the volume fraction. So, in RNS the growth kinetics should not depend on  $f$ .

4. In our analysis of ripening in normalized space, we obtain the expression for driving force by decoupling free energies. As for mobility, we take LSW-mobility (though not used explicitly in the original LSW- papers) and recalculate it in new dimensions, corresponding to the normalized space.

5. We investigate only asymptotic regime of ripening, when scaling is already established. In this regime all characteristic lengths including screening length and average inter-particle distance (size of Wigner-Seitz cell) change proportionally, so that the number of cells inside  $\lambda$ - sphere remains constant (in our case of large volume fractions it is just one Wigner-Seitz cell).

6. As was pointed out by Ardell [11], if the volume fraction is really large (in geometric sense), precipitates can overlap the neighboring Wigner-Seitz cells, due to non-spherical shape and random space distribution. In our treatment we neglected these geometric considerations, being more interested in a general picture.

7. Universality of our PSD does not mean that RNS is applicable to all values of  $f$ . It is designed for the case of large volume fractions ( $f >$  few percents), when the mean free path of

diffusing atoms is about the size of Wigner-Seitz cell around the precipitate. Our approach cannot be applied to the limiting LSW case of  $f \rightarrow 0$ . We may indicate at least one mathematical reason why this is so. In our decoupling of surface energies in eq. (16), we treated the second term (reservoir) as constant, arguing that for infinitesimal change of the central precipitate, the other (N-1) precipitates have not enough time to change. It is okay for normal grain growth, as well as for large  $f$  in RNS, but it is not so for very small volume fractions in LSW. Indeed, let  $N$  be the number of precipitates in  $\lambda$  - sphere of influence. One can show that the ratio of the characteristic time for disappearance of one precipitate in this sphere to the characteristic time of change of average size tends to zero with  $f \rightarrow 0$ . It means, that in LSW-limit the  $N$  is changing so fast, that this fast blinking of  $N$  does not allow us to consider the contribution of reservoir to normalized energy as constant. Thus, in LSW limit the decoupling in normalized space fails. So, LSW and RNS are for ripening phenomena in different volume fractions. However, almost all experiments are usually made in RNS-region.

8. Our estimation of critical volume fraction is very approximate, due to very strong (sixth power) dependence of this value on the ratio of  $\lambda / L$  (see Eq. (5)). For example, if we don't neglect the factor 3 under the square root in Eq. (5) and take into account the difference between cubed average and averaged cube (see Eq. (29)), the critical volume fraction becomes significantly less - just about 0.1%. On the other hand, one can take as cross-over case  $\lambda = 3L$  (external boundaries of neighboring cells) instead of  $\lambda = 2L$ , and it will return us to about 1%. Yet, these possible changes of the large volume criterion don't change the presented picture.

9. We have formulated our analysis for the original LSW case of ripening of almost pure B precipitates in a dilute solution of B in A. So, in our equations  $D$  was just the diffusivity of B impurity in A, and  $\alpha = C^{eq} \frac{2\gamma\Omega}{kT}$ . These two parameters,  $D$  and  $\alpha$ , can be found from Eqs. (31, 32) by simultaneous measuring the rate parameters for mean size and average super-saturation:

$$k_{growth} \equiv \frac{\langle r \rangle^3 - \langle r_0 \rangle^3}{t} \cong 2.14D\alpha, \quad k_{comp} \equiv \frac{1}{(\Delta)^3 t} = 4.09 \frac{D}{\alpha^2}. \quad (33)$$

So, if the  $C^{eq}$  is known, the diffusivity  $D$  and surface tension  $\gamma$  can be determined.

10. In case of ripening of precipitates of intermediate phase in concentrated alloys, all main equations of presented model remain valid, but expressions for diffusivity and for  $\alpha$ , should be, of course, changed. In the case of LSW ripening, it was made by Calderon et al

[20] and Ardell et al [21]. Value of  $\alpha$  should be calculated as  $\alpha = \frac{2\gamma\Omega}{(C_{\beta}^{eq} - C_{\alpha}^{eq}) \cdot g_{\alpha}''}$  with  $g_{\alpha}''$

being the second derivative of Gibbs free energy per atom of the parent phase. As for rescaling of diffusivity, we should be cautious. According to Ardell et al [22], we should treat  $D$  as an interdiffusion coefficient, determined by the Darken's expression [23] with Manning's corrections [24]. Yet, Darken's approach is based on the account of Kirkendall shift of lattice planes. Mechanism of Kirkendall shift is the dislocation climbing in the

processes of vacancy generation and annihilation – building up of extra-planes in one part of the diffusion couple (containing the slower diffusing species) and dismantling of planes in another part (containing the faster species). In many cases [20,21], experiments are made in well homogenized alloys with inter-particle spacing not less than the mean free path of vacancy migration between sources and sinks. As was shown, for example in Ref. [25], in this case Darken's analysis is not applicable because the redistribution of species in mesoscopic regions between vacancy sources and sinks is governed not by Darken's interdiffusivity  $D_D = C_B D_A + C_A D_B$ , but instead by effective diffusivity

$$D_{eff} = \frac{D_A D_B}{C_A D_A + C_B D_B} \quad (\text{known, for example, from diffusion theory of ionic crystals}).$$

The main difference is that Darken's diffusivity in concentrated alloys is determined mainly by the fast species, but the effective diffusivity is determined by the slow species.

11. Alternative developments of LSW approach can be found in [26-28]

### Conclusion

Ripening cannot be described by one general theory for all possible volume fractions,  $f$ . LSW theory is correct for negligibly small  $f$ , and it can be modified in terms of perturbation theory for cases of still very small  $f$ . Yet, there exists a critical value of volume fraction (about 1 %), above which LSW is not to be used even with perturbation, because the screening length is reduced to inter-particle distance. For these "large" volume fractions (usually occurs in most experiments) each precipitate can exchange atoms only with nearest neighbors, and the ripening process becomes similar to grain growth but with the mobility inversely proportional to size due to diffusive nature of exchange. For the large volume fraction cases, we propose a new approach, based on translating the basic growth/shrinkage equations into "velocity = mobility x driving force" and a transition from real space to normalized size space. In the normalized space, the surface energy related driving force for an arbitrary particle can be decoupled from the rest of the reservoir. Thus, the concept of thermodynamics in normalized space enables us to take into account a cooperative character of ripening with only the nearest-neighbor diffusive interactions. The predicted PSD looks reasonable and fits experimental data (for "large" volume fractions) much better than LSW. The RNS's PSD has no cut-off. It is broader and less peaked, and it has a small positive skewness (instead of a large negative one in LSW).

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### Appendix A. Dependence of composition noise on volume fraction

We shall analyze the noise effect for the case of very small volume fractions, where we can use the coarsened space scale. We divide the space around a “central” particle into a series of concentric spheres of radii  $l$  and thickness  $dl \ll l$ , but containing enough precipitates (physically small volumes). The number of precipitates inside each spherical slice is  $n4\pi l^2 dl$ . Each ( $k$ -th) precipitate gives the following contribution to the deviation of super-saturation around the central particle:

$$\delta C_1[k] = \frac{r[k] \cdot \Delta[k] - \alpha}{l} \cdot \text{Exp}\left(-\frac{l}{\lambda}\right) \approx \frac{r[k] \cdot \bar{\Delta} - \alpha}{l} \cdot \text{Exp}\left(-\frac{l}{\lambda}\right). \quad (\text{A1})$$

Here we treat the  $r[k]$  (and corresponding  $\delta C_1[k]$ ) as random values, uncorrelated with the central particle size, also not between each other. The dispersion of contribution from one particle is then equal to

$$\langle (\delta C_1)^2 \rangle \approx \frac{\langle r^2 \rangle \cdot \bar{\Delta}^2 - \alpha^2}{l^2} \cdot \text{Exp}\left(-\frac{2l}{\lambda}\right) = \bar{\Delta}^2 \cdot \frac{\langle r^2 \rangle - \langle r \rangle^2}{l^2} \cdot \text{Exp}\left(-\frac{2l}{\lambda}\right). \quad (\text{A2})$$

(Here we used the relations  $\langle r \rangle = \frac{\alpha}{\Delta}$ ,  $\langle \delta C_1 \rangle = 0$ .)

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

$$\begin{aligned} \langle (\delta C)^2 \rangle &\approx \int_0^\infty dl \cdot 4\pi l^2 \cdot n \cdot \bar{\Delta}^2 \cdot \frac{\langle r^2 \rangle - \langle r \rangle^2}{l^2} \cdot \text{Exp}\left(-\frac{2l}{\lambda}\right) = \\ &= 2\pi\lambda n \bar{\Delta}^2 \cdot (\langle r^2 \rangle - \langle r \rangle^2) = \Delta^2 \cdot \frac{\langle r \rangle}{2\lambda} \cdot \left(\frac{\langle r^2 \rangle}{\langle r \rangle^2} - 1\right) = \Delta^2 \frac{\langle r \rangle}{2\lambda} \cdot s^2 \end{aligned} \quad (\text{A3})$$

with  $s$  being the standard deviation of size distribution (0.215 in LSW).

In terms of volume fractions it translates to the following “noise level”

$$\nu \equiv \frac{1}{\Delta} \sqrt{\langle (\delta C)^2 \rangle} \approx f^{1/4} \cdot s. \quad (\text{A4})$$

Eqs. (A3-A4) demonstrate why a mean-field approximation should work well in the limiting case  $f \rightarrow 0$ . The inputs of large amount of precipitates from  $\lambda$ - sphere almost compensate each other, allowing the use of the concept of average concentration. Note that one cannot just neglect the contributions from distant precipitates: in Eq. (A3) the input of

integral  $\int_L^\infty$  (from distant precipitates – small individual inputs, but a lot) is much larger than

that of integral  $\int_0^L$  (from nearest neighbors), if  $\lambda \gg L (f \rightarrow 0)$ .

The noise level even for  $f = 1\%$ , should be 6.8%, which is significant enough, especially in the vicinity of critical size. Moreover, the feedback will play its role – the noise

will broaden the PSD, and this broadening in turn will make the noise even larger.

Noise analysis above was based on using the coarsened space scale with “elementary volume”  $1/n$  much less than the volume of  $\lambda$  - sphere. Certainly, such continuous description fails when the screening length  $\lambda$  becomes of the order of or less than  $2L$ , i.e., the average distance between the neighboring precipitates (if  $f \geq f^* \approx (1/2)^6$ ). For volume fractions about or higher than this threshold, we should consider  $L$ - sphere instead of  $\lambda$  - sphere: each precipitate in this case is diffusively interacting only with its nearest neighbors. Then the noise level will be  $\nu \approx Z^{1/2} f^{1/3} \cdot s, Z \propto 10^1$  (more than 30% at  $f=10\%$ ).

### Appendix B. “Uphill diffusion” of sizes during ripening

To have some transparent physical picture of correlations, we shall analyze the following very simplified model of ripening of a precipitate with its nearest neighbors for an understanding of the kinetic process. Let the precipitates form the simple cubic lattice in space with a lattice parameter of  $2L$ , each precipitate being characterized by indexes  $(i, j, k)$  along axes  $X, Y, Z$  and size (radius)  $r[i, j, k]$ . For our case of “large”  $f$  the average supersaturation  $\Delta[i, j, k]$  around each precipitate is determined only by 6 nearest neighbors and can be taken as

$$\Delta[i, j, k] = \frac{\alpha}{6} \left( \frac{1}{r[i+1, j, k]} + \frac{1}{r[i-1, j, k]} + \frac{1}{r[i, j+1, k]} + \frac{1}{r[i, j-1, k]} + \frac{1}{r[i, j, k+1]} + \frac{1}{r[i, j, k-1]} \right) \quad (\text{B1})$$

Then the growth/shrinkage equation for  $(i, j, k)$  precipitate can be written as:

$$\frac{dr[i, j, k]}{dt} = \frac{D \cdot \left( \Delta[i, j, k] - \frac{\alpha}{r[i, j, k]} \right)}{r[i, j, k]} = \frac{D\alpha L^2}{6} \left( \frac{1}{L^2} \left( \frac{1}{r[i+1, j, k]} - \frac{2}{r[i, j, k]} + \frac{1}{r[i-1, j, k]} \right) + \frac{1}{L^2} \left( \frac{1}{r[i, j+1, k]} - \frac{2}{r[i, j, k]} + \frac{1}{r[i, j-1, k]} \right) + \frac{1}{L^2} \left( \frac{1}{r[i, j, k+1]} - \frac{2}{r[i, j, k]} + \frac{1}{r[i, j, k-1]} \right) \right) \quad (\text{B2})$$

Note, that the expressions in the brackets, in case of small differences between radii, can be interpreted as the second derivatives of curvature  $1/r$  over  $x, y$  and  $z$  in finite differences, and the expression in large brackets – as Laplacian of curvature in finite differences. Multiplying both sides of Eq. (B2) by  $-1/(r[i, j, k])^2$ , one obtains the finite-difference analogue of diffusion equation, but for inverse radii instead of concentration, and with negative effective diffusivity instead of positive one:

$$\frac{\partial}{\partial t} \left( \frac{1}{r(t, x, y, z)} \right) \approx -\frac{D\alpha L^2}{6r^2} \cdot \nabla^2 \left( \frac{1}{r} \right). \quad (\text{B3})$$

Equation (B3) is formally similar to uphill diffusion and it means that if some precipitate is growing, its neighbor will be most probably shrinking, making the local supersaturation larger (accelerating the growth of the “central” precipitate). Vice versa, a shrinking



precipitate will, most probably, have the growing neighbors, making local super-saturation smaller than the mean-field value. Certainly, we cannot use Eq. (B3) for quantitative analysis, since finite differences can be treated as derivatives only for smooth  $r(x, y, z)$  dependence. Yet, qualitatively it is clear that the mean-field approach in real space fails for “large” volume fractions, with a few percents treated as “large”.

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**Анотація.** *А.М. Гусак, К.Н. Ту. Ще раз про Освальдівське дозрівання. В той час як ЛСВ теорія оствальдівського дозрівання припускає дуже малу об'ємну частку фази, що виділяється, більшість експериментів проведені в умовах об'ємних часток принаймні в кілька відсотків. Ми називаємо об'ємну частку «великою», якщо довжина дифузійного екранування не перевищує середньої відстані між частинками ( $f$  більше за десь один відсоток). У цьому випадку шум концентрацій та ближні дифузійні взаємодії роблять підхід ЛСВ не валідним. Аби обійти вказану проблему, ми спочатку переформулюємо основне рівняння росту чи зменшення в ЛСВ теорії у вигляді «швидкість = рухливості, помноженій на рушійну силу». Далі ми застосовуємо підхід «нормалізованого простору», розвинутий нещодавно для росту зерен, до коалесценції. При цьому ми беремо рухливість обернено пропорційною розміру системи.*

**Ключові слова:** огрубіння, дифузія, осаджування, розподіл за розмірами, середньо-польовий аналіз.

**Аннотація.** *А.М. Гусак, К.Н. Ту. Еще раз об Освальдовском созревании. В то время как ЛСВ теория оствальдовського созревания предполагает очень малую объемную долю выделившейся фазы, большинство экспериментов проведены в условиях объемных долей по крайней мере в несколько процентов. Мы называем объемную долю «большой», если длина диффузионного экранирования не превышает среднего расстояния между частицами ( $f$  больше где-то, чем один процент). В этом случае шум концентраций и ближние диффузионные взаимодействия делают подход ЛСВ НЕ валидным. Чтобы обойти указанную проблему, мы сначала переформулируем основное уравнение роста или уменьшения в ЛСВ теории в виде «скорость = подвижности, умноженной на движущую силу». Далее мы применяем подход «нормализованного пространства», развитый недавно для роста зерен, до коалесценции. При этом мы берем подвижность обратно пропорциональной размеру системы.*

**Ключевые слова:** огрубение, диффузия, осаждение, распределение по размерам, средне-полевой анализ.

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