JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS, 2024, Vol. 165, No. 2, pp. 205–215

SOLIDS AND LIQUIDS

ON THE THEORY OF HOMOGENEOUS NUCLEATION OF INCOHERENT INCLUSIONS IN SOLID SOLUTIONS

© 2024 **M.S. Veshchunov**

Nuclear Safety Institute (IBRAE), Russian Academy of Sciences, Moscow 115191, Russia

e-mail: *msvesh@gmail.com*

Received August 16, 2023

Revised August 16, 2023

Accepted September 07, 2023

Abstract. Based on a critical analysis of the traditional theory of homogeneous nucleation of incoherent precipitates of a new phase in solid solutions, it is shown that the elastic energy associated with a difference in the atomic volumes of two phases does not contribute to the nucleation barrier due to the absorption of thermal point defects at the particle-matrix interface (in contrast to the traditional approach). Correspondingly, a new kinetic model is developed for the rate of nucleation of incoherent precipitates in a supersaturated solid solution of alloying atoms, which has also been generalized to take into account excess vacancies formed under non-equilibrium conditions of quenching tests.

Keywords: *incoherent inclusions*, *solid solutions*, *homogeneous nucleation*, *Reiss theory*

DOI: 10.31857/S00444510240207e4

1. INTRODUCTION

When the transformation takes place in the solid state, i.e. between two solid phases, elastic misfit strain energy is generally present due to volume and/or shape incompatibilities between the cluster and the matrix. However, the changes in volume and shape cannot occur freely because of the rigidity of the surrounding matrix, and elastic strains are induced. The elastic strain energy and the surface energy created by the new phase nuclei make a positive contribution to the free energy and therefore act as a barrier to nucleation. The magnitude of the elastic energy term generally depends upon factors such as the cluster shape, the mismatch between the cluster and the matrix, and whether the interface between the matrix and cluster is coherent, semicoherent, or incoherent [1–3].

The interfacial energy of incoherent solid/solid interfaces is typically about (0.7–1) J·m^{-2}, whereas that of an interface that is coherent is lower by a factor of 3 or more. Homogeneous nucleation is therefore often expected in cases where the nucleus interface is coherent and the interfacial energy is relatively low.

However, the large difference in atomic volumes and the difference in crystal structures may result in a largely incoherent precipitate/matrix interface. For instance, it appears that there is no coherent clustering of silicon in aluminium alloys. Pure silicon has a diamond cubic structure and there is no evidence that a low energy face-centred cubic modification exists [4]. Besides, silicon has a greater atomic volume than Al with the deformation strain of 0.2, which can be too large for formation of the coherent interface. The precipitation of silicon from a supersaturated solid solution of Al (1% Si) in the form of equiaxed particles randomly distributed inside the grains was observed by X-ray diffraction analysis, as well as by light and electron microscopy [5, 6]. Similar observations using a transmission electron microscope in Al-Si alloys after various quenching and pre-aging treatments were presented in [7].

Modern principles of strengthening, fracture and precipitation in alloys suggest that ultra-fine dispersoids in f.c.c. Al-matrix represent the ideal microstructure if ultra-high strength and resistance to fracture are desired. The basis of such a microstructure is provided only by two binary alloy systems: Al-Si and Al-Ge. Therefore, these alloys can serve both as models for mechanistic studies of the nucleation of incoherent phases and as the basis for a new class of technical aluminium alloys [8].

In the traditional nucleation theory for a transformation where strain energy effects are not negligible (see, e.g. [1–3]), the formation of a nucleus of given size will require an increase in the Gibbs free energy of the nucleus formation, ΔG_0, with the addition of the elastic energy term. The elastic energy is proportional to the number x of atoms in the nucleus, so that

$$\Delta G_0(x) = x(-\Delta g_b + \Delta g_{el}) + \Delta G_{surf}, \qquad (1)$$

where $\Delta g_b = kT\ln S_x$ is the bulk free energy change per atom involved in the formation of the nucleus in the solid solution with the supersaturation S_x; Δg_{el} is the elastic energy per atom; $\Delta G_{surf} = \gamma 4\pi R^2$ is the surface energy of the nucleus with surface tension γ.

For an incoherent spherical nucleus of radius $R_x = \left(3\frac{\Omega}{4\pi}\right)^{1/3} x^{1/3}$, the misfitting sphere model of Nabarro [9] may be applied to give the total strain energy (cf. [3]),

$$\Delta G_{el} = x\Delta g_{el} = 6\mu\left(\frac{3K}{3K+4\mu}\right)\delta^2 V_p, \qquad (2)$$

where δ is the transformation strain (for simplicity assumed to be $\ll 1$) due to forming the particle of a volume $V_p = x\Omega$ placed in a spherical cavity of a volume $V_m = x\Omega_m$, calculated from the relation $V_p / V_m = (1+\delta)^3 \approx 1 + 3\delta$; Ω and Ω_m are the atomic volumes in the particle and in the matrix respectively; μ is the shear modulus of the matrix, and K is the bulk modulus of the particle. The common boundary between the inclusion and the matrix will occupy a position intermediate between the surfaces of the cavity and the inclusion before matching, with the misfit strain $\varepsilon = \delta / [1 + 4\mu / 3K]$. However, in the case $3K \gg 4\mu$ when all the strain is taken by the matrix and thus $\varepsilon \approx \delta$, this equation can be simplified,

$$\Delta G_{el} = x\Delta g_{el} \approx 6\mu\delta^2 V_p. \qquad (3)$$

Minimization of Eq. (1), $\partial\Delta G_0(x)/\partial x = 0$, gives the critical nucleus size,

$$x^* = \frac{32\pi}{3}\left(\frac{\gamma}{kT\ln S_x - \Delta g_{el}}\right)^3 \Omega^2 = \frac{32\pi}{3}\left(\frac{\gamma}{kT\ln S_x - 6\mu\Omega\delta^2}\right)^3 \Omega^2, \qquad (4)$$

and the formation free energy of the critical nucleus,

$$\Delta G_0(x^*) = \frac{16\pi}{3}\frac{\gamma^3\Omega^2}{\left(kT\ln S_x - 6\mu\Omega\delta^2\right)^2}, \qquad (5)$$

which demonstrates that the misfit strain reduces the effective driving force for precipitation and increases the critical supersaturation to $S_x^* = \exp\left(6\mu\Omega\delta^2 / kT\right) > 1$ [1–3].

This article will present a critical analysis of the traditional theory of the nucleation of incoherent precipitates in solid solutions based on Eqs (3) and (4). As a result, it will be shown that taking into account thermal point defects in the parent phase, which can be absorbed at the particle-matrix interface during particle nucleation, leads to the removal of the nucleation barrier associated with the elastic strain energy created by the nuclei of the new phase. On this basis, a new model for the nucleation rate of incoherent precipitates will be developed within the framework of the Reiss theory for binary homogeneous nucleation as applied to a binary system of an oversaturated solid solution and thermal vacancies. The kinetic model can also be generalized to take into account excess vacancies formed under non-equilibrium conditions (e.g. during quenching).

2. CRITICAL ANALYSIS OF THE TRADITIONAL THEORY

It should be noted that Eqs (3) and (4) are definitely valid for coherent particles, since vacancies can only be trapped (or *ad*sorbed) at the particle-matrix interface and thus do not change the elastic energy of the particle.

However, for incoherent particles, at the interface of which with the matrix vacancies and self-interstitials are *ab*sorbed, the situation can change significantly: due to the absorption of vacancies and emission of self-interstitials (with the net number $n = n_v - n_i$), the interface of an oversized particle relocates outward leading to a simultaneous increase in the volume of the cavity (in which the particle is inserted), $V_m \to V_m' = (x+n)\Omega_m$, the radius of the interface,

$$R \to R' = \left(3\frac{\Omega_m}{4\pi}\right)^{1/3}(x+n)^{1/3} = \left[3\frac{\Omega}{4\pi}(1+\varphi)\right]^{1/3}(x+n)^{1/3}$$

and its surface area, $S \to S'$. In turn, this leads to a decrease in the elastic energy ΔG_{el} (due to a decrease in the transformation strain $\delta \to \delta' = \left(V_p - V_m'\right)/3V_p$) and an increase in the surface energy ΔG_{surf}.

Assuming that the elastic strain in the matrix near the interface is small (which will be self-consistently confirmed below) and thus the chemical potential of point defects in equilibrium with the interface is close to zero, then the free energy of the system of equilibrium point defects in the matrix (with zero chemical potential) does not change due to their absorption.

In this case, Eq. (1) takes the form

$$\Delta G_0(x,n) = -kTx\ln S_x + 4\pi\gamma\left(\frac{3}{4\pi}\Omega_m\right)^{\frac{2}{3}} \times \times (x+n)^{\frac{2}{3}} + \frac{2\mu\Omega}{3}\left(\frac{1}{1+\varphi}\right)^2 x\left(\varphi - \frac{n}{x}\right)^2, \tag{6}$$

where $\varphi = (\Omega - \Omega_m)/\Omega_m$.

Minimization of Eq. (6) with respect to the two variables, $\partial\Delta G_0(x,n)/\partial x = \partial\Delta G_0(x,n)/\partial n = 0$, gives a new expression for the critical nucleus size,

$$x^* = \frac{288\pi\gamma^3\Omega^2}{\left[4\mu\Omega(1-q)\right]^3 q} \approx \approx \frac{32\pi}{3}\left(\frac{\gamma}{kT\ln S_x}\right)^3 \Omega^2\left(1 - \frac{3kT}{8\mu\Omega}\ln S_x\right), \tag{7}$$

where $q = \left(1 - \frac{3kT}{2\mu\Omega}\ln S_x\right)^{\frac{1}{2}}$, or $q \approx 1 - \frac{3kT}{4\mu\Omega}\ln S_x$ in the first approximation in a small parameter $3kT/4\mu\Omega \ll 1$, and

$$\frac{n^*}{x^*} = (\varphi+1)q - 1 \approx \varphi - \frac{3kT}{2\mu\Omega}(1+\varphi)\ln S_x, \tag{8}$$

whereas the formation free energy of the critical nucleus is calculated as

$$\Delta G_0^* \equiv \Delta G_0\left(x^*, n^*\right) = = \frac{48\pi\gamma^3\Omega^2\left[4\mu\Omega(q-1) + 6kT\ln S_x\right]}{\left[4\mu\Omega(1-q)\right]^3 q} \approx \approx \frac{16\pi}{3\left(kT\ln S_x\right)^2}\gamma^3\Omega^2\left[1 + \frac{3}{4}\frac{kT}{\mu\Omega}\left(\frac{1}{1+\varphi}\right)^2 \ln S_x\right] \approx \approx \frac{16\pi}{3}\frac{\gamma^3\Omega^2}{\left(kT\ln S_x\right)^2}, \tag{9}$$

which demonstrates that the elastic strain in the matrix is almost completely compensated by absorbed point defects, and, consequently, Eqs (4) and (5) are invalid for incoherent precipitates. Therefore, the conclusion of the traditional theory that the strain energy created by the nuclei of the new phase acts as a barrier to nucleation is not correct and must be amended when evaluating the nucleation rate of incoherent particles (as shown below).

It is interesting to note from Eq. (8) that for a relatively small misfit strain of oversized particles with $0 < \varphi < \frac{3kT}{4\mu\Omega}\ln S_x$, the critical nucleus does not absorb but emits vacancies, $n^* < 0$; this occurs because, at such misfits, the decrease in the nucleus surface energy due to the emission of vacancies prevails over the increase in the elastic strain energy. This additionally demonstrates the importance of self-consistent consideration of changes in the nucleus volume and surface due to absorption/emission of point defects.

In typical experiments with supersaturated alloys (see, e.g. [5–7]), the maximum number of particles was nucleated when the samples were quenched, creating an excess of vacancies in the matrix (with a supersaturation level $S_v = c_v / c_v^{(0)}$, where c_v is the dimensionless non-equilibrium concentration of vacancies and $c_v^{(0)}$ is its thermal value), which can significantly accelerate the nucleation process. More generally, an excess of self-interstitials in the quenched (non-equilibrium) matrix (with supersaturation $S_i = c_i / c_i^{(0)}$), should be additionally taken into account. However, under the condition $c_i^{(0)} / c_v^{(0)} \ll 1$ before quenching which is normally realised in metals (since self-interstitials have rather high formation enthalpies compared to vacancies [10]), fast recombination during subsequent cooling leads to the survival of only excess vacancies.

The influence of excess vacancies on the nucleation barrier was considered by Russel [11]. His predictions, while qualitatively passable, turned out to be insufficient due to some inconsistencies in the model formulation, which can be avoided after some modification of his model. In particular, in the free energy of formation of an incoherent particle, the change in its volume due to the absorption of vacancies was taken into account, but the increase in the interface area was neglected (which makes this approach inconsistent, as explained above).

A more adequate result can be obtained by generalizing the model presented above to take into account excess vacancies formed under non-equilibrium (quenching) conditions, which makes it possible to refine Russel's model. For this, an additional term, $-kTn\ln S_v$, describing the variation of the free energy of n vacancies due to absorption at the interface from the matrix, should be implemented in Eq. (1), leading to

$$\Delta G_0(x,n) = -kTx\ln S_x - kTn\ln S_v + \\ +4\pi\gamma\left(\frac{3}{4\pi}\Omega_m\right)^{\frac{2}{3}}(x+n)^{\frac{2}{3}} + \\ +\frac{2}{3}\mu\Omega\frac{1}{(1+\varphi)^2}x\left(\varphi - \frac{n}{x}\right)^2, \tag{10}$$

which minimization with respect to x and n in the critical point gives in the first approximation in $3kT/4\mu\Omega \ll 1$,

$$\frac{n^*}{x^*} = (\varphi+1)\tilde{q} - 1 \approx \varphi - (\varphi+1)\frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}, \tag{11}$$

where $\tilde{q} = \left(1 - \frac{3kT}{2\mu\Omega}\ln\frac{S_x}{S_v}\right)^{1/2}$, and

$$x^* = \frac{288\pi\gamma^3\Omega^2}{\left[3kT(1+\varphi)\ln S_v + 4\mu\Omega(1-\tilde{q})\right]^3\tilde{q}} \approx \\ \approx \frac{32\pi}{3}\left(\frac{\gamma}{kT}\right)^3\frac{\Omega^2}{\left[\ln S_x + \varphi\ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right]^3} \times \\ \times\left(1 + \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right). \tag{12}$$

Correspondingly, the expression for the formation free energy of the critical nucleus takes the form

$$\Delta G_0^* = 48\pi\gamma^3\Omega^2\frac{\left[4\mu\Omega(q-1) + 6kT\ln S_x + 3kT\left[-2 + (1+\varphi)\tilde{q}\right]\right]}{\left[4\mu\Omega(1-\tilde{q}) + 3kT(1+\varphi)\ln S_v\right]^3\tilde{q}} \approx \\ \approx \frac{16\pi}{3}\frac{\gamma^3\Omega^2}{(kT)^2}\frac{1}{\left[\ln S_x + \varphi\ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right]^3} \times \\ \times\left\{\begin{matrix}\ln S_x + \varphi\ln S_v + \frac{3kT}{2\mu\Omega}\ln\frac{S_x}{S_v}\ln S_v + \\ +\frac{3}{4}\frac{kT}{\mu\Omega}\left[\left(\frac{1}{1+\varphi}\right)^2 + \frac{3}{2}\right]\left(\ln\frac{S_x}{S_v}\right)^2\end{matrix}\right\}, \tag{13}$$

with the critical supersaturation $\ln S_x^* \approx -\varphi\ln S_v$.

Therefore, the results of calculations [11] with the overestimated nucleation barrier

$$\Delta G_0^* \approx 16\pi\gamma^3\Omega^2 \Big/ \left[3(kT)^2\left(\ln S_x + \varphi\ln S_v - \frac{9kT(1-\nu)}{8\mu\Omega(1+\nu)}\ln^2 S_v\right)^2\right],$$

where ν is Poisson's ratio (which appeared due to the erroneous use of the expression for the strain energy of coherent particles as applied to incoherent particles), led to an underestimation of the effect of excess vacancies on nucleation barrier (along with an overestimation of the critical supersaturation S_x^*), or even to the cancellation of this effect at typical values of $\varphi \approx 0.1$ and $\ln S_v \approx 5$ (when $\varphi\ln S_v \approx \frac{9kT(1-\nu)}{8\mu\Omega(1+\nu)}\ln^2 S_v$).

3. BINARY NUCLEATION

The problem of nucleation of equiaxed incoherent precipitates (observed in [5, 6]) is an example of homogeneous nucleation in binary systems where the nuclei can be considered as a spherical particle of a new phase in the parent solid phase containing solute atoms (and vacancies). However, the classical nucleation theory [12–14] was developed mainly in relation to one-component (unary) systems.

This theory was generalized to the kinetics of nucleation in binary mixtures by Reiss [15]. In his theory, the parent phase is thought of as a mixture of molecules (monomers) of two components X and Y with number densities N_x and N_y (corresponding to dimensionless concentrations c_x and c_y), respectively, together with clusters of all sizes and compositions. A particular molecular cluster is characterized by the numbers of single molecules (or monomers) x and y of species X and Y, respectively, that it contains. Reiss showed that the critical point of unstable equilibrium corresponds in this case to a saddle point $\left(x^*, y^*\right)$ on the free energy surface $\Delta G_0(x,y)$. He characterized the rate of the transition by a two-dimensional flux vector (in the phase space of cluster sizes x, y) at the critical point, $\boldsymbol{J}\left(x^*, y^*\right)$, oriented in the direction of the steepest descent of the free energy surface (the axis of the pass x').

Accordingly, in Reiss' expression for the nucleation rate

$$\dot{N} = J\left(x^*, y^*\right) \approx -f_0\left(x^*, y^*\right)\frac{\beta_x^*\beta_y^*\left(1 + \mathrm{tg}^2\theta\right)}{\beta_y^* + \beta_x^*\mathrm{tg}^2\theta} \times \\ \times D'_{11}\left(\frac{1}{D_{12}^2 - D_{11}D_{22}}\right)^{1/2}, \tag{14}$$

where $f_0(x,y)$ is the equilibrium size distribution function,

$$f_0(x,y) = F\exp\left[-\Delta G_0(x,y)/kT\right], \tag{15}$$

F is the kinetic factor discussed below in Section 3.1; θ is the angle between the original axis x and the axis of the pass x'; $\beta_i^* = \beta_i\left(x^*, y^*\right) = 4\pi D_i c_i R^* \Omega^{-1}$, $i = x, y$, are the arrival rates of monomers X and Y to the critical cluster $\left(x^*, y^*\right)$ of radius R^*; $D_{ij} = \frac{1}{2}\frac{\partial^2 \Delta G_0(x,y)}{\partial x_i \partial x_j}\Big|_{x^*,y^*}$ are elements of the matrix $\mathbf{D} = \left(D_{ij}\right)$, which determinant is negative in the saddle point (in accordance with the classification of the critical points, cf. [16]), and, thus, $\det \mathbf{D} = D_{11}D_{22} - D_{12}^2 < 0$;

$$D'_{11} = \frac{1}{2}\frac{\partial^2 \Delta G_0(x',y')}{\partial x'^2}\Big|_{x^*,y^*} = \tag{16}$$
$$= D_{11}\cos^2\theta + D_{22}\sin^2\theta + 2D_{12}\sin\theta\cos\theta,$$

is the second derivative of ΔG_0 in the direction x' of the orthogonal coordinate system (x', y') obtained by rotating the original coordinate system (x, y) through the angle θ, which should be negative, $D'_{11} < 0$, to provide a maximum of the free energy at the critical point in the direction of the x'-axis.

Reiss' theory was modified by Langer [17] (with subsequent reiteration by Stauffer [18]), who corrected the orientation of the flux vector in the direction parallel to the direction of the unstable mode at the saddle point (the new axis of the pass x'), using a formal approach based on additional trial assumption (ansatz) to solve the steady state equation for the non-equilibrium size distribution function in the critical zone.

The modified value of θ was explicitly calculated in [18] and later refined in [19] as

$$\operatorname{tg}\theta = \begin{cases} s + \left(r + s^2\right)^{1/2}, & D_{21} < 0, \\ s - \left(r + s^2\right)^{1/2}, & D_{21} > 0, \end{cases} \tag{17}$$

where $r = \beta_x^* / \beta_y^*$, $s = \left(d_a - r d_b\right)/2$, $d_a = -D_{11}/D_{12}$ and $d_b = -D_{22}/D_{12}$.

3.1. Pre-exponential kinetic factor

In the Reiss theory, given the total number density of N_{xy} clusters small compared to the number density of single molecules (monomers) of X and Y in the parent phase, $N_{xy} \ll N_x, N_y$, respectively, the pre-exponential factor F of the equilibrium size distribution function in Eq. (14) is equal to the total number density of monomers

$$F = N_x + N_y. \tag{18}$$

Accordingly, in three different situations investigated by Reiss [6], it was assumed that no third inert gas was present in the parent phase. As applied to a lattice gas (with a lattice site density N_0), this assumption corresponds to the complete filling of the lattice sites with monomers, i.e. $N_x + N_y = N_0$. This approach was a generalization of the Frenkel model [20], which characterizes the cluster size distribution in a one-component system.

The correctness of such approach as applied to vapours in an inert atmosphere (with $N_x + N_y \ll N_0$, where N_0 is the total density of the gas mixture, including inert gas) was widely criticized in the literature. In particular, Lothe and Pound [21] suggested that degrees of freedom corresponding to the translation of clusters have been neglected in the development of nucleation theory. As a result, they predicted that the pre-exponential factor is proportional to the total number density of gas molecules (or lattice sites in the case of a lattice gas) N_0 rather than vapour molecules, leading to a large discrepancy with the previous approach. A similar conclusion as applied to the lattice gas was made in a large number of subsequent works, reviewed and supported in [22]. For binary vapours in an inert carrier gas, the approach of Lothe and Pound was generalized in [23].

This disagreement ('translation paradox') was discussed by Reiss and Katz [24], who evaluated the partition function of the system taking into account permutations of monomers among clusters and showed that Lothe and Pound's correction to the nucleation theory does not arise (for unary vapours). However, in their subsequent paper [25], where the main qualitative conclusions of [24] were reaffirmed, a correction factor of several orders of magnitude was calculated (however, much smaller than the Lothe and Pound correction). Presumably for this reason, Katz disregarded his previous results [24] and modified the Frenkel model in his subsequent works (e.g. in [26, 27]).

Therefore, the contradiction between different approaches has not been completely resolved and required further analysis. Such an analysis for unary systems was carried out in the recent work of the author [28] within the framework of the thermodynamic approach [29], taking into account the interaction of monomers with clusters (considered in the statistical mechanics approach [24, 25] and disregarded in the Lothe and Pound model [21, 22]). A generalization of this consideration to binary systems is presented in the Appendix A, where the validity of Eq. (18) is justified in relation to binary solid solutions.

3.2. Nucleation rate

When applying the Reiss theory to the nucleation of incoherent particles, the index x will be assigned to solute atoms and the index y to vacancies in the matrix. Results of calculations of the elements of the matrix $\mathbf{D} = \left(D_{ij}\right)$ and other related parameters of Eq. (14) are presented in the Appendix B, where it is assumed that $D_v c_v^{(0)} \geq D_x c_x$, taking into account that in the majority of metals, the self-diffusion coefficient D_s is determined by the vacancy mechanism and thus $D_s \approx D_v c_v^{(0)}$ [10], and $D_x \approx D_s$ for Si in Al [30], whereas the typical concentration of Si in Al in the precipitation tests [5–7] was a few percent, $c_x \ll 1$. In the case of thermal vacancies in the matrix (with $c_v^{(0)} \ll c_x$), the nucleation rate of incoherent particles (number per unit volume per unit time) takes the form

$$\dot{N} \approx 4\pi D_x c_x^2 \frac{\gamma}{kT}\left(\frac{kT}{4\mu\Omega}\right)^{\frac{1}{2}} \ln^{-\frac{1}{2}} S_x \exp\left(-\frac{16\pi\gamma^3\Omega^2}{3(kT)^3 \ln^2 S_x}\right). \quad (19)$$

In the case of quenched samples with an excess of vacancies in the matrix, a more general expression is derived in the Appendix B,

$$\dot{N} \approx \frac{\gamma}{kT}\left(\frac{kT}{4\mu\Omega}\right)^{\frac{1}{2}} \frac{4\pi D_x c_x\left(c_x + c_v\right)}{\left[\ln S_x + \varphi \ln S_v + \dfrac{3}{8}\dfrac{kT}{\mu\Omega}\left(\ln\dfrac{S_x}{S_v}\right)^2\right]^{\frac{1}{2}}} \times$$
$$\times \exp\left\{-\frac{16\pi\gamma^3\Omega^2}{3(kT)^3\left[\ln S_x + \varphi \ln S_v + \dfrac{3}{8}\dfrac{kT}{\mu\Omega}\left(\ln\dfrac{S_x}{S_v}\right)^2\right]^2}\right\}. \quad (20)$$

From this equation, it may be concluded that an excess of vacancies in quenched samples not only reduces the nucleation barrier, but also increases the pre-exponential factor due to increased diffusion of dissolved atoms $D_x \propto c_v$ in materials with a vacancy diffusion mechanism.

As noted in [1], the experimental measurement of nucleation rates during precipitation in solid solutions is extremely difficult, since measurable rates can only be obtained in a very limited range of experimental conditions. An additional difficulty is related to the calculation of the actual number of particles formed, since there is often a significant simultaneous coarsening of the particles. Therefore, the common procedure is to find the thermodynamic driving force that is needed to obtain measurable amounts of nucleation. Since the nucleation rate is so sensitive to the value of the driving force, it is not necessary to know with high precision the many other (kinetic) factors in the overall expression for the nucleation rate. Therefore, the key problem of the theory of nucleation in solid solutions, in view of the many uncertainties involved, is a qualitatively correct understanding of the underlying mechanisms and their consistency with experimental observations. In this regard, the obtained Eqs (19) and (20) for the nucleation rate can be used to adequately interpret available and new observations.

4. CONCLUSION

The traditional theory for a homogeneous nucleation of incoherent precipitates in solid solutions (cf. [1–3]), is critically analysed. It is shown that the prediction of the theory that the formation of a nucleus of a given size will require an increase in the free energy of nucleus formation due to the elastic energy associated with a difference in the atomic volumes of the two phases becomes incorrect for incoherent precipitates. Namely, it is shown that taking into account thermal point defects in the parent phase which can be absorbed at the particle-matrix interface during the nucleation of particles, leads to relaxation of the emerging nucleus, removal of the contribution of elastic strain energy to the nucleation barrier, and restoration of the critical supersaturation $S_x^* \approx 1$ (overestimated in the traditional approach).

On this basis, within the framework of the Reiss theory for binary homogeneous nucleation, a kinetic model is developed for the rate of nucleation of incoherent precipitates as applied to a binary system of a supersaturated solid solution of alloying atoms and thermal vacancies in the matrix.

The model is generalized to take into account excess vacancies formed under non-equilibrium conditions of quenching tests in dilute alloys (e.g. Al-Si). It is shown that an excess of vacancies in the quenched samples lowers the nucleation barrier, shifts the critical oversaturation to the value $S_x^* \approx -\varphi \ln S_v$ (which may differ significantly from the estimates of the simplified thermodynamic model [11]), and increases the kinetic pre-exponential nucleation rate factor.

ACKNOWLEDGEMENTS

The author thanks Dr. V. Tarasov (IBRAE, Moscow) for careful reading of the manuscript and valuable recommendations.

Appendix A.

Calculation of the pre-exponential factor of the equilibrium size distribution function

Although the Lothe and Pound approach [21] correctly identified the limitations of the earlier approach (in which the influence of an inert carrier gas was ignored), it inherited the main drawback of this approach, considering the system of monomers and clusters as an ideal mixture.

Indeed, such consideration is valid only in the case of Boltzmann statistics (to which the ideal gas obeys), when all particles are distributed over different thermodynamic states completely independently of each other [29]. For clusters of finite sizes, their interaction with monomers (described in the statistical mechanics approach [24, 25] by permutations of monomers among clusters), cannot be neglected, since clusters, in contrast to monomers, cannot be considered as point particles.

In accordance with general thermodynamics, the additivity of thermodynamic quantities, such as free energy or entropy, is preserved only as long as the interaction between different parts of the system is negligible, as in the case of ideal gas mixtures, for which, for example, the entropy of the mixture is equal to the sum of the entropies of each of gases. Therefore, for a non-ideal mixture of several substances (for example, monomers and clusters), the entropy is no longer equal to the sum of the entropies of each of the substances [29].

To find the excess entropy of a mixture of monomers and clusters, let $\Phi_0\left(P,T,N_x,N_y\right)$ be the Gibbs free energy of an ideal solid solution in the crystal matrix (with the number density of lattice sites N_0) of monomers X and Y (with the number density N_x and N_y, respectively), whose chemical potentials are $\mu_i\left(P,T,c_i\right)=\psi_i\left(P,T\right)+kT\ln c_i$, where $i=x,y$, and $c_i=N_i/N_0\ll 1$. Let α_{xy} denote the small change which would occur in the free energy if one spherical cluster X_xY_y consisting of $\left(x,y\right)$ monomers (a nucleus of the new phase) was added to the system. In the thermodynamic approach, clusters are considered as 'macroscopic' systems with $n_x,n_y\gg 1$. Due to the interactions of clusters with monomers, $X_xY_y\pm X=X_{x\pm1}Y_y$, and $X_xY_y\pm Y=X_xY_{y\pm1}$, this value should be sought as a function of N_x and N_y, i.e. $\alpha_{xy}=\alpha_{xy}\left(P,T,N_x,N_y\right)$. Due to $N_{xy}\ll N_x,N_y$, where N_{xy} is the number (per unit volume) of clusters of size $\left(x,y\right)$, interactions between clusters can be neglected, and thus the free energy takes the form

$$\Phi=N_x\mu_x+N_y\mu_y+N_{xy}\alpha_{xy}\left(P,T,N_x,N_y\right)+ \\ +kT\ln\left(N_{xy}!\right), \tag{A.1}$$

where the latter term, $kT\ln\left(N_{xy}!\right)\approx kTN_{xy}\ln\left(N_{xy}/e\right)$, takes into account that all (spherical) clusters of one size $\left(x,y\right)$ are identical and, being macroscopic bodies, are uniformly distributed in the external medium (represented by the lattice gas).

This consideration is fundamentally different from the distribution of a new ideal lattice gas with density in the existing lattice mixture of lattice gases, which becomes part of the 'medium' and transforms the configurational entropy

$$kT\ln\left(\frac{N_0!}{\left(N_0-N_x-N_y\right)!N_x!N_y!}\right)\approx \\ \approx -kT\left[N_x\ln\left(\frac{N_x}{N_0}\right)+N_y\ln\left(\frac{N_y}{N_0}\right)\right],$$

(which enters through chemical potential terms) in the

$$kT\ln\left(\frac{N_0!}{\left(N_0-N_x-N_y-N_z\right)!N_x!N_y!N_z!}\right).$$

Consequently, the additional entropy term in Eq. (A.1) will be of the form $kTN_z\ln\left(\frac{N_z}{N_0}\right)$, instead of $kTN_z\ln\left(N_z/e\right)$, with simultaneous vanishing of the interaction term $N_z\alpha_z$.

$$\Phi=N_x\mu_x+N_y\mu_y+kTN_{xy}\ln\left[\frac{N_{xy}}{e}\exp\left(\frac{\alpha_{xy}}{kT}\right)\right]. \tag{A.2}$$

Since Φ must be a homogeneous function of the first order in N_x, N_y and N_{xy} [29], the term $\exp\left[\alpha_{xy}\left(P,T,N_x,N_y\right)/kT\right]$ in the argument of the logarithm should be sought in the most general form $f_{xy}\left(P,T\right)/\left(N_x+\beta N_y\right)$. Given that after redefining $x\leftrightarrow y$, the free energy should not change, we can conclude that $\beta=1$. Accordingly,

$$\Phi=N_x\mu_x+N_y\mu_y+kTN_{xy}\ln\left[\frac{N_{xy}}{e\left(N_x+N_y\right)}f_{xy}\left(P,T\right)\right], \tag{A.3}$$

or, introducing a new function $\psi_{xy}\left(P,T\right)=$ $=kT\ln f_{xy}\left(P,T\right)$,

$$\Phi=N_x\mu_x+N_y\mu_y+N_{xy}\psi_{xy}\left(P,T\right)+ \\ +kTN_{xy}\ln\left[\frac{N_{xy}}{e\left(N_x+N_y\right)}\right]. \tag{A.4}$$

Comparison of Eq. (A.4) with Eq. (A.1) shows that

$$N_{xy}\alpha_{xy}\left(P,T,N_x,N_y\right) = \\ = N_{xy}\psi_{xy}\left(P,T\right) - kTN_{xy}\ln\left(N_x + N_y\right). \tag{A.5}$$

Therefore, since the first term in Eq. (A.5), $N_{xy}\psi_{xy}\left(P,T\right)$, does not depend on the number of monomers, the value $\psi_{xy}\left(P,T\right)$ is the standard free energy of a cluster, while the second term of Eq. (A.5), $kTN_{xy}\ln\left(N_x + N_y\right)$, is the excess entropy of the mixture.

This leads to the following expressions for the chemical potentials of the ‘solvents’

$$\mu'_x = \frac{\partial\Phi}{\partial N_x} = \mu_x - kTc_{xy} \approx \mu_x, \tag{A.6}$$

$$\mu'_y = \frac{\partial\Phi}{\partial N_y} = \mu_y - kTc_{xy} \approx \mu_y, \tag{A.7}$$

where $c_{xy} \approx N_{xy} / \left(N_x + N_y\right) \ll 1$, and of the ‘solute’

$$\mu_{xy} = \frac{\partial\Phi}{\partial N_{xy}} = kT\ln c_{xy} + \psi_{xy}. \tag{A.8}$$

Therefore, from the equilibrium condition of the chemical reaction $xX + yY = X_xY_y$,

$$x\mu_x + y\mu_y = \mu_{xy}, \tag{A.9}$$

the mass action law can be derived as

$$c_{xy} \approx N_{xy} / \left(N_x + N_y\right) = K_{xy}\left(T\right), \tag{A.10}$$

with the equilibrium constant

$$K_{xy}\left(T\right) = \exp\left(-\frac{\Delta G_0\left(x,y\right)}{kT}\right), \tag{A.11}$$

where $\Delta G_0\left(x,y\right) = \psi_{xy} - x\mu_x - y\mu_y$ is the Gibbs free energy of formation of a cluster.

If concentrations of other clusters are also small, their contributions to the total free energy of the system are linear; therefore, the equilibrium size distribution function has the form

$$f_0\left(x,y\right) = \left(N_x + N_y\right)\exp\left(-\Delta G_0\left(x,y\right) / kT\right), \tag{A.13}$$

which is derived, as mentioned above, in the thermodynamic approach for ‘macroscopic’ clusters with $x, y \gg 1$. For this reason, the assertion in Ref. [27] that this expression for a cluster size of 1 does not return the number of monomers N_x is irrelevant.

Appendix B.

Calculation of the nucleation rate parameters

The first and the second derivatives of the free energy, Eq. (9), are calculated as

$$\frac{\partial\Delta G_0\left(x,n\right)}{\partial n} = -kT\ln S_v + \frac{8}{3}\pi\gamma\left(\frac{3}{4\pi}\Omega_m\right)^{\frac{2}{3}} \times \\ \times x^{-\frac{1}{3}}\left(1+\frac{n}{x}\right)^{-\frac{1}{3}} - \frac{4\mu\Omega}{3}\frac{1}{\left(1+\varphi\right)^2}\left(\varphi - \frac{n}{x}\right), \tag{B.1}$$

$$\frac{\partial\Delta G_0\left(x,n\right)}{\partial x} = -kT\ln S_x + \frac{8}{3}\pi\gamma\left(\frac{3}{4\pi}\Omega_m\right)^{\frac{2}{3}} \times \\ \times x^{-\frac{1}{3}}\left(1+\frac{n}{x}\right)^{-\frac{1}{3}} + \frac{2\mu\Omega}{3}\frac{1}{\left(1+\varphi\right)^2}\left[\varphi^2 - \left(\frac{n}{x}\right)^2\right], \tag{B.2}$$

$$\frac{\partial^2\Delta G_0\left(x,n\right)}{\partial n^2} = -\frac{8}{9}\pi\gamma\left(\frac{3}{4\pi}\frac{\Omega}{1+\varphi}\right)^{\frac{2}{3}} \times \\ \times x^{-\frac{4}{3}}\left(1+\frac{n}{x}\right)^{-\frac{4}{3}} + \frac{4\mu\Omega}{3}\frac{1}{\left(1+\varphi\right)^2}\frac{1}{x}, \tag{B.3}$$

$$\frac{\partial^2\Delta G_0\left(x,n\right)}{\partial x^2} = -\frac{8}{9}\pi\gamma\left(\frac{3}{4\pi}\frac{\Omega}{1+\varphi}\right)^{\frac{2}{3}} \times \\ \times x^{-\frac{4}{3}}\left(1+\frac{n}{x}\right)^{-\frac{4}{3}} + \frac{4\mu\Omega}{3}\frac{1}{\left(1+\varphi\right)^2}\frac{1}{x}\left(\frac{n}{x}\right)^2, \tag{B.4}$$

$$\frac{\partial^2\Delta G_0\left(x,n\right)}{\partial n\partial x} = -\frac{8}{9}\pi\gamma\left(\frac{3}{4\pi}\frac{\Omega}{1+\varphi}\right)^{\frac{2}{3}} \times \\ \times x^{-\frac{4}{3}}\left(1+\frac{n}{x}\right)^{-\frac{4}{3}} - \frac{4\mu\Omega}{3}\frac{1}{\left(1+\varphi\right)^2}\frac{1}{x}\frac{n}{x}, \tag{B.5}$$

Accordingly, the elements $D_{ij} = \frac{1}{2}\left.\frac{\partial^2\Delta G_0\left(x,y\right)}{\partial x_i\partial x_j}\right|_{x^*,y^*}$ of the matrix **D** calculated in the first approximation in a small parameter $3kT / 4\mu\Omega \sim 10^{-2} \ll 1$ using Eq. (10) take the form

$$D_{11} = \left.\frac{\partial^2\Delta G_0\left(x,n\right)}{\partial x^2}\right|_{x^*,n^*} \approx \frac{4\mu\Omega}{3}\frac{1}{\left(1+\varphi\right)^2}\frac{1}{x^*} \times \\ \times\left[\begin{aligned}&\left(\varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right)^2 - \frac{kT}{4\mu\Omega}\left(1+\varphi\right)^{\frac{4}{3}} \times \\ &\times\left(\ln S_x + \varphi\ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right)\end{aligned}\right], \tag{B.6}$$

$$D_{22} = \left.\frac{\partial^2 \Delta G_0(x,n)}{\partial n^2}\right|_{x^*,n^*} \approx \frac{4\mu\Omega}{3}\frac{1}{(1+\varphi)^2}\frac{1}{x^*}\left(1-\frac{kT}{4\mu\Omega}\ln S_x\right), \qquad \text{(B.7)}$$

$$D_{12} = \left.\frac{\partial^2 \Delta G_0(x,n)}{\partial n \partial x}\right|_{x^*,n^*} \approx -\frac{4\mu\Omega}{3}\frac{1}{(1+\varphi)^2}\frac{1}{x^*} \times \left[\left(\varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right) + \frac{kT}{4\mu\Omega}(1+\varphi)^{\frac{4}{3}}\left(\ln S_x + \varphi \ln S_v\right)\right], \qquad \text{(B.8)}$$

and thus

$$\det \mathbf{D} = D_{11}D_{22} - D_{12}^2 \approx -\left(\frac{1}{x^*}\frac{4\mu\Omega}{3}\right)^2\left(\frac{1}{1+\varphi}\right)^{\frac{8}{3}} \times \frac{kT}{4\mu\Omega}\left(\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right), \qquad \text{(B.9)}$$

which is negative above the critical supersaturation, $\ln S_x > \ln S_x^* \approx -\varphi \ln S_v$, and thus confirms that (x^*, y^*) is a saddle point. This leads to

$$(-\det \mathbf{D})^{\frac{1}{2}} = \frac{1}{x^*}\frac{4\mu\Omega}{3}\left(\frac{1}{1+\varphi}\right)^{\frac{4}{3}} \times \left[\frac{kT}{4\mu\Omega}\left(\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right)\right]^{\frac{1}{2}}. \qquad \text{(B.10)}$$

For simplicity, only relatively large values of $|\varphi| \gg \left|\frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right| \sim 0.01$, will be further analysed, taking into account that for Si (with $\Omega = a_{\mathrm{Si}}^3 / 8$ and $a_{\mathrm{Si}} = 0.5431$ nm) in Al (with $\Omega_m = a_{\mathrm{Al}}^3 / 4$ and $a_{\mathrm{Al}} = 0.4049$ nm) $\varphi \approx 0.2$; for Ge (with $\Omega = a_{\mathrm{Ge}}^3 / 8$ and $a_{\mathrm{Ge}} = 0.5658$ nm) in Al $\varphi \approx 0.41$; and a negative value $\varphi \approx -0.1$ for incoherent CuAl$_2$ phase in Al. In these cases,

$$\left|\varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right| \gg \frac{kT}{4\mu\Omega}(1+\varphi)^{\frac{4}{3}}\left(\ln S_x + \varphi \ln S_v\right) \sim 0.01,$$

and thus Eq. (B.8) can be simplified as

$$D_{12} \approx -\frac{4\mu\Omega}{3}\left(\frac{1}{1+\varphi}\right)^2\frac{1}{x^*}\left(\varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right). \qquad \text{(B.8')}$$

In the considered case $\beta_x^* / \beta_v^* = D_x c_x / D_v c_v \ll 1$, from Eq. (17) one obtains

$$\mathrm{tg}\theta \approx \varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}, \text{ if } D_{21} < 0, \quad \text{or } \varphi - \frac{3kT}{4\mu\Omega}\ln S_x > 0, \qquad \text{(B.11)}$$

$$\mathrm{tg}\theta \approx -\left|\varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right|, \text{ if } D_{21} > 0, \quad \text{or } \varphi - \frac{3kT}{4\mu\Omega}\ln S_x < 0, \qquad \text{(B.12)}$$

or, more generally,

$$\mathrm{tg}\theta \approx \varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v} \ll 1, \qquad \text{(B.13)}$$

$$\cos^2\theta = \frac{1}{1+\mathrm{tg}^2\theta} \approx \frac{1}{1+\left(\varphi - \frac{3kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right)^2} \approx 1, \qquad \text{(B.14)}$$

and thus, taking into account that $\beta_x^* << \beta_v^*$ (as explained in Section 3.2),

$$\frac{\beta_x^*\beta_v^*\left(1+\mathrm{tg}^2\theta\right)}{\beta_v^* + \beta_x^*\mathrm{tg}^2\theta} \approx \beta_x^*\left(1+\mathrm{tg}^2\theta\right). \qquad \text{(B.15)}$$

By substituting Eqs (B.13)–(B.15) in Eq. (16), one obtains

$$D'_{11} \approx -\frac{1}{3}\left(\frac{1}{1+\varphi}\right)^{\frac{2}{3}}\frac{1}{x^*}kT\left(\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right), \qquad \text{(B.16)}$$

which is negative above the critical supersaturation, $\ln S_x > \ln S_x^* \approx -\varphi \ln S_v$, and thus ensures a maximum of the free energy at the critical point in the direction of the x'-axis (and a positive sign of the r.h.s of Eq. (13)).

Taking into account Eq. (B.15) and

$$R^* = \left[\frac{3\Omega}{4\pi(1+\varphi)}\right]^{1/3}\left(x^* + n^*\right)^{1/3} \approx \left(1 - \frac{kT}{4\mu\Omega}\ln\frac{S_x}{S_v}\right)\frac{2\gamma\Omega/(kT)}{\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2} \approx \frac{2\gamma\Omega/(kT)}{\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2}, \qquad \text{(B.17)}$$

Eq. (14) takes the form

$$\dot{N} \approx \frac{\gamma}{kT}\left(\frac{kT}{4\mu\Omega}\right)^{\frac{1}{2}} \frac{4\pi D_x c_x\left(c_x + c_v\right)}{\left[\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right]^{\frac{1}{2}}} \times$$
$$\times \exp\left\{-\frac{16\pi\gamma^3\Omega^2}{3(kT)^3\left[\ln S_x + \varphi \ln S_v + \frac{3}{8}\frac{kT}{\mu\Omega}\left(\ln\frac{S_x}{S_v}\right)^2\right]^2}\right\}. \quad \text{(B.18)}$$

Taking into account that $c_v^{(0)}$ can be generally neglected compared to c_x, in the absence of excess vacancies this equation is reduced to

$$\dot{N} \approx 4\pi D_x c_x^2 \frac{\gamma}{kT}\left(\frac{kT}{4\mu\Omega}\right)^{\frac{1}{2}} \ln^{-\frac{1}{2}} S_x \exp\left(-\frac{16\pi\gamma^3\Omega^2}{3(kT)^3 \ln^2 S_x}\right). \text{(B.19)}$$

It should be noted that the above expression for the cavity volume, $V_m = (x+n)\Omega_m$, used in Eqs (6) and (10), is applicable only in the case $\Omega / \Omega_m \le 2$ which corresponds to $\varphi \le 1$ while in the case $2 < \Omega / \Omega_m \le 3$ and $\varphi \le 2$ the correct expression is $V_m = (2x+n)\Omega_m$. Therefore, the transformation strain $\delta(x,n)$ should be recalculated from the expression

$$\frac{V_p - V_m}{V_p} = 1 - \frac{(2x+n)\Omega_m}{x\Omega} =$$
$$= \left(\varphi - 1 - \frac{n}{x}\right)\frac{1}{1+\varphi} = \left(\tilde{\varphi} - \frac{n}{x}\right)\frac{1}{2+\tilde{\varphi}} =,$$
$$= (1+\delta)^3 \approx 1 + 3\delta$$

where $\tilde{\varphi} = \varphi - 1 < 1$.

REFERENCES

1. R.W. Balluffi, S. M. Allen, and W.C. Carter, Kinetics of materials, John Wiley & Sons, 2005.
2. R.E. Smallman, A. H.W. Ngan, Physical metallurgy and advanced materials, 7th ed. Elsevier, 2007.
3. J.W. Christian, The theory of transformations in metals and alloys, Pergamon, Oxford, 1975.
4. D. Turnbull, H. S. Rosenbaum, and H.N. Treaftis, Kinetics of clustering in some aluminium alloys, Acta Metallurgica 8 (1960) 277–295.
5. H.S Rosenbaum, D Turnbull, On the precipitation of silicon out of a supersaturated aluminum-silicon solid solution, Acta Metallurgica 6 (1958) 653–659.
6. H.S Rosenbaum, D Turnbull, Metallographic investigation of precipitation of silicon from aluminum, Acta Metallurgica 7 (1959) 664–674.
7. E. Ozawa, and H. Kimura, Excess vacancies and the nucleation of precipitates in aluminum-silicon alloys, Acta Metallurgica 18 (1970) 995–1004.
8. E.Hornbogen, and E. A. Starke Jr., Overview no. 102 Theory assisted design of high strength low alloy aluminum, Acta Metallurgica et Materialia 41 (1993) 1-16.
9. F.R.N. Nabarro, The influence of elastic strain on the shape of particles segregating in an alloy, Proc. Phys. Soc. 52 (1940) 90–104.
10. H. Mehrer, Diffusion in solids: fundamentals, methods, materials, diffusion-controlled processes, Springer Series in Solid State Science, Vol. 155, Springer (2007).
11. K.C. Russel, The role of excess vacancies in precipitation, Scripta Metallurgica 3 (1969) 313–316.
12. M. Volmer, A. Weber, Keimbildung in übersättigten Gebilden, Z. Phys. Chem. 119 (1926) 277–303.
13. R. Becker, W. Doering, Kinetische Behandlung der Keimbildung in übersättigten Dämpfen, Ann. Phys. 24 (1935) 719–752.
14. Ja.B. Zeldovich, On the theory of new phase formation: cavitation, Acta Physicochim. URSS 18 (1943) 1.
15. H. Reiss, The kinetics of phase transitions in binary systems, J. Chem. Phys. 18 (1950) 840–848.
16. A. Katok, B. Hasselblatt, Introduction to the Modern Theory of Dynamical Systems, Cambridge: Cambridge University Press (1995).
17. J.S. Langer, Statistical theory of the decay of metastable states, Annals of Physics 54 (1969) 258–275.
18. D. Stauffer, Kinetic theory of two-component ("hetero-molecular") nucleation and condensation, J. Aerosol Sci. 7 (1976) 319–333.
19. L.M. Berezhkovskii and V.Yu. Zitserman, Direction of the nucleation current through the saddle point in the binary nucleation theory and the saddle point avoidance, J. Chem. Phys. 102 (1995) 3331–3336.
20. J. Frenkel, Kinetic Theory of Liquids, Dover Publication, New York, 1955.
21. J. Lothe, G. M. Pound, Reconsiderations of nucleation theory, J. Chem. Phys. 36 (1962) 2080–2085.
22. D. Kashchiev, Nucleation: Basic Theory with Applications, Butterworth Heinemann, Oxford, Boston, 2000.
23. H. Reiss, J. L. Katz, Resolution of the translation – rotation paradox in the theory of irreversible condensation, J. Chem. Phys. 46 (1967) 2496–2499.

24. H. Reiss, J. L. Katz, and E.R. Cohen, Translation–rotation paradox in the theory of nucleation, J. Chem. Phys. 48 (1968) 5553–5560.
25. J.L. Katz, H. Wiedersich, Nucleation of voids in materials supersaturated with vacancies and interstitials, J. Chem. Phys. 55 (1971) 1414–1425.
26. J.L. Katz, Homogeneous nucleation theory and experiment: A survey, Pure&Appl. Chem, 64 (1992) 1661–1666.
27. M.S. Veshchunov, On the theory of void nucleation in irradiated crystals, J. Nucl. Mater. 571 (2022) 154021.
28. L.D. Landau and E.M. Lifshitz, Theoretical Physics, Vol. 5: Statistical Physics, Pergamon Press, 1980.
29. S.-I. Fujikawa, , K.-I. Hirano, and Y. Fukushima, Diffusion of silicon in aluminium, Metallurgical Transactions A 9 (1978) 1811–1815.