

# Numerical integration of the Gibbs–Thomson equation for multicomponent systems

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The differential form of the Gibbs–Thomson equation is derived for non-stoichiometric, partially stoichiometric and fully stoichiometric precipitates in a multicomponent system. This form can be readily used in a numerical integration scheme based on separation of variables. The validity of the proposed approach has been demonstrated with binary (Al–Sc) and ternary (Al–Mn–Si) systems. Good agreement with other approaches (e.g. analytical or Thermo-Calc) has been shown. The proposed approach aims at bridging the gap between open thermodynamic databases and precipitation models.

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## 1. Introduction

The Gibbs–Thomson effect describes the influence of interface curvature on equilibrium phase compositions. It is the basis of many phenomena, including nucleation and coarsening. In binary alloys, the modification of the equilibrium phase composition is often given by:

$$X_{eq,r}^z = X_{eq,\infty}^z \exp\left(\frac{2\gamma\kappa V_m}{RT}\right) \quad (1)$$

where  $T$  is the temperature,  $\kappa$  the interface curvature,  $\gamma$  the interfacial energy,  $R$  the molar gas constant and  $V_m$  the precipitate molar volume. Although frequently encountered in the literature, this equation holds only in systems with a pure precipitate phase (i.e. which contains no alloying elements). For a general binary system with a stoichiometric precipitate phase, a general form of the Gibbs–Thomson equation is given in Ref. [1], where its approximate solutions under various situations are discussed. The method proposed in Ref. [1] is also extendable to multicomponent systems if thermodynamic models of the alloy system are simple, so that the solubility product method can be employed to describe the phase diagram. On the other hand, using a

constructed molar Gibbs energy diagram, Qian [2] proposed a general description of the Gibbs–Thomson effect in a dilute binary system, where the precipitate phase is non-stoichiometric. Both of these works are based on the Gibbs energy minimization principle; however they took a different mathematical formalism. It would be desirable to have a single general mathematical framework that could deal with both stoichiometric and non-stoichiometric precipitates.

Moreover, simple systems, where ideal thermodynamic models hold and where an analytical expression of the Gibbs–Thomson effect can be derived, are rare. The thermodynamic models of real alloys are more complex and, in general, such an analytical solution does not exist. A numerical method is therefore needed to quantify the Gibbs–Thomson effects.

It is possible to evaluate the Gibbs–Thomson effect with the numerical Gibbs energy minimization technique rooted in the CALPHAD community for phase diagram calculation. Indeed, from a CALPHAD point of view, the Gibbs–Thomson effect leads to a special phase diagram for the system in which the molar Gibbs energy of the precipitate phase increases by  $2\gamma\kappa V_m$  due to the presence of the interfacial energy (spherical shape precipitates). Here it is useful to define the collections of these special phase diagrams as a “Gibbs–Thomson phase diagram”. A Gibbs–Thomson phase diagram is a diagram that has one more dimension (i.e. the curvature) than the general

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phase diagram. The utilization of the Gibbs energy minimization technique for evaluating the Gibbs–Thomson effect has been successfully implemented in commercial software such as Thermo-Calc [3]. However, this technique, only commercially available, is difficult to adapt and/or modify. This situation has prevented the deployment of open thermodynamic databases that could be connected to precipitation models, in which the evaluation of Gibbs–Thomson is an essential component.

Instead of performing an algebraic analysis (as in the solubility product method), or a Gibbs energy minimization (as in the CALPHAD approach), a numerical integration technique (originally proposed in Ref. [4]) is employed to calculate the Gibbs–Thomson phase diagram. The proposed approach bridges the gap between open thermodynamic databases and precipitation models.

This paper is organized as follows: it starts with the derivation of the equilibrium conditions for a two-phase mixture system in the presence of the Gibbs–Thomson effect. These conditions, being equivalent to the equal chemical potential conditions, are applicable to any matrix-precipitate system regardless of the nature of the precipitate phase (stoichiometric, non-stoichiometric or partially stoichiometric). Then, the integration method is briefly described and employed to calculate the Gibbs–Thomson phase diagram. Finally, the approach is discussed and compared with the results obtained from other approaches for the Al–Sc and Al–Mn–Si systems.

### 1.1. Differential form of equilibrium conditions

Let us consider a multicomponent two-phase system, where a spherical precipitate  $\beta$  of radius  $R$  is in equilibrium with a matrix  $\alpha$ . Transferring  $dn$  atoms of  $\beta$  precipitate to the  $\alpha$  matrix will change the system Gibbs energy by:

$$dG = -dnG_n^\beta + \sum_{i=0}^N dnX_i^\beta \mu_i^\alpha \quad (2)$$

where  $G_n^\beta$  is the molar Gibbs energy of the  $\beta$  phase,  $X_i^\beta$  is the molar fraction of element  $i$  in the  $\beta$  phase and  $\mu_i^\alpha$  is the chemical potential of element  $i$  in the  $\alpha$  phase. At equilibrium  $dG = 0$ , the differentiation of Eq. (2) leads to:

$$dG_n^\beta = \sum_{i=0}^N (X_i^\beta d\mu_i^\alpha + dX_i^\beta \mu_i^\alpha) \quad (3)$$

Note that  $G_n^\beta$  depends on the radius  $R$  (or curvature  $\kappa = R^{-1}$ ) of the precipitates, and also on the mole fractions of all non-stoichiometric elements  $X_i^\beta$ , except the base element,<sup>1</sup> whose index is 0:

$$G_n^\beta = G_n^\beta(\kappa, X_1^\beta, \dots, X_N^\beta) \quad (4)$$

Moreover, for all non-stoichiometric elements, chemical potentials are equal in both phases:  $\mu_i^\alpha = \mu_i^\beta$ ; and, for

all stoichiometric elements,  $dX_i^\beta = 0$  (due to  $X_i^\beta = \text{constant}$ ). Eq. (3) is then equivalent to:

$$2\gamma V^\beta d\kappa + \sum_{i=1}^N \left( \frac{\partial G_n^\beta}{\partial X_i^\beta} \right)_{X_i+X_0} dX_i^\beta = \sum_{i=0}^N X_i^\beta d\mu_i^\alpha + \sum_{i=0}^N dX_i^\beta \mu_i^\beta \quad (5)$$

where  $V^\beta$  is the mean atomic volume in the precipitate and  $\gamma$  is the surface energy associated with the  $\alpha/\gamma$  interface. Note that in Eq. (5), for all partial derivatives,  $X_0 + X_i$  is constant (i.e.  $dn_i = -dn_0$ ). Using the form of  $\mu_i^\alpha$  demonstrated in Ref. Appendix A and under the assumption that  $\sum dX_i = 0$ , the differential form of the equilibrium condition is finally obtained, i.e.:

$$2\gamma V^\beta d\kappa = \sum_{i=0}^N X_i^\beta d\mu_i^\alpha \quad (6)$$

Note that Eq. (6) is the Gibbs–Duhem equation for the precipitate under isobaric and isothermal conditions. It could be easily obtained from Eq. (3) for the case of fully stoichiometric precipitates by stating that (i)  $G_n^\beta$  depends only on  $\kappa$  and (ii) all  $dX_i^\beta$  terms are equal to zero. It can also be derived for the pure non-stoichiometric case, as is done in many textbooks. However, the derivation of the Gibbs–Duhem relation for partially stoichiometric precipitates is not straightforward and, to the authors' knowledge, cannot be found in the literature.

As far as the matrix is concerned, under isothermal and isobaric conditions, the Gibbs–Duhem relation states:

$$\sum_{i=0}^N X_i^\alpha d\mu_i^\alpha = 0 \quad (7)$$

The combination of Eqs. (7) and (6) then leads to the equilibrium condition:

$$\sum_{i=0}^N (X_i^\beta - X_i^\alpha) d\mu_i^\alpha - 2V^\beta \gamma d\kappa = 0 \quad (8)$$

Using (i) the obvious summation ( $X_0^\alpha = 1 - \sum_{i=1}^N X_i^\alpha$ ), (ii) the form of  $\mu_i^\alpha$  demonstrated in Ref. Appendix A, and (iii) under the assumption that, for all partial derivatives,  $dn_i = -dn_0$  (i.e.  $X_0^\alpha + X_i^\alpha$  is constant), the equilibrium condition is:

$$\sum_{i=1}^N (X_i^\beta - X_i^\alpha) d \left( \frac{\partial G_n^\alpha}{\partial X_i^\alpha} \right)_{X_i+X_0} - 2V^\beta \gamma d\kappa = 0 \quad (9)$$

Finally, as the function  $\partial G^\alpha / \partial X_i$  depends on the variables  $(X_1^\alpha, X_2^\alpha, \dots, X_N^\alpha)$ , the differential Gibbs–Thomson equation takes the following form:

$$\sum_{i=1}^N \sum_{j=1}^N (X_i^\beta - X_i^\alpha) \left( \frac{\partial^2 G_n^\alpha}{\partial X_i^\alpha \partial X_j^\alpha} \right) dX_j^\alpha - 2V^\beta \gamma d\kappa = 0 \quad (10)$$

Note that Eq. (10) is similar to Eq. (6) of Ref. [5], for which justification was far from being obvious. This form is very versatile as it is valid for stoichiometric, partially stoichiometric and non-stoichiometric cases.

For all non-stoichiometric elements the differential form of the equilibrium condition is obvious:  $d\mu_i^\alpha = d\mu_i^\beta$ ,

<sup>1</sup>The base element is the reference element used to conserve the total number of atoms of a phase. For any variation of mole fraction  $X_i$ , we have  $dX_i = -dX_0$ .

whereas for all stoichiometric elements  $dX_i^\beta = 0$ . Using, once more, the form of  $\mu_i^\alpha$  derived in Appendix A leads to a set of  $N$  linear equations, defining the tie-line:

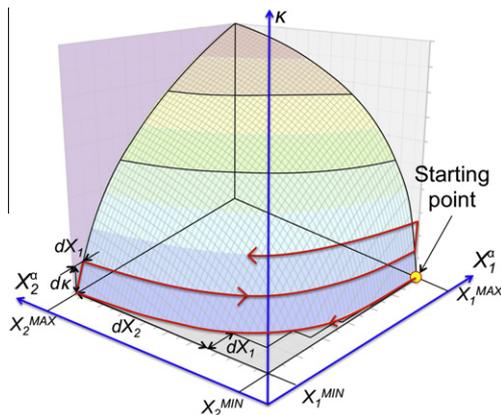
$$\begin{cases} \sum_{j=1}^N \left( \frac{\partial^2 G_n^\alpha}{\partial X_i \partial X_j} \right) dX_j^\alpha = \sum_{j=1}^N \left( \frac{\partial^2 G_n^\beta}{\partial X_i \partial X_j} \right) dX_j^\beta & \text{non-stoich.} \\ dX_i^\beta = 0 & \text{stoich.} \end{cases} \quad (11)$$

## 1.2. Integration-based numerical method

One of the main advantages of Eqs. (10) and (11) is that they are linear in  $dX^\alpha$  and  $dX^\beta$ , which is extremely convenient for numerical integration. Let us assume that we know the initial values of all variables at one particular point, i.e. the values of  $X_0^\alpha, \dots, X_N^\alpha$ , as well as  $X_0^\beta, \dots, X_N^\beta$  are known and  $\kappa = 0$ . The goal of the integration-based method is to provide values for the solubility limit domain in the  $\alpha$  phase, as well as the associated tie-lines (i.e. precipitate composition). For the sake of simplicity, let us consider a ternary system with base element indexed 0. The following algorithm is used, with initial known values  $X_1^\alpha = X_1^{MAX}$ ,  $X_2^\alpha = X_2^{MIN}$ ,  $dX_1^\alpha = -dX$  and  $\kappa = 0$  (see Fig. 1):

- ①  $d\kappa = 0$  and  $dX_2^\alpha \neq 0$   
Get  $dX_2^\alpha$  from Eq. (10) and  $X_{1/2}^\alpha \leftarrow X_{1/2}^\alpha + dX_{1/2}^\alpha$ ,  
Get  $dX_{1,2}^\beta$  from Eq. (11) and  $X^\beta \leftarrow X^\beta + dX^\beta$
- ② if  $(X_1^\alpha < X_1^{MAX})$  and  $(X_1^\alpha > X_1^{MIN})$  go to ①
- ③  $d\kappa \neq 0$ ,  $\kappa \leftarrow \kappa + d\kappa$  and  $dX_2^\alpha = 0$   
Get  $dX_1^\alpha$  from Eq. (10) and  $X_{1/2}^\alpha \leftarrow X_{1/2}^\alpha + dX_{1/2}^\alpha$ ,  
Get all  $dX^\beta$  from Eqs. (11) and  $X^\beta \leftarrow X^\beta + dX^\beta$
- ④ if  $(X_1^\alpha < X_1^{MIN})$   $dX_1^\alpha \leftarrow dX$ ,  
if  $(X_1^\alpha > X_1^{MAX})$   $dX_1^\alpha \leftarrow -dX$ ,  
if  $(\kappa < \kappa_{MAX})$  go to ①

This approach presents the main advantage of being (i) simple to implement and, (ii) extremely efficient in terms of computer performance (when coupled to an open thermodynamic database). Moreover, it can be easily applied to precipitation models (e.g. [6,7]). For such models, at each time step, the growth rate of pre-



**Figure 1.** Integration path (red line) on the Gibbs–Thomson surface, i.e. the surface showing the matrix solute content (phase diagram) for different values of curvature  $\kappa$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cipitates ( $dR/dt$ ) is calculated, leading to a new value of  $R$  (and  $\kappa$ ) and the previous algorithm is then followed from step ③ to ④ to obtain the new precipitate and matrix concentrations.

## 2. Results and discussion

In this section, the proposed approach is now applied to various systems to compute the Gibbs–Thomson phase diagram: (i) an ideal solution model for a binary system, (ii) Al–Sc binary alloy, and (iii) Al–Mn–Si ternary alloy.

The Gibbs–Thomson effect in an A–B binary system containing a dilute ideal solid solution and a stoichiometric precipitate phase in equilibrium has been studied in Ref. [1]. It will be demonstrated here that the same results could be derived from the proposed integration-based approach. It starts with a ideal solution model for the solid solution phase, which reads:

$$G_n^\alpha = (1 - X_B^\alpha)G_A + X_B^\alpha G_B + RT[(1 - X_B^\alpha) \ln(1 - X_B^\alpha) + X_B^\alpha \ln X_B^\alpha] \quad (12)$$

Inserting the previous equation into Eq. (10) leads to:

$$RT \frac{X_B^\beta - X_B^\alpha}{(1 - X_B^\alpha)X_B^\alpha} dX_B^\alpha - 2\gamma V^\beta d\kappa = 0 \quad (13)$$

Note that the previous equation is exactly the same as Eq. (10) of Ref. [1] and Eq. (2.127) of Ref. [8], which is considered as a general form of the Gibbs–Thomson equation for a binary system with a ideal solid solution phase and pure-stoichiometric phase.

Under a dilute ideal solution approximation, integration of Eq. (13), and bearing in mind the initial value of this equation is  $X_2^\alpha = X_2^{\infty}$  when the curvature is zero, gives:

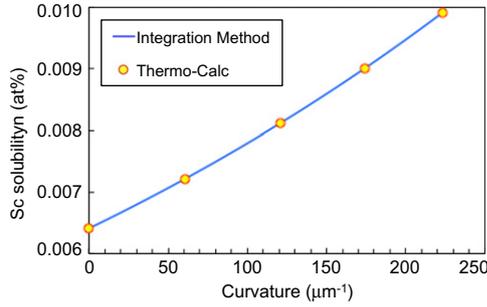
$$X_B^\alpha = X_B^{\infty} \exp\left(\frac{2\gamma V^\beta \kappa}{X_B^\beta RT}\right) \quad (14)$$

This is identical to Eq. (17) of Ref. [1], which is the solution of the general Gibbs–Thomson equation under the dilute solid-solution approximation.

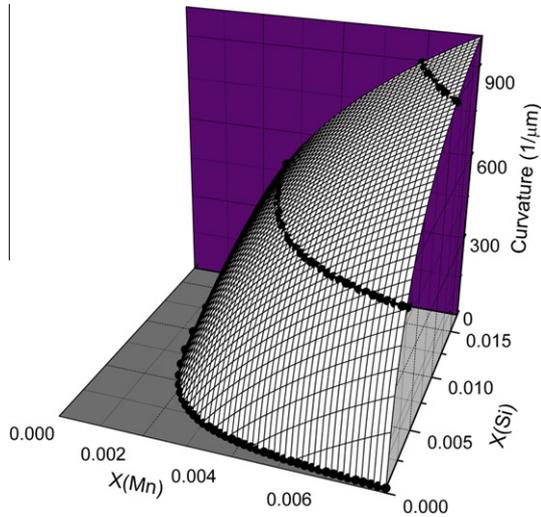
As a second application to a binary system, the proposed numerical integration method is applied to an Al–Sc alloy with a face-centered cubic (fcc) phase and  $\text{Al}_3\text{Sc}$  precipitate phase in equilibrium. For the sake of validation, the thermodynamic model of the fcc phase is taken directly from the TTAL6 database (Thermotech Al-based Alloys Database, version 6.1) and the programming interface of Thermo-Calc (version S), TQ, is used to compute the partial derivatives of the molar Gibbs energy of each phase. The surface energy and molar volume are taken as  $0.127 \text{ J m}^{-2}$  and  $10^{-5} \text{ m}^3 \text{ mol}^{-1}$ , respectively.

The calculated relation between the equilibrium matrix phase Sc composition and curvature is plotted in Figure 2 with the solid line together with the one calculated by Thermo-Calc based on the same dataset (solid circle markers). They are in good agreement, indicating the validity of the proposed methodology and its implementation.

The proposed integration method is now applied to compute the Gibbs–Thomson phase diagram of an



**Figure 2.** Sc solubility limit in fcc phase at 350 °C as a function of curvature computed by the proposed integration method compared with Thermo-Calc.



**Figure 3.** Gibbs–Thomson phase diagram (surface showing matrix solute content vs. curvature) of the Al–Mn–Si system at 600 °C calculated by the integration method together with the solubility limit line (markers) for various curvatures calculated by Thermo-Calc.

Al–Mn–Si system consisting of a fcc phase (matrix) in equilibrium with spherical precipitates at 600 °C. Thermodynamic models of matrix and precipitate phases are directly taken from TTAL6 database and the programming interface of Thermo-Calc, TQ, is used to compute the partial derivatives. The surface energy and molar volume are taken as  $0.127 \text{ J m}^{-2}$  and  $10^{-5} \text{ m}^3 \text{ mol}^{-1}$ , respectively.

Figure 3 shows the calculated Gibbs–Thomson phase diagram (surface) with Mn atomic fraction as the  $X$  axis, Si atomic fraction as the  $Y$  axis and the curvature as the  $Z$  axis. This diagram can be validated by comparing with some sections calculated using Thermo-Calc. As can be seen in Figure 3, they are in very good agreement, confirming the applicability of the proposed approach to the alloy systems with complex thermodynamic models.

### 3. Conclusions

In this paper an original approach is proposed to compute the Gibbs–Thomson phase diagram. The meth-

od is based on the differential form of the Gibbs–Thomson equation, which is valid for non-stoichiometric, partially stoichiometric and fully stoichiometric precipitates. The integration is performed on a line, on which only two compositions are allowed to vary. It has been validated by comparing its results with the Gibbs energy minimization technique implemented in commercial software. The proposed approach might be useful in precipitation modelling where the evaluation of the Gibbs–Thomson effect is an essential component.

### Appendix A. Derivation of the chemical potential $\mu_i^\alpha$ [9]

The chemical potential  $\mu_i^\alpha$  of atomic species  $j$  in phase  $\alpha$  containing  $N^\alpha$  atoms is given by:

$$\begin{aligned}\mu_i^\alpha &= \frac{\partial G^\alpha}{\partial n_i^\alpha} = \frac{\partial(N^\alpha G_m^\alpha)}{\partial n_i^\alpha} = G_m^\alpha + N^\alpha \frac{\partial G_m^\alpha}{\partial n_i^\alpha} \\ &= G_m^\alpha + N^\alpha \sum_{j=0}^{N^\alpha} \frac{\partial G_m^\alpha}{\partial X_j^\alpha} \frac{\partial X_j^\alpha}{\partial n_i^\alpha}\end{aligned}$$

$G^\alpha$  and  $G_m^\alpha$  are the Gibbs energy and the molar Gibbs energy of phase  $\alpha$ . Assuming that  $\partial X_j / \partial n_i = -n_j / N^{\alpha 2}$  for  $i \neq j$  and  $\partial X_j / \partial n_i = (N^\alpha - n_j) / N^{\alpha 2}$  for  $i = j$ , we have:

$$\frac{\partial G^\alpha}{\partial n_i^\alpha} = G_m^\alpha + (1 - X_i^\alpha) \frac{\partial G_m^\alpha}{\partial X_i^\alpha} - \sum_{j \neq i}^{N^\alpha} X_j^\alpha \frac{\partial G_m^\alpha}{\partial X_j^\alpha}$$

which gives for the chemical potential:

$$\mu_i^\alpha = G_m^\alpha + \frac{\partial G_m^\alpha}{\partial X_i^\alpha} - \sum_{i=1}^{N^\alpha} X_j^\alpha \frac{\partial G_m^\alpha}{\partial X_j^\alpha}$$

If the base element (see definition in text) is indexed 0, we finally have:

$$\mu_i^\alpha - \mu_0^\alpha = \left( \frac{\partial G_m^\alpha}{\partial X_i^\alpha} \right)_{X_i + X_0}$$

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