

Generalization of the Lifshitz–Slyozov–Wagner coarsening theory to non-dilute multi-component systems

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Abstract

The coarsening of precipitates in a matrix with a non-zero volume fraction is treated by assuming that the exchange of matter between the precipitates occurs by diffusion in the matrix within finite zones surrounding the precipitates. The thermodynamic extremal principle is used for the derivation of evolution equations for the precipitate radii. Accordingly, non-steady-state and steady-state distribution functions are deduced, depending on the system parameter characterizing the finite diffusion zones. The distribution functions tend exactly to the established Lifshitz–Slyozov–Wagner distribution for a zero volume fraction of the precipitates. The steady-state distribution functions are expressed by means of distinct volume-fraction-dependent parameters, which are presented by analytical expressions and in diagrams. To treat non-steady-state systems, ensembles of up to 10^6 precipitates can easily be handled by standard computational methods.

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1. Introduction

Nowadays, the understanding, modelling and simulation of structural materials, represented by multi-component and multi-particle (precipitate) systems, are a central goal in materials science research and the development of materials designed to meet specific properties. One of the most relevant topics in this field is the nucleation, growth and coarsening of precipitates, consisting of several components forming multiple stoichiometric phases (see Refs. [1–3] or the software systems Matcalc (<http://matcalc.tuwien.ac.at/>) and Thermocalc (<http://www.thermocalc.com/>)).

To handle such very complex systems, the evolution equations are usually given only for discrete parameters as follows. The precipitates are modelled as ellipsoidal

objects [4], in the simplest case as spheres with radii $R_k, k = 1, \dots, N$. Furthermore, the mean concentrations of the component $i, i = 1, \dots, n$ are assumed to be c_i^* in the precipitates of a given phase and \bar{c}_i in the matrix. Since the exchange of matter between the individual precipitates is only possible by a diffusive process, the tracer diffusion coefficients D_i of component i in the matrix must also be known. The diffusive process can be described following the leading differential equations, as recently summarized and described in detail in Refs. [5,6]. As the simplest case, Fick's laws 1 and 2 can be applied. The fluxes of the components are described as simple functions of the radial distance r from the centre of the precipitate and their divergences are either spatially constant quantities or zero in the steady-state approximation. Formulating the mass balances for the precipitates as well as for the matrix yields, for a dilute distribution of the precipitates (volume fraction $Z \rightarrow 0$) for R_k , the following equation, with t being the time

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and a dot denoting the time derivative, see e.g. Ref. [7] and later Ref. [8]:

$$\frac{dR_k}{dt} = \dot{R}_k = \frac{A}{R_k} \left(\frac{1}{R_c} - \frac{1}{R_k} \right). \quad (1)$$

The quantity A includes the interface energy γ of the precipitate and an averaged diffusion coefficient, see Section 2. The radius $R_c(t)$ is the so-called critical radius, since obviously for $R_k > R_c$ growth and for $R_k < R_c$ shrinkage of the precipitate k occurs. In accordance with observations, steady-state coarsening occurs, which can be expressed by the fact that the normalized distribution function, expressed in the variable $u_k = R_k/R_c$, remains constant in time. Here the ground-breaking works by Lifshitz and Slyozov [9] from 1958 and by Wagner [10] from 1961, and a following paper [11] by Hillert from 1965 must be mentioned. These researchers found that the conditions for the steady state provide explicit relations for the steady-state value of \dot{R}_c and the maximum value u_0 of u_k .

Eq. (1) can be rewritten in variables u (label k is omitted) as

$$\dot{u} = A \frac{(u-1)}{R_c^3 u^2} - u \frac{\dot{R}_c}{R_c}. \quad (2)$$

The necessary conditions for the steady state (see Refs. [9–11] for a detailed explanation) are given by

$$\dot{u}(u_0) = 0 \quad \text{and} \quad \left. \frac{\partial \dot{u}}{\partial u} \right|_{u_0} = 0. \quad (3)$$

The conditions of Eq. (3) also express that \dot{u} has a double root u_0 . Assuming A to be a constant, the solution of Eqs. (2) and (3) with respect to u_0 yields $u_0 = 3/2$ and the value of \dot{R}_c , and the critical radius $R_c(t)$ can be obtained by integration of \dot{R}_c as

$$R_c^3(t) - R_c^3(t = t_0) = \frac{4A}{9}(t - t_0). \quad (4)$$

The quantity $4A/9$ is very often denoted as the kinetic factor K or K_0 in the literature.

The steady-state distribution function $f(R, t)$ can be expressed in a form with $g(u)$ being independent of time (compare, e.g. Refs. [12,13]), as

$$f(R, t) = \frac{1}{R_c^4(t)} g(u). \quad (5)$$

The function $g(u)$ can be derived, based on the so-called continuity equation (see, e.g. Ref. [12]):

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R}(\dot{R}f) = \frac{\partial f}{\partial t} + \dot{R} \frac{\partial f}{\partial R} + \frac{\partial \dot{R}}{\partial R} f = 0. \quad (6)$$

The result is the very prominent Lifshitz–Slyozov–Wagner (LSW) distribution.

Finally, it should be mentioned that also a second way is open by the direct solution of the multi-particle/matrix diffusion problem. This has been shown by Voorhees and Glicksman (see their pioneering papers, Refs. [14,15]), using the potential-theoretic method. In this case the

diffusion boundary value problem for several spherical sources and sinks with individual potentials is solved, which allows a proper representation of the diffusional process in the matrix. Of course, the implementation of this concept is only possible within an adequately powerful computational framework.

For the sake of completeness it must be mentioned that, with permanently increasing computer power, the phase field method has been engaged to model individual multi-particle diffusion problems as a third applicable concept. Here, as rather early contributions, the papers by Wen et al. [16] and Ardell and co-workers [17] and the recent paper by Kundin and Rezende [18] can be referenced.

However, tools for the design of rather complex materials cannot deal with local details but should provide an overall picture of the microstructure and also have to include details of the nucleation of the precipitates, see e.g. Matcalc (<http://matcalc.tuwien.ac.at/>) or Ref. [3]. Consequently, a concept as outlined above leading to a generalized steady-state LSW-type size distribution function of precipitates for non-dilute systems is still of high actuality.

The goal of this paper is, therefore, to follow the procedure according to Eqs. (2–6) for a non-zero volume fraction Z of precipitates. The leading evolution equations for the individual precipitates are derived by application of the thermodynamic extremal principle (TEP), see Refs. [19,20] and for an overview see Ref. [7]. It is shown that from the evolution equations the rate of the critical radius as well as the steady-state distribution function for multi-particle, multi-component material systems can be derived in analytical form. Corresponding references to the open literature are given in Section 2.

2. Derivation of the growth rate \dot{R}_k for the precipitate k by application of the thermodynamic extremal principle (TEP)

The evolution equations for the diffusion-controlled coarsening of the precipitates in a multi-component system can be derived very effectively by application of the TEP (see, e.g., Refs. [7,8,19,20]). The necessary assumptions are:

1. the precipitates are approximated by spheres,
2. coarsening is driven by the reduction of the total Gibbs energy of matrix/precipitate interfaces,
3. the total volume of precipitates is conserved,
4. the interaction of precipitates by diffusion of components is ensured by overlapping spherical diffusion zones of radius L around all precipitates (later denoted as our concept) or of the radius $R_k + \beta_A R_c$ around the precipitate k (later denoted as the Ardell concept).

To account for a non-dilute volume fraction of precipitates in our concept it is necessary to develop an acceptable model for the diffusional zone radius L , which scales with the mean centre-to-centre distance of the precipitates. As during coarsening the volume fraction Z of the precipitates

conserves, and one can assume that the precipitate microstructure remains self-similar during coarsening, a dimensional consideration leads to

$$L/R_c = l = \kappa Z^{-1/3}, \quad (7)$$

where κ is a fitting parameter, which is obtained later (Section 3.1, last paragraph) by comparison of our results with those by Voorhees and Glicksman [14,15], specifically Fig. 18 of Ref. [15]. Furthermore, we assume that the non-dilute volume fraction reduces the effective diffusivity in the diffusion zone by a factor of $1 - Z$, as the precipitates can be considered as regions of substantially lower diffusivity compared to the matrix.

The total Gibbs energy G of the system is given by

$$G = 4\pi\gamma \sum_{k=1}^N R_k^2, \quad (8)$$

where γ is the specific Gibbs energy of matrix/precipitate interfaces. It should be mentioned that Cho and Ardell [21] argued that the elastic strain energy due to the misfit of the precipitates may eliminate nearly completely the influence of the volume fraction Z with the consequence that it should be considered in the total Gibbs energy. This, however, is in contradiction with the fact that the elastic strain energy scales with the total volume of the precipitates (see, e.g. the treatment by Fratzl et al. [22]), which is conserved during the coarsening process, and consequently the total elastic strain energy keeps constant. The volume conservation in the rate form reads as

$$\sum_{k=1}^N R_k^2 \dot{R}_k = 0. \quad (9)$$

To calculate the total dissipation, let us assume that there are spherically symmetric, sufficiently overlapping diffusion zones around all precipitates. The radii U_k of the zones, where the diffusion fluxes are assumed to be divergence-free, are given by $U_k = L$ in our concept or by $R_k + \beta_A R_c$ in the Ardell concept [23]. The radial diffusive flux $j_{ik}(r)$ of component i in the matrix surrounding the precipitate k is given by

$$j_{ik}(r) = (\bar{c}_i - c_i^*) \frac{R_k^2}{r^2} \dot{R}_k, \quad R_k \leq r \leq U_k, \quad (10)$$

which agrees with the flux in a Laplace-type diffusion field cell as applied by Marsh and Glicksman [24]. If an infinite mobility of the interfaces between the precipitates and the matrix is assumed, then the total dissipation Q in the system is only due to diffusion and is given by Ref. [19,20] as

$$Q = \frac{R_g T}{V} \sum_{k=1}^N \int_{R_k}^{U_k} 4\pi r^2 \frac{j_{ik}^2}{c_i^* D_i} dr, \quad (11)$$

where D_i is the tracer diffusion coefficient of component i in the matrix and $V = 1 - Z$ for our concept and $V = 1$ for the Ardell concept. Putting Eqs. (10) and (11) together and performing the integral one obtains for our concept

$$Q = \frac{4\pi\beta}{1-Z} \sum_{k=1}^N R_k^4 \left(\frac{1}{R_k} - \frac{1}{L} \right) \dot{R}_k^2 \quad (12)$$

and for the Ardell concept

$$Q = 4\pi\beta \sum_{k=1}^N R_k^4 \left(\frac{1}{R_k} - \frac{1}{R_k + \beta_A R_c} \right) \dot{R}_k^2 \quad (13)$$

with the material-related quantity β derived as $\beta = R_g T \sum_{i=1}^n \left[(c_i^* - \bar{c}_i)^2 / (\bar{c}_i D_i) \right]$.

With the volume conservation, Eq. (9), as a constraint the direct application of the TEP [8,19,20] provides the evolution equations of the precipitate radii for our concept:

$$\dot{R}_k = \frac{2\gamma(1-Z)}{\beta} \frac{1}{(1-R_k/L)R_k} \left(\frac{1}{R_c} - \frac{1}{R_k} \right), \quad (14)$$

and for the Ardell concept

$$\dot{R}_k = \frac{2\gamma}{\beta} \frac{1 + \beta_A R_k/R_c}{R_k} \left(\frac{1}{R_c} - \frac{1}{R_k} \right). \quad (15)$$

The critical radius R_c can be calculated by inserting the evolution equations (Eqs. (14) and (15)) in the constraint (Eq. (9)). In the case of our concept accounting for Eq. (7), R_c must be determined numerically due to the dependence of L on R_c via Eq. (7); for the Ardell concept the constraint leads to a quadratic equation for R_c .

Eqs. (14) and (15) can be rewritten in a general form as

$$\dot{R}_k = A z(R_k/R_c) \frac{1}{R_k} \left(\frac{1}{R_c} - \frac{1}{R_k} \right), \quad (16)$$

with the kinetic constant $A = 2\gamma V/\beta$ and the function $z(R_k/R_c)$ accounting for non-zero volume fraction of precipitates Z being $z(R_k/R_c) = 1$ for dilute systems ($Z = 0$, $L/R_c \rightarrow \infty$, $\beta_A \rightarrow 0$, LSW theory).

The function $z(R_k/R_c)$ becomes $1/(1 - R_k/L)$ for our concept and can be rewritten as $z(u_k) = 1/(1 - u_k/l)$ a parameter depending only on Z , see Eq. (7). Also other functions for $z(u_k)$, as well as other proposals for the dependence on Z , were suggested in the past. Ardell [23] used $z_A(u_k) = 1 + \beta_A u_k$ in 1972, which agrees exactly with our derivation leading to Eq. (15). In the following text, the subscript A is used for the Ardell concept. Brailsford and Wynblatt [25] applied a more detailed diffusion model in 1979, leading to a two-parametric function $z(u_k) = (1 + \beta_1(Z))/(1 + \beta_1(Z) - \beta_2(Z)u_k)$, which agrees with our $z(u_k)$ for $\beta_1(Z) = 0$ and $\beta_2(Z) = 1/l$. Tsumuraya and Miyata published an overview paper [26] presenting six different relations for $z(u_k)$ in 1983, which are principally either of the type suggested by Ardell or of our type. Brown [27,28], offered again a study on different types of $z(u_k)$ and showed that several types of particle size distribution functions exhibit a cubic growth law in the form of Eq. (4). Furthermore, the concept followed by Enomoto and co-workers [29–33] should be mentioned; this is based on statistical-mechanics diffusion-controlled droplet coarsening, considering the soft-collision process to meet the interaction of particles by means of surrounding diffusive fluxes. They presented

a dependence of the kinetic factor K , see Eq. (4) and below, on Z as $K(Z) = K_0(1 + \alpha\sqrt{Z})$, with α being a known coefficient (see also the comments below). Finally, it should be noted that Davies et al. [34] offered a different concept to include Z by adding a so-called “encountering term” to the continuity equation, see Eq. (6), and the discussion below Eq. (34). Two recent contributions with respect to $z_A(u_k) = 1 + \beta_A u_k$ are discussed in detail.

Pletcher et al. [35] gave a direct geometrical and physical interpretation to β_A as being approximately $\beta_A = \sqrt{3Z}$, according to the “diffusion screening length” $R_D = R_c/\sqrt{3Z}$. Of course, this consideration limits β_A by $\sqrt{3}$. As is shown in Section 3.1, however, mathematically sound results exist for any positive β_A .

The most recent contribution to this topic stems from Streitenberger [36] from 2013, who introduced for $z(u)$ the Ansatz $A_1 + A_2 + A_2 u$, which is equivalent to $z_A(u) = 1 + \beta_A u$ with $\beta_A = A_2/(A_1 + A_2)$ and the kinetic factor A in Eq. (16) replaced by $A/(A_1 + A_2)$.

It is interesting to note that the function $z(u_k)$, as derived according to our concept and also suggested by Brown in Ref. [28], is exactly in accordance for the case of a two-particle basis, with the results by Voorhees and Glicksman [14,15], compare Section 2, Eqs. (2.31)–(2.32) in Ref. [28] with Appendix A in this paper. Our quantity L corresponds to the ratio of the lattice parameter a_0 and the so-called Madelung constant in Refs. [14,15].

3. Steady state solutions

3.1. The steady-state condition

We skip again the subscript “ k ”, when it is not explicitly necessary. In the general case the evolution equation (Eq. (2)) can be written in the form

$$\dot{u} = Az(u) \frac{(u-1)}{R_c^3 u^2} - u \frac{\dot{R}_c}{R_c}. \quad (17)$$

The steady-state conditions of Eq. (3) then provide

$$\frac{A}{R_c^2 \dot{R}_c} z(u_0) \cdot (u_0 - 1) = u_0^3 \cdot \frac{A}{R_c^2 \dot{R}_c} \left(\left. \frac{dz}{du} \right|_{u_0} \cdot (u_0 - 1) + z(u_0) \right) = 3u_0^2. \quad (18)$$

Eliminating $A/R_c^2 \dot{R}_c$ yields

$$u_0(u_0 - 1) \left(\left. \frac{dz}{du} \cdot \frac{1}{z} \right|_{u_0} - 2u_0 + 3 \right) = 0. \quad (19)$$

Eq. (19) leads for our case to a quadratic equation:

$$u_0(u_0 - 1)/(1 - u_0) - 2u_0 + 3 = 0,$$

and for the Ardell case to an other quadratic equation:

$$1/(1/\beta_A + u_{0,A}) \cdot u_{0,A}(u_{0,A} - 1) - 2u_{0,A} + 3 = 0, \quad (20)$$

with the solutions

$$u_0 = \frac{1}{3} \left(2 + l \left(1 - \sqrt{1 - 5l - 4/l^2} \right) \right), \quad l \geq 4, \quad (21)$$

$$u_{0,A} = 1 + \left(\sqrt{1 + (1 + \beta_A)\beta} - 1 \right) / \beta_A, \quad \beta_A \geq 0. \quad (22)$$

The following limiting cases can be distinguished: the LSW case for $Z \rightarrow 0$, $l \rightarrow \infty$, $\beta_A \rightarrow 0$ yields

$$u_0 = 3/2 + 3/25l, \quad u_{0,A} = 3/2 + \beta_A/2. \quad (23)$$

As one can immediately see from Eq. (22), the steady-state solution exists in our case only for $l \geq 4$; however, no upper limit exists for β_A . Then $l \rightarrow 4$ and $\beta_A \rightarrow \infty$ yield

$$u_0 = 2(1 - \sqrt{\Delta l/3}) \text{ for } l = 4 + \Delta l, \quad 0 \leq \Delta l \ll l, \quad u_{0,A} = 2 - 1/\beta_A. \quad (24)$$

The evolution equation for R_c can now directly be calculated from Eq. (18)₁ as

$$\frac{dR_c^3}{dt} = \frac{3Az(u_0)(u_0 - 1)}{u_0^3}, \quad (25)$$

yielding

$$R_c^3(t) - R_c^3(t = t_0) = \frac{3Az(u_0)(u_0 - 1)}{u_0^3} (t - t_0). \quad (26)$$

The multiplier of $(t - t_0)$ on the right-hand side of Eq. (26) can be compacted into a single kinetic factor $K(l)$ or $K(Z)$, see Eq. (4) and the text below. Voorhees and Glicksman offered in Fig. 18 of Ref. [15] relative kinetic factors $K(Z)/K_0$ (K_0 is the kinetic factor for the LSW concept) as functions of Z according to the derivations of several authors as listed above. In a later review paper from 1992, Voorhees [37] compared again several results from the past in Fig. 3 there. The results by Voorhees et al. can be considered as key results due to their derivation from a multi-source/sink diffusion problem and lead, in the tendency, to the lower curves compared to those stemming from the concepts above. A further diagram was provided in Chapter 10.4, Fig. 4 of the book by Sahm et al. [38], demonstrating also the curves by Voorhees and Glicksman as the lower ones.

We calibrate now the fitting parameter κ in the relation $l = \kappa Z^{-1/3}$, see Eq. (7), in such a way that our ratio $K(Z)/K_0$ for the limiting value $l = 4$ is identical to that by Voorhees and Glicksman, Fig. 18 of Ref. [15]. With the right-hand side of Eq. (26) and $u_0 = 2$ for $l = 4$ we find $K(Z)/K_0 = (1 - Z)27/16$. Using this linear relation in Fig. 18 of Ref. [15] leads to $Z = 0.095$ and finally to $\kappa = 1.825$. The calibration can be demonstrated in Fig. 1, where the dependence of $K(Z)/K_0$ is plotted vs. the volume Z using the kinetic constant in Eq. (26) for our concept as well as the Ardell concept with $\beta_A = \sqrt{3Z}$ from Pletcher et al. [35]. Both concepts are compared with data by Voorhees and Glicksman [15] and Voorhees [37]. Fig. 1 demonstrates also that our concept delivers a steady solution only for $Z \leq 0.095$. It may also be of interest that all recent theoretical concepts show a vertical tangent of the $K(Z)/K_0$ curve

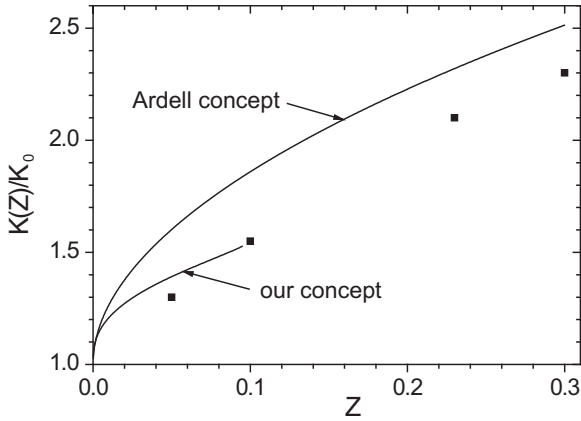


Fig. 1. Dependence of the relative kinetic factor $K(Z)/K_0$ for our concept and the Ardell concept with $\beta_A = \sqrt{3Z}$ (Pletcher et al. [35]) vs. the volume fraction Z . Full squares are due to data provided by Voorhees [15,37].

at $Z = 0$, which need not to be the case for data provided by Voorhees and Glicksman [15] and Voorhees [37].

3.2. The steady-state distribution function

First, we would like to remark that the derivations below are valid for any case of $z(u)$, and no distinction between the different concepts is necessary.

To derive the steady-state distribution function one can start with the distribution function in the form of Eq. (5). Then the individual terms in the continuity equation, Eq. (6), can be expressed as

$$\frac{\partial f}{\partial t} = -\frac{4}{R^5} g \dot{R}_c + \frac{1}{R^4} \frac{dg}{du} \cdot \frac{-R}{R_c^2} \dot{R}_c = -\frac{\dot{R}_c}{R_c^5} \left(4g + u \frac{dg}{du} \right), \quad (27)$$

$$\frac{\partial f}{\partial R} = \frac{1}{R^4} \cdot \frac{1}{R_c} \frac{dg}{du}. \quad (28)$$

According to Eq. (16) we have

$$\begin{aligned} \dot{R} &= Az(R/R_c) \frac{1}{R} \left(\frac{1}{R_c} - \frac{1}{R} \right) = \frac{Az(u)}{R_c^2} \frac{1}{u} \left(1 - \frac{1}{u} \right) \\ &= \dot{R}_c \left(\frac{h(u)}{u^2 + u} \right), \end{aligned} \quad (29)$$

with the auxiliary function $h(u)$:

$$h(u) = \frac{A}{R_c^2 \dot{R}_c} z(u)(u-1) - u^3, \quad (30)$$

which can be rewritten with Eq. (25) as

$$h(u) = \frac{u_0^3}{z(u_i)(u_0-1)} z(u)(u-1) - u^3, \quad (31)$$

and depends only on u . The function $h(u)$ helps to compact the following equations.

The derivative $\partial \dot{R} / \partial R$ can directly be calculated from Eq. (29)₃ as

$$\frac{\partial \dot{R}}{\partial R} = \frac{\partial \dot{R}}{\partial u} \frac{\partial u}{\partial R} = \frac{\dot{R}_c}{R_c} \frac{d}{du} \left(\frac{h(u)}{u^2} + u \right). \quad (32)$$

Inserting Eqs. (5), (27–29), (32) in the continuity equation, Eq. (6) provides the differential equation for $g(u)$ as

$$\frac{g}{u^3} \left(u \frac{dh}{du} - 2h - 3u^3 \right) + \frac{dg}{du} \frac{h(u)}{u^2} = 0. \quad (33)$$

It should be noted that the present continuity equation contains no source/sink term. Davies et al. [34] offered a solution of the continuity equation for $Z > 0$ with an “encountering term” as the source/sink term. Such a concept may be useful if matter is supplied from outwards to the system during the coarsening process but shows no significant advantage in the actual case.

The function $g(u)$ can immediately be formulated by the following integral:

$$\ln(g(u)) = \int_{u_s}^u - \frac{\bar{u} dh/d\bar{u} - 2h(\bar{u}) - 3\bar{u}^3}{\bar{u} h(\bar{u})} d\bar{u} + \zeta. \quad (34)$$

The integral is performed with respect to an arbitrarily chosen fixed lower bound u_s ; the quantity ζ is an integration constant. The analytical integrability of Eq. (34) depends on the structure of $h(\bar{u})$, and always exists, if $h(\bar{u})$ is a rational function as in our case or in all the cases listed in Ref. [26].

The detailed analytical calculation of the integral on the right-hand side of Eq. (34) is performed in Appendix B, yielding the following distribution function:

$$\begin{aligned} g(u) &= \bar{\zeta} \frac{(1 - u/l)u^2 \cdot \exp(B_4/(u_0 - u))}{(1 - u/\bar{u}_6)^{-B_6}(u_0 - u)^{-B_3}(u - \bar{u}_5)^{-B_5}} \\ &\text{for } u \leq u_0, \quad g(u) = 0 \quad \text{for } u \geq u_0. \end{aligned} \quad (35)$$

The integration constant $\bar{\zeta}$ can be determined from the condition

$$\int_0^{u_0} g(u) du = 1. \quad (36)$$

For our concept the roots u_0 , \bar{u}_5 , \bar{u}_6 as well as the exponents B_3 to B_6 can be taken from Fig. 2a and b and are derived in Appendix B, Eqs. (B.7) and (B.8). For $l \rightarrow \infty$ the distribution function $g(u)$ takes the LSW form with $B_3 = -3/2$, $B_5 = -7/3$ and $B_6 = -1$ together with $\bar{u}_5 = -3$ and $\bar{u}_6 \rightarrow \infty$.

For the Ardell concept the role of a non-zero volume fraction Z is expressed by the dimension-free parameter β_A , and the steady-state distribution function reads as

$$\begin{aligned} g_A(u) &= \bar{\zeta}_A \frac{u^2 \exp(B_{4,A}/(u_{0,A} - u))}{(u_{0,A} - u)^{-B_{3,A}}(u - \bar{u}_{5,A})^{-B_{5,A}}} \\ &\text{for } u \leq u_{0,A}, \quad g_A(u) = 0 \quad \text{for } u \geq u_{0,A}. \end{aligned} \quad (37)$$

The integration constant $\bar{\zeta}_A$ is calculated in an analogous way to $\bar{\zeta}$, see Eq. (36).

The roots $u_{0,A}$, $\bar{u}_{5,A}$ as well as the exponents $B_{3,A}$ to $B_{5,A}$ can be taken from Fig. 3a and b and are derived in Appendix B, Eqs. (B.9) and (B.10). For $\beta_A \rightarrow 0$ the distribution $g_A(u)$ also takes the LSW form, see above.

Fig. 4a and b demonstrate steady state distribution functions for the according system parameters. Since we obtained a closed-form analytical solution for the

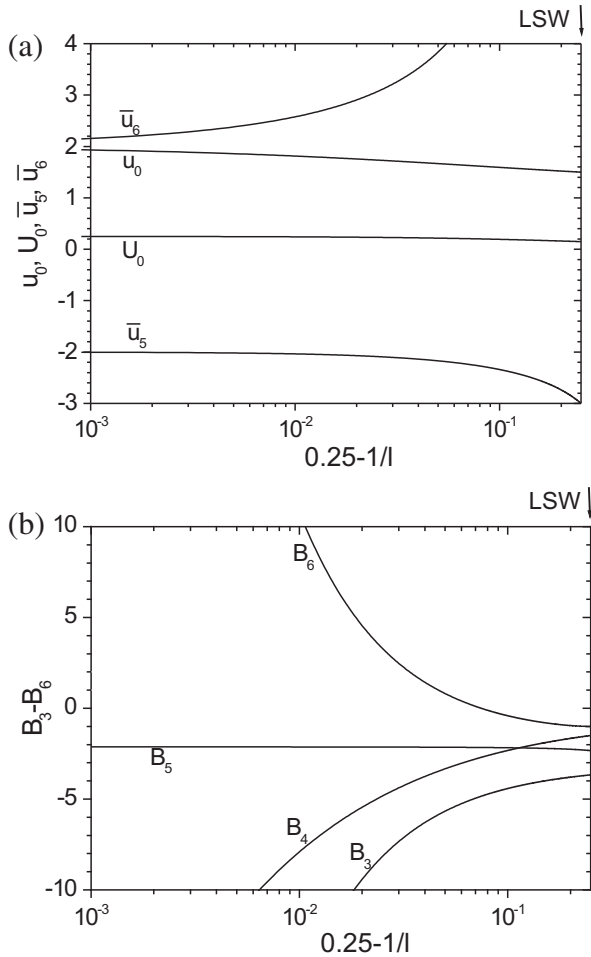


Fig. 2. Dependence of steady-state quantities on the system parameter l . The volume fraction Z can be reflected by the relation $l = \kappa/\sqrt[3]{Z}$ with $\kappa = 1.825$ for our concept. (a) Dependence of $u_0 = R_0/R_c$, U_0 and the roots \bar{u}_5 , \bar{u}_6 . (b) Dependence of the exponents B_3 to B_6 .

steady-state distribution function $g(u)$ or $g_A(u)$ meeting a finite volume fraction Z of precipitates, see Fig. 4, it seems to be reasonable to check whether other groups have also found such a type of solution in the past. Ardell mentioned in his seminal paper [23] from 1972 that an explicit analytical formulation for $g_A(u)$ is only possible for $\beta_A = 0$ or $\beta_A \rightarrow \infty$. However, as our derivations above show, an analytical $g_A(u)$ is possible for the whole range $0 \leq \beta_A \leq \infty$. Also Brailsford and Wynblatt [25] found a closed form solution for Ardell's concept for the whole range of β_A , which is equivalent to $k_T r^*$ in their notation. A comparison with the results in Fig. 3a and b shows exact agreement. Their ρ_c and ρ_0 correspond to $u_{0,A}$ and $\bar{u}_{5,A}$, respectively, and their a , b , c to $-B_{5,A}$, $-B_{3,A}$, $B_{4,A}$, respectively. Tsumuraya and Miyata [26] gave analytical expressions for u_0 (in their notation ρ_M) and $A/R_c^2 \bar{R}_c$, (in their notation v), according to six types of $z(u)$, which, as already mentioned, can be reduced to our type as well as to Ardell's type; their expressions agree then with our results. Enomoto and co-workers obtained, in a series of papers [29–31], using a statistical-mechanics approach for the diffusion process, exactly the same analytical relations as Brailsford

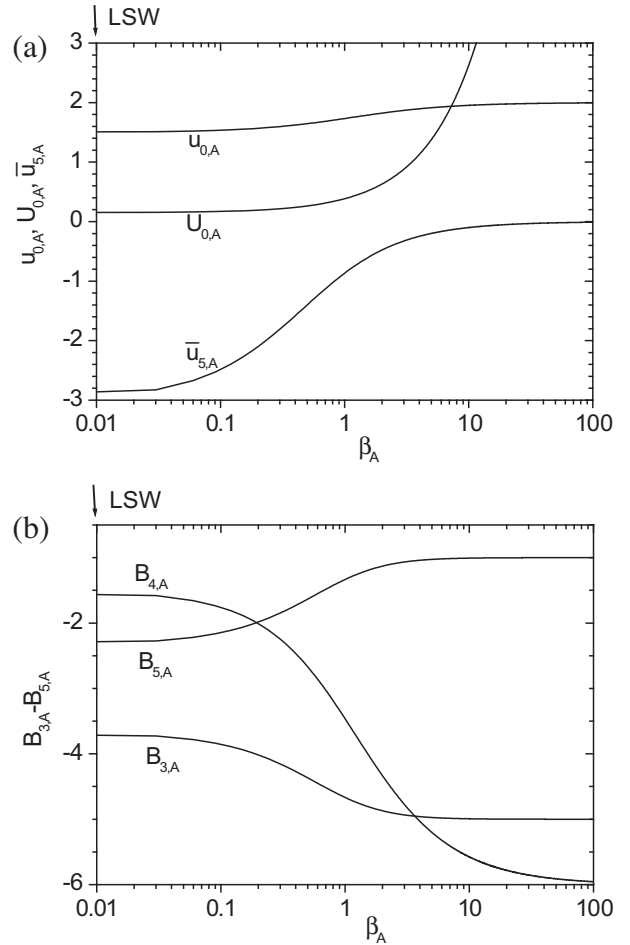


Fig. 3. Dependence of steady-state quantities on the system parameter β_A . The volume fraction Z can be reflected by the relation $\beta_A = \sqrt{3Z}$ for the Ardell concept, subscript “A”. (a) Dependence of $u_{0,A}$, $U_{0,A}$ and the root $\bar{u}_{5,A}$. (b) Dependence of the exponents $B_{3,A}$ to $B_{5,A}$.

and Wynblatt [25], which agree, as mentioned above, with our results for Ardell's proposal; see also the two following papers [32,33], where these authors introduced several approaches for the kinetic parameter K , see Eq. (4). In the context of analytical solutions, the papers by Brown [27,28] should also be mentioned, since this author derived analytical expressions for the distribution function but up to a final integral, which was performed numerically. Brown used as a parameter the quantity v , which corresponds to our expression $(AR_c^2 \bar{R}_c)z(u)$. Insofar, the numerical results by Brown for constant parameters v cannot directly be compared with the results of the authors mentioned above as well as our group. Most recently, Streitenberger [36] reported an exact analytical solution for g_A with $z_A(u) = A_1 + A_2(u+1)$, which can be linearly related to $z_A(u) = 1 + \beta_A u$, and agrees with the current solution (Eq. (37)).

A final remark concerning the limit case for $u_0 = 2$ due to $\beta_A \rightarrow \infty$ is of practical relevance. Streitenberger [36] pointed to the fact that the steady-state distribution function $g_A(u)$ (in his notation $\phi(u)$) becomes identical for $u_0 = 2$ to the so-called “Wagner” steady-state distribution,

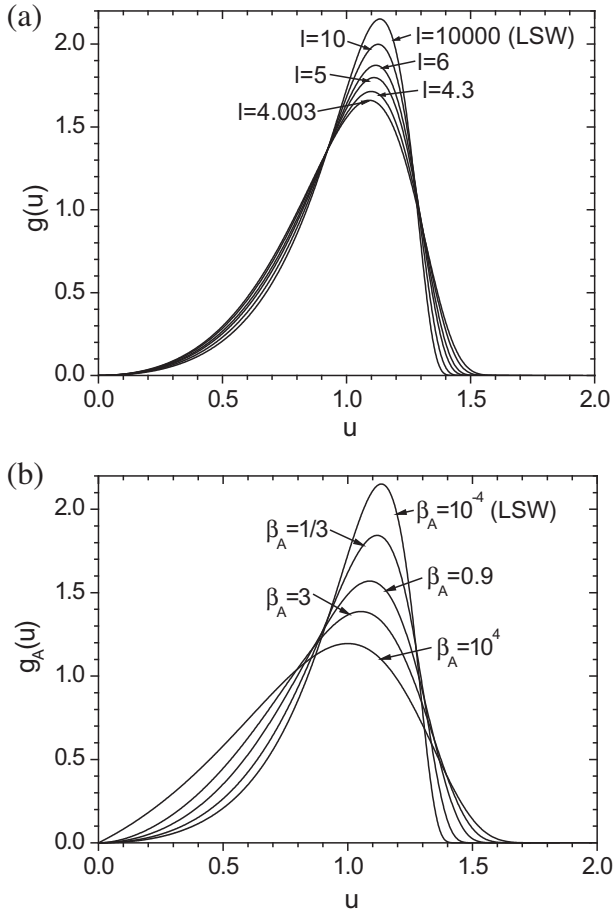


Fig. 4. Steady state distribution function $g(u)$, see Eq. (5), as function of the dimension-free particle radius $u = R/R_c$. The system parameter l or β_A reflects the volume fraction Z of the precipitates. (a) Our concept: system parameter $l = \kappa / \sqrt[3]{Z}$; (b) the Ardell concept: system parameter $\beta_A = \sqrt{3}Z$.

see e.g. Ref. [10], valid for interface-reaction-driven coarsening (which is equivalent to Hillert's theory of grain growth).

It may be useful for comparing distribution functions to have available not only their maximum width, represented by u_0 or $u_{0,A}$, but also the maximum value of $g(u)$ or $g_A(u)$ as g_{\max} or $g_{\max,A}$ at the positions $u = u_m$ or $u_{m,A}$. The positions u_m and $u_{m,A}$ can be found from the extremum condition $dg/du = 0$ and $dg_A/du = 0$ by using Eq. (33), yielding

$$u \frac{dh}{du} = 2h + 3u^2. \quad (38)$$

Inserting $h(u)$ from Eq. (30) one finds after some algebra for our case with $z(u) = 1/(1 - u/l)$ the value u_m as admissible root of the polynomial

$$\frac{4}{l}u^4 - 4u^3 + \frac{u_0^3}{z(u_0)(u_0 - 1)} \left[\frac{2}{l}u^2 - \left(\frac{3}{l} + 1 \right)u + 2 \right] = 0, \quad (39)$$

and, in an equivalent way for $u_{m,A}$ with $z_A(u) = 1 + \beta_A u$, as

$$-4u^3 + \frac{u_{0,A}^3}{z_A(u_{0,A})(u_{0,A} - 1)} [-(1 - \beta_A)u + 2] = 0. \quad (40)$$

For $l \rightarrow \infty$, $\beta_A \rightarrow 0$, i.e. for the LSW distribution, one obtains $u_m = 1.13454$. Both the quantities u_m and $u_{m,A}$ as well as the values g_{\max} and $g_{\max,A}$ are depicted in Fig. 5a and b. The extrema g_{\max} and $g_{\max,A}$ decrease with an increasing volume fraction Z of precipitates, since $1/l$ is proportional to $\sqrt[3]{Z}$ and β_A can be assumed as proportional to \sqrt{Z} . If one compares the experimental data from Pletcher et al. [35] for $Z = 0.27$ (Fig. 13c in Ref. [35]) and uses their $\beta_A = \sqrt{3}Z$, then their measured maximum value of $g_{\max,E} \approx 1.52$ agrees well with the according $g_{\max,A}$ value in Fig. 5b. As one can easily observe, the positions of the maxima of $g(u)$ or $g_A(u)$ slightly decrease and their values show a remarkable reduction with an increasing volume fraction Z of precipitates.

4. Examples of non-steady-state coarsening and general discussion

To demonstrate our model some examples are presented in this chapter.

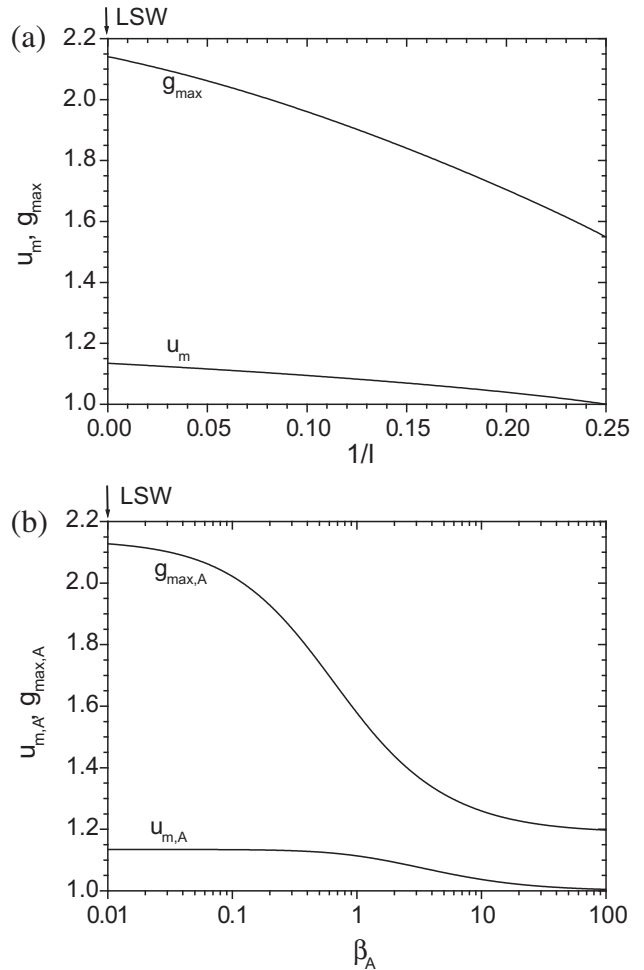


Fig. 5. Dependence of the steady-state quantities position u_m and extremum of $g(u)$ as g_{\max} . The system parameters l and β_A reflect the volume fraction Z of the precipitates. (a) Our concept; (b) the Ardell concept.

The product of the distribution function $f(R)$ and dR represents the number dN of precipitates of the radius in the interval $(R, R + dR)$. This can be written in finite differences as

$$\Delta N = f(R)\Delta R. \quad (41)$$

If the distribution function $f(R)$ is known and the precipitates in the ensemble are sorted according to the decreasing radius, choosing $\Delta N = 1$ and approximating R by $(R_k + R_{k+1})/2$ in Eq. (41) allow calculating the difference $\Delta R = R_k - R_{k+1}$. Then Eq. (41) can be rewritten as

$$1 = f((R_k + R_{k+1})/2)(R_k - R_{k+1}). \quad (42)$$

Eq. (42) is used for calculation of the values $R_k, k = 1, \dots, N$ by assuming $R_N = 0$ with $N = \int_0^\infty f(R)dR$. This ensemble of radii of precipitates represents the starting condition for evolution equations, Eq. (16). The smallest grains with the highest indices are eliminated from the ensemble, immediately after their radius reaches a negative value during the numerical time integration. After the evolution equations are integrated in time numerically, Eq. (42) is used again for the calculation of the distribution function.

First of all the evolution of the normalized distribution function $g^*(u, \bar{t})$ (the non-steady-state distribution function is denoted with the superscript *) for different values of l (and consequently different values of Z , see Eq. (7)) starting with the LSW distribution is calculated. The time is normalized as $\bar{t} = t \cdot Az(u_0)/R_{c0}^3$ with R_{c0} being the initial value of R_c .

The evolution of the ensemble of grains is calculated according to Eqs. (7), (9), and (14) for $l = 4.003$ ($Z = 0.095$) and $l = 2.673$ ($Z = 0.318$) with the initial number of 10^6 grains having the LSW distribution and shown in Fig. 6. For $l = 4.003$ ($Z = 0.095$) the calculation is stable for any time and approaches the steady-state distribution shown in Fig. 4a. For $l = 2.673$ ($Z = 0.318$) the calculation is stable only for a limited time and the width of the normalized distribution $g^*(u, \bar{t})$ continuously increases. Shortly after the normalized time $\bar{t} = 1000$ the calculation collapses. The reason is that the value of the radius of the largest grain approaches the value of L and the rate of the largest radius (see Eq. (14)) diverges. This is, of course, not realistic. On the other hand, however, the width, height and the shape of the normalized distribution $g^*(u, \bar{t})$ agree perfectly with the measured normalized distribution functions summarized by Marder [39] and presented in Figs. 8, 9 and 13 there. It should be noted that during the normalized time period $\bar{t} = 1000$ the precipitates coarsened by a factor of more than 10 (the number of precipitates decreased more than 1000 times), which corresponds to typical experiments. It should also be pointed out that the Ardell model provides too narrow distribution functions, which do not fit well with experiments presented by Marder. Since Marder's overview dates back more than 25 years, three recent contributions are mentioned, too, reporting particle size distributions g for rather high volume fractions:

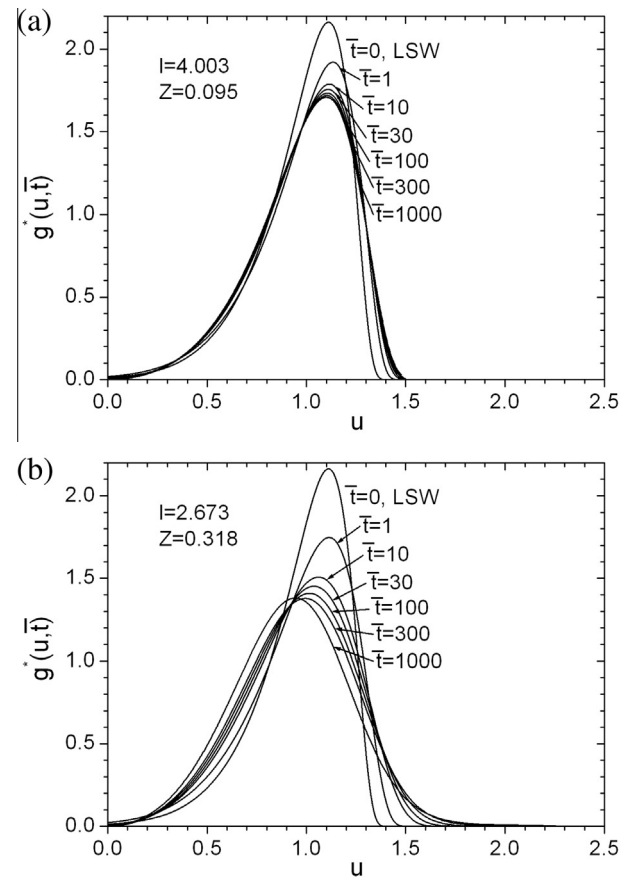


Fig. 6. Evolution of non-steady-state distribution functions $g^*(u, \bar{t})$ based on our concept as function of the dimension-free particle radius $u = R/R_c$ for different instants of normalized time \bar{t} ; LSW distribution as starting distribution; parameter set (see Eq. (7)) $\kappa = 1.825$: (a) $Z = 0.095$, (b) $Z = 0.318$.

- (1) Rowenhorst et al. [40], Pb–Sn, $Z = 0.52$, $g_{\max, E} \approx 1.20$,
- (2) Pletcher et al. [35], Al–Li, $Z = 0.27$, $g_{\max, E} \approx 1.52$,
- (3) Werz et al. [41], Al–Cu, $Z = 0.74$, $g_{\max, E} \approx 1.05$.

Checking the a/m maxima with $g_{\max, A}$ (i.e. the Ardell concept) and using for $\beta_A = \sqrt{3Z}$ (the proposal by Pletcher et al. [35]), we receive $g_{\max, A}$ values for (1) 1.35, for (2) 1.60 and for (3) 1.28. The maxima $g_{\max, A}$ are too high compared with the experimental results. However, if we look for a non-steady-state distribution, we can use Fig. 6b for comparison with (2), since the volume fractions Z are rather similar (0.32 and 0.27, respectively). The values of g_{\max} for higher times (showing a somewhat asymptotic behaviour) are surprisingly near to those observed by Pletcher et al. [35], Fig. 13c there.

To demonstrate the conditions for the non-steady-state coarsening the kinetics of the critical radius R_c and the maximum grain radius R_{\max} in the ensemble are calculated for $l = 4.003$ ($Z = 0.095$), leading to a steady-state coarsening and for $l = 2.673$ ($Z = 0.318$), which does not allow a steady-state coarsening. In the first case a strict cubic time law is observed for both R_c and R_{\max} , see Fig. 7a, while in

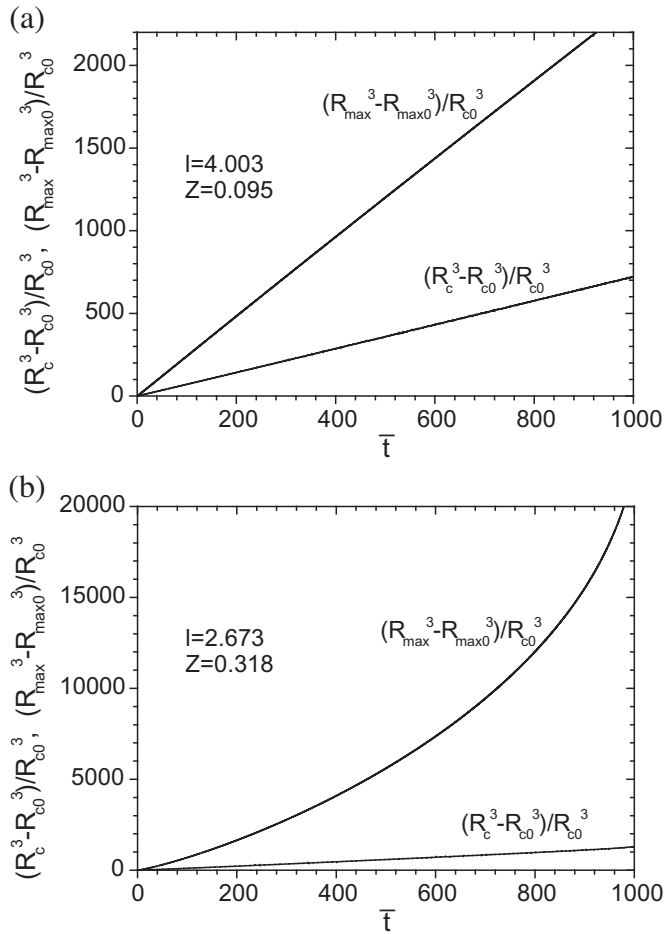


Fig. 7. Coarsening kinetics of the critical radius R_c and the maximum grain radius R_{\max} , normalized with respect to the starting value R_{c0} based on our concept as function of the normalized time \bar{t} ; parameter set (see Eq. (7)) $\kappa = 1.825$: (a) $Z = 0.095$; (b) $Z = 0.318$.

the second case the cubic time law is kept approximately only for R_c and it is violated for R_{\max} . The reason for this fact is again the singularity in Eq. (14) for R_{\max} tending to L , which follows from the requirement that the radius L of the diffusion zone is constant for all precipitates and scales with R_c (see Section 2). To remove this singularity a new model could be developed, which allows increasing the radius L for large precipitates. Such a model could be considered as a compromise between the Ardell model, assuming the external radius of the diffusion zone given by $R_k + 1/\beta_A$ (with $1/\beta_A$ is fixed for diffusion zones of all precipitates), and our model, assuming an external radius of the diffusion zone fixed for all precipitates and given by L .

5. Conclusion

The present model for coarsening of non-dilute precipitates in multi-component systems is based on the exchange of matter between an ensemble of precipitates via diffusion in the matrix. For the system the Gibbs energy function and the dissipation function are derived. Two different

parameters, l or β_A , appear in the dissipation function to account for the finite volume fraction of the precipitates with the physical meaning that both parameters describe the radius of the diffusion zone surrounding each precipitate, as $L = lR_c$ and $R_k + \beta_A R_c$, respectively, with R_c being the critical radius. The TEP is applied, which allows formulating the evolution equation of each individual precipitate and calculation of the evolution of the distribution function of ensembles of precipitates. Up to 10^6 precipitates can be handled without any computational problem on a PC. Also (self-similar) steady-state distribution functions are derived and presented also in an analytical form. It should be emphasized that steady state solutions are possible only for values of $l \in \langle 4, \infty \rangle$ and for values of $\beta_A \in (0, \infty)$. For $l < 4$ only non-steady-state distribution functions can be calculated, which become lower and significantly wider than the well-established LSW-coarsening distribution function as well as the steady-state distribution functions published by several authors. These non-steady-state distribution functions agree very well with sets of experimentally found distribution functions for finite volume fractions of precipitates reported by Marder [39] and recently by Pletcher et al. [35].

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Appendix A. Comparison with the results from Voorhees and Glicksman [14]

Voorhees and Glicksman presented in their paper [14] an exact solution for a two-particle basis (R_1, R_2) as

$$\dot{R}_1 = \frac{1}{R_1^2} \frac{R_1 - R_2}{R_1 + R_2 - 2R_1R_2 \cdot M/a_0}, \quad (\text{A.1})$$

with M being Madelung’s constant and a_0 the lattice parameter. The evolution equation for R_2 can be obtained by the exchange of indices in Eq. (A.1) and the equations fulfil automatically the volume conservation condition of Eq. (9). In an alternative way the equations can be reformulated after some algebra as

$$\dot{R}_k = \frac{1}{(1 - R_k/(a_0/M))R_k} \left(\frac{1}{R_c} - \frac{1}{R_k} \right), \quad k = 1, 2, \quad (\text{A.2})$$

with

$$R_c = \frac{R_1 + R_2 - 2R_1R_2/(a_0/M)}{2 - (R_1 + R_2)/(a_0/M)}. \quad (\text{A.3})$$

Comparing Eqs. (A.2) and (14) shows clearly that L in our relation corresponds directly to a_0/M in Ref. [14]. With respect to the constant A , note that Voorhees and Glicksman assumed $2\gamma(1 - Z)/\beta = 1$.

Appendix B. Integration of the differential equation for the distribution function

We study now the integral in Eq. (34) and introduce for easier writing an abbreviation in Eq. (31) as

$$\frac{A}{R_c^2 \dot{R}_c} = \frac{u_0^3}{z(u_0)(u_0 - 1)} = \frac{1}{U_0}. \quad (\text{B.1})$$

For Ardell's proposal we use instead of U_0 the abbreviation $U_{0,A}$. Then the integrand in Eq. (34) can be formulated after some algebra as

$$\frac{N}{D} = \frac{4U_0\bar{u}^3 - (2 - \bar{u})z(\bar{u}) - \bar{u}(\bar{u} - 1)dz/d\bar{u}}{U_0\bar{u}h(\bar{u})}. \quad (\text{B.2})$$

If we use for our concept $z(\bar{u}) = (1 - \bar{u}/l)$ in the numerator N in Eq. (B.2), we obtain for the integrand

$$\begin{aligned} \frac{N}{D} &= \frac{4U_0\bar{u}^3(1 - \bar{u}/l)^2 - 2\bar{u}^2/l + \bar{u}(1 + 3/l) - 2}{(1 - \bar{u}/l)\bar{u}[U_0(1 - \bar{u}/l)h(\bar{u})]} \\ &= \frac{4U_0\bar{u}^3(1 - \bar{u}/l)^2 - 2\bar{u}^2/l + \bar{u}(1 + 3/l) - 2}{(1 - \bar{u}/l)\bar{u}P_4(\bar{u})}. \end{aligned} \quad (\text{B.3})$$

The numerator N is a polynomial of fifth order in \bar{u} and degenerates for $l \rightarrow \infty$ to a polynomial of third order. The denominator D is a polynomial of sixth order in \bar{u} since after inserting $z(\bar{u}) = (1 - \bar{u}/l)$ into $h(\bar{u})$ the polynomial $P_4(\bar{u}) = -U_0\bar{u}^3(1 - u/l) + \bar{u} - 1$ is of fourth order, see Eq. (30). Moreover, a comparison of Eqs. (18)₁ and (30) indicates that $h(\bar{u})$ has two roots u_0 given by Eq. (22)₁ due to the steady-state conditions, see Eq. (3). Thus, $P_4(\bar{u})$ must have also two roots u_0 . For $l \rightarrow \infty$ the denominator D degenerates to a polynomial of fourth order. We perform now a polynomial decomposition of N/D according to the roots of D , being $\bar{u}_1 = l$, $\bar{u}_2 = 0$, the double-root $\bar{u}_3 = \bar{u}_4 = u_0$ due to the steady-state conditions and the roots \bar{u}_5 , \bar{u}_6 of the equation

$$P_4(\bar{u})/(\bar{u} - u_0)^2 = [\bar{u}^2 + (2u_0 - l)\bar{u} + (4u_0 - 3l)](-U_0/l^2) = 0. \quad (\text{B.4})$$

Eq. (B.4) can be found by performing the division in an algebraic way, using Eq. (B.1) as the relation between U_0 and u_0 and Eq. (20) to express $3u_0^2 = 2(l + 2)u_0 - 3l$. The roots \bar{u}_5 , \bar{u}_6 follow from the quadratic equation, Eq. (B.4), as

$$\bar{u}_5, \bar{u}_6 = \frac{(l - 2u_0)}{2} \left(1 \pm \sqrt{1 + 4(3l - 4u_0)/(l - 2u_0)^2} \right).$$

In the limiting case for $l \rightarrow \infty$ the roots \bar{u}_1 and \bar{u}_6 tend to infinity and play no role in the final solution. The four roots $\bar{u}_2 = 0$, $\bar{u}_3 = \bar{u}_4 = 3/2$ and $\bar{u}_5 = -3$ survive, which yield in a straightforward way the LSW solution.

The integral of N/D can now be found by partial decomposition of the integrand as

$$\begin{aligned} \frac{N}{D} &= \frac{(-l^2/U_0) \cdot N}{(\bar{u} - l)\bar{u}(\bar{u} - u_0)^2(\bar{u} - \bar{u}_5)(\bar{u} - \bar{u}_6)} \\ &= \frac{B_1}{\bar{u} - l} + \frac{B_2}{\bar{u}} + \frac{B_3}{\bar{u} - u_0} + \frac{B_4}{(\bar{u} - u_0)^2} + \frac{B_5}{\bar{u} - \bar{u}_5} + \frac{B_6}{\bar{u} - \bar{u}_6}. \end{aligned} \quad (\text{B.5})$$

A numerical analysis has brought out that B_1 and B_2 are independent of l with the values $B_1 = 1$ and $B_2 = 2$. This fact leads to a reduced formulation of the partial decomposition as

$$\frac{N}{D} - \left(\frac{1}{\bar{u} - l} + \frac{2}{\bar{u}} \right) = \frac{7\bar{u}^4 - 13l\bar{u}^3 + 6l^2\bar{u}^2 + \bar{u}l/U_0 - l^2/U_0}{(\bar{u} - u_0)^2(\bar{u} - \bar{u}_5)(\bar{u} - \bar{u}_6)}, \quad (\text{B.6})$$

to obtain the constants B_3 to B_6 .

The indefinite integral of Eq. (B.5) with respect to \bar{u} can be easily performed as

$$\begin{aligned} \int \frac{N}{D} d\bar{u} &= \ln [(1 - \bar{u}/l)(1 - \bar{u}/\bar{u}_6)^{B_6}] \\ &\quad + \ln [\bar{u}^2(u_0 - \bar{u})^{B_3}(\bar{u} - \bar{u}_5)^{B_5} \cdot \exp(B_4/(u_0 - \bar{u}))] + \ln \bar{\zeta}, \end{aligned} \quad (\text{B.7})$$

with $\bar{\zeta}$ being an integration constant. The first contribution on the right-hand side of Eq. (B.7) disappears for large values of l , since \bar{u}_6 tends also to infinity.

In the case of Ardell's proposal $z_A(\bar{u}) = (1 + \beta_A\bar{u})$, we obtain for the integrand

$$\frac{N_A}{D_A} = \frac{4U_{0,A}\bar{u}^3 + (1 - \beta_A)\bar{u} - 2}{\bar{u}[U_{0,A}h(\bar{u})]}. \quad (\text{B.8})$$

The four roots of D_A are denoted as $\bar{u}_{2,A}$, $\bar{u}_{3,A} = \bar{u}_{4,A}$, $\bar{u}_{5,A}$. The first three ones follow immediately as $\bar{u}_{2,A} = 0$, $\bar{u}_{3,A} = \bar{u}_{4,A} = \bar{u}_{0,A}$. The fourth one is obtained by division of $U_{0,A}h(\bar{u})$, being a polynomial of third order, by $(\bar{u} - u_{0,A})^2$ and reads as $\bar{u}_{5,A} = -2u_{0,A} + \beta_A/U_{0,A} = -2u_{0,A} + u_{0,A}^3/(u_{0,A} - 1)(1/\beta_A + u_{0,A})$. The quantity $u_{0,A}$ as a function of β_A must be taken from Eq. (22)₂. In the limiting case for $\beta_A \rightarrow 0$ one obtains $\bar{u}_{2,A} = 0$, $\bar{u}_{3,A} = \bar{u}_{4,A} = 3/2$ and $\bar{u}_{5,A} = -3$, which yields again in a straightforward way the LSW solution. For $\beta_A \rightarrow \infty$ one gets $\bar{u}_{2,A} = 0$, $\bar{u}_{3,A} = \bar{u}_{4,A} = 2$ and $\bar{u}_{5,A} = 0$.

The integrand can be decomposed as

$$\begin{aligned} \frac{N_A}{D_A} &= \frac{-1/U_{0,A} \cdot N_A}{\bar{u}(\bar{u} - u_{0,A})^2(\bar{u} - \bar{u}_{5,A})} \\ &= \frac{B_{2,A}}{\bar{u}} + \frac{B_{3,A}}{\bar{u} - u_{0,A}} + \frac{B_{4,A}}{(\bar{u} - u_{0,A})^2} + \frac{B_{5,A}}{(\bar{u} - \bar{u}_{5,A})}. \end{aligned} \quad (\text{B.9})$$

Again a numerical analysis has brought $B_{2,A} = 2$ and leads also to a reduced formulation of the partial decomposition as

$$\frac{N_A}{D_A} - \frac{2}{\bar{u}} = \frac{-6\bar{u}^2 + 2\beta_A \bar{u}/U_{0,A} + (1 - \beta_A)/U_{0,A}}{(\bar{u} - u_{0,A})^2(\bar{u} - \bar{u}_{5,A})}, \quad (\text{B.10})$$

to obtain the constants $B_{3,A}$ to $B_{5,A}$. The indefinite integral of Eq. (B.9) with respect to \bar{u} can easily be performed as

$$\int \frac{N_A}{D_A} d\bar{u} = \ln [u^2(u_{0,A} - \bar{u})^{B_{3,A}}] + \ln [(\bar{u} - \bar{u}_{5,A})^{B_{5,A}}] + B_{4,A}/(u_{0,A} - \bar{u}) + \ln \bar{\zeta}_A, \quad (\text{B.11})$$

with $\bar{\zeta}_A$ being an integration constant.

The coefficients B_3 to B_6 and $B_{3,A}$ to $B_{5,A}$ can be found in analytical form; however, they are rather lengthy rational functions. So we decided to provide only diagrams presenting the coefficients together with the quantities u_0 , U_0 , \bar{u}_5 , \bar{u}_6 and $u_{0,A}$, $U_{0,A}$, $\bar{u}_{5,A}$, see Figs. 2a and b, 3a and b.

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