

Gibbs–Thomson effects in phase transformations

Michel Perez *

GEMPPM, INSA Lyon, UMR CNRS 5510, 25, avenue Capelle, 69621 Villeurbanne, France

Received 28 June 2004; received in revised form 6 December 2004; accepted 18 December 2004

Abstract

During phase transformations, like precipitation or solidification, processes such as nucleation, growth and coarsening depend strongly on interfacial effects, named Gibbs–Thomson effects. Based, on simple thermodynamics considerations, a formulation of the Gibbs–Thomson equation is proposed and different approximation solutions of this equation found in the literature are discussed.

© 2004 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Phase transformation; Precipitation; Gibbs–Thomson effects

1. Introduction

In order to predict and model phase transformations, like solidification, precipitation or massive transformation, it is necessary to evaluate with accuracy the Gibbs free energy of the multiphased system. The influence of interfaces on equilibrium (i.e. the interface curvature) has to be taken into account. This is the so called Gibbs–Thomson effect that modifies the solubility limits given by equilibrium thermodynamics (phase diagram). Most of the time such effects are very small, but in some particular cases, like nucleation or coarsening, the Gibbs–Thomson effect has to be incorporated in the solubility limits.

Indeed, the corrected solubility limit $X_{\text{eq},r}$ of B atoms in α matrix in equilibrium with β phase occurring as spherical particles of radius r is often given as a function of r [1–5]:

$$X_{\text{eq},r}^{\alpha} = X_{\text{eq},\infty}^{\alpha} \exp\left(\frac{2\gamma V_m}{rRT}\right), \quad (1)$$

where T is the temperature, γ the surface energy, R the molar gas constant and V_m is the molar volume.

Although Eq. (1) is almost always used in the literature as the Gibbs–Thomson correction, it does not apply to a compound β phase, like A_xB_y . In this paper, a more general expression for the Gibbs–Thomson correction is proposed. After having evaluated the Gibbs free energy of a binary solution, the equilibrium between the solid solution α and the β phase will lead to the general form of the Gibbs–Thomson correction. Finally, different approximations of the literature are compared with the numerical evaluation of the GT correction.

2. Equilibrium between two phases

We first evaluate the Gibbs free energy of a binary solution of n_A , A atoms and n_B , B atoms. This solution is called α phase. If we assume that the free energy is due to the bond energies between adjacent atoms (regular solution hypothesis) its Gibbs free energy is written as follows:

$$G^{\alpha} = n_A \left[G_A + kT \ln \frac{n_A}{n_A + n_B} \right] + n_B \left[G_B + kT \ln \frac{n_B}{n_A + n_B} \right] + \Omega \frac{n_A n_B}{n_A + n_B}, \quad (2)$$

* Tel.: +33 4 7243 8063; fax: +33 4 7243 8539.

E-mail address: michel.perez@insa-lyon.fr

where G_A , G_B are the molar free energies of pure A and pure B phase respectively, and $\Omega = z(H_{AA}/2 + H_{BB}/2 - H_{AB})$. H_{AA} , H_{BB} , H_{AB} are the A–A, B–B and A–B bond energies and z is the coordination number. The exceptional case where $\Omega = 0$ is called an ideal solution.

Now, we introduce another phase (called β) of composition A_xB_y . We note X_p , the molar concentration of B in the β phase: $X_p = y/(x + y)$. For the sake of simplicity, the β phase is considered as perfectly ordered (no configurational entropy). Its free Gibbs energy is given by:

$$G^\beta = n^\beta G_n^\beta, \quad (3)$$

where G_n^β is the free energy per atom of β phase (i.e. chemical potential) and n^β is the number of atom in β phase.

If the α phase is in equilibrium with the β phase, transferring a small amount of A and B atoms from the α phase of composition X_{eq_∞} to the β phase (composition X_p) will not change the global energy of the system. If dn atoms of β phase are transferred:

$$dn(1 - X_p) \left. \frac{\partial G^\alpha}{\partial n_A^\alpha} \right|_{X_{eq_\infty}} + dnX_p \left. \frac{\partial G^\alpha}{\partial n_B^\alpha} \right|_{X_{eq_\infty}} = dn \frac{\partial G^\beta}{\partial n}. \quad (4)$$

For a dilute regular solid solution, this is equivalent to:

$$G_n^\beta = (1 - X_p)[G_A^\alpha + kT \ln(1 - X_{eq_\infty})] + X_p[G_B^\alpha + \Omega + kT \ln X_{eq_\infty}]. \quad (5)$$

3. Gibbs–Thomson equation

If we take into account the increase in free energy due to the presence of the interface (of surface S^β), the Gibbs energy of a β phase particle of n^β atoms is then:

$$G^\beta = n^\beta G_n^\beta + \gamma S^\beta. \quad (6)$$

If we assume that β phase is spherical of radius r , the average atomic volume v_{at}^β is linked with the radius through:

$$\frac{4}{3}\pi r^3 = n^\beta v_{at}^\beta. \quad (7)$$

The partial derivative of the β phase Gibbs free energy is then given by:

$$\frac{\partial G^\beta}{\partial n^\beta} = G_n^\beta + \frac{8\pi r \gamma}{4\pi r^2 / v_{at}^\beta} = G_n^\beta + \frac{2\gamma v_{at}^\beta}{r}. \quad (8)$$

The equilibrium condition between the α phase (new composition X_{eq_r}) and the β precipitate (composition X_p) is then:

$$G_n^\beta + \frac{2\gamma v_{at}^\beta}{r} = (1 - X_p)[G_A^\alpha + kT \ln(1 - X_{eq_r})] + X_p[G_B^\alpha + \Omega + kT \ln X_{eq_r}]. \quad (9)$$

We now subtract the two equilibrium relations with (Eq. (9)) and without (Eq. (5)) the interfacial effect, leading to the general form of the Gibbs–Thomson equation:

$$\frac{2\gamma v_{at}^\beta}{rkT} = (1 - X_p) \ln \left(\frac{1 - X_{eq_r}}{1 - X_{eq_\infty}} \right) + X_p \ln \left(\frac{X_{eq_r}}{X_{eq_\infty}} \right). \quad (10)$$

This equation can be easily generalized in the case of a multicomponent alloy ABC... at equilibrium with a β phase of composition $A_xB_yC_z...$. If $X_A, X_B, X_C, ...$ are the matrix mole fraction surrounding the β phase, the generalized form of the Gibbs–Thomson is then:

$$\frac{2\gamma v_{at}^\beta}{rkT} (x + y + z + \dots) = x \ln \left(\frac{X_{A_r}}{X_{A_\infty}} \right) + y \ln \left(\frac{X_{B_r}}{X_{B_\infty}} \right) + z \ln \left(\frac{X_{C_r}}{X_{C_\infty}} \right) + \dots \quad (11)$$

It is very interesting to note that if the radius is equal to the nucleation radius $r = R^*$, resulting from the classical nucleation theory [1], a direct comparison between the Gibbs–Thomson equation and the equation giving the driving force for nucleation gives $X_{eq_r} = X_0$ (X_0 is the matrix mole fraction of solute atoms). In that case, the driving force exactly compensate the surface force. The evaluation of the Gibbs–Thomson equation and the classical nucleation theory are fully consistent because they come out of the same thermodynamical approach and formalism.

Even for binary alloys, the Gibbs–Thomson equation does not have trivial solutions. However, three simple approximations can be made: (1) $X_p = 1$; (2) $X_{eq_r} \approx X_{eq_\infty}$; (3) $X_{eq_r} \ll 1$ and $X_{eq_\infty} \ll 1$.

(1) The simpler approximation $X_p = 1$ leads to the famous Gibbs–Thomson factor:

$$X_{eq_r} = X_{eq_\infty} \exp \left(\frac{2\gamma v_{at}^\beta}{rkT} \right). \quad (12)$$

Eq. (12) is equivalent to Eq. (1): the molar volume being replaced by the atomic volume. This approximation is the most frequently encountered in the literature. Indeed, some authors [5,6] use it erroneously because it applies only to pure precipitates or phase ($X_p = 1$) and leads to non-negligible errors in the case of compounds precipitate or phases (see Section 4).

(2) Another approximation leads to an analytical formulation of the Gibbs–Thomson term: $X_{eq_r} \approx X_{eq_\infty}$. Indeed, the Gibbs–Thomson equation can be put in the following form:

$$\frac{2\gamma v_{at}^\beta}{rkT} = (1 - X_p) \ln \left(1 + \frac{X_{eq_\infty} - X_{eq_r}}{1 - X_{eq_\infty}} \right) + X_p \ln \left(1 + \frac{X_{eq_r} - X_{eq_\infty}}{X_{eq_\infty}} \right). \quad (13)$$

In that case, series expansion of logarithmic terms gives:

$$\frac{2\gamma v_{\text{at}}^{\beta}}{rkT} = (1 - X_p) \frac{X_{\text{eq}_{\infty}} - X_{\text{eq}_r}}{1 - X_{\text{eq}_{\infty}}} + X_p \times \frac{X_{\text{eq}_r} - X_{\text{eq}_{\infty}}}{X_{\text{eq}_{\infty}}}. \quad (14)$$

Leading to the following form, called the ‘general case’ by Doherty in Ref. [7], also used by Fujita and Bhadeshia [8] and very similar to the expression given by Hillert [9] and Morral and Purdy [10]:

$$X_{\text{eq}_r} = X_{\text{eq}_{\infty}} \left(1 + \frac{2\gamma v_{\text{at}}^{\beta}}{rkT} \frac{1 - X_{\text{eq}_{\infty}}}{X_p - X_{\text{eq}_{\infty}}} \right). \quad (15)$$

- (3) Another approximation is the case of diluted solid solutions: $X_{\text{eq}_r} \ll 1$ and $X_{\text{eq}_{\infty}} \ll 1$. In that case, the first term of the Gibbs–Thomson equation is negligible compared to the second one, except when $X_{\text{eq}_r} \approx X_{\text{eq}_{\infty}}$ (non-trivial). We can then put: $\varepsilon = X_{\text{eq}_r} - X_{\text{eq}_{\infty}}$, leading to:

$$\frac{2\gamma v_{\text{at}}^{\beta}}{rkT} = (1 - X_p)(-\varepsilon) + X_p \frac{\varepsilon}{X_{\text{eq}_{\infty}}}. \quad (16)$$

In that form, the first term of the Gibbs–Thomson equation is still negligible compared to the second one. The equilibrium concentration is then:

$$X_{\text{eq}_r} = X_{\text{eq}_{\infty}} \exp \left(\frac{2\gamma v_{\text{at}}^{\beta}}{X_p rkT} \right). \quad (17)$$

To the knowledge of the present author, Gibbs–Thomson effects are very rarely described using Eq. (17), despite its simplicity.

In the next section, these three approximations will be compared with numerical resolution of the Gibbs–Thomson equation (Eq. (10)) in two cases: Cu_4Ti precipitates in a binary CuTi alloy and cementite precipitation in a low carbon steel.

4. Applications

4.1. Cu_4Ti precipitation in a binary CuTi alloy

Comparison of the numerical solution of the Gibbs–Thomson equation and the three mentioned approximations for the case of Cu_4Ti precipitation in a CuTi alloy is shown in Fig. 1. Table 1 gives the parameters used to evaluate X_{eq_r} . Experimental measurements performed by Miyazaki et al. [5] are also shown in Fig. 1. Note that the very good fit between the Gibbs–Thomson equation and experimental data is due to the fact that surface tension γ and solubility limit $X_{\text{eq}_{\infty}}$ proposed by Qian et al. [11] were fitted with the measurements of Miyazaki et al. [5].

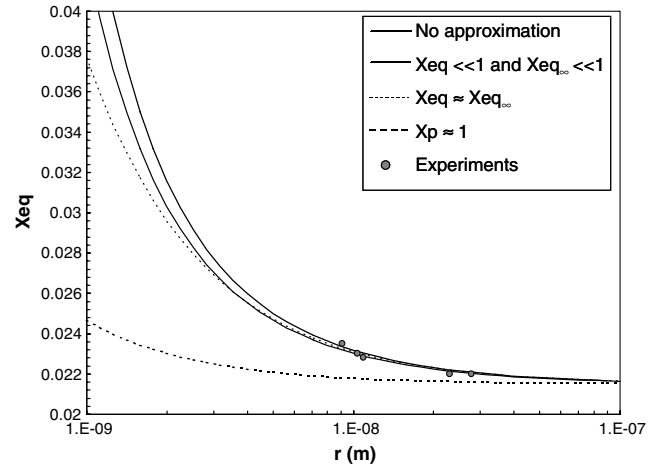


Fig. 1. The exact solution of Eq. (10) is compared with the three different approximations for the case of Cu_4Ti precipitation in Cu-Ti alloy. Eq. (17) gives the best approximate values.

Table 1
Parameters for Cu_4Ti precipitation at 600 °C

X_p	Carbon mole fraction of Cu_4Ti	0.2
$X_{\text{eq}_{\infty}}$	Solubility limit (flat interface)	0.0214 [11]
v_{at}^{β}	Mean atomic volume of Cu_4Ti	$1.31 \times 10^{-29} \text{ m}^3$ [11]
γ	Surface tension	0.063 J/m^2 [11]

However, we clearly observe that the first approximation ($X_p = 1$, Eq. (17)) is clearly unsuitable for radii smaller than 10 nm. For lower radii, the approximation ($X_{\text{eq}_r} \ll 1$ and $X_{\text{eq}_{\infty}} \ll 1$, Eq. (17)) seems to be better than the other one ($X_{\text{eq}_r} \approx X_{\text{eq}_{\infty}}$, Eq. (15)). Note that for small radii, the Gibbs–Thomson equation has no solution: the β phase is unstable due to the high amount of interfacial energy stored in the precipitates.

4.2. Cementite precipitation in a low carbon steel

Fig. 2 shows the evolution of X_{eq_r} as a function of the precipitate radius for the case of cementite precipitation in a low carbon steel that has been studied in a previous work [12]. Table 2 gives the parameters used to evaluate X_{eq_r} . In this case the first approximation ($X_p = 1$, Eq. (17)) is clearly untrue for radii smaller than 100 nm. The second one ($X_{\text{eq}_r} \approx X_{\text{eq}_{\infty}}$, Eq. (15)) is still valid for radii larger than 10 nm, whereas the third one ($X_{\text{eq}_r} \ll 1$ and $X_{\text{eq}_{\infty}} \ll 1$, Eq. (17)) remains valid in the whole range of radii.

4.3. Discussion

To extend the validity of Eq. (12), many authors express the Gibbs–Thomson equation as formulated in Eq. (1) with the ambiguous term V_m , which is given to be the ‘molar volume’ of β phase. If it means the volume of one mole of β atoms, Eqs. (12) and (1) are strictly

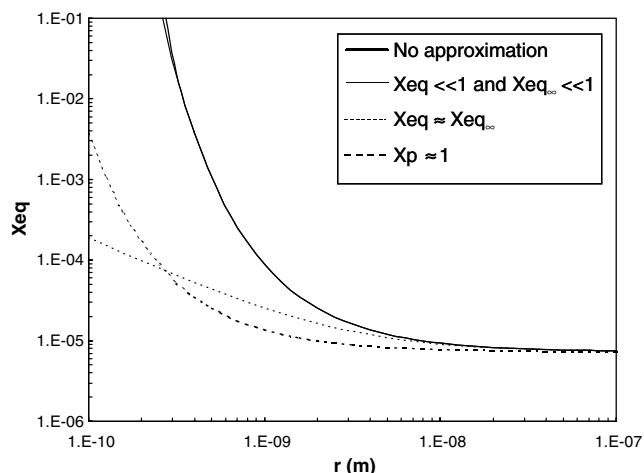


Fig. 2. The exact solution of the Gibbs–Thomson equation (10) is compared with the three different approximations for the case of Fe_3C precipitation in Fe–C alloy: the approximation $X_{\text{eq}} \ll 1$ and $X_{\text{eq}_\infty} \ll 1$, Eq. (17) is remarkably good in the whole domain.

Table 2
Parameters for low carbon steel at 200 °C

X_p	Carbon mole fraction of Fe_3C	0.25
X_{eq_∞}	Solubility limit (flat interface)	7.3×10^{-6} [13,12]
v_{at}^β	Mean atomic volume of Fe_3C	$1.17 \times 10^{-29} \text{ m}^3$ [1,12]
γ	Surface tension	0.174 J/m^2 [12]

equivalents, and as seen previously, not a very accurate approximation. If it means the volume of one mole of A_xB_y , the frequently encountered approximation (Eq. (1)) is then equivalent to the proposed approximation (Eq. (17)) only in a particular case where $\gamma = 1$.

5. Conclusion

In order to take into account the presence of interfaces during phase transformation, it is necessary to add the capillarity term ($2\gamma v_{\text{at}}/r$) in the Gibbs free energy of the multiphased system. This leads to the general formulation of the Gibbs–Thomson effect giving a relation between the matrix composition at the interface with (i) a precipitate of radius r and (ii) a precipitate of infinite radius (flat interface).

For practical reasons, approximations of this formulation are often used in the literature. However, it has

been showed that for compound precipitates, some of these approximations are not valid in the considered precipitates radii range. A very simple approximation has been proposed, giving values of composition very close to the exact solution of the Gibbs–Thomson equation in a wide range of radii. In any case, the chosen approximation has to be compared with the numerical solution of the Gibbs–Thomson equation in order to check its domain of validity.

Acknowledgments

C. Sigli from Pechiney-Alcan and G. Purdy are gratefully acknowledged for stimulating discussions and helpful comments.

References

- [1] Porter DA, Easterling KE. Phase transformation in metals and alloys. London: Chapman and Hall; 1992. 514 p.
- [2] Philibert J, Vignes A, Bréchet Y, Combrade P. Métallurgie: du minéral au matériau. Paris: Masson; 1998. 1107 p.
- [3] Madras G, McCoy B. Temperature effects for crystal growth: a distribution kinetics approach. Acta Mater 2003;51:2031–40.
- [4] Myhr OR, Grong O, Anderson SG. Modelling of the age hardening behaviour of Al–Mg–Si alloys. Acta Mater 2001;49: 65–75.
- [5] Miyazaki T, Koyama T, Kobayashi S. A new characterization method of the microstructure using the macroscopic composition gradient in alloys. Met Trans A 1996;27:945–9.
- [6] Kim HK, Tu KN. Kinetic analysis of the soldering reaction between eutectic SnPb alloy and Cu accompanied by ripening. Phys Rev B 1996;53(23):16027–33.
- [7] Cahn RW, Haasen P. Physical metallurgy. Amsterdam: North Holland; 1996. 1830 p.
- [8] Fujita N, Bhadeshia HKDH. Modelling simultaneous alloy carbide sequence in power plant steel. ISIJ Int 2002;42:760–9.
- [9] Hillert M. Phase equilibria, phase diagrams and phase transformation. Cambridge: Cambridge University Press; 1998. 538 p.
- [10] Morral JE, Purdy GR. Thermodynamic of particle coarsening. J Alloys Compd 1995;220:132–5.
- [11] Quian M, Lim LC. Re-evaluation of the experimental results reported by Miyazaki et al. on the Gibbs–Thomson effect. Scripta Mater 1998;39(10):1451–5.
- [12] Perez M, Deschamps A. Microscopic modelling of simultaneous two-phase precipitation: application to carbide precipitation in low-carbon steels. Mater Sci Eng A 2003;A360:214–9.
- [13] Zhu A, Neife SI, Pink E. Characterization of medium and low temperature carbides in a low carbon steel by internal friction. Steel Res 1996;67(11):507–12.