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# CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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## Modelling precipitation kinetics: Evaluation of the thermodynamics of nucleation and growth

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### ABSTRACT

Modelling of (solid-state) precipitation kinetics in terms of particle nucleation and particle growth requires evaluation of the thermodynamic relations pertaining to these mechanisms, i.e. evaluation of the nucleation barrier and of the Gibbs–Thomson effect. In the present work, frequently occurring problems and misconceptions of the thermodynamic evaluation are identified and a practical approach with regard to kinetic modelling is proposed for combined and unified analysis of the thermodynamics of nucleation and growth, based on the fundamental thermodynamic equilibrium consideration in a particle–matrix system. A computationally efficient method for numerical determination of the thermodynamic relations is presented which allows an easy and flexible implementation into kinetic modelling.

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### 1. Introduction

The dispersion of small second-phase particles within a parent-phase matrix, e.g. as resulting from a solid-state precipitation reaction, strongly influences the properties of the two-phase system. In materials science, precipitation reactions are therefore widely used as a method to enhance materials performance in numerous fields of application [1]. Precise control of the reaction kinetics allows to tailor the microstructure evolving upon precipitation and thus to tune the material properties.

Upon precipitation, particles of a solute(s)-rich  $\beta$  phase are formed within an  $\alpha$ -phase matrix initially supersaturated in solute (s), leaving behind a solute(s)-depleted  $\alpha$ -phase matrix. The kinetics of the precipitation reaction, typically described in terms of nucleation and growth of precipitate particles, strongly vary with the degree of solute supersaturation, i.e., at constant temperature, with phase composition. In order to account for this effect in a model for precipitation kinetics the kinetics must be coupled to the thermodynamics of the alloy system. The numerical efficiency of the kinetic model and the quality of its results are therefore directly linked to the evaluation of the system's thermodynamics. Typical examples are models of Kampmann–Wagner-numerical (KWN) type [2] (see e.g. [3–6] and Section 4): in this frequently applied type of modelling approach, the evolution of

the particle size distribution is computed on the basis of numerical integration of a composition-dependent nucleation rate and a size- and composition-dependent growth rate for discrete time steps and discrete particle-size classes. Such models thus require numerous evaluations of thermodynamic relations. Unfortunately, up to now the current corresponding modelling practice often involves usage of incompatible thermodynamic models for nucleation and growth and redundant thermodynamic evaluations (see below). The present work proposes a practical route for the thermodynamically correct and numerically efficient coupling of kinetic model and thermodynamic description (for KWN-type modelling).

In terms of thermodynamics, formation and stability of a precipitate-phase particle are (in the simplest case) defined by two counteracting factors (see e.g. [7]): (i) The release of energy due to the decomposition of the supersaturated matrix phase into solute-depleted matrix phase and solute-rich precipitate phase. This release of energy can be described as a difference of chemical Gibbs energies  $G_c^j(x^j)$  of the (homogeneous) phases  $j = \alpha, \beta$ , defined by their respective compositions  $x^j$ . (ii) The increase in energy due to the development of a particle–matrix interface.<sup>1</sup>

In the rate equations for nucleation and growth as typically used in KWN-type kinetic models, this stability consideration is represented by two different concepts: the energy barrier for

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<sup>1</sup> Within the scope of this work, only the case of a, in the Gibbsian sense, “sharp” interface, i.e. an interface with a width small compared to the size of the particle will be considered.

nucleation and the Gibbs–Thomson effect, affecting the growth (rate) of a particle. In the classical theory of nucleation [8,9], the rate of nucleation  $\dot{N}$  is dominated by an energy barrier  $\Delta G^*$  for formation of a particle of critical size  $r^*$  above which the particle is stable:

$$\dot{N} \propto \exp\left(-\frac{\Delta G^*}{kT}\right), \quad (1)$$

where  $k$  and  $T$  denote the Boltzmann constant and the absolute temperature, respectively.<sup>2</sup> For the case of a precipitation reaction,  $\Delta G^*$  and  $r^*$  are functions of the change in chemical Gibbs energy  $\Delta g_c(x^{\alpha,m}, x^{\beta,p})$  upon nucleation (with  $-\Delta g_c(x^{\alpha,m}, x^{\beta,p})$  being the chemical driving force for nucleation) for given compositions  $x^{\alpha,m}$  and  $x^{\beta,p}$  of the  $\alpha$ -phase matrix and the  $\beta$ -phase precipitate, respectively, and of the interface energy  $\gamma$  per unit area, i.e.  $\Delta G^* = \Delta G_c^*(\Delta g_c(x^{\alpha,m}, x^{\beta,p}), \gamma)$  and  $r^* = r^*(\Delta g_c(x^{\alpha,m}, x^{\beta,p}), \gamma)$ , thus reflecting the two competing energy contributions. Growth of a solute-rich particle leads to solute depletion of the surrounding matrix; particle growth can then (in any case eventually) become rate-controlled by solute diffusion through the solute-depleted matrix towards the particle. The growth rate of a spherical particle of radius  $r$  in a binary<sup>3</sup> system A–B is then often described by [12,13]

$$\frac{dr}{dt} = \frac{x^{\alpha,m} - x^{\alpha,int} D}{k' x^{\beta,int} - x^{\alpha,int} r}, \quad (2)$$

with the diffusion coefficient  $D$  of the solute component in the matrix and the atom fractions<sup>4</sup> of solute  $x^{\alpha,m}$  in the  $\alpha$ -phase matrix remote from the particle, and  $x^{\alpha,int}$  and  $x^{\beta,int}$  in the  $\alpha$ -phase matrix and in the  $\beta$ -phase particle at the particle–matrix interface, respectively; the factor  $k'$  accounts for the difference in molar volume of the  $\alpha$  phase and the  $\beta$  phase. For  $x^{\alpha,m} > x^{\alpha,int}$ , i.e. for a positive growth rate (considering precipitation of a solute-rich  $\beta$  phase,  $k' x^{\beta,int} - x^{\alpha,int}$  is generally positive), the particle is stable and grows; for  $x^{\alpha,m} < x^{\alpha,int}$ , the particle is unstable and shrinks.  $x^{\alpha,int}$  and  $x^{\beta,int}$  are often taken according to local establishment of thermodynamic equilibrium at the interface.<sup>5</sup> For a small particle size, i.e. for a large ratio of interface area to particle volume, the state of equilibrium between the  $\alpha$ -phase matrix and the  $\beta$ -phase precipitate can strongly deviate from the state of equilibrium between the  $\alpha$ - and  $\beta$ -bulk phases, i.e. the  $\alpha$  phase and the  $\beta$  phase in the absence of the interface. This is the so-called Gibbs–Thomson effect, which, in compliance with the two counteracting contributions of composition-dependent chemical Gibbs energy and interface energy, can be expressed by functions  $x^{\alpha,int}$  and  $x^{\beta,int}$  depending on particle size (i.e. interface area) and interface energy  $\gamma$  per unit area, i.e.  $x^{\alpha,int} = x^{\alpha,int}(r, \gamma)$  and  $x^{\beta,int} = x^{\beta,int}(r, \gamma)$ .

Kinetic modelling of nucleation and growth thus requires evaluation of the thermodynamics of the system defined by chemical energy and interface energy. Usually, the interface energy  $\gamma$  per area is taken as being constant within a certain range of composition, particle size and morphology. This assumption effectively allows to reduce the evaluation of the thermodynamics for the kinetic modelling to determination of (i) the nucleation barrier as a function of the composition-dependent chemical driving force for nucleation  $-\Delta g_c(x^{\alpha,m}, x^{\beta,p})$  and (ii) the compositions  $x^{\alpha,int}(r)$  and  $x^{\beta,int}(r)$  as a function of particle size  $r$  (cf. Section

2). Analytical expressions for  $\Delta g_c(x^{\alpha,m}, x^{\beta,p})$ ,  $x^{\alpha,int}(r)$  and  $x^{\beta,int}(r)$ , based on simple thermodynamic solution models for the chemical Gibbs energies of the  $\alpha$  and the  $\beta$  phase, are an often used, numerically efficient way to implement thermodynamic data into the numerical kinetic modelling. For instance, the Gibbs–Thomson effect in a binary system is often accounted for by application of the equation [14]

$$x^{\alpha,int}(r) = x^\alpha \left( r \rightarrow \infty \right) \exp\left(\frac{2\gamma V_{\text{mol}}^\beta}{RT} \frac{1}{r}\right) \quad (3)$$

for the composition of the matrix at the particle–matrix interface, where  $x^\alpha(r \rightarrow \infty)$  is the solute concentration of the  $\alpha$  phase in the reference state of equilibrium between the  $\alpha$  phase and the  $\beta$  phase with  $r \rightarrow \infty$ , i.e. between the bulk phases in the absence of the interface.  $V_{\text{mol}}^\beta$  is the mean molar volume of the  $\beta$ -phase and  $R$  denotes the gas constant. Eq. (3) is based on the assumption that the thermodynamic behaviour of the  $\alpha$ -matrix phase can be described with the regular solution model and that the  $\beta$ -precipitate phase is a pure phase, i.e.  $x^{\beta,int}(r) = x^\beta(r \rightarrow \infty) = 1$ . The applicability of such analytical expressions can thus be severely limited by the limited capability of the underlying simple solution models to adequately describe the actual thermodynamic behaviour of the  $\alpha$  phase and the  $\beta$  phase.

Hence, in recent years, direct numerical derivation of the relations  $\Delta g_c(x^{\alpha,m}, x^{\beta,p})$ ,  $x^{\alpha,int}(r)$  and  $x^{\beta,int}(r)$  from a comprehensive thermodynamic assessment of the alloy system (which is typically based on more complex solid solution models for the chemical Gibbs energies) has become more frequently applied, especially for multi-component systems (see, e.g., [5,6]). This trend is facilitated by the increasing availability of such thermodynamic assessments, e.g. in form of CALPHAD data, and commercial software for thermodynamic analysis (e.g. [15]). On the one hand, the numerical determination of the chemical driving force for nucleation,  $-\Delta g_c(x^{\alpha,m}, x^{\beta,p})$ , for a given composition  $x^{\alpha,m}$  of the matrix phase, can be performed straightforwardly, for instance by application of the parallel tangent/maximum chemical driving force approach [16] (see Section 2). On the other hand, the numerical evaluation of the Gibbs–Thomson effect, i.e. the determination of the compositions  $x^{\alpha,int}(r)$  and  $x^{\beta,int}(r)$ , is much more elaborate [17–19], since it requires the evaluation of a thermodynamic equilibrium state including the energy contribution of the interface, e.g. by minimisation of the total Gibbs energy [15]. In view of the correspondingly larger complexity and computational effort, direct numerical evaluation of the Gibbs–Thomson effect is in practice often avoided and simple analytical expressions such as Eq. (3), based on generally invalid solid solution models, are adopted instead. Obviously, problems of inconsistency arise when the relations  $\Delta g_c(x^{\alpha,m}, x^{\beta,p})$  for nucleation and  $x^{\alpha,int}(r)$  and  $x^{\beta,int}(r)$  for growth are derived, analytically or numerically, by adoption of differing, incompatible thermodynamic solution models for nucleation and for growth. This is a common shortcoming in kinetic models of precipitation kinetics based on the KWN-approach (e.g. [2,3]).<sup>6</sup> The problem becomes even more aggravated when an elastic strain energy contribution due to a precipitate/matrix misfit is taken into consideration only for nucleation but not for growth (or vice versa) without more ado (e.g. [22,23]). As a consequence, the kinetic model predictions may be strongly biased or

<sup>2</sup> For a full expression of  $\dot{N}$  according to classical nucleation theory, see e.g. [10].

<sup>3</sup> For multinary systems, see e.g. [11].

<sup>4</sup> For binary systems, the convention  $x^j = x_B^j$  will be used.

<sup>5</sup> cf. footnote at the end of Section 2.3.

<sup>6</sup> Naturally, this problem does not appear in kinetic models without discrimination of nucleation kinetics and growth kinetics, as in cluster dynamics models, cf. e.g. [20]. Also, in kinetic models involving a consideration of the total (Gibbs) energy of the system [21], such problems are more readily avoided.

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