Chapter 5

Capillarity in multicomponent systems

In the preceding chapter, it was assumed that the interface between the matrix and the growing precipitate was under local equilibrium, therefore allowing the use of the equilibrium phase diagram to determine its composition. It was also mentioned that several effects may invalidate this hypothesis. In particular, capillarity, which is a modification of the interface equilibrium due to the contribution of the interface energy, affects particularly the early stages of growth. Capillarity is also at the origin of the coarsening phenomenon.

Because the problem of multicomponent capillarity has no simple solutions, many works have used the Gibbs-Thomson equation developed for a binary system. In this chapter, the validity of this approach is discussed, and two better methods are proposed and compared.

5.1 Introduction

As presented in chapter 3, the CALPHAD method allows predictions of the phase behaviour of complex, multicomponent systems. Software such as MT-DATA or ThermoCalc use thermodynamic databases to calculate equilibrium phase compositions and amounts for given composition, temperature and pressure. However, the equilibrium at an interface between two phases can be modified by curvature, an effect commonly referred to as "capillarity", and most often described by the Gibbs-Thomson equation (e.g. [101]

page 149). These concepts have been introduced in chapter 3.

There are two aspects in the treatment of the capillarity problem. One solution is to re-calculate the thermodynamic equilibrium when the Gibbs free energy of one phase is raised by an amount which allows for the creation of new interfacial energy as the particle grows (Eq. 22.29 in [84]). This is possible using thermodynamic calculation packages such as MT-DATA, as described later.

On the other hand, there is an interest in being able to estimate the capillarity correction without such software, particularly when this correction has to be estimated within a separate model. For binary solutions, this can be done using the Gibbs-Thomson equation, or a generalised form for multicomponent alloys.

In the following, a two-phase system is considered, with the matrix referred to as γ and the precipitate as θ. The problem is to estimate how the equilibrium between the two phases is modified when the Gibbs energy of θ is raised by a given amount, in the case of capillarity, $\sigma_{\gamma\theta} \, \partial O/\partial n$; $\sigma_{\gamma\theta}$ being the γ/θ interface energy per unit area, and $\partial O/\partial n$ the increase in area when the number of moles n of θ increases.

5.2 Capillarity effects in a binary two phase system

The solution of the capillarity problem in a binary, two-phase system is well known and is presented here to be used as a guide towards the solution in a ternary system. This section is essentially after Hillert [101]. A binary system A-B is considered, with two phases γ and θ.

The precipitate θ is here considered to have a fixed chemical composition. Figure 5.1 illustrates the problem: the Gibbs free energy of θ (G_θ) is raised by a term $\sigma_{\gamma\theta} \, \partial O/\partial n$. The mathematical treatment is however more readable and easier to develop rigorously if the Gibbs energy addition is written in a general manner, $V_m^\theta \, \Delta P$ where V_m^θ is the molar volume of θ and $\Delta P = \int \mathrm{d}P$ a pressure increase.

The initial interface compositions are given by the two contact points of the common tangent to the γ and θ free energy curves. If the difference in composition between the matrix and the precipitate is sufficiently large, when compared to the composition change due to capillarity, the addition of $V_m^\theta \mathrm{d}P$ causes the slope of the common tangent to change as:
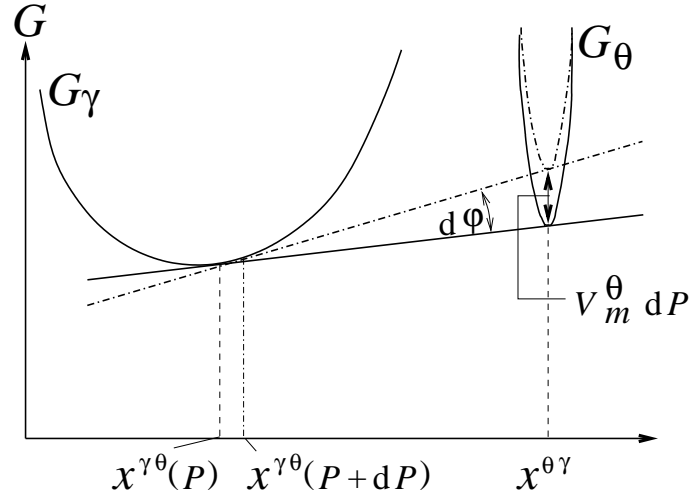
Figure 5.1: The effect of an increase in the Gibbs energy of a stoichiometric compound θ on the matrix composition. G denotes the Gibbs energy of the phase identified by the subscript.

$$(x^{\theta\gamma} - x^{\gamma\theta})\mathrm{d}\varphi = V_m^\theta \mathrm{d}P \tag{5.1}$$

where $x^{\theta\gamma}$ is the mole fraction of solute in phase θ in equilibrium with γ, similarly for $x^{\gamma\theta}$; $\mathrm{d}\varphi$ is the difference between the slopes at the two contact points (figure 5.1):

$$\mathrm{d}\varphi = \left.\frac{\partial G_\gamma}{\partial x^\gamma}\right|_{x^{\gamma\theta}(P+\mathrm{d}P)} - \left.\frac{\partial G_\gamma}{\partial x^\gamma}\right|_{x^{\gamma\theta}(P)} = \frac{\partial^2 G_\gamma}{\partial x^{\gamma2}}\,\mathrm{d}x^{\gamma\theta} \tag{5.2}$$

where $\mathrm{d}x^{\gamma\theta} = x^{\gamma\theta}(P+\mathrm{d}P) - x^{\gamma\theta}(P)$ is the composition change of the matrix in equilibrium with the precipitate. Assuming a dilute solution:

$$\frac{\partial^2 G_\gamma}{\partial x^{\gamma2}} = \frac{RT}{x^\gamma} \tag{5.3}$$

therefore:

$$\mathrm{d}x^{\gamma\theta} = \frac{x^{\gamma\theta}}{x^{\theta\gamma} - x^{\gamma\theta}}\frac{V_m^\theta \mathrm{d}P}{RT} \tag{5.4}$$

and for a reasonably small change, it is possible to integrate assuming that $x^{\theta\gamma} - x^{\gamma\theta}$ is constant:

$$\ln\frac{x^{\theta\gamma}(P)}{x^{\theta\gamma}(P=0)} = \frac{V_m^\theta \Delta P}{RT(x^{\theta\gamma} - x^{\gamma\theta})} \tag{5.5}$$

This is valid regardless of the nature of the Gibbs energy increase; in the case of capillarity with a spherical interface of radius r, $P = 0$ corresponds to a flat interface, that is $r = \infty$, and the increase of Gibbs energy is $2V_m^\theta \sigma_{\gamma\theta}/r$, so that:

$$\ln \frac{x^{\theta\gamma}(r)}{x^{\theta\gamma}(r = \infty)} = \frac{2V_m^\theta \sigma_{\gamma\theta}}{r} \frac{1}{RT(x^{\theta\gamma} - x^{\gamma\theta})} \tag{5.6}$$

5.3   Ternary systems

Probably because the literature does not offer a simple solution for multicomponent capillarity, various works dealing with multicomponent alloys have used either the standard form of the Gibbs-Thomson equation, or methods based on it.

For example, Faulkner [102] used directly the Gibbs-Thomson equation to calculate the influence of the curvature of $M_{23}C_6$ on the expected chromium content of the surrounding austenite, in an austenitic steel (Fe-18Cr-10Ni-Mn-C wt%). Such a procedure was recognised to be incorrect by Fujita and Bhadeshia [93] since the binary equation gives a different critical radius (at which growth becomes impossible) for each of the solutes in a multicomponent solution. However, the technique used by Fujita and Bhadeshia, who used the Gibbs-Thomson equation for a particle with a fixed radius and then calculated the capillarity corrected phase boundary, also has its problems. In a multicomponent system, the different components are not independent, and this does not appear when equation 5.6 is applied in turn to each component.

Consider now a ternary system A-B-C where C is the solvent. The mole fractions of A and B in both the matrix (γ) and the precipitate (θ) are likely to be modified by the curvature of the interface and are therefore functions of r.

The derivation of a correct set of equations is better understood with the help of figure 5.2. MN is an equilibrium tie-line as shown in figure 5.2. Since it is assumed that the composition of θ is constant, the new tie-line M′N′ will remain in the same vertical plane. Equation 5.1 becomes:

$$Z \, \mathrm{d}\varphi = V_m^\theta \, \mathrm{d}P \tag{5.7}$$

where Z is the distance between the compositions defined by M and N. Considering the change of slope along the tie-line, it can be shown, using the same idea as in equation 5.2,
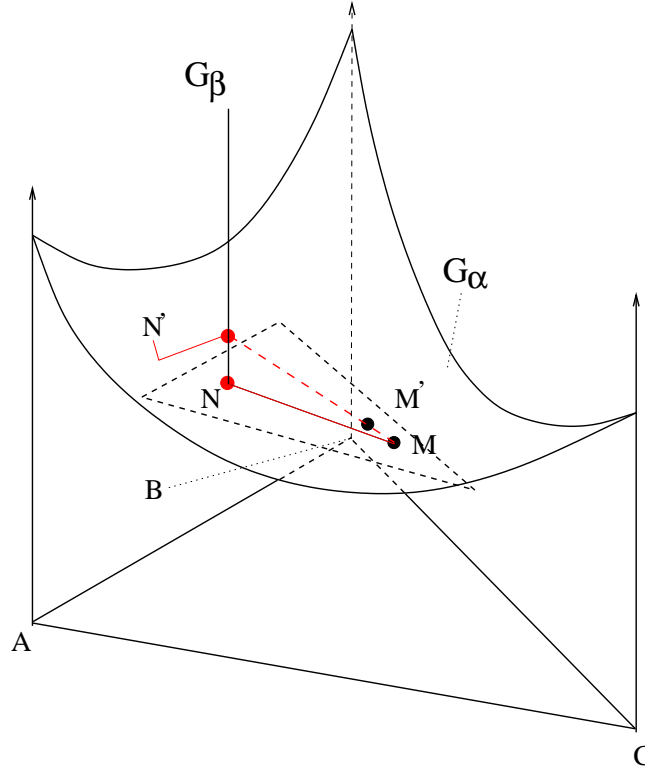
Figure 5.2: The effect of raising the molar Gibbs energy of the θ phase in a ternary system. The points of contact with the tangent plane, M and N move to M' and N'. $G_\theta + V_m^\theta \mathrm{d}P$ has its minimum value at N'.

that:

$$V_m^\theta \, \mathrm{d}P = \left(a\frac{\partial^2 G_\gamma}{\partial x_A^{\gamma\,2}} + b\frac{\partial^2 G_\gamma}{\partial x_A^\gamma \partial x_B^\gamma} \right) \mathrm{d}x_A^\gamma + \left(b\frac{\partial^2 G_\gamma}{\partial x_B^{\gamma\,2}} + a\frac{\partial^2 G_\gamma}{\partial x_A^\gamma \partial x_B^\gamma} \right) \mathrm{d}x_B^\gamma \qquad (5.8)$$

where $a = (x_A^\theta - x_A^\gamma)$ and $b = (x_B^\theta - x_B^\gamma)$. Equation 5.8 is in fact similar to the one proposed by Morral and Purdy [103], since $V_m^\theta \, \mathrm{d}P$ is replaced by $2V_m^\theta/r$ for a spherical particle:

$$(\Delta x^{\gamma\theta}] \, [G] \, [\Delta x^\gamma) = \frac{2\sigma_{\gamma\theta} V_m^\theta}{r} \qquad (5.9)$$

where ( ] indicates a row vector, while [ ) a column vector, and the matrix $[G]$ is defined by:

$$G_{ij} = \frac{\partial^2 G_\gamma}{\partial x_i \partial x_j} \qquad (5.10)$$

If a dilute solution is assumed, the cross derivatives are zero and the others can be estimated as in equation 5.3. Given that $\mathrm{d}x_A^\gamma/\mathrm{d}x_B^\gamma = (x_A^\theta - x_A^\gamma)/(x_B^\theta - x_B^\gamma)$, equation 5.8

becomes:

$$
\begin{aligned}
\mathrm{d}x_A^\gamma &= \frac{ax_A^\gamma x_B^\gamma}{a^2 x_B^\gamma + b^2 x_A^\gamma} \frac{V_m^\theta \mathrm{d}P}{RT} \\
\mathrm{d}x_B^\gamma &= \frac{(x_B^\theta - x_B^\gamma)}{(x_A^\theta - x_A^\gamma)} \, \mathrm{d}x_A^\gamma
\end{aligned}
\tag{5.11}
$$

These equations involve, as expected, both x_A^γ and x_B^γ; the system can easily be integrated numerically, and there is no difficulty in generalising to any number of components. For n components a system of $(n-1)$ equations are obtained.

It is noticeable that the interdependence does not require the presence of thermodynamic interactions between the components, as equation 5.11 has been derived assuming an ideal solution. Rather, the interdependence can be explained, geometrically, by the need to consider the slope along the tie-line. Applying directly the Gibbs-Thomson equation is equivalent to consider individually the components of this slope along the axis x_A and x_B.

It would be useful to compare these solutions against an exact calculation done using MT-DATA, in which the capillarity effect can be incorporated by raising the free energy of one of the phases by a quantity $\Delta P\, V_m^\theta$, equivalent to $\sigma \partial O / \partial n$.

5.4 An exact calculation using MT-DATA

Softwares such as MT-DATA rely on thermodynamic solution models to estimate the Gibbs energy of a given phase. Such models have been presented in chapter 3. The Gibbs energy of a phase like austenite is usually calculated using a sublattice model [81], which involves, in particular, terms called unaries ($G_{i:j}^0$ in eq. 5.12) which, for the example of a phase with two sublattices, contribute to the total free energy as follows:

$$
G_{unaries} = \sum_{i \in I} \sum_{j \in II} y_i^I y_j^{II} G_{i:j}^0
\tag{5.12}
$$

where I is the first sublattice and II the second, i are all the elements able to enter the first sublattice and j those entering on the second, y_i^I the site fraction occupancy on the first sublattice by element i. Most commonly, temperature and pressure dependence of

the unaries are described using the G-HSER format [83]:

$$G^{T,P} - H^{SER} = a + bT + cT\ln T + eT^2 + fT^3 + i/T + \int_0^P V_m^{P,T}\mathrm{d}P \qquad (5.13)$$

in which $G^{T,P}$ is the molar Gibbs energy at (T,P) and H^{SER} is the enthalpy of the element or substance in its defined reference state at 298.15 K. Although the data contained in the SGTE solutions and substances databases do not include any pressure dependent terms for most of the condensed phases, it is possible to construct modified databases containing such terms. In the case of a sublattice model, one has to modify all the unaries for a given phase. By inserting a constant molar volume in the databases, one can, while using MT-DATA, add a given Gibbs energy to the phase of interest by setting the pressure to the appropriate value. As an example, table 5.1 lists all the non-zero unaries data for $M_{23}C_6$ (three sublattices).

Cr:Cr:C	Fe:Cr:C	Mn:Cr:C	Ni:Cr:C	V:Mn:C
Cr:Fe:C	Fe:Fe:C	Mn:Fe:C	Ni:Fe:C	
Cr:Mn:C	Fe:Mn:C	Mn:Mn:C	Ni:Ni:C	
Cr:Mo:C	Fe:Mo:C			
Cr:Ni:C	Fe:Ni:C			
Cr:V:C	Fe:V:C	Mn:V:C		V:V:C

Table 5.1: Some unaries data for $M_{23}C_6$. Missing unary like Mn:Mo:C have to be created so that the sum in equation 5.12 adds up to one mole of component. However, most of the time, missing unaries may make insignificant contributions as they involve minor elements.

For phases such as NbN, TiN, *etc...* which are modelled as pure substances, however, the SGTE databases often only contain coefficients to describe the temperature dependence of the heat capacity. This format does not accept pressure dependent terms and it was therefore necessary to create datasets in the G-HSER format for the relevant phases. In the C_P-format [83], the variation of the heat capacity within the temperature range i, for which $T \in [T_{min,i}, T_{min,i+1}]$ where $T_{min,i}$ is the minimum temperature for the range i, is given by:

$$C_{Pi}(T) = A_i + B_i T + C_i T^2 + D_i T^{-2} \qquad (5.14)$$

with possibly a transition term $\Delta_i H_i$ between the ranges i and $i+1$, the parameters required for the G-HSER format can be calculated from the relationships between Gibbs

energy and heat capacity:

$$
\begin{aligned}
a_i &= \mathrm{H}(T_{min,i}) - A_i\,T_{min,i} - B_i\,T_{min,i}^2/2 - C_i\,T_{min,i}^2/3 + D_i/T_{min,i} \\
b_i &= A_i - \mathrm{S}(T_{min,i}) + A_i\,\ln(T_{min,i}) + B_i\,T_{min,i} + C_i\,T_{min,i}^2/2 - D_i/(2\,T_{min,i}^2) \\
c_i &= -Ai \\
d_i &= -B_i/2 \\
e_i &= -Ci/6 \\
f_I &= -D_i/2 \\
\mathrm{H}(T_{min,i}) &= \Delta_f\mathrm{H}(298) + \sum_{j<i}\left(\int_{T_{min,j}}^{T_{min,j+1}} C_{Pj}\,\mathrm{d}T\right) + \sum_{j<i}(\Delta_t\mathrm{H}_j) \\
\mathrm{S}(T_{min,i}) &= \mathrm{S}_{298} + \sum_{j<i}\left(\int_{T_{min,j}}^{T_{min,j+1}} \frac{C_{Pj}}{T}\,\mathrm{d}T\right) + \sum_{j<i}\left(\frac{\Delta_t\mathrm{H}_j}{T_{min,j+1}}\right)
\end{aligned}
\tag{5.15}
$$

where enthalpies and entropies, $\Delta_f\mathrm{H}(298)$, S_{298}, and the $\Delta_t\mathrm{H}_j$ are found in the databases.

A pressure dependence term was added to various precipitates expected to form in steels, so as to increase the molar Gibbs energy of the phases of interest by 10^{-6} J per Pa. In this way, setting a pressure of 1 Pa allows the user to perform an ordinary equilibrium calculation since the added Gibbs energy is negligible. Databases incorporating such
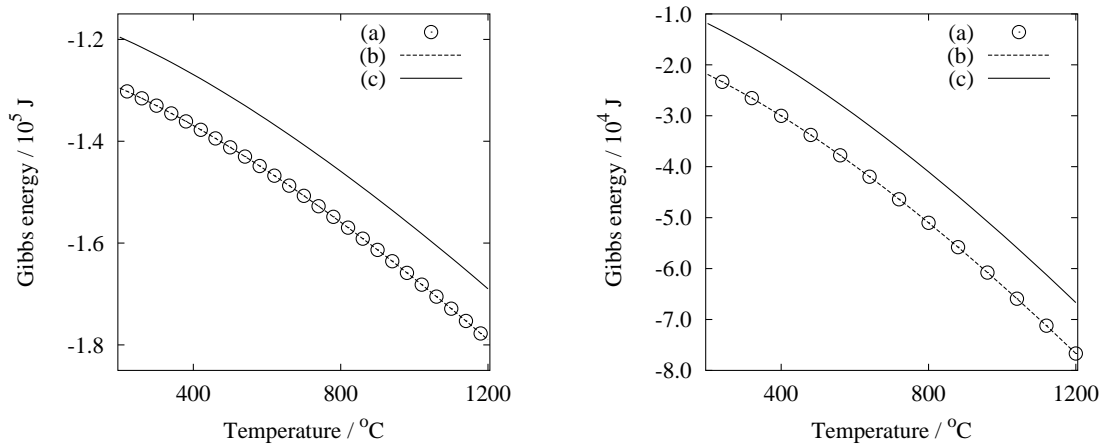

Figure 5.3: Verification of the effect of pressure setting on the Gibbs energy of NbN and $M_{23}C_6$ calculated with MT-DATA. The calculation using the original database (a) is identical to that with the modified database and the pressure set to $P = 1$ Pa (b). Setting the pressure to $P = 10^{10}$ Pa raises the Gibbs energy of the phases by 10^4 J per mole of components (c).

modifications have been created for $M_{23}C_6$, HCP_A3 (e.g. Cr_2N, Mo_2C), NbN, TiN, NbC and TiC, $NbC_{0.479}$, $NbC_{0.877}C$ and $Nb_{0.98}C$. Figure 5.3 shows the Gibbs energy of NbN and $M_{23}C_6$ calculated in different conditions. By setting the pressure to 1 Pa when using a thermodynamic calculation software such as MT-DATA or ThermoCalc in conjunction with the modified databases, the user can calculate the ordinary equilibrium (because the Gibbs energy increase is negligible), while the equilibrium when G_θ is raised by 500 J would be calculated by setting the pressure to 5×10^8 Pa.

5.5   Comparisons and comments

5.5.a   The dilute solution approximation

To validate the simple expression proposed for a ternary system (equation 5.11), a system consistent with the approximations made above (precipitate of fixed composition, ideal solution) was chosen: Fe, Nb, C, allowing austenite (γ) and NbC. Because NbC is modelled as a pure substance, its composition cannot change as assumed in the derivation.

By setting a small total amount of Nb (0.03 mole %) and C (0.06 mole %) in the austenite, it is possible to match reasonably well the approximation of a dilute solution, as shown in table 5.2. The second part of this table is for the example used later and shows that the dilute solution approximation does not lead to significant error. When the

For $x_{Nb}^\gamma = 0.0003$ and $x_C^\gamma = 0.0006$, at 1173 K				
	Calculated with MT-DATA		Ideal solution approximation	
	Nb	C	Nb	C
Nb	3.25×10^7	-2.98×10^5	3.25×10^7	0
C	-2.98×10^5	1.63×10^7	0	1.62×10^7
For the composition chosen in example (0.2 Nb, 0.1 C wt%):				
	Calculated with MT-DATA		Ideal solution approximation	
	Nb	C	Nb	C
Nb	8.33×10^6	-2.97×10^5	8.32×10^6	0
C	-2.97×10^5	2.23×10^6	0	2.15×10^6

Table 5.2: The Hessian matrix of G (that is $\left[\partial^2 G_\gamma / \partial x_i \partial x_j\right]_{(i,j)}$) (J / mol) calculated with MT-DATA (left) and calculated using the dilute solution approximation (right).

concentration is further raised, RT/x_i^γ is still a good approximation for $\partial^2 G_\gamma/\partial x_i^{\gamma\,2}$, but the cross derivatives cannot reasonably be neglected.

5.5.b   Effect of a Gibbs energy increase

In this example, the precipitate is NbC, which is modelled as a pure substance. The composition change of the matrix (γ) in equilibrium with NbC when the latter's Gibbs energy is increased by a constant term is considered.

Table 5.3 shows the expected composition change of the austenite in equilibrium with NbC at 1200 K, comparing the results of equation 5.5 and of equation 5.11 integrated to the value calculated with MT-DATA. The bulk composition is 0.2 wt% Nb, 0.1 wt% C. In this case, the C is in excess for the formation of NbC, and the modification of the Nb

PV_m^θ / (J/mol)	$\Delta x_C^{\gamma\theta}$ calculated with:		
	MT-DATA	Eq. 5.5	Integration of Eq. 5.11
1000	2.4×10^{-6}	7.74×10^{-4}	2.4×10^{-6}
5000	1.85×10^{-5}	6.03×10^{-3}	1.84×10^{-5}

Table 5.3: The modification of the carbon content (mole fraction) of the matrix in equilibrium with NbC when a constant Gibbs free energy is added, as calculated by MT-DATA and according to different equations.

content is well approximated by any formula. If the situation is opposite (Nb in excess), the effect of capillarity on Nb is overestimated by equation 5.5.

This shows clearly that a straightforward application of the Gibbs-Thomson formula leads to an error which can be large. With the correct multicomponent treatment (Eq. 5.11), the agreement is excellent.

Figure 5.4 shows the shift of the austenite/austenite+NbC boundary when the molar Gibbs energy of NbC is raised by 10000 J/mol. It should be noticed that, although the boundary calculated according to the method proposed by Fujita and Bhadeshia [93] does not lie very far from the exactly calculated one, the error on individual points is significant.
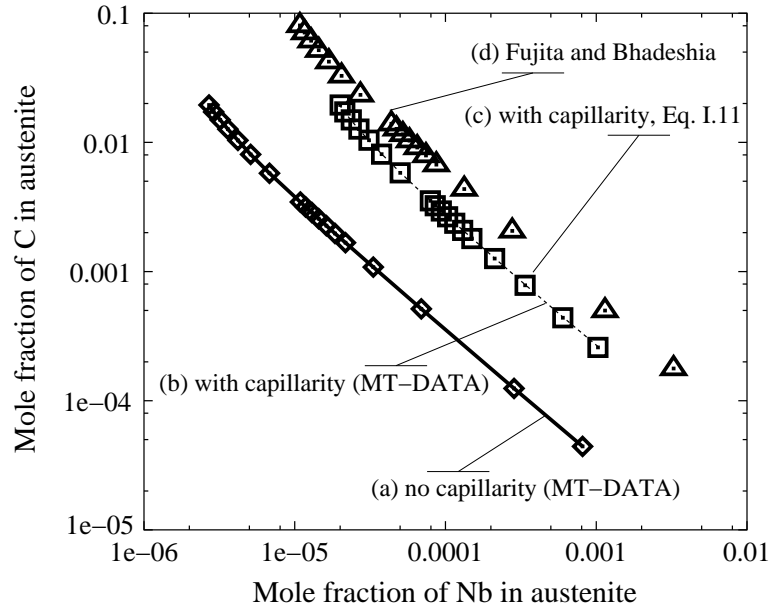
Figure 5.4: The shift of the $\gamma/\gamma + \mathrm{NbC}$ boundary at 1200 K for $PV_m^\theta = 0$ (a), calculated with MT-DATA for $PV_m^\theta = 10000$ J/mol (b), for the same addition using Fujita and Bhadeshia's method (c) and using equations 5.11 (d).

5.6   Consequences and conclusions

5.6.a   Example

To illustrate the effect of the correction proposed to the Gibbs-Thomson equation, the model proposed by Fujita and Bhadeshia [93] for $\mathrm{Mo_2C}$ precipitation was used. The program available on MAP (http://www.cam.ac.uk/map/mapmain.html) was used as provided, then corrected to estimate capillarity effects using the system of equations 5.11.

Figure 5.5 shows the differences between the two curves; when additions of Mo and C are nearly stoichiometric, the error due to the use of the standard Gibbs-Thomson equation is relatively small (see figure 5.4, an example with Nb and C) and only the last part of the curve in which the transformation is mainly due to growth of the existing precipitates is significantly affected. When the additions of Mo and C are far from stoichiometric, the error is more important and so is the difference between the two curves. The trend is expected: it has been shown that use of the Gibbs-Thomson equation leads to large overestimation of the capillarity effect, and consequently, the effect on kinetics is exaggerated.
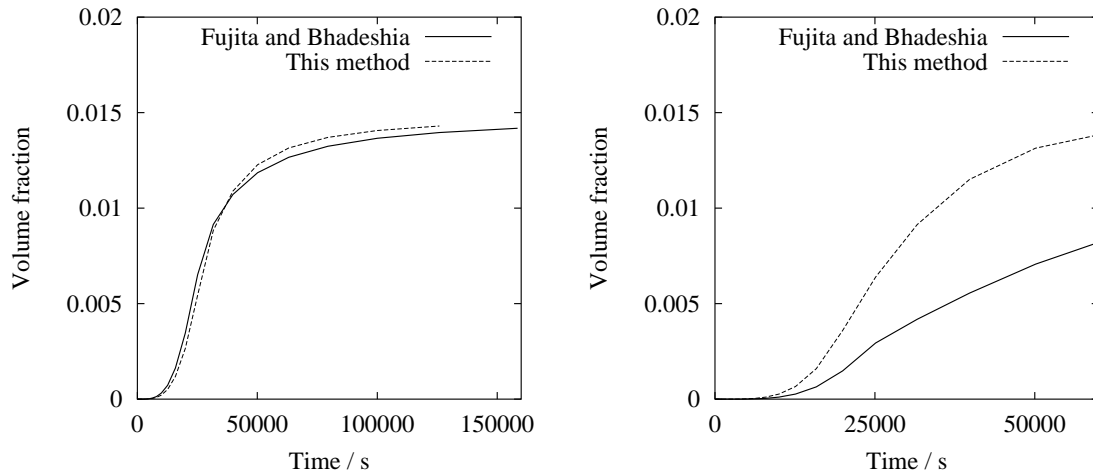
Figure 5.5: The volume fraction of Mo$_2$C in Fe-Mo-C steel. On the left, with all parameters as given on MAP (http://www.cam.ac.uk/map/mapmain.html), the initial mole fraction of Mo is twice that of C. On the right, the mole fraction of Mo and C have been chosen so as to give about the same amount of Mo$_2$C, but with a Mo addition ten times that of carbon, and the error due to the use of the Gibbs-Thomson equation is much larger, as can be seen on figure 5.4 with Nb and C for example.

5.6.b Conclusions

The Gibbs-Thomson equation has been applied in a number of studies dealing with multicomponent alloys, for example [93, 102]. It has been shown that the error can be large. This means that estimation of the coarsening rate, and of the influence of interface curvature on the kinetics of precipitation might be overestimated.

A simple solution has been proposed for a ternary system, one which can easily be extended to any number of components. It shows excellent agreement with the exact recalculation of the modified equilibrium when the assumptions are justified, that is in the case of a precipitate with fixed composition, in a matrix behaving like a dilute solution. When the precipitate is a solution whose composition is likely to change, the equation proposed estimates quite well the matrix composition change, but can not be applied to the precipitate, for which the approximation of dilute solution can not be made. It seems that solving analytically the problem of the precipitate composition change would be as complicated as recalculating the equilibrium, which can be made easily with thermodynamic calculation packages like MT-DATA.