Journal of Non-Crystalline Solids 125 (1990) 129–138
North-Holland

Non-stationary nucleation and cluster growth in quasi-binary non-ideal solutions

Jörn Bartels, Frank Schweitzer and Jürn Schmelzer

Universität Rostock, Sektion Physik, Universitätsplatz 3, Rostock, 2500 German Democratic Republic

Received 26 February 1990
Revised manuscript received 14 May 1990

A kinetic theory of nucleation and cluster growth in non-ideal quasi-binary liquid and solid solutions with, in general, concentration dependent diffusion coefficients of the segregating particles is developed. This theory allows one, in a straightforward way, to account for the influence of elastic strains, evolving in solid solutions as the result of cluster formation and growth, on the kinetics of the phase transformation. Specific properties of the solution or the evolving elastic fields have to be incorporated explicitly only in the final expressions describing nucleation and growth. The theory is applied to special cases demonstrating the consequences of depletion of segregating particles, the non-ideality of the solution and effects due to elastic strains on the kinetics of the segregation process. It is shown that, due to the non-steady character of the nucleation process, resulting from time-lag and depletion effects, the incorporation of the non-ideality of the solution and elastic strains into the description leads not only to a variation of the nucleation rate but changes also a number of other significant characteristics of the phase transformation, e.g., the cluster distribution function and the rate of the decomposition process.

1. Introduction

Nucleation and cluster growth is one major way thermodynamic phase transitions of first order may proceed. Despite the long history of investigations on this topic due both to widespread technological applications and the complexity of this phenomenon, it is also at present an actively developing field of research both from theoretical and experimental points of view [1,2].

Two problems that have attracted much attention in the last years are the influence of depletion on nucleation, in particular, and on the whole course of the transition, in general, and the effects due to the evolution, in the course of the transition, of elastic strains of different types [3–5]. Due to time-lag effects and variations of the state of the system in the course of the transition, the classical steady-state approximation for the nucleation rate cannot be applied. Moreover, the non-ideality of most solutions also affects both nucleation and growth.

Thus, a general theory of nucleation and cluster growth in non-ideal solutions under the influence of different kinds of elastic strains is required. In the present paper such a theory is developed and applied to quasi-binary solutions.

Starting with some basic equations of the linear thermodynamics of irreversible processes, in sections 2 and 3 macroscopic growth equations for spherical clusters in quasi-binary non-ideal solid or liquid solutions are developed for two different diffusion mechanisms of the components (exchange of places and relatively independent diffusion of both components).

The general method for incorporation of the effects of elastic strains of different types into the description of this process is given in section 4. In comparison with a previous study [6], where ideal solutions and concentration-independent diffusion

0022-3093/90/$03.50

coefficients are assumed, the generalization with respect to this part consists in the incorporation of the non-ideality of the solution and the concentration dependence of the diffusion coefficients into the theory.

In section 5 the kinetic equations, describing nucleation and cluster growth or shrinkage, are formulated and the transition probabilities are determined.

The general theory is applied to special cases. It is demonstrated that the account of the non-ideal character of the solution and the evolving elastic fields has a significant effect not only on the nucleation rate but on all characteristics of the phase transformation such as cluster distribution, rate of decomposition, and density profile of the segregating particles in the vicinity of the cluster.

2. Diffusion-limited cluster growth: two cases

In the framework of the linear thermodynamics of irreversible processes [7] the basic equations for the derivation of the growth equations for clusters of a new phase are given by

$$\bar{j}_i = \sum_k L_{ik} \bar{X}_k, \quad \bar{X}_k = -\text{grad } \mu_k, \tag{1}$$

where $\bar{j}_i$ are the density of fluxes of particles of the ith component due to gradients in the chemical potential μ_i. The pressure p and temperature T are kept constant. The L_{ik} are the Onsager coefficients obeying the relation [7]

$$L_{ik} = L_{ki}. \tag{2}$$

We consider here growth processes in non-ideal binary solutions, where the clusters consist mainly of one component.

Two cases are considered. If, as assumed first, the diffusion proceeds via an exchange of places of the particles of the different components, in addition to eqs. (1) and (2) the relation

$$\bar{j}_1 + \bar{j}_2 = 0 \tag{3}$$

has to be fulfilled, resulting in

$$\begin{aligned} \bar{j}_1 &= -L_{11} \text{ grad } (\mu_1 - \mu_2) \\ \bar{j}_2 &= -L_{22} \text{ grad } (\mu_2 - \mu_1). \end{aligned} \tag{4}$$

It follows immediately from eqs. (3) and (4) that in this first case the relation $L_{11} = L_{22}$ holds.

A substitution of the expression for the chemical potentials μ_i according to [8]

$$\mu_i = \mu_{0i}(p, T) + kT \ln(x_i f_i) \tag{5}$$

into eqs. (4) yields

$$\bar{j}_i = -\frac{L_{ii} kT}{c_i(1-x_i)} \left[1 + \frac{x_i}{f_i} \frac{\partial f_i}{\partial x_i}\right] \text{grad } c_i, \tag{6}$$

where x_i is the molar fraction and f_i the activity coefficient of the component i, k is the Boltzmann constant, and μ_{0i} is the reference value of the chemical potential. Defining the partial diffusion coefficient D_i of the component i by [7]

$$\bar{j}_i = -D_i \text{ grad } c_i, \tag{7}$$

one obtains

$$D_i = \frac{L_{ii} kT}{c_i(1-x_i)} \left[1 + \frac{x_i}{f_i} \frac{\partial f_i}{\partial x_i}\right] \tag{8}$$

or

$$D_i = D_i^{(id)} \left[1 + \frac{x_i}{f_i} \frac{\partial f_i}{\partial x_i}\right], \tag{9}$$

with

$$D_i^{(id)} = \frac{L_{ii} kT}{c_i(1-x_i)}. \tag{10}$$

c_i is the volume density of particles of component i.

Since the coefficients, L_{ii}, in eqs. (4) are a measure of the frequency of exchange of particles of the different components, L_{ii} must be also a function of both x_1 and x_2, so that divergencies of $D_i^{(id)}$ do not occur.

It was assumed in the derivation, that the condition $c_1 + c_2 = c =$ constant is, at least approximately, fulfilled. With eq. (3) and the Gibbs–Duhem relation [8] this condition yields

$$D_1 = D_2; \quad D_1^{(id)} = D_2^{(id)}. \tag{11}$$

Returning to the chemical potential the expression for $\bar{j}_i$ may be written also as

$$\bar{j}_i = -\frac{D_i^{(id)} c_i}{kT} \text{grad } \mu_i \tag{12}$$

since after the substitution of eq. (5) into eq. (12) eqs. (7) and (8) result, again.

As the second case, we consider the situation that $L_{ik} = 0$ holds for $i \neq k$. In this case we obtain for each component

$$\bar{j}_i = -L_{ii} \operatorname{grad} \mu_i \tag{13}$$

and with eq. (5)

$$\begin{aligned} \bar{j}_i &= -D_i^{(id)} \left[1 + \frac{x_i}{f_i} \frac{\partial f_i}{\partial x_i}\right] \operatorname{grad} c_i, \\ D_i^{(id)} &= \frac{kTL_{ii}}{c_i}. \end{aligned} \tag{14}$$

Since by assumption the diffusion process of the components proceeds, in this second case, independently of each other, L_{ii} and, consequently, $D_i^{(id)}$ do not depend on the concentration of the other components. Again, the density of fluxes $\bar{j}_i$ may be written in the form given by eq. (12) with $D_i^{(id)}$ determined here by eq. (14).

Thus, independently of the diffusion mechanism, also in non-ideal solutions, the density of fluxes may be expressed via eq. (12), with a coefficient $D_i^{(id)}$ we consider in the following as concentration independent.

3. Steady-state solution of the diffusion equation

For spherical symmetry the differential equation for the determination of the stationary concentration profile of the segregating component in the surrounding of a cluster with a radius R reads [6,10]

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial c}{\partial r}\right] + \frac{c}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial \phi}{\partial r}\right] + \frac{\partial c}{\partial r} \frac{\partial \phi}{\partial r} = 0 \tag{15}$$

with

$$\phi = \ln f. \tag{16}$$

Taking into account the boundary conditions

$$\begin{aligned} c(r = R) &= c_R, \\ c(r \to \infty) &= c_\infty, \end{aligned} \tag{17}$$

the solution of eq. (15) can be obtained as (see also refs. [6,10])

$$\begin{aligned} c(r) = {} & \frac{c_\infty \exp[\phi(\infty)] - c_R \exp[\phi(R)]}{\int_R^\infty \frac{\mathrm{d}r}{r^2} \exp[\phi(r)]} \\ & \times \exp[-\phi(\infty)] \int_R^r \frac{\mathrm{d}r}{r^2} \exp[\phi(r)] \\ & + c_R \exp[\phi(R) - \phi(r)]. \end{aligned} \tag{18}$$

The density of fluxes through the surface of the cluster with the radius R reads then

$$j_R = -D \frac{c_\infty \exp[\phi(\infty)] - c_R \exp[\phi(R)]}{R^2 \int_R^\infty \frac{\mathrm{d}r}{r^2} \exp[\phi(r)]} \tag{19}$$

and with eq. (16)

$$j_R = -D \frac{c_\infty f(\infty) - c_R f(R)}{R^2 \int_R^\infty \frac{\mathrm{d}r}{r^2} f(r)}. \tag{20}$$

D is the measured diffusion coefficient of the segregating component at a concentration, c_R. We identify this concentration, c_R, in the immediate vicinity of the cluster with the equilibrium solubility of a cluster with radius R. For the completion of the derivation, the equilibrium solubility, c_R, of a cluster with a radius R, has to be determined for non-ideal solutions. From the necessary extremum conditions for the Gibbs free energy $\Delta G = -n_\alpha \Delta g + \sigma A + \ldots$ of the heterogeneous system cluster in the matrix, one obtains for quasi-binary solutions [3,6]

$$\mu_\beta(c_R) - \mu_\alpha = (2\sigma / c_\alpha R). \tag{21}$$

Δg is the bulk contribution to the change of G due to the formation of a cluster with n_α particles, and a density of particles, c_α, a surface area, A, and a specific interfacial energy, σ. Δg can be expressed as $\Delta g = \mu_\beta - \mu_\alpha$, which is used in the derivation of eq. (21). μ_α is the chemical potential of the evolving phase at a pressure p and a temperature T, μ_β and $\mu_\beta(c_R)$ are the chemical potentials of the segregating particles far away from and in the immediate vicinity of the cluster, respectively. It follows from the equilibrium conditions at a planar interface that $\mu_\alpha = \mu_\beta(c')$. c' is the equilibrium solubility of the considered component for a planar interface between both phases. One obtains with eq. (5)

$$c_R f(c_R) = c' f(c') \exp[2\sigma/c_\alpha kTR]. \tag{22}$$

With eq. (22), eq. (20) results in

$$j_R = -D\frac{c_\infty f(\infty) - c' f(c') \exp[2\sigma/c_\alpha kTR]}{R^2 \int_R^\infty \frac{\mathrm{d}r}{r^2} f(r)}. \tag{23}$$

By the introduction of a new variable of integration $y = R/r$ we obtain further

$$j_R = -\frac{Dc' f(c')}{R\int_0^1 \mathrm{d}y f(y)}\left[\frac{c_\infty f(\infty)}{c' f(c')} - \exp\frac{2\sigma}{c_\alpha kTR}\right]. \tag{24}$$

Equation (22) represents at the same time a relation determining the critical cluster size for non-ideal solutions in dependence on the actual supersaturation

$$R_c = \frac{2\sigma}{c_\alpha kT \ln[cf(c)/c'f(c')]}, \tag{25}$$

where c is the density of segregating particles at a sufficiently large distance from the growing cluster. Taking into account the notations (17) it has to be identified with c_∞.

With eq. (25), eq. (24) may be expressed as

$$j_R = -\frac{Dc' f(c')}{R\int_0^1 \mathrm{d}y f(y)}\left[\exp\frac{2\sigma}{c_\alpha kTR_c} - \exp\frac{2\sigma}{c_\alpha kTR}\right] \tag{26}$$

which for small values of the exponent is reduced to

$$j_R = -\frac{2\sigma Dc' f(c')}{c_\alpha kTR\int_0^1 \mathrm{d}y f(y)}\left[\frac{1}{R_c} - \frac{1}{R}\right]. \tag{27}$$

Assuming incompressibility of the cluster phase the change of the radius of the cluster is connected with the flux through the surface via [9,3]

$$\frac{\mathrm{d}R}{\mathrm{d}t} = -\frac{j_R}{c_\alpha} \tag{28}$$

and we obtain, finally,

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{2\sigma Dc' f(c')}{c_\alpha^2 kT\int_0^1 \mathrm{d}y f(y)}\frac{1}{R}\left[\frac{1}{R_c} - \frac{1}{R}\right]. \tag{29}$$

For perfect solutions ($f = 1$) this equation is reduced to the well-known expression (e.g., ref. [9])

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{2\sigma Dc'}{c_\alpha^2 kT}\frac{1}{R}\left[\frac{1}{R_c} - \frac{1}{R}\right]. \tag{30}$$

A comparison of eqs. (29) and (30) indicates that in the estimation of the diffusion coefficient from experimentally observed growth curves, which are based usually on eq. (30), corrections due to the non-ideality of the solution have to be incorporated.

4. Influence of elastic strains on the growth rate

In solid binary solutions the processes of diffusion, growth and dissolution of clusters of a new phase are, in general, influenced by the evolving elastic strains [11]. This influence is to be taken into account in two ways, via modifications of the diffusion process (diffusion coefficient) and via a variation in the equilibrium solubility. It has to be expressed differently in the two cases considered here, so we have to study them separately.

4.1. Diffusion by exchange of places

First we consider, again, the situation that the diffusion process takes place via an exchange of places of the particles of the different components, a process described by eqs. (3)–(2).

With the general thermodynamic relationship [8]

$$(\partial\bar{G}/\partial x_1) = \mu_1 - \mu_2, \tag{31}$$

eqs. (4) read

$$\bar{j}_i = -L_{ii}\,\mathrm{grad}(\partial\bar{G}/\partial x_i). \tag{32}$$

$\bar{G}$ is the molar free enthalpy of the solution.

The influence of elastic strains on growth thus may be expressed via an additional term $G^{(\epsilon)}$ in G:

$$G = G^{(\mathrm{ch})} + G^{(\epsilon)}, \tag{33}$$

where the first term, $G^{(\mathrm{ch})}$, represents G in the absence of elastic strains.

Neglecting the composition dependence of the elastic moduli, it can be shown, that $G^{(\epsilon)}$ for the considered first mechanism of diffusion and the resulting strains does not depend on composition [3,6,10,11]. Thus $\partial G^{(\epsilon)}/\partial x_{\mathrm{i}} = 0$ and eqs. (15)–(20) remain valid.

However, taking into account the influence of elastic strains, the generalized Gibbs–Thomson equation reads, now,

$$\mu_\beta(c_R) - \left[\mu_\alpha + \frac{1}{c_\alpha}\frac{\partial G^{(\epsilon)}}{\partial V_\alpha}\right] = 2\sigma/c_\alpha R \tag{34}$$

(compare eq. (21)). If the chemical potentials are expressed through concentrations and activity coefficients in analogy to eq. (22) we obtain

$$c_R f(c_R) = c' f(c') \exp\left[\frac{1}{c_\alpha kT}\left(\frac{2\sigma}{R} + \frac{\partial G^{(\epsilon)}}{\partial V_\alpha}\right)\right] \tag{35}$$

and for small values of the exponent

$$c_R f(c_R) = c' f(c')\left[1 + \frac{1}{c_\alpha kT}\left(\frac{2\sigma}{R} + \frac{\partial G^{(\epsilon)}}{\partial V_\alpha}\right)\right]. \tag{36}$$

The total energy of elastic deformations, $G^{(\epsilon)}$, evolving in diffusion processes due to exchange of places of particles of the different components with different values of the volume per particle may be written as [6,11,12]

$$G^{(\epsilon)} = \epsilon V_\alpha, \tag{37}$$

where V_α is the volume of the cluster, and ϵ can be expressed through the elastic constants of both cluster and matrix phases.

Instead of eq. (22), one obtains then

$$c_R f(c_R) = c' f(c') \exp\left[\frac{1}{c_\alpha kT}\left(\frac{2\sigma}{R} + \epsilon\right)\right]. \tag{38}$$

Elastic strains of the considered type thus result effectively only in an increase of the equilibrium concentration, c_R, by a factor $\exp(\epsilon/c_\alpha kT)$.

4.2. Relatively independent diffusion of both components

We consider now the second possible case, that both components are mobile and cross-effects may be neglected ($L_{12} = L_{21} = 0$; eqs. (13)–(14)). The influence of elastic strains on the diffusion process may be taken into account then by an additional term $\mu_{\mathrm{i}}^{(\epsilon)}$ in the expression for the flux of particles (compare eq. (12), [13])

$$j_i = -\frac{D_i^{(id)} c_i}{kT} \operatorname{grad}\left(\mu_i + \mu_i^{(\epsilon)}\right). \tag{39}$$

With the notation

$$\phi_i = \ln f_i + \phi_i^{(\epsilon)}; \quad \phi_i^{(\epsilon)} = \mu_i^{(\epsilon)}/kT, \tag{40}$$

we arrive at eqs. (15)–(19), again, now with ϕ given by eq. (40).

For the segregating particles $\mu_{\mathrm{i}}^{(\epsilon)}$ may be expressed via the volume density of energy of elastic deformations $g^{(\epsilon)}$ as [13]

$$\mu^{(\epsilon)} = \frac{\omega}{c_\alpha} g^{(\epsilon)}, \tag{41}$$

where ω is some constant of proportionality. Thus we obtain for this component

$$\phi = \ln f + \phi^{(\epsilon)}; \quad \phi^{(\epsilon)} = \frac{\omega}{c_\alpha kT} g^{(\epsilon)}. \tag{42}$$

In the second case, the total energy of elastic deformations, $G^{(\epsilon)}$, depends not only on the elastic constants of both phases but also on the mobility of the non-segregating component. In general, $(\partial G^{(\epsilon)}/\partial V_\alpha)$ is an increasing function of the cluster size and the elastic strains may result in an inhibition of growth with an increasing size of the cluster. Models describing the mobility of the matrix particles and its effect on $G^{(\epsilon)}$ are developed, e.g., in refs. [3,6,13]. Thus, via an influence on $G^{(\epsilon)}$ the motion of the first component has a sometimes considerable effect on the segregation of the second one which makes the assumptions, leading to eqs. (13)–(14) and (39), (40), less restrictive.

5. Non-steady state nucleation and elastic strains: kinetic equations

If, as we assume here, nucleation and cluster growth proceed via addition or evaporation of monomers only, then this process may be described by a system of rate equations of the form [14–17]

$$\partial N(n,\ t)/\partial t = I(n-1,\ t) - I(n,\ t) \tag{43}$$

with

$$I(n,\ t) = w_n^+(t) N(n,\ t) - w_{n+1}^- N(n+1,\ t). \tag{44}$$

$N(n,\ t)$ is the number of clusters consisting at the time, t, of n monomers. w_n^+ and w_n^- are the transition rates for addition and evaporation, respectively, of monomers to/from a cluster consisting of n particles.

The transition rates are connected with the average or deterministic velocity of cluster growth via

$$\mathrm{d}n/\mathrm{d}t = \langle w_n^+ - w_n^- \rangle \tag{45}$$

or through (cf. eq. (27))

$$\mathrm{d}n/\mathrm{d}t = -4\pi R_n^2 j_R, \tag{46}$$

where R_n is the radius of a cluster consisting of n particles.

With eq. (19) we obtain

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 4\pi R_n \frac{D}{R_n \displaystyle\int_{R_n}^{\infty} \frac{\mathrm{d}r}{r^2} \exp[\phi(r)]} \times \left[c_\infty \exp(\phi(\infty)) - c_R \exp(\phi(R)) \right]. \tag{47}$$

An introduction of the reduced variable $y = R_n/r$ yields

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 4\pi R_n \frac{D}{\displaystyle\int_0^1 \mathrm{d}y \exp[\phi(y)]} \times \left[c_\infty \exp(\phi(\infty)) - c_R \exp(\phi(R)) \right]. \tag{48}$$

In the case of a concentration dependence of the diffusion coefficient for D its value in the immediate vicinity of the cluster is to be taken (compare eqs. (7), (19) and (27)).

Introducing an effective diffusion coefficient $D^{(\mathrm{e})}$ by

$$D^{(\mathrm{e})} = \frac{D(c_R)}{\displaystyle\int_0^1 \mathrm{d}y \exp[\phi(y)]}, \tag{49}$$

the expressions for w_n^+ and w_n^- may be written as

$$\begin{aligned} w_n^+ &= 4\pi R_n D^{(\mathrm{e})} c_\infty \exp(\phi(\infty)), \\ w_n^- &= 4\pi R_n D^{(\mathrm{e})} c_R \exp(\phi(R)). \end{aligned} \tag{50}$$

Note, that eqs. (49) and (50) are valid independent of any specific properties of the solution and the type of the evolving strains. Thus, only at this point a specification of the character of the solution and the properties of the strain fields is needed to describe a particular system of interest.

Moreover, it has to be taken into account, that the total number of segregating particles is conserved:

$$\sum n N_n = \text{constant}. \tag{51}$$

Equation (43) represents thus a system of coupled equations which can be solved numerically only. Moreover, since monomers are consumed in the process of cluster formation and growth, the concentration of free particles, c_∞, is also a function of the actual cluster-distribution and consequently of time.

6. Numerical solution of the kinetic equations for special cases

6.1. Numerical method

With the transition rates (eq. (50)) determined in the preceding chapter, we study, now, nucleation and cluster growth in a non-ideal solution in the presence of elastic strains expressed via eqs. (33) and (37).

We assume the usual initial and boundary conditions

$$\begin{aligned} &\text{(i)} \quad N(n,\ t=0) = 0 \quad \text{for } n \geq 2 \\ &\text{(ii)} \quad N(n > n^*,\ t) = 0. \end{aligned} \tag{52}$$

The first of these conditions (i) implies that the segregating component is present in the system in the initial state in form of monomers only.

The second condition (ii) gives a restriction for the size of the clusters, for which the evolution in time can be described. It holds always for sufficiently short time intervals and results in a restriction of the number of equations (equal to n^*) of the form (43) which have to be solved simultaneously.

If one is interested to follow the time evolution of the size distribution for larger periods of time, in order to save computer time, one of the following two methods can be used.

The first method consists in the description of the growth of sufficiently large clusters n ($n > n^* \gg n_c$, where n_c corresponds to the critical cluster size) instead of eqs. (43) and (44) by a deterministic growth equation (such as eq. (28) (see, for example, refs. [15–17]). This approach neglects, however, diffusion processes in the space of cluster sizes and a possible broadening of the distribution connected with this process [18].

To avoid these uncertainties, we retain here the description by eqs. (43) and (44) but carry out the calculations only for certain values, $N(n, t)$, with non-equidistantly distributed grid points n. For $n \leq 100$ the smallest possible difference between two grid points, $\Delta n = 1$, is maintained; for $n > 100$, $\Delta n > 1$.

To carry out the calculations the functions $N(n \pm 1)$ in eqs. (43) and (44) have to be expressed via $N(n)$. This expression is possible through a Taylor-expansion, where only the first three terms are retained:

$$N(n \pm 1) = N(n) \pm (\partial/\partial n) N(n) + \tfrac{1}{2}(\partial^2/\partial n^2) N(n). \tag{53}$$

The aim of the calculations is to demonstrate:

(1) the influence of the depletion of monomers of the segregating component;

(2) the influence of the non-ideality of the solution; and

(3) the influence of (a special type of) elastic strains on the kinetics of the phase transition. As an example the process of AgCl precipitation in a sodium borate liquid is considered. Thermodynamic and material constants are taken from refs. [19,20].

It has been shown in the cited papers that the mentioned system (AgCl in a sodium borate liquid) can be well-described as a regular solution [21] defined by

$$\ln f = \frac{Q}{kT}(1 - x)^2, \quad Q = 4.72 \times 10^{-20}\ \text{J}, \tag{54}$$

where x is the molar fraction of the segregating component, and k the Boltzmann constant. We apply expression (54) in our calculations as an example for a non-ideal solution and compare the results with the corresponding curves for perfect or ideal solutions ($f_i = 1$).

Other values of the parameters are $c_\alpha = 2.3 \times 10^{28}$ m^{-3}, $\sigma = 0.08$ N m^{-1}, and $c' = 1.4 \times 10^{26}$ m^{-3}. The prefactor $D^{(e)} \exp[\phi(c')]$ was determined from the $\langle R(t) \rangle^3$ plots of the asymptotic stage of Ostwald ripening ($\langle R \rangle$ is the average radius of the ensemble of clusters). Its value for $T = 730$ K is found to be equal to 5.8×10^{-16} m^2 s^{-1}.

6.2. Results

Starting with a sharp initial distribution of the segregating particles, consisting at $t = 0$ of monomers only, the results of the numerical calculations show in a first stage a very fast process of establishment of a primary distribution for small cluster sizes. This process results in finite systems, when the number of particles is conserved, in an instantaneous decrease of the supersaturation due to the consumption of monomers connected with the formation of this primary cluster distribution. This effect is investigated in more detail elsewhere [22].

In fig. 1, based on a numerical solution of eq. (43), the rate of formation of clusters with a radius R is shown in dependence on time. Depletion effects – both the decrease of the initial supersaturation as the result of the establishment of a primary cluster distribution and the consumption of monomers in its further evolution – lead to a time-dependence of the nucleation rate and to a lower value of the maximum nucleation rate as compared with the value I_{class} obtained from the classical steady-state approximation for a given supersaturation, which results in

$$I_{\text{class}} = w^+(R_c) Z \exp(\Delta G(R_c)/kT). \tag{55}$$

Z is the Zeldovich factor and $\Delta G(R_c)$ is the change of the Gibbs free energy connected with the formation of a cluster with a critical size R_c [14].

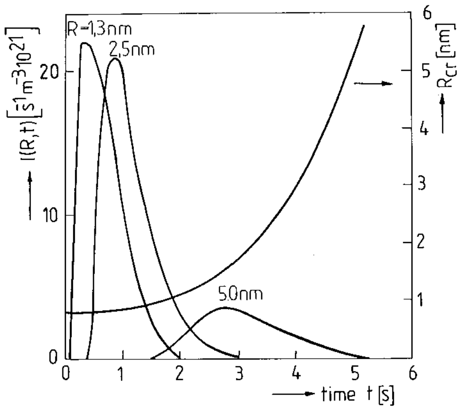

Fig. 1. Rate of thermally activated nucleation of clusters of different sizes $I(R, t)$ versus time for a regular solution without elastic strains according to eq. (44). The values of the parameters are: $c_\alpha = 2.3 \times 10^{28}$ m^{-3}, $c = 4.2 \times 10^{26}$ m^{-3}, $c' = 1.4 \times 10^{26}$ m^{-3}, $\sigma = 0.08$ N m^{-1}, $D^{(c)} \exp[\phi(c')] = 5.8 \times 10^{-16}$ m^2 s^{-1}, $T = 730$ K. The solution is described by the following expression for the segregating particles: $\ln f = Q/kT(1-x)^2$, with $Q = 4 \times 72 \cdot 10^{-20}$ J. The value of the steady-state nucleation rate I_{class} corresponding to these parameters is equal to $I_{\text{class}} = 2000 \times 10^{21}$ m^{-3} s^{-1} (cf. eq. (54)).

Equation (55) can be supplemented by an expression for the calculation of the time-lag needed for the establishment of the steady-state nucleation rate [23] for clusters of a critical size R_c.

From the example presented in fig. 1, two more conclusions can be drawn. First, the time-lag for the establishment of the maximum nucleation rate of clusters of a given size, R, depends on R. This dependence has to be taken into account in experimental investigations, where usually not clusters of a critical size but of a size corresponding to the lower resolution limit of the experimental apparatus, e.g., $R \sim 2.5$ nm for SAXS, are detected. Moreover, the value of the maximum rate of nucleation depends also on R which is due to an interplay of depletion, nucleation and growth.

Taking the time interval of formation of clusters of a radius $R = 2.5$ nm as a measure of the length of the nucleation period, it can be seen from fig. 1, that the duration of the nucleation period is about 3 s. This estimation remains nearly the same if other measures of the length of the nucleation stage are used, connected with the rate of thermally activated formation of supercritical clusters [24].

Figure 2 gives an illustration of the influence of the non-ideal (regular) character of the solution on nucleation. For comparison the cluster distribution is shown at certain moments of time for ideal (dashed curves) and regular solutions (full curves). The consideration of the non-ideality results in a decrease of the total number of clusters and a decrease of the initial rate of evolution of the cluster distribution.

At a later stage, when the period of nucleation is finished, the situation changes. Now, the average cluster size of the distribution evolving in a regular solution becomes larger compared with an ideal solution. This is due to the higher number of clusters formed initially in the ideal solution and the resulting depletion. For a further growth of the larger clusters, the smaller clusters have to be dissolved. The time needed for the process of dissolution contributes significantly to the hindrance of the growth of the larger clusters.

The effects discussed in connection with fig. 2 are generally observed, if the initial supersaturation is decreased [15,16]. Thus, the account of the non-ideal character of the solution can be interpreted as a special form of a decrease of the initial supersaturation (compare, for example, eq. (25).

Moreover, it has to be expected, that elastic strains of the form (37) will lead to the same consequences. This is indeed the case, as shown at part in fig. 3, where the rates of formation of clusters of a radius $R = 5$ nm are shown as a

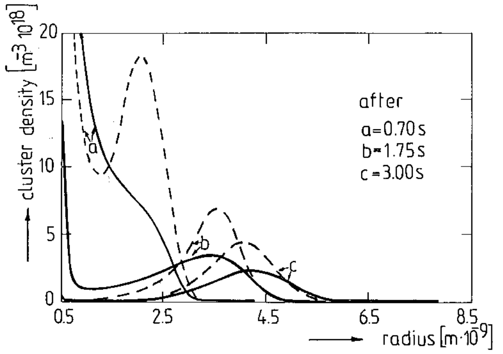

Fig. 2. Evolution of the cluster size distribution in the nucleation stage for ideal (dashed curves) and regular (full curves) solutions and the same initial concentration of segregating particles.

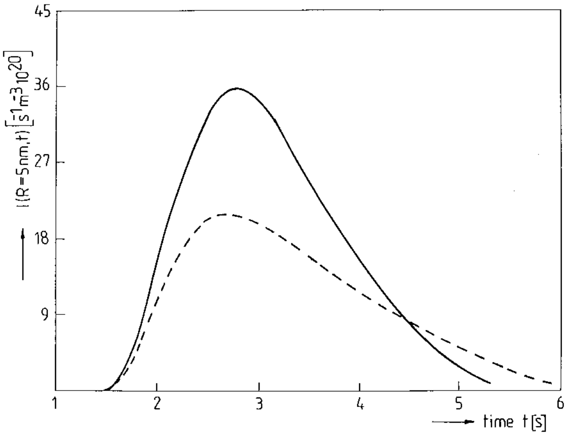

Fig. 3. Rate of formation I of clusters of the size $R = 5$ nm versus time without ($\epsilon = 0$, full line) and with elastic strains ($\epsilon = 6.1 \times 10^7$ J m^{-3}, dashed line) of the form $G^{(\epsilon)} = \epsilon V$ (cf. eq. (37)).

function of time for $\epsilon = 0$ and $\epsilon \neq 0$ and the same initial concentration of segregating particles.

Figure 4 gives the effective supersaturation $\Delta g/kT = \ln(fc/f'c') - \epsilon/c_\alpha$ as a function of time for both cases ($\epsilon = 0$ – full line; $\epsilon \neq 0$ – dashed line). Since the initial concentration of monomers is equal in both cases the elastic strains decrease the initial supersaturation compared with $\epsilon = 0$. As can be seen, the state characterized by a lower supersaturation relaxes at a slower rate into the equilibrium state.

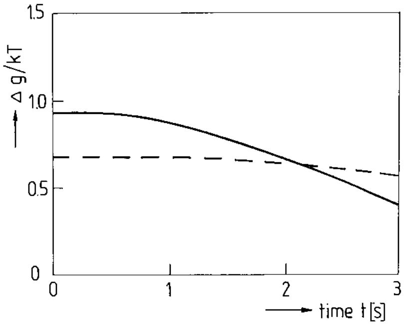

Fig. 4. Evolution of the effective supersaturation $\Delta g/kT$ in time without ($\epsilon = 0$, full line) and with consideration of the elastic strains ($\epsilon = 6.1 \times 10^7$ J m^{-3}, dashed curve).

7. Conclusions

It has been shown in the present study that due to the non-steady character of the nucleation process, resulting from time-lag and depletion effects, incorporation of the non-ideality of the solution and elastic strains leads not only to a change of the nucleation rate but also to significant variations of a number of other characteristics of the phase transformation process in quasi-binary solutions (cluster distribution function, time-lag in dependence on cluster size, rate of the decomposition process in different stages of the phase transformation). Consequently, a detailed study of the evolution of the distribution function with respect to cluster sizes and its dependence on the initial supersaturation, on specific properties of the system under investigation, including different models for the evolving strains, is believed to be of theoretical and practical interest. Such a study is expected to be of particular interest for viscoelastic materials such as glasses and polymers in the vicinity of the glass transformation temperature. The analysis can be carried out straightforwardly based on the general rate or kinetic equations outlined here.

References

[1] J.D. Gunton, M. San Miguel and P.S. Sahni, in: Phase Transitions and Critical Phenomena, Vol. 8, eds. C. Domb, M.S. Green and J.L. Lebowitz (Academic Press, London, 1983) p. 267.

[2] S. Komura and H. Furukawa, eds., Dynamics of Ordering Processes in Condensed Matter (Plenum, New York, 1988).

[3] H. Ulbricht, J. Schmelzer, R. Mahnke and F. Schweitzer, Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions (Teubner, Leipzig, 1988).

[4] J. Schmelzer and I. Gutzow, Z. Phys. Chem. (Leipzig) 269 (1988) 753.

[5] R. Pascova, I. Gutzow and J. Schmelzer, J. Mater. Sci. 25 (1990) 921.

[6] J. Schmelzer, I. Gutzow and R. Pascova, J. Cryst. Growth, in press.

[7] R. Haase, Thermodynamik der Irreversiblen Prozesse (Thermodynamics of Irreversible Processes) (Springer, Darmstadt, 1963).

[8] R. Haase, Thermodynamik der Mischphasen (Thermodynamics of Mixtures) (Springer, Berlin, 1956).

[9] I.M. Lifshitz and V.V. Slyozov, J. Exper. Theor. Phys. (USSR) 25 (1958) 479.

[10] I.M. Lifshitz and V.V. Slyozov, Solid State Phys. (USSR) 1 (1959) 1401.

[11] J.W. Christian, The Theory of Transformations in Metals and Alloys (Pergamon, London, 1974).

[12] F.R. Nabarro, Proc. R. Soc. (London) 175A (1940) 519.

[13] J. Crank, The Mathematics of Diffusion, 2nd Ed. (Clarendon, Oxford, 1975).

[14] R. Becker and W. Döring, Ann. Phys. 24 (1935) 719.

[15] J. Bartels, J. Schmelzer and F. Schweitzer, in: Irreversible Processes and Self-organization, eds. W. Ebeling and H. Ulbricht, Teubner-Texte zur Physik, Vol. 23 (Teubner, Leipzig, 1990) p. 47.

[16] F. Schweitzer and J. Bartels, in: Phase Transitions in Binary Systems: Theory and Experiment, Rostocker Physikalische Manuskripte 12 (1988) 70.

[17] K.F. Kelton, J. Non-Cryst. Solids 79 (1986) 295.

[18] H. Trinkaus and M.H. Yoo, Philos. Mag. A55 (1987) 269.

[19] I. Gutzow and R. Pascova, Glastechn. Ber. 56 (1983) 324.

[20] R. Pascova, I. Gutzow and I. Tomov, J. Mater. Sci. 25 (1990) 914.

[21] R. Becker, Ann. Phys. 32 (1938) 128.

[22] J. Bartels, J. Schmelzer and F. Schweitzer, Z. Phys. Chem. 166 (1990) 119.

[23] D. Kashchiev, Surf. Sci. 14 (1969) 209.

[24] J. Schmelzer and H. Ulbricht, J. Colloid Interface Sci. 117 (1987) 325.