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Eutectic Growth in Two-Phase Multicomponent Alloys

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Abstract

A theory of two-phase eutectic growth for a multicomponent alloy is presented. Using the same hypotheses as the Jackson-Hunt theory, we find that the growth law of the microstructure given by Jackson and Hunt for binary alloys can be generalized to systems with N elements. Thermodynamic parameters involved in this theory are linked to the Gibbs free energies of the phases which makes it possible to compute these parameters with CALPHAD tools. A model is derived from this general theory for ternary alloys which does not contain any assumptions on the alloy thermodynamic properties, contrary to previous models. We find that a small addition of a ternary alloying element with a small diffusivity to a binary alloy can significantly alter the spacing of the eutectic.

Keywords: Eutectic solidification ; Multicomponent ; Ternary alloys ; CALPHAD ; Diffusion

1. Introduction

Eutectic alloys possess many advantages compared to single-phase systems. Indeed, they have a low melting point compared to pure components and their composite microstructure gives them superior mechanical properties.

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For binary eutectics, Hillert [1] and later Jackson and Hunt [2] analytically determined a scaling law for the microstructure developed by regular eutectics during directional steady state solidification. Moreover, they have established a link between the microstructure developed and the thermodynamic and thermophysical properties of alloys. This scaling parameter has been proved to be very useful in characterizing the eutectic microstructure of many regular binary alloys [3].

However, a analogous theory for alloys with many components and growing as a two-phase eutectic does not exist. Such multicomponent two-phase eutectics are common and have been studied in, Al-Cu-Ag [4], Fe-Si-Mn, Fe-Si-Co [5], Al-Cu-Ni [6] and Ni-Al-Cr-Mo [7]. Moreover, most commercially relevant materials contain still more alloying elements. Unfortunately, a comprehensive model for the growth of these multicomponent two-phase eutectics does not exist. However, there has been progress towards a general theory. Catalina et al. [8] proposed a model for eutectic growth of two-phase eutectics containing N elements, but restricted the treatment to the case where one of the phases has no solid solubility for the solute elements. Fridberg and Hillert [9] published a model for the growth process of a binary alloy containing a small amount of an additional element. Later, Plapp and Karma [10] analyzed the effect of a small addition of a third element on the morphology of a symetrical binary eutectic. In ternary alloys, McCartney et al. [11] and DeWilde et al. [12] gave two different models. In the McCartney-Hunt model, simplifying approximations were employed on the alloy phase diagram and the diffusion process. DeWilde et al. employed an approximation for the manner in which the long-range diffusion field decays and for concentration profiles in the liquid phase. While all of these treatments provide important insights into eutectic solidification of multicomponent alloys, they lack the generality needed for many applications.

In this paper, we present a method to compute the mean undercooling of a two-phase eutectic as a function of the eutectic spacing and the velocity for any alloy containing N elements in the spirit of the Jackson Hunt model (Section II). This general method removes the approximations introduced in the models [8, 11, 12] mentioned above. It is then applied to binary alloys and compared to the Jackson-Hunt theory in section III. The model derived from this general method for ternary alloys is given in section IV. This model is then used to analyze the influence of the addition of a low concentration of a third element on the microstructure of a binary alloy. We finally discuss in section VI the use of this model as a way to predict of the eutectic microstructure evolution of an alloy with the addition of a new element. We conclude this paper by a summary of results presented and possible future continuation of this work.

2. Two-phase eutectic growth of alloys with N elements

In this section, we present our general methodology to compute the mean undercooling of any two-phase eutectic alloy with N elements.

We study the directional solidification at steady state of a two-phase eutectic with an initial concentration $(C_2^\infty, \dots, C_N^\infty)$. In this work, the choice of the element 1, which concentration depends on independent concentrations of elements 2 to N is arbitrary. We assume that this eutectic develops a lamellar morphology such as the one presented in Fig 1.

By definition, the two-phase eutectic temperature (T_E) is the temperature at which three phases, α, β and liquid are in equilibrium. For systems with more than three elements, this temperature depends on the alloy composition. All quantities referring to the eutectic temperature will be identified with a superscript 'E'. We assume that for any position x at the interface, the solid/liquid interface is at thermodynamic equilibrium at a temperature $T_u(x)$. So for any

position x of the interface, the chemical potentials of any specie $i = 1..N$ in the liquid phase and in the solid phase ϕ are equal:

$$\mu_i^{\phi}(C_2^{\phi}, .., C_N^{\phi}, T_u, p^{\phi}) = \mu_i^{l}(C_2^{l}, .., C_N^{l}, T_u, p^{l}) \;\; i = 1, 2 \dots N \tag{1}$$

where C_i is the mole fraction of component i, p is the pressure, and ϕ can be either one of the two solid phases. For a given phase, assuming that $C_2^l .., C_N^l, p^l$ and p^{ϕ} are known, this gives N equations and N unknowns. Thus once the composition of the liquid at the interface and the pressure in the solid phase are known, and by assuming that p^l does not change from that at the equilibrium state, the composition of the solid phase is known and the undercooling is fixed.

The variations in the rejection of solutes in front of solid phases, α and β, induce changes in the concentrations in the liquid phase at the interface compared with the equilibrium state, $(C_2^{lE}, .., C_N^{lE})$. In addition, the interface curvature due to the surface energies equilibrium at the trijunctions (points where the two solid phases are in contact with the liquid phase) induces a variation of the internal pressure in solid phases. Since local equilibrium is assumed to hold, these variations in the liquid composition induce changes in concentrations in solid phases from their equilibrium values, and a change in the interface temperature from T_E. The compositions of the solid, liquid and the temperature are related by N chemical potential equations for each solid phase. Unfortunately, these equations are nonlinear, and thus we assume small deviations from the equilibrium temperature, and phase compositions to relate the solid phase compositions and undercooling temperature to the liquid composition. The development of these N equalities (Eq. (1)) for each phase is given in the appendix A. This development leads to a matrix expressing the change in the concentration in solid phases from equilibrium, $\Delta C_i^{\phi} = C_i^{\phi E} - C_i^{\phi}$ $(i = 2 \dots N)$ and the undercooling $\Delta T = T_E - T_u$ as a function of the concentration in the liquid

phase $\Delta C_i^l = C_i^{lE} - C_i^l$ and of pressure in the solid phase Δp^ϕ.

At a given point x along the interface, the undercooling ΔT is thus expressed as a sum of a solutal (ΔT_C) and a curvature (ΔT_R) undercooling (see appendix A) :

$$\Delta T(x) = \Delta T_C(x) + \Delta T_R(x) \tag{2}$$

where

$$\Delta T_C(x) = \sum_{i=2}^{N} m_i^\phi (C_i^{lE} - C_i^l(x)) \tag{3}$$

$$\Delta T_R(x) = -\frac{V_m^\phi}{\Delta S_{\phi l}} \Delta p^\phi(x) \tag{4}$$

where m_i^ϕ is a slope of a liquidus surface, V_m^ϕ is a molar volume, and $\Delta S_{\phi l}$ are defined in appendix A as functions of derivatives of molar Gibbs free energies of the solid and liquid phases. As $\Delta p^\phi = -\sigma_{\phi l}\kappa(x)$ where $\sigma_{\phi l}$ is the ϕ/l surface energy and $\kappa(x)$ is the interface curvature at x, Eq. (4) can be re-written:

$$\Delta T_R(x) = \Gamma_{\phi/l}\kappa(x) \tag{5}$$

where $\Gamma_{\phi/l} = \frac{V_m^\phi}{\Delta S_{\phi l}}\sigma_{\phi l}$ is the ϕ/l Gibbs Thomson coefficient.

As stated by Jackson and Hunt [2], the mean undercooling at the interface can be computed on half of a eutectic period :

$$\overline{\Delta T} = \frac{2}{\lambda}\int_0^{\lambda/2} \Delta T(x)dx \tag{6}$$

From Eq. (2), this mean eutectic undercooling can be separated as a mean solutal undercooling $\overline{\Delta T}_C$ and a mean curvature undercooling $\overline{\Delta T}_R$. Hillert [1], and Jackson and Hunt [2] have shown that for microstructures similar to Fig.

1, the mean curvature undercooling has the expression:

$$\overline{\Delta T}_R = \frac{K_R}{\lambda} \tag{7}$$

with

$$K_R = 2\left(\Gamma_{\alpha/l}\sin(\mid \theta_\alpha \mid) + \Gamma_{\beta/l}\sin(\mid \theta_\beta \mid)\right) \tag{8}$$

where angles θ_α and θ_β are defined in the Figure 1.

To define the mean solutal undercooling given in Equation (3) requires an expression for the liquid concentration of the different elements at the interface. This necessitates a solution to the diffusion equation in the liquid phase for all independent elements i:

$$D_i \nabla^2 C_i^l + \vec{V}\cdot\vec{\nabla}C_i^l = 0 \quad i = 2, 3 \ldots N \tag{9}$$

where $D_i = \tilde{D}_{ii}$ are the diagonal terms of the interdiffusion coefficient matrix for element i. Here we neglect off-diagonal terms since there is very little information on the magnitude or even the sign of these coefficients. Solutions of these equations should satisfy the boundary conditions:

$$C_i = C_i^\infty \qquad z \to \infty \tag{10}$$

$$\frac{\partial C_i}{\partial x} = 0 \qquad x = 0, \lambda/2 \tag{11}$$

Therefore, the liquid concentration of any element i can be expressed as:

$$C_i^l(x,z) = C_i^\infty + E_i^0 \exp(-\frac{V}{D_i}z) + \sum_{n=1}^{\infty} E_i^n \exp(-\frac{2\pi n}{\lambda}z)\cos(\frac{2\pi n}{\lambda}x) \tag{12}$$

for small Peclet numbers, $Pe_i = \frac{V\lambda}{2D_i} \ll 1$.

Assuming that all phases have the same molar volume, the conservation of

matter at the interface gives for any element i:

$$D_i \frac{\partial C_i^l}{\partial z}\bigg|_{z=0} = V(C_i^\phi - C_i^l) \quad i = 1 \dots N \tag{13}$$

2.1. Binary alloys: Jackson-Hunt-Hillert

For binary alloys, Hillert [1] and Jackson and Hunt [2] used Eq. (13) and the hypothesis of a constant concentration in the liquid phase at the interface to compute E_i^n coefficients for $n > 0$. In addition, for a microstructure similar to the one of Fig. 1, the solid/liquid interface could be reasonably supposed to be isothermal. Using this hypotheses, Jackson and Hunt observed that the E_i^0 term of Eq. (12) could be eliminated from the mean undercooling expression by using the relation:

$$\overline{\Delta T}^{iso} = \frac{m_2^\beta \overline{\Delta T}^\alpha - m_2^\alpha \overline{\Delta T}^\beta}{m_2^\beta - m_2^\alpha} \tag{14}$$

This approach masks the fact that the hypothesis of an isothermal interface gives a condition on the average liquid composition at the interface and so on the E_i^0 coefficients. Indeed, this growth condition requires in general a variation of the average liquid composition compared to the eutectic composition that equalizes the average undercooling of the two solid phases. As the interface is supposed to be at the thermodynamic equilibrium, this variation of composition in the liquid phase induces variations of compositions in solid phases and so an evolution of the solid fraction of phases compared to the one corresponding to phases composition at the eutectic temperature. One can note that inversely, a variation of phases solid fractions would induce variations of compositions in the solid phases and so a variation of the average liquid composition at the interface. The relation used by Jackson and Hunt accounts these variations in the mean undercooling expression in an implicit way and avoids the computation of these

variations.

Jackson and Hunt finally obtain an expression for the mean undercooling of an isothermal interface as a function of the growth velocity and the eutectic spacing:

$$\overline{\Delta T}^{iso} = K_1 V \lambda + \frac{K_2}{\lambda} \tag{15}$$

In addition, Jackson and Hunt observed that the eutectic spacing corresponding to the minimum undercooling (λ_m) satisfies the relation:

$$\lambda_m^2 V = \frac{K_2}{K_1} \tag{16}$$

This λ_m is a scaling parameter of the microstructure developed at a given velocity. Although it has been shown that eutectics do not grow with a unique eutectic spacing at a given velocity, the microstructure developed is usually close to the one at λ_m. This is why Eq. (16) is frequently used to characterize the microstructure developed by 2-phase eutectics. Moreover, the stability of this theory according to perturbations of the position of the trijunction has been analyzed by Datye and Langer [13]. It was shown that for a given concentration and growth velocity, the Jackson Hunt law is only stable over a range of eutectic spacings close the λ_m.

Unfortunately, Eq. (14) cannot be used for the N-component eutectic growth problem. We thus explicitly determine the general expression of the average concentration at the interface as a function of the volume fraction of the solid phases without any hypotheses on the undercooling and then compute the variation of the phase fractions corresponding to a shift of the average liquid concentration to make the interface isothermal. We finally determine the expression of the mean undercooling corresponding to the isothermal growth.

2.2. Approach

We first determine the expression for the liquid concentration of all independent elements i, the coefficients E_i^0 and E_i^n (for $n > 0$), assuming that the Peclet number of any element i ($Pe_i = \frac{V\lambda}{2D_i}$) is small compared to 1. We then use the isothermal hypotheses to obtain an expression for the solid fraction variation with the undercooling, and finally express the mean undercooling of an isothermal interface as a function of the growth velocity and eutectic spacing. All of these steps imply a development of expressions at first order in Peclet numbers. For consistency, we therefore suppose that $\max((Pe_2)^2, \ldots, (Pe_N)^2) < \min(Pe_2, \ldots, Pe_N)$ which implies that $\max(Pe_2, \ldots, Pe_N) < \frac{\min(D_2,\ldots,D_N)}{\max(D_2,\ldots,D_N)}$.

2.2.1. Liquid concentration field

In this section we determine the coefficients E_i^0 and E_i^n, that are needed in the general expression of the liquid concentration of element i (Eq. 12). This entire analysis is performed at the solid-liquid interface, which corresponds to $z = 0$. Therefore, the z-dependence of C_i^l (see Eq. (12)) does not appear in this section. Introducing Eq. (12) in Eq. (13) and expressing the function $C_i^l(x) - C_i^\phi(x)$ as a Fourier series we obtain for $i = 2 \ldots N$:

$$E_i^n = \frac{Pe_i}{\pi n} \frac{4}{\lambda} \int_0^{\lambda/2} (C_i^l(x) - C_i^\phi(x)) \cos(\frac{2\pi n}{\lambda} x) dx \quad \text{for } n > 0 \tag{17}$$

So E_i^n coefficients are at least first order in the Peclet numbers. To proceed with the calculation of E_i^n coefficients, a relationship between $C_i^l(x)$ and $C_i^\phi(x)$ is needed. For this, we use the relation obtained in Appendix A,

$$\Delta C_i^\phi(x) = \sum_{j=2}^{N} \Lambda_{ij}^\phi \Delta C_j^l(x) \tag{18}$$

where Λ_{ij}^{ϕ} are certain solute distribution coefficients associated with the phase ϕ and assuming the effect of curvature on solid phase concentration can be neglected, see appendix A. The Λ_{ij}^{ϕ} coefficients are functions of derivatives of chemical potentials that are function of concentration of elments and temperature. The full expression of Λ_{ij}^{ϕ} coefficients is presented in appendix A for ternary alloys. This link between phase compositions is represented by a tie line in binary phase diagrams and by a tie triangle in isothermal cross section of a ternary phase diagram. The tie triangle at equilibrium and that at an undercooling are shown in Figure 2. So as the liquid composition along the interface deviates from its equilibrium value, the tie triangle changes in shape, as given by the red dot-dash lines. This change in shape is thus given by $(\overline{\Delta C_2}^{\phi}, .., \overline{\Delta C_N}^{\phi})$ for a certain $(\overline{\Delta C_2}^{l}, .., \overline{\Delta C_N}^{l})$

The approximation of E_i^n to first order in Peclet number implies that in Eq. (17), $C_i^l(x) - C_i^{\phi}(x)$ needs only to be approximated at zero order in Peclet number. Eqs (12) evaluated at $z = 0$ and Eq. (18) give for any position x at the interface:

$$C_i^l(x)\big|_{Pe_i^0} = C_i^{\infty} + E_i^0\big|_{Pe_i^0} \tag{19}$$

$$C_i^{\phi}(x)\big|_{Pe_i^0} - C_i^{\phi E} = \sum_{j=2}^{N} \Lambda_{ij}^{\phi}(C_j^l(x)\big|_{Pe_i^0} - C_i^{lE}) \tag{20}$$

where the index Pe_i^0 indicates that the expression is truncated at the zero order in Peclet numbers. Introducing Eq. (19) in Eq. (20) we thus obtain for both solid phases ϕ:

$$(C_i^l(x) - C_i^{\phi}(x))\big|_{Pe_i^0} = C_i^{\infty} + E_i^0\big|_{Pe_i^0} - \sum_{j=2}^{N} \Lambda_{ij}^{\phi}(C_j^{\infty} + E_j^0\big|_{Pe_j^0} - C_j^{lE}) - C_i^{\phi E} \tag{21}$$

By introducing Eq. (21) in Eq. (17) we get for $n > 0$:

$$E_i^n = \frac{V\lambda}{D_i}\frac{\sin(n\pi f_\alpha)}{(n\pi)^2}E_i \tag{22}$$

where

$$E_i = \Delta C_i + \sum_{j=2}^{N} \Delta\Lambda_{ij}(C_j^\infty + E_j^0\big|_{Pe_j^0} - C_j^{lE}) \tag{23}$$

with $\Delta C_i = C_i^{\beta E} - C_i^{\alpha E}$ and $\Delta\Lambda_{ij} = \Lambda_{ij}^\beta - \Lambda_{ij}^\alpha$. .

It remains to determine the coefficient E_i^0. For this, we use the conservation of matter between the solid phases and the liquid phase which implies that for each element i:

$$f_\alpha\overline{C_i^\alpha} + f_\beta\overline{C_i^\beta} = C_i^\infty \tag{24}$$

and at the eutectic temperature:

$$f_\alpha^E C_i^{\alpha E} + f_\beta^E C_i^{\beta E} = C_i^\infty \tag{25}$$

where $\overline{C_i^\alpha}$ (resp $\overline{C_i^\beta}$) is the average concentration of element i in the solid phase α (resp β). These two equalities imply that for each element $i = 2 \dots N$:

$$-\Delta f_\alpha \Delta C_i = f_\alpha(\overline{C_i^\alpha} - C_i^{\alpha E}) + f_\beta(\overline{C_i^\beta} - C_i^{\beta E}) \tag{26}$$

where $\Delta f_\alpha = f_\alpha^E - f_\alpha$. This system of equalities can be linked to variations of composition in the liquid phase using Eq. (18) averaged on the length of solid phases α and β.

The integration of Eq. (12) on each solid phase and using Eq. (22) gives

that for $i = 2 \dots N$:

$$\overline{C_i^l}^{\alpha} = C_i^{\infty} + E_i^0 + \frac{V\lambda}{D_i}\frac{1}{f_\alpha}E_i Q \tag{27}$$

$$\overline{C_i^l}^{\beta} = C_i^{\infty} + E_i^0 - \frac{V\lambda}{D_i}\frac{1}{f_\beta}E_i Q \tag{28}$$

with $Q = \sum_{n=1}^{\infty} \frac{\sin^2(n\pi f_\alpha)}{(n\pi)^3}$. Introducing (18) and (27-28) into (26) for each element i leads to the system of equations for E_i^0:

$$\left[\bar{\Lambda}\right] \times \begin{bmatrix} C_2^{\infty} + E_2^0 - C_2^{lE} \\ \vdots \\ C_N^{\infty} + E_N^0 - C_N^{lE} \end{bmatrix} = \begin{bmatrix} -\Delta f_\alpha \Delta C_2 \\ \vdots \\ -\Delta f_\alpha \Delta C_N \end{bmatrix} + Q \left[\Delta\Lambda\right] \times \begin{bmatrix} \frac{V\lambda}{D_2} E_2 \\ \vdots \\ \frac{V\lambda}{D_N} E_N \end{bmatrix} \tag{29}$$

where $\left[\bar{\Lambda}\right]$ is the matrix of coefficients $\overline{\Lambda}_{ij} = f_\alpha \Lambda_{ij}^{\alpha} + f_\beta \Lambda_{ij}^{\beta}$ and $\left[\Delta\Lambda\right]$ is the matrix of coefficients $\Delta\Lambda_{ij}$. Solving Eq (29) for $E_i^0\big|_{Pe_i^0}$ along with Eq (23) yields E_i as a function of $\Delta f_\alpha, \Delta C_i$ and $\overline{\Lambda}_{ij}$ coefficients. We note that the E_i coefficient is different from ΔC_i only if the phase fractions evolve compared to those at the eutectic temperature. Using Eq. (29) enables us to obtain a full expression for the composition field for all i independent concentrations in the liquid phase. We observe that the expression for the liquid phase concentration depends on the volume fraction of solid phases, as was discussed in part 2.1.

Integrating Eqs (3) and (4) on both solid phase interfaces, we obtain the mean undercooling of the α phase and of the β phase:

$$\overline{\Delta T}^{\alpha} = \sum_{i=2}^{N} m_i^{\alpha}(C_i^{lE} - \overline{C_i^l}^{\alpha}) + \frac{2\Gamma_{\alpha/l}\sin(\mid \theta_\alpha \mid)}{f_\alpha \lambda} \tag{30}$$

$$\overline{\Delta T}^{\beta} = \sum_{i=2}^{N} m_i^{\beta}(C_i^{lE} - \overline{C_i^l}^{\beta}) + \frac{\Gamma_{\beta/l}\sin(\mid \theta_\beta \mid)}{f_\beta \lambda} \tag{31}$$

where expressions of $\overline{C_i^l}^\alpha$ and $\overline{C_i^l}^\beta$ are given in Eqs (27) and (28). We thus observe that, for a given growth velocity V and eutectic spacing λ, $\overline{\Delta T}^\alpha$ and $\overline{\Delta T}^\beta$ are two different functions of the phase fraction f_α. This phase fraction is unknown at that point. The simple approximation of setting $f_\alpha = f_\alpha^E$ yields, in general, to very different average temperatures at the two solid-phase interfaces. The hypotheses that the system grows with an iosthermal interface implies therefore an evolution of solid fractions from (f_α^E, f_β^E). In the following, we compute the change in the phase fraction from that at equilibrium that is necessary to make the interface isothermal for a given growth velocity and eutectic spacing, which yields the mean undercooling of the interface.

2.2.2. Isothermal Interfaces

In this section, we determine the phase fraction variation induced by requiring an isothermal interface for a given growth velocity and eutectic spacing. For this, the interface is considered isothermal if the mean undercoolings of the α phase and the β phase are equal:

$$\overline{\Delta T}^\alpha(f_\alpha) = \overline{\Delta T}^\beta(f_\alpha) \tag{32}$$

A Taylor expansion of this equality to first order in the variation of f_α gives:

$$\Delta f_\alpha^{\text{iso}} \left(\frac{\partial \overline{\Delta T}^\beta}{\partial f_\alpha}\bigg|_{f_\alpha^E} - \frac{\partial \overline{\Delta T}^\alpha}{\partial f_\alpha}\bigg|_{f_\alpha^E} \right) = \overline{\Delta T}^\beta(f_\alpha^E) - \overline{\Delta T}^\alpha(f_\alpha^E) \tag{33}$$

with $\Delta f_\alpha^{\text{iso}} = f_\alpha^E - f_\alpha^{\text{iso}}$ where f_α^{iso} is the solid fraction corresponding to the undercooling of an isothermal interface.

Using the expressions for the undercoolings of each phase (Eqs. (30) and (31)), and the expressions for the mean liquid concentrations at each phase

interface (Eqs. (27) and (28)) we obtain:

$$\overline{\Delta T}^{\beta}(f_{\alpha}^{E}) - \overline{\Delta T}^{\alpha}(f_{\alpha}^{E}) = V\lambda\alpha_C + \frac{\alpha_R}{\lambda} \tag{34}$$

where

$$\alpha_R = 2\left[\frac{\Gamma_{\beta/l}\sin(\mid\theta_\beta\mid)}{f_{\beta}^{E}} - \frac{\Gamma_{\alpha/l}\sin(\mid\theta_\alpha\mid)}{f_{\alpha}^{E}}\right] \tag{35}$$

and α_C will be given for binary (section 3) and ternary (section 4) eutectics. We rename for simplicity

$$-\Delta' = \left.\frac{\partial\overline{\Delta T}^{\beta}}{\partial f_\alpha}\right|_{f_\alpha^E} - \left.\frac{\partial\overline{\Delta T}^{\alpha}}{\partial f_\alpha}\right|_{f_\alpha^E} \tag{36}$$

We assume for the following that $\Delta' \approx \Delta'_0$ where Δ'_0 is independent of velocity and the eutectic spacing. The validity of this hypotheses is discussed in appendix B. This neglects the influence of the variation of f_α on $\overline{\Delta T}_R^{\alpha}$ and $\overline{\Delta T}_R^{\beta}$ and on terms proportional to Pe_i in $\overline{\Delta T}_C^{\alpha}$ and $\overline{\Delta T}_C^{\beta}$, which is small in most cases.

Using (34) and (36) in (33) we thus get the expression of the variation of f_α necessary to yield an isothermal interface:

$$\Delta f_{\alpha}^{\mathrm{iso}} = -\left(V\lambda\frac{\alpha_C}{\Delta'_0} + \frac{1}{\lambda}\frac{\alpha_R}{\Delta'_0}\right) \tag{37}$$

The general expression of Δ'_0 for a given phase diagram is given in appendix B. For binary alloys, this expression gives $\Delta'_0 = \Delta m_2 \Delta C_2/\overline{\Lambda_{22}}^{E}$ where $\Delta m_2 = m_2^{\beta} - m_2^{\alpha}$. We show in appendix A that this coefficient is always positive for binary alloys. This means that if $\overline{\Delta T}^{\beta}(f_{\alpha}^{E}) > \overline{\Delta T}^{\alpha}(f_{\alpha}^{E})$ the fraction of α phase has to be increased to make the interface isothermal and if $\overline{\Delta T}^{\beta}(f_{\alpha}^{E}) < \overline{\Delta T}^{\alpha}(f_{\alpha}^{E})$ the fraction of β phase has to be increased to make the interface isothermal, which makes sense intuitively, as already discussed by Magnin and Trivedi [3].

2.2.3. Undercooling of isothermal interface

We now determine the expression for the mean undercooling of the isothermal interface. The mean undercooling defined in Eq. (6) can be computed using Eqs. (7) and (3), as a function of the volume fraction of phases using the liquid concentrations obtained in section 2.2.1. For small changes of the volume fractions of the solid phases compared to their equilibrium values, (f_α^E, f_β^E), the mean undercooling can be approximated by a Taylor expansion to first order in the change of f_α from f_α^E. Moreover, we have seen in section 2.2.2 that for a given growth velocity and eutectic spacing, the system enforces an isothermal condition by changing the average concentration at the interface which corresponds to a variation of phases fractions $\Delta f_\alpha^{\text{iso}}$.

We can thus express the mean undercooling of an isothermal interface as:

$$\overline{\Delta T}^{\text{iso}}(f_\alpha) = \overline{\Delta T}_C(f_\alpha^E) - \Delta f_\alpha^{\text{iso}} \left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E} + \overline{\Delta T}_R \tag{38}$$

In order to use the expression of $\overline{\Delta T}^{\text{iso}}$ given in (38), we need an expression for $\overline{\Delta T}_C(f_\alpha^E)$ and $\left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E}$. Using the expression of the liquid concentration developed in section 2.2.1 we obtain :

$$\overline{\Delta T}_C(f_\alpha^E) = \sum_{i=2}^{N} (C_i^{lE} - C_i^\infty - E_i^0\big|_{f_\alpha^E}) \overline{m_i}^E + \sum_{i=2}^{N} \frac{V\lambda}{D_i} (E_i Q)\big|_{f_\alpha^E} \Delta m_i \tag{39}$$

with $\overline{m_i}^E = f_\alpha^E m_i^\alpha + f_\beta^E m_i^\beta$. The system of equations for E_i^0 (Eq. 29) shows that for $i = 2 \dots N$, $C_i^{lE} - C_i^\infty - E_i^0\big|_{f_\alpha^E}$ is proportional to Pe_i, so we can write:

$$\overline{\Delta T}_C(f_\alpha^E) = V\lambda K_C \tag{40}$$

The expression of K_C will be given for binary and ternary alloys in sections 3 and 4 respectively. For the term involving $\left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E}$ in Eq. (38), it is unclear

if this quantity has to be evaluated at first order in Peclet numbers or at zero order, as the order of $\Delta f_\alpha^{\rm iso}$ in Peclet has not been determined. For simplicity, we approximate $\left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E}$ at zero order in Peclet number. This hypothesis is discussed in appendix B by analyzing the order of $\Delta f_\alpha^{\rm iso}$. Introducing Eq. (40) and (37) in (38) we thus obtain the undercooling of the isothermal interface:

$$\overline{\Delta T}^{\rm iso} = V\lambda K_1 + \frac{K_2}{\lambda} \tag{41}$$

where K_1 and K_2 coefficients are:

$$K_1 = K_C + l_N \alpha_C \tag{42}$$

$$K_2 = K_R + l_N \alpha_R \tag{43}$$

and

$$l_N = \frac{1}{\Delta_0'} \left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E, Pe_i^0} \tag{44}$$

For a given growth velocity, we thus have now established the link between the mean temperature at the isothermal interface and the eutectic spacing for any 2-phase eutectic with N elements.

From Eq. (41) we obtain the eutectic spacing corresponding to the minimum undercooling :

$$\lambda_m^2 V = \frac{K_2}{K_1} \tag{45}$$

This expression shows that the growth law (Eq. 15) determined by Jackson and Hunt [2] for binary alloys can be generalized to two-phase eutectics with N-elements. However, the analytical expressions for K_C, l_N and α_C can be quite complicated for N large. The thermodynamic parameters needed to evaluate these coefficients ($C_i^{\phi E}$,m_i^ϕ, Λ_{ij}^ϕ) can be found using CALPHAD descriptions of the free energies. These coefficients are therefore only given here for binary

alloys (in section 3) and for ternary alloys (in section 4). In a similar way as the Jackson-Hunt theory, this general model takes into account interfacial energies of the two solid phases through the expression of the undercooling of the isothermal interface through Gibbs-Thomson coefficients ($\Gamma_{\alpha l}$, $\Gamma_{\beta l}$) and trijunction angles (θ_α, θ_β). The diffusion properties of the alloy are also introduced in the theory through the interdiffusion coefficients of each independent element $\{D_2, \ldots, D_N\}$. As in the Jackson-Hunt model, this theory includes thermodynamic properties of the alloy which correspond to the equilibrium concentration of elements in solid phases ($C_i^{\alpha E}$, $C_i^{\beta E}$), the liquidus slopes corresponding to each phase (m_i^α and m_i^β) and certain solute distribution coefficients ($[\Lambda^\alpha]$ and $\left[\Lambda^\beta\right]$) defined in Appendix A. The expressions of liquidus slopes and solute distribution coefficients as functions of derivatives of chemical potentials for a given temperature and concentration are given in Appendix A. These derivatives can be computed from the expression of the Gibbs free energy of phases using CALPHAD descriptions of the free energies.

Catalina et al. [8] have recently proposed a model for the growth of two-phase eutectics with N elements in the limit that the composition of the β phase is a constant $[\Lambda^\beta] = 0$. Moreover, this model only takes into account diagonal terms of the $[\Lambda^\alpha]$ matrix. Our model is thus a generalization of this approach. To illustrate the predictions of the model, we examine the coefficients K_1 and K_2 for binary and ternary alloys.

3. Binary alloys

In this section, we illustrate how the general theory can be used to describe the well-known results in a binary alloy. From the development of the solute concentration expression at the interface given in section 2.2.1, we obtain the

concentration at the interface:

$$C_2^l(x) = C_2^\infty + E_2^0 + \frac{V\lambda}{D_2} E_2 \sum_{n=1}^{\infty} \frac{\sin(n\pi f_\alpha)}{(n\pi)^2} \cos(\frac{2\pi}{\lambda} x) \tag{46}$$

with

$$E_2^0 = C_2^{lE} - C_2^\infty - \frac{\Delta C_2}{\overline{\Lambda}_{22}} \Delta f_\alpha + Q \frac{\Delta\Lambda_{22}}{\overline{\Lambda}_{22}} \frac{V\lambda}{D_2} E_2 \tag{47}$$

$$E_2 = \Delta C_2 \left(1 - \frac{\Delta\Lambda_{22}}{\overline{\Lambda}_{22}} \Delta f_\alpha \right) \tag{48}$$

Donaghey and Tiller [14] give a detailed development at first order in Peclet number of the concentration in the liquid phase for binary alloys. Our expressions for the parameters E_2^0 and E_2 defined in Eqs (47) and (48) are identical the one obtained by Donaghey and Tiller [14].

The solutal undercooling at any position x of the interface is determined by introducing this expression of the solute concentration at the interface in Eq. (3). The integration of $\Delta T_C(x)$ on half of the eutectic spacing gives coefficients K_C and the $\left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E, Pe_2^0}$ term in l_2 (see Eq. (44)) and its integration on each solid phase interface gives the coefficient α_C (see Eq. (34)) and the Δ_0' term in l_2 (see Eq. (44)) and obtains:

$$l_2 = -\frac{\overline{m}_2^E}{\Delta m_2} \tag{49}$$

$$K_C = Q^E \frac{\Delta C_2}{D_2} \left[\Delta m_2 - \frac{\Delta\Lambda_{22}}{\overline{\Lambda_{22}}^E} \overline{m}_2^E \right] \tag{50}$$

$$\alpha_C = Q^E \frac{\Delta C_2}{D_2} \left[-\frac{\Delta\Lambda_{22}}{\overline{\Lambda_{22}}^E} \Delta m_2 + \left(\frac{m_2^\beta}{f_\beta^E} + \frac{m_2^\alpha}{f_\alpha^E} \right) \right] \tag{51}$$

where $\overline{m}_2 = f_\alpha m_2^\alpha + f_\beta m_2^\beta$. The coefficients m_i^ϕ are signed and so, for binary alloys, the m_2^α coefficient is negative and the solute distribution coefficients Λ_{22}^α and Λ_{22}^β are usually noted k^α and k^β for binary alloys. In arriving at these

results, we employ the result that follows from Eqs. (85) in Appendix A that relates the second derivates of the free energy to the slope of the liquidus:

$$m_2^{\phi} = -\frac{\left(C_2^{lE} - C_2^{\phi E}\right) \frac{\partial^2 G_m^l}{\partial (C_2^l)^2}}{\Delta S_{\phi l}} \tag{52}$$

where G_m^l is the molar Gibbs free energy of the liquid phase. This expression for the slope of the phase ϕ liquidus curve is the well-known Gibbs-Konovalov relation [15].

By introducing Eqs. (49), (50) and (51) in expressions of coefficients K_1 and K_2 (eqs. (42) and (43)) we obtain that :

$$K_1 = \left(\frac{-m_2^{\alpha} m_2^{\beta}}{\Delta m_2 f_{\alpha}^E f_{\beta}^E}\right) Q^E \frac{\Delta C_2}{D_2} \tag{53}$$

$$K_2 = \frac{-2m_2^{\alpha}\Gamma_{\beta/l}\sin(\mid \theta_{\beta} \mid)}{f_{\beta}^E \Delta m_2} + \frac{2m_2^{\beta}\Gamma_{\alpha/l}\sin(\mid \theta_{\alpha} \mid)}{f_{\alpha}^E \Delta m_2} \tag{54}$$

The K_1 and K_2 coefficients are identical to those obtained by Jackson and Hunt [2]. The coefficients that set the $\lambda_m^2 V$ relationship should indeed be the same as those of Jackson and Hunt, since the same hypotheses and approximations are used in our approach and were also used by Jackson and Hunt. However, our treatment yields the expression for the E_2^0 coefficient, and thus we can determine the effects of the asymmetry of the phase diagram on the volume fraction of the phases.

Magnin and Trivedi [3] published a eutectic growth model similar to ours for binary alloys. In their study, they determined the expression of the liquid concentration at the interface by using the conservation of matter at the interface (Eq. (13)) and taking into account the density differences between phases. They obtain the same expression for the mean undercooling as Jackson and Hunt, and K_1 and K_2 coefficients are identical with ours (Eqs (42) and (43)), in the

limit where the density of the phases are identical. However, our K_C and α_C coefficients are different, as Magnin and Trivedi did not take into account the terms at first order in Peclet number in their E_2^0 parameter (the last term in the expression of E_2^0 in Eq. (47)).

We showed above that if the interface is isothermal and undercooled then the fraction of the phases can change from their equilibrium values. To illustrate this for a binary alloy, we examine the difference of undercooling between the two solid phases if the phase fractions do not change with the growth conditions and thus the interface is nonisothermal. From eq. (34) we observe that $|\overline{\Delta T}^{\beta}(f_\alpha^E) - \overline{\Delta T}^{\alpha}(f_\alpha^E)|$ is a function of λ at a given velocity. If α_R and α_C have the same sign, then $|\overline{\Delta T}^{\beta}(f_\alpha^E) - \overline{\Delta T}^{\alpha}(f_\alpha^E)|$ has a minimum with the expression:

$$|\overline{\Delta T}^{\beta}(f_\alpha^E) - \overline{\Delta T}^{\alpha}(f_\alpha^E)|\big|_{min} = 2\sqrt{\alpha_C \alpha_R V} \tag{55}$$

From Eq. (35) and (51) we observe that the coefficients α_R and α_C are large if the two solid phases have asymetrical properties and a low diffusion coefficient. For example, if we take, for a model binary alloy: $\Delta C_2 = 90\%$ and $D_2 = 5 \times 10^{-10}\,\mathrm{m^2/s}$, $f_\alpha = 0.2$, $\Gamma_{\alpha/l}\sin(\mid \theta_\alpha \mid) = 1 \times 10^{-7}\,\mathrm{K.m}$, $\Gamma_{\beta/l}\sin(\mid \theta_\beta \mid) = 1 \times 10^{-8}\,\mathrm{K.m}$, $m_2^\alpha = -50\,\mathrm{K.at\%}$, $m_2^\beta = 5\,\mathrm{K.at\%}$, $\Lambda_{22}^\alpha = 0.1$, $\Lambda_{22}^\beta = 0.2$ we find that for $V = 100\,\mu\mathrm{m/s}$ $|\overline{\Delta T}^{\beta}(f_\alpha^E) - \overline{\Delta T}^{\alpha}(f_\alpha^E)|\big|_{min} = 17.7\,K$. For a standard thermal gradient $G = 9\,\mathrm{K/mm}$, this difference of undercooling would induce a difference of position of 2 mm between the α/l and the β/l interfaces which would be observable if the eutectic was not growing with an isothermal interface. From these properties and using the expression of Δ_0' given in Appendix B, we compute the change in the α phase fraction needed to insure an isothermal interface is $\Delta f_\alpha^{\mathrm{iso}} = -1.3 \times 10^{-3}$. Such a small variation of solid fraction would certainly be difficult to observe in experiments. However, other choices of materials parameters may yield larger changes. If α_C and α_R do not have

the same sign then, at a given velocity, the function $|\overline{\Delta T}^{\beta}(f_{\alpha}^{E}) - \overline{\Delta T}^{\alpha}(f_{\alpha}^{E})|$ has a zero value for a certain λ_0. For this λ_0 the interface is isothermal at $f_\alpha = f_\alpha^E$. However, for eutectic spacings far from this λ_0 the difference of undercooling in front of the two solid phases can be very different for $f_\alpha = f_\alpha^E$.

4. Ternary alloys

We now apply the general method to ternary two-phase eutectics. The coefficients used in the theory are given and compared to those in binary alloys. The ternary model is compared to previous models available in the literature. Finally, we evaluate the evolution of the $\lambda_m^2 V$ law for a binary alloy with the addition of a small amount of element 3, when the system stays in a two-phase eutectic microstructure.

4.1. General model in ternary alloys

Using the same process as described in section 3, we obtain that the coefficients l_3, K_C and α_C defined in section 2 for a ternary alloy are:

$$l_3 = -\frac{\Delta C_2\left(\overline{m_2}^E\overline{\Lambda_{33}}^E - \overline{m_3}^E\overline{\Lambda_{32}}^E\right) + \Delta C_3\left(-\overline{m_2}^E\overline{\Lambda_{23}}^E + \overline{m_3}^E\overline{\Lambda_{22}}^E\right)}{\Delta C_2\left(\Delta m_2\overline{\Lambda_{33}}^E - \Delta m_3\overline{\Lambda_{32}}^E\right) + \Delta C_3\left(-\Delta m_2\overline{\Lambda_{23}}^E + \Delta m_3\overline{\Lambda_{22}}^E\right)} \tag{56}$$

$$K_C = Q^E\sum_{i=2}^{3}\frac{\Delta C_i}{D_i}\left[\Delta m_i - \overline{m_2}^E\left(\frac{\Delta\Lambda}{\overline{\Lambda}}\right)_{2i}^{E} - \overline{m_3}^E\left(\frac{\Delta\Lambda}{\overline{\Lambda}}\right)_{3i}^{E}\right] \tag{57}$$

$$\alpha_C = Q^E\sum_{i=2}^{3}\frac{\Delta C_i}{D_i}\left[-\Delta m_2\left(\frac{\Delta\Lambda}{\overline{\Lambda}}\right)_{2i}^{E} - \Delta m_3\left(\frac{\Delta\Lambda}{\overline{\Lambda}}\right)_{3i}^{E} + \left(\frac{m_i^\beta}{f_\beta^E} + \frac{m_i^\alpha}{f_\alpha^E}\right)\right] \tag{58}$$

where

$$\left(\frac{\Delta\Lambda}{\overline{\Lambda}}\right)_{2i}^{E} = \frac{\overline{\Lambda}_{33}^{E}\Delta\Lambda_{2i} - \overline{\Lambda}_{23}^{E}\Delta\Lambda_{3i}}{\overline{\Lambda}_{22}^{E}\overline{\Lambda}_{33}^{E} - \overline{\Lambda}_{32}^{E}\overline{\Lambda}_{23}^{E}} \tag{59}$$

$$\left(\frac{\Delta\Lambda}{\overline{\Lambda}}\right)_{3i}^{E} = \frac{\overline{\Lambda}_{22}^{E}\Delta\Lambda_{3i} - \overline{\Lambda}_{32}^{E}\Delta\Lambda_{2i}}{\overline{\Lambda}_{22}^{E}\overline{\Lambda}_{33}^{E} - \overline{\Lambda}_{32}^{E}\overline{\Lambda}_{23}^{E}} \tag{60}$$

We observe that coefficients l_3, K_C and α_C obtained for ternary alloys have a similar form as coefficients obtained for binary alloys presented in Eq. (49-51). However, whereas l_2 only depends on liquidus slopes m_2^{α} and m_2^{β} and on the phase fractions, coefficient l_3 also depends on differences of concentration in solid phases ΔC_2 and ΔC_3 and on the $\overline{\Lambda}_{ij}$ coefficients.

McCartney and Hunt [11] assume that the ratio $(E_3^0+C_3^{\infty}-C_3^E)/(E_2^0+C_2^{\infty}-C_2^E)$ is independent of the conditions for eutectic growth. In addition, they assume that the non-diagonal terms in the $\left[\bar{\Lambda}\right]$ matrix are negligible compared to diagonal terms and that $\overline{\Lambda}_{22}^{E} \simeq \overline{\Lambda}_{33}^{E}$, which limits this model to systems with specific thermodynamic properties. To illustrate this statement, we have computed the $\left[\bar{\Lambda}\right]$ matrix in the ternary eutectic Al-Cu-Ag with an alloy composition of: $14.8\text{at}\%Cu - 5\text{at}\%Ag$. For this, we have used the expression of the Gibbs free energies for the liquid phase, the α phase and the $\theta - Al_2Cu$ phase given in Ref. [16, 17] and computed the equilibrium composition of each phase at the eutectic temperature using ThermoCalc. We have obtain $\left[\bar{\Lambda}\right] = \begin{bmatrix} 0.46 & 0.20 \\ 0.48 & 0.94 \end{bmatrix}$. Therefore, in this case, non-diagonal terms are of similar order to diagonal terms and $\overline{\Lambda}_{22}^{E} \neq \overline{\Lambda}_{33}^{E}$. In a future paper, the calculations of the thermodynamic properties of Al-Cu-Ag will be given in detail. Finally, McCartney et al. have used the assumption that $D_2 = D_3$ to obtain their final expression of the interface undercooling. Recently, DeWilde et al. [12] proposed a new model for the directional growth of ternary two-phase eutectics. In this model, the mean solutal

undercooling of each solid phase is expressed as a sum of absolute values of undercoolings corresponding to each element. In addition, this model neglects the dependence of E_i^0 on the change of the phase fractions with the undercooling. This approximation eliminates the Δ_0' term in the expression of Δ' given Eq. (90) but keeps the $V\lambda\xi_C + \frac{\xi_R}{\lambda}$ term (see Appendix B). We note that none of these assumptions made by McCartney et al. or DeWilde et al. are used in our theory.

Some binary eutectics stay in a two-phase microstructure with the addition of a ternary element. In this case, if all parameters involved in coefficients K_1 and K_2 are known for the ternary alloy, one could predict the evolution of the microstructure with the addition of the element 3 at a given velocity by comparing K_2/K_1 for the binary and the ternary alloys using Eq. (16). In the general case, this comparison is difficult due to the large number of parameters involved in these ratios. In particular, the eutectic temperature of the ternary eutectic might be different than the one of the binary system which would affect all parameters involved in the growth law that depend on temperature such as the interfacial energies, and diffusion coefficients. From Eqs. (57) and (58), we see that if element 3 is a slow diffuser compared to element 2, the coefficients K_C and α_C are particularly sensitive to the thermodynamic parameters associated with element 3 and so the eutectic microstructure might change drastically compared to the binary alloy. We also note that if the solubility of element 3 is the same in the 2 phases and if the cross coefficients of the $[\Lambda^\phi]$ matrices are negligible, the coefficients K_1 and K_2 of the ternary alloy have the same form as the one of the binary alloy. Therefore, if the addition of component 3 does not affect element 2 thermodynamics (Λ_{22}^ϕ and m_2^ϕ with $\phi = \alpha, \beta$) and diffusion (D_2) coefficients, then element 3 has no effect on the eutectic spacing.

4.2. Limit of small additions of a third element

To illustrate the effects of component 3 on the growth law $\lambda_m^2 V = \frac{K_2}{K_1}$ of a binary alloy, we consider the limit of a ternary alloy with a dilute amount of component 3. To perform such a study, we have to limit the number of parameters evolving with the addition of element 3. Therefore, we assume that the capillary lengths, and the phases fractions do not change significantly with the addition of component 3. Coefficients K_R and α_R are therefore identical to those of a binary alloy. Moreover, the variation of the thermodynamic properties of element 2 (Λ_{22}^{ϕ} and m_2^{ϕ} with $\phi = \alpha, \beta$) with the addition of element 3 is neglected. We recall in this part that, according to our notations, for an element i, $\Delta C_i = C_i^{\beta} - C_i^{\alpha}$. In addition, for a small addition of element 3, we should have $|\Delta C_3| \ll |\Delta C_2|$. To simplify the problem, we also assume that the Λ_{23}^{ϕ} and Λ_{32}^{ϕ} coefficients for the α and β phases are negligible. In this case, coefficients K_1 and K_2 of the ternary alloy growth law can be expressed as:

$$K_1^t = K_1^b + \Delta C_3 q_1 \tag{61}$$

$$K_2^t = K_2^b + \Delta C_3 q_2 \tag{62}$$

where the 'b' superscript refers to the binary alloy and the 't' superscript refers to the ternary alloy and

$$q_1 = Q^E \left\{ \frac{\Omega}{D_2} + \frac{\Pi}{D_3} \right\} \tag{63}$$

$$q_2 = \frac{1}{\Delta C_2} \frac{\overline{\Lambda_{22}}^E}{\overline{\Lambda_{33}}^E} \left(\frac{m_2^{\alpha} m_3^{\beta} - m_3^{\alpha} m_2^{\beta}}{(\Delta m_2)^2} \right) \alpha_R \tag{64}$$

with

$$\Omega = -\frac{\overline{\Lambda_{22}}^E}{\overline{\Lambda_{33}}^E}\frac{1}{\Delta m_2}\left(\overline{m_3}^E - \Delta m_3\frac{\overline{m_2}^E}{\Delta m_2}\right)\left[-\Delta m_2\frac{\Delta\Lambda_{22}}{\overline{\Lambda_{22}}^E} + \frac{m_2^\beta}{f_\beta} + \frac{m_2^\alpha}{f_\alpha}\right] \quad (65)$$

$$\Pi = \Delta m_3 - \frac{\overline{m_2}^E}{\Delta m_2}\left(\frac{m_3^\beta}{f_\beta} + \frac{m_3^\alpha}{f_\alpha}\right) + \frac{\Delta\Lambda_{33}}{\overline{\Lambda_{33}}^E}\left(\overline{m_2}^E\frac{\Delta m_3}{\Delta m_2} - \overline{m_3}^E\right) \quad (66)$$

and so

$$\lambda_{mt}^2 V = \frac{K_2^b}{K_1^b} + \frac{\Delta C_3}{K_1^b}\left(q_2 - \frac{K_2^b}{K_1^b}q_1\right) \quad (67)$$

In these expressions, the thermodynamic coefficients $\overline{\Lambda_{33}}^E$, m_3^α and m_3^β can be determined from the Gibbs free energies of the phases as shown in appendix A. If m_3^α and/or m_3^β is small compared to other slopes, then the q_1 coefficient will be insensitive to D_3. So changes on liquidus curves of both solid phases with the addition of element 3 are necessary conditions for D_3 to have an effect on the eutectic spacing.

In the general case, there are many factors that lead to a change in $\lambda_m^2 V$ with the addition of a third element as shown in Eqs (63-64). However, if $f_\alpha = 0.5$ and the phase diagram of the binary alloy is symmetric ($m_2^\beta = -m_2^\alpha$ and $\Lambda_{22}^\beta = \Lambda_{22}^\alpha$), then the term depending on D_2 in eq. (63) disappears. According to Eq. (18), and assuming that Λ_{33}^α and Λ_{33}^β are independent of the temperature, we obtain that the difference of concentration of element 3 between the β phase and the α phase can be replaced by $\Delta C_3 = \Delta\Lambda_{33}C_3^E$. In addition, by introducing Eq. (18) in Eq. (25) we obtain that $\overline{\Lambda_{33}}^E C_3^E = C_3^\infty$. Moreover, if the binary alloy has equal solid/liquid surface energies for the α and the β phase, then q_2 can be neglected and eq. (67) becomes:

$$\lambda_{mt}^2 V\big|_{symmetrical} = \frac{K_2^b}{K_1^b}\left[1 - \frac{C_3^\infty}{\Delta C_2}\frac{D_2}{D_3}\frac{1}{2m_2^\beta}\frac{\Delta\Lambda_{33}}{\overline{\Lambda_{33}}^E}\left(\Delta m_3 - \overline{m_3}^E\frac{\Delta\Lambda_{33}}{\overline{\Lambda_{33}}^E}\right)\right] \quad (68)$$

For this particular case, the evolution of $\lambda_m^2 V$ with the addition of element

3 can be analyzed according to element 3 parameters. In fig. 3, we present the variation of the $\lambda_m^2 V$ according to C_3^∞ for 3 different sets of (m_3^α,m_3^β,$\Delta\Lambda_{33}$) coefficients and for different diffusion coefficients D_3 in a model ternary eutectic. In this figure, parameters used for element 2 are: $D_2 = 1 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$, $\Delta C_2 = 80\,(at\%)$ and $m_2^\beta = 10\,K/(at\%)$ and $m_3^\alpha = -10\,K/(at\%)$.

We note from Eq. (68) that whatever the (m_3^α,m_3^β,$\Delta\Lambda_{33}$) coefficients, the change in $\lambda_m^2 V$ with C_3^∞ diminishes in magnitude with the increase of D_3. So $\lambda_{mt}^2 V$ will be particularly sensitive to the addition of element 3 if the element 3 is a slow diffuser, as can be observed in fig. 3 in all cases displayed. We also remark that the solid-liquid equilibrium implies that $C_3^E > (C_3^\alpha, C_3^\beta)$. Therefore, $\overline{\Lambda_{33}}^E < 1$ and $\mid \Delta\Lambda_{33}/\overline{\Lambda_{33}}^E \mid < 2$. We note from Eq. (68) that the more similar the Λ_{33}^α and Λ_{33}^β distribution coefficients, the less $\lambda_m^2 V$ varies with the addition of element 3. In addition, for small values of $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E$, the variation of $\lambda_m^2 V$ is proportional to Δm_3. In Fig. 3, we have represented ywo cases for $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E = 0.1$. We can see that the variation of $\lambda_m^2 V$ is negligible when $\Delta m_3 = 1\,K/(at\%)$ and non-negligible when $\Delta m_3 = 20\,K/(at\%)$. In addition, it is clear from Fig. 3 that the third alloying element can affect the eutectic spacing even is $D_2 = D_3$. This is due to the asymmetry of the phase diagram.

In the opposite limit, if element 3 is almost not soluble in one phase, for example $\Lambda_{33}^\alpha \simeq 0$, then $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E \simeq \Lambda_{33}^\beta/(2 \times \Lambda_{33}^\beta) \simeq 2$. In this case, $\Delta m_3 - \overline{m_3}^E \frac{\Delta\Lambda_{33}}{\overline{\Lambda_{33}}^E} \simeq 2m_3^\beta$. Conversely, if $\Lambda_{33}^\beta \simeq 0$, then $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E \simeq (-\Lambda_{33}^\alpha/(2\times\Lambda_{33}^\alpha) \simeq -2$ and $\Delta m_3 - \overline{m_3}^E \frac{\Delta\Lambda_{33}}{\overline{\Lambda_{33}}^E} \simeq -2m_3^\alpha$. In Fig. 3 we represent $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E = 1.9$ and $m_3^\alpha = -10\,K/(at\%)$ and $m_3^\beta = -9\,K/(at\%)$. We can see that this last case is the most favorable the change the microstructure of the eutectic with the addition of element 3.

It has however to be noted that the addition of a third element to a binary eutectic may induce an instability of the eutectic front. Indeed, Plapp and

Karma [10] have shown that for a given system, there exists a critical velocity v_c such that the eutectic front becomes unstable for solidification speeds higher than v_c. This critical velocity is proportional to D_3. Therefore, the slower the diffusion of element 3, the smaller the critical velocity. For the model system studied previously and taking $C_3^\infty = 1\,at\%$, $m_3^\alpha = m_3^\beta = -10\,K/(at\%)$, $D_3 = 0.5 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$ and $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E = 1.9$ we obtain v_c of the order of $0.1\,\mu m/s$ which is relatively small. Therefore, for velocities higher than v_c, the evolution of the microstructure induced by the addition of 3 predicted by our theory might not been observed.

This symmetrical study is restrictive but only limits the complexity of the microstructure evolution related to properties inherent to the binary alloy. We note indeed that tendencies highlighted in this symmetrical case can be generalized to non-symmetrical binary eutectics.

5. Discussion

The eutectic growth model developed in this paper is equivalent to the Jackson-Hunt theory for binary alloys. It is well-known that the Jackson-Hunt theory is a satisfactory model of eutectic growth of regular binary alloys. This theory can therefore be used to analyze regular eutectics containing any number of elements and their growth properties in a similar way as the Jackson-Hunt model. However, it has been shown for binary systems that rather than growing only with the eutectic spacing λ_m predicted by the Jackson-Hunt theory, eutectics can grow with a range of eutectic spacing around λ_m at a given velocity. Indeed, Karma and Sarkissian [18] have revealed that the regular microstructure drawn on Fig. 1 is stable up to a critical spacing which can be as high as $2\lambda_m$. Akamatsu et al. [19] have shown experimentally and theoretically that the lower stability bound of this range of eutectic spacings can be as low as $0.7\lambda_m$.

They have also observed that the eutectic spacing developed is dependent on the history of the solidification process. So even if all parameters involved in the theory are known perfectly, the theory will only give an approximate value of the eutectic spacing developed experimentally for a given velocity.

However, the model presented will provide guidance on how the eutectic spacing in an alloy changes with the addition of a new element through a change in the $\lambda_m^2 V$ law for the multicomponent system. To determine the change it is necessary to know thermodynamic, diffusion and curvature parameters involved in the $\lambda_m^2 V$ result given above. Among these parameters, thermodynamic coefficients (liquidus slopes and distribution coefficients) can be obtained as soon as the expression of the Gibbs free energies of the solid and liquid phases are known. Such expressions are generally gathered in thermodynamic databases such as Pandat [20] or ThermoCalc [21]. Nowadays, we are still far from knowing the thermodynamic properties of any multicomponent alloy. Nevertheless, the development of computational tools offers promising ways to accelerate our knowledge on thermodynamic properties of multicomponent systems [22]. Experimental values of diffusion coefficients in liquids with more than 2 elements are rare [23]. For metals, this lack of experimental studies is partly due to the fact that diffusion coefficients are particularly sensitive to fluid flow [24]. For binary and ternary mixtures, some methods are nevertheless available to compute interdiffusion coefficients from ab initio Molecular Dynamics simulations [25]. Finally, solid/liquid surface energies appear in the expression of Gibbs-Thomson coefficients and angles of curvature at the trijunction. Angles of curvature depend also on the different interphase surface energies [3]. A review of the current knowledge on interface properties in multicomponent systems has been published by Hecht et al. [23]. They find that very little is known about the interfacial properties in multicomponent systems, especially with more than two

components. However, some experimental and numerical methods are available to obtain information on how the interfacial properties change with the addition of an element, at least in dilute ternary alloys [26, 27, 28]. Therefore, determining the evolution of interfacial properties with the addition of an element seems to be the the largest challenge in using this model. Computations and experiments that give these interface properties as a function of alloy composition would be very helpful. For now, we can nevertheless consider that solid/liquid surface energies are expected to decrease with the absorption of a third element [29] which would lower Gibbs-Thomson coefficients.

This work can be continued by developing the theory for 3D rod-like microstructures in a similar way as in the Jackson-Hunt theory [2]. Moreover, it was assumed in the theory presented that all phases have the same density, which is not the case in most alloys. It would thus be important to add the effect of these differences of density in the theory in the future. Finally, this theory is accurate to only first order in Peclet numbers, which is not true during rapid solidification. This approximation may be removed by using an algorithm similar to the one of Ludwig et al. [30] which enables the growth law of the eutectic to be determined for any Peclet number value in binary alloys.

In section 4.2, we have seen that, according to the model of Plapp and Karma [10], the eutectic front of a binary eutectic containing a small amount of a slow diffuser can become morphologically unstable and form eutectic colonies. We note that this theory is based on a ternary eutectic model containing more approximations than the one presented in this paper. It would therefore be interesting to integrate the approach used here to model the morphological instability of the eutectic interface model in a N component alloy with no assumptions on the symmetry of the phase diagram.

6. Conclusion

We examine the steady state growth of multicomponent 2-phase eutectics. Using the same hypotheses as the Jackson-Hunt theory [2], we show that the growth law relating the mean undercooling of the interface ($\overline{\Delta T}$), the eutectic spacing (λ), and the growth velocity (V): $\overline{\Delta T} = K_1 V\lambda + \frac{K_2}{\lambda}$ determined by Jackson and Hunt for binary alloys can be generalized to all regular 2-phase eutectics, whatever the number of elements. A method is given to express the K_1 and K_2 coefficients in terms of the alloy thermodynamic and thermophysical properties. Thermodynamic parameters involved in this general theory have been linked to Gibbs free energy functions of the phases and can therefore be computed for any alloy with CALPHAD free energies.

A model has been derived from this theory for ternary 2-phase eutectics. It was shown that non-diagonal terms of the matrix of coupling between variations of concentrations in solid phases and variations of concentration in the liquid phase can be non-negligible, contrary to what was assumed in previous models [11, 8, 4]. From the ternary model, we have analyzed the influence of a small addition of a third element to a binary alloy on the scaling law for the microstructure. We have shown, in particular, that slow diffusers can have a large influence on the microstructure. However, this effect can be limited by the thermodynamic properties of the alloy as described in section 4.2.

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Appendices

A. Equilibrium at the interface

Linearisation of equations

We analyze here the thermodynamic equilibrium between the solid phase ϕ and the liquid phase l at the interface. We suppose that this interface is curved. We note T the temperature of the interface at this position, $(C_2^l, .., C_N^l)$ the composition of the liquid phase at the interface (resp $(C_2^\phi, .., C_N^\phi)$ in the solid phase ϕ), and p^l the internal pressure in the liquid phase (resp p^ϕ). The interface thermodynamic equilibrium implies that for every element $i = 1..N$,

the chemical potential of the phase ϕ (μ_i^ϕ) and of the liquid phase (μ_i^l) are equal:

$$\mu_i^\phi(C_2^\phi, .., C_N^\phi, T, p^\phi) = \mu_i^l(C_2^l, .., C_N^l, T, p^l) \tag{69}$$

If the temperature T of the interface is close to the equilibrium eutectic temperature T_E, the equality (69) can be linearly expanded about the equilibrium state of a flat interface at the eutectic temperature:

$$\sum_{j=2}^{N} \left.\frac{\partial \mu_i^\phi}{\partial C_j^\phi}\right|_{C_k^{\phi E} \neq C_j^{\phi E}, T_E} \Delta C_j^\phi + \left.\frac{\partial \mu_i^\phi}{\partial T}\right|_{C_j^{\phi E}} \Delta T + \left.\frac{\partial \mu_i^\phi}{\partial p}\right|_{C_j^{\phi E}, T_E} \Delta p^\phi = \sum_{j=2}^{N} \left.\frac{\partial \mu_i^l}{\partial C_j^l}\right|_{C_j^{lE} \neq C_i^{lE}, T_E} \Delta C_j^l + \left.\frac{\partial \mu_i^l}{\partial T}\right|_{C_j^{lE}} \Delta T \tag{70}$$

where all ΔX quantities correspond to the difference between the value of X at the eutectic temperature and the value of X at T: $\Delta X = X^E - X$. In this development, we supposed that the pressure of the liquid does not change from the equilibrium state.

For the following we use the notation: $\Delta S_i^\phi = \left.\frac{\partial \mu_i^\phi}{\partial T}\right|_{C_j^{\phi E}} - \left.\frac{\partial \mu_i^l}{\partial T}\right|_{C_j^{lE}}$ and $\mu_{ij}^\phi = \left.\frac{\partial \mu_i^\phi}{\partial C_j^\phi}\right|_{C_k^{\phi E} \neq C_j^{\phi E}, T_E}$ (we use the same notation for the liquid phase). Also $\left.\frac{\partial \mu_i^\phi}{\partial p}\right|_{C_j^{\phi E}, T} = V_{m,i}^\phi$ where $V_{m,i}^\phi$ is the partial molar volume of element i in the solid phase ϕ. We note that for all i, ΔS_i^ϕ is positive. Indeed, at $T > T_E$ the liquid phase is more stable than the phase ϕ and at $T < T_E$ the solid phase ϕ is more stable than the liquid phase. Therefore, the function $\mu_i^\phi(C_2^{\phi E}, \ldots, C_N^{\phi E}) - \mu_i^l(C_2^{lE}, \ldots, C_N^{lE})$ is an increasing function of the temperature.

Using these notations, we can transform the system of N equations (70) to

the following matrix system:

$$\begin{bmatrix} \mu_{12}^{\phi} & \dots & \mu_{1N}^{\phi} & \Delta S_1^{\phi} \\ & & \vdots & \\ \mu_{N2}^{\phi} & \dots & \mu_{NN}^{\phi} & \Delta S_N^{\phi} \end{bmatrix} \times \begin{bmatrix} \Delta C_2^{\phi} \\ \vdots \\ \Delta C_N^{\phi} \\ \Delta T \end{bmatrix} = \begin{bmatrix} \mu_{12}^{l} & \dots & \mu_{1N}^{l} & V_{m,1}^{\phi} \\ & & \vdots & \\ \mu_{N2}^{l} & \dots & \mu_{NN}^{l} & V_{m,N}^{\phi} \end{bmatrix} \times \begin{bmatrix} \Delta C_2^{l} \\ \vdots \\ \Delta C_N^{l} \\ -\Delta p^{\phi} \end{bmatrix} \tag{71}$$

Defining $[A]$ as the $(N \times N)$ matrix on left hand side of the matrix equation (71), the multiplication of this equality by the inverse of matrix $[A]$ gives a matrix equation expressing variations of concentration in the solid phase ΔC_i^{ϕ} and the variation of temperature ΔT according to variations of concentration in the liquid phase ΔC_j^{l} and the variation of pressure in the solid phase Δp^{ϕ}:

$$\begin{bmatrix} \Delta C_2^{\phi} \\ \vdots \\ \Delta C_N^{\phi} \\ \Delta T \end{bmatrix} = \begin{bmatrix} \Lambda_{22}^{\phi} & \dots & \Lambda_{2N}^{\phi} & \Theta_2^{\phi} \\ & \ddots & \vdots & \\ \Lambda_{N2}^{\phi} & \dots & \Lambda_{NN}^{\phi} & \Theta_N^{\phi} \\ m_2^{\phi} & \dots & m_N^{\phi} & \Omega^{\phi} \end{bmatrix} \times \begin{bmatrix} \Delta C_2^{l} \\ \vdots \\ \Delta C_N^{l} \\ -\Delta p^{\phi} \end{bmatrix} \tag{72}$$

In this $(N \times N)$ matrix, coefficients Λ_{ij}^{ϕ} are called distribution coefficients and m_i^{ϕ} coefficients are the slopes of the phase ϕ liquidus surface corresponding to variations of concentration of elements i. Coefficients of this matrix depend on partial derivatives of chemical potentials μ_i^{ψ} (where ψ can be the solid phase ϕ or the liquid phase) according to independent elements concentration and temperature. These derivatives can be computed from the expressions of phases molar Gibbs free energies G_m^{ψ} as for each element $i = 1 \dots N$ [29]:

$$\mu_i^{\psi} = G_m^{\psi} + \sum_{j=2}^{N} (\delta_{ij} - C_j^{\psi}) \frac{\partial G_m^{\psi}}{\partial C_j} \bigg|_{C_k^{\psi} \neq C_j^{\psi}, T} \tag{73}$$

where G_m^{ψ} depends on independent elements concentrations $(C_2^{\psi}, .., C_N^{\psi})$ and on

590 temperature.

In Calphad, the molar Gibbs free energy of a phase ψ is expressed according to the concentration of all elements $(C_1^\psi, \ldots, C_N^\psi)$ and according to temperature. We call this function $G_{m,1N}^\psi$. To change this function to a one independent on C_1^ψ ($G_{m,2N}^\psi$), we replace C_1^ψ by $1 - \sum_{i=2}^{N} C_i^\psi$ in the expression of $G_{m,1N}^\psi$. In that way, for all element $i = 2 \ldots N$:

$$\frac{\partial G_{m,2N}^\psi}{\partial C_i^\psi} = \frac{\partial G_{m,1N}^\psi}{\partial C_i^\psi} - \frac{\partial G_{m,1N}^\psi}{\partial C_1^\psi} \tag{74}$$

Curvature parameters

In this section we analyze terms linking the variations of temperature ΔT and of elements concentration in the solid phase ΔC_i^ϕ to the variation of pressure induced by the interface curvature.

In eq. (72), the coefficient Ω^ϕ is defined as:

$$\Omega^\phi = \sum_{k=1}^{N} A_{Nk}^{-1} V_{m,k}^\phi \tag{75}$$

where coefficients A_{ij}^{-1} are coefficients of the inverse matrix of $[A]$. By definition A_{Nk}^{-1} coefficients can be written:

$$A_{Nk}^{-1} = \frac{1}{\det(A)} (-1)^{N+k} B_{kN} \tag{76}$$

where coefficient B_{ij} is the determinant of the $(N-1) \times (N-1)$ matrix corresponding to $[A]$ withour row i and column j. We note that B_{kN} can be written: $B_{kN} = \det([C_k][G_{cc}^\phi])$ where G_{cc}^ϕ is the Hessian of phase ϕ Gibbs free energy (according to independent concentrations $(C_2^\phi, .., C_N^\phi)$) and $[C_k]$ is a matrix which only depends on independent elements concentration and such that $\det(C_k) = C_k^\phi (-1)^{k+1}$. In addition, $\det(A) = \sum_{k=1}^{N} (-1)^{N+k} B_{kN} \Delta S_k$. We thus

get that:

$$\Omega^{\phi} = \frac{V_m^{\phi}}{\Delta S_{\phi l}} \tag{77}$$

where $V_m^{\phi} = \sum_{k=1}^{N} C_k^{\phi} V_{m,k}^{\phi}$ is the molar volume of phase ϕ and $\Delta S_{\phi l} = \sum_{k=1}^{N} C_k^{\phi} \Delta S_k^{\phi}$ is the molar entropy of fusion of an infinitesimal amount of phase ϕ in the liquid phase [15].

For $k = 1 \dots (N-1)$, coefficient Θ_{k+1} introduced in eq. (72) is defined as:

$$\Theta_{k+1} = \sum_{j=1}^{N} A_{kj}^{-1} V_{m,j}^{\phi} \tag{78}$$

which can be re-written $\Theta_{k+1} = \dfrac{\sum_{j=1}^{N} (-1)^{k+j} B_{jk} V_{m,j}^{\phi}}{\sum_{j=1}^{N} A_{jk} (-1)^{k+j} B_{jk}}$. If we suppose that terms of the same type (A_{jk}, B_{jk}, $V_{m,k}^{\phi}$) are of the same order, we obtain that $\Theta_{k+1} \sim \frac{V_{m,j}^{\phi}}{A_{jk}} = \frac{V_{m,j}^{\phi}}{\mu_{j(k+1)}^{\phi}}$. If, in addition, we assume that all terms of $[G_{cc}]$ and all elements concentration have respectively the same order we obtain that:

$$\Theta_{k+1} \sim \frac{V_m^{\phi}}{\frac{\partial^2 G_m^{\phi}}{\partial C_{k+1} \partial C_i}} \tag{79}$$

The pressure variation induced by the interface curvature is defined as: $\Delta p^{\phi} = \sigma_{\phi l} \kappa(x)$, where $\sigma_{\phi l}$ is the solid phase ϕ/liquid interface energy and $\kappa(x)$ is the interface curvature in position x. Therefore, the effect of curvature variation on ΔC_i^{ϕ} (for $i = 2 \dots N$) is of the same order as $\frac{V_m^{\phi}}{\frac{\partial^2 G_m^{\phi}}{\partial C_i \partial C_j}} \sigma_{\phi l} \kappa(x)$.

From the data given in Kurz and Fisher [31] of pure materials, we find $V_m^{\phi} \sim 10^{-5}\, m^3/\text{mol}$ and $\sigma_{\phi l} \sim 10^{-2} - 10^{-1}\, J/m^2$. By only taking into account the entropy of mixing term of solid phase ϕ solidifying at $T \sim 10^2\, K$ we get that $\frac{\partial^2 G_m^{\phi}}{\partial C_i \partial C_j} \sim 10^4\, K/\text{mol}$. For alloys with a eutectic spacing around $\lambda \sim 10^{-6}\, m$ we

have $\kappa(x) \sim 10^6\, m^{-1}$. Based on these ranges, we find that the effect of curvature alone on ΔC_i^ϕ (for $i = 2 \dots N$) is of the order of $10^{-17} - 10^{-16}$, so this effect is negligible.

Coefficients of binary alloys

In this section, we develop the expression of Λ_{22}^ϕ and m_2^ϕ coefficients for binary alloys. In this particular case, Eq. (72) gives that:

$$\Lambda_{22}^\phi = \frac{\mu_{12}^l \Delta S_2^\phi - \mu_{22}^l \Delta S_1^\phi}{\mu_{12}^\phi \Delta S_2^\phi - \mu_{22}^\phi \Delta S_1^\phi} \tag{80}$$

$$m_2^\phi = \frac{\mu_{12}^\phi \mu_{22}^l - \mu_{22}^\phi \mu_{12}^l}{\mu_{12}^\phi \Delta S_2^\phi - \mu_{22}^\phi \Delta S_1^\phi} \tag{81}$$

In binary alloys, Eq. (73) induces that

$$\mu_{12}^\phi = -C_2^\phi \frac{\partial^2 G_m^\phi}{\partial C_2^2} \tag{82}$$

$$\mu_{22}^\phi = (1 - C_2^\phi) \frac{\partial^2 G_m^\phi}{\partial C_2^2} \tag{83}$$

(these expressions are also valid for the liquid phase). Eqs.(80) and (81) can therefore be re-written:

$$\Lambda_{22}^\phi = \frac{C_1^l \Delta S_1^\phi + C_2^l \Delta S_2^\phi}{C_1^\phi \Delta S_1^\phi + C_2^\phi \Delta S_2^\phi} \frac{\frac{\partial^2 G_m^l}{\partial (C_2^l)^2}}{\frac{\partial^2 G_m^\phi}{\partial (C_2^l)^2}} \tag{84}$$

$$m_2^\phi = -\frac{\left(C_2^{lE} - C_2^{\phi E}\right) \frac{\partial^2 G_m^l}{\partial (C_2^l)^2}}{\Delta S_{\phi l}} \tag{85}$$

We note that as ΔS_1^ϕ, ΔS_2^ϕ, $\frac{\partial^2 G_m^l}{\partial (C_2^l)^2}$ and $\frac{\partial^2 G_m^\phi}{\partial (C_2^l)^2}$ are all positive, the coefficient Λ_{22}^ϕ is always positive.

Coefficients of ternary alloys

In this section, we develop the expression of Λ_{ij}^{ϕ} and m_i^{ϕ} coefficients for ternary alloys. In this particular case, the $(N \times N)$ matrix defined in Eq. (72) can be expressed as:

$$\begin{bmatrix} \Lambda_{22}^{\phi} & \Lambda_{23}^{\phi} & \Theta_2^{\phi} \\ \Lambda_{32}^{\phi} & \Lambda_{33}^{\phi} & \Theta_N^{\phi} \\ m_2^{\phi} & m_3^{\phi} & \Omega^{\phi} \end{bmatrix} = [A]^{-1} \times \begin{bmatrix} \mu_{12}^{l} & \mu_{13}^{l} & V_{m,1}^{\phi} \\ \mu_{22}^{l} & \mu_{23}^{l} & V_{m,2}^{\phi} \\ \mu_{32}^{l} & \mu_{33}^{l} & V_{m,3}^{\phi} \end{bmatrix} \tag{86}$$

where $[A]^{-1}$ is the inverse matrix of $[A]$ defined in Eq. (71). For ternary alloys, $[A]^{-1}$ can be expressed as:

$$[A]^{-1} = \frac{1}{\det(A)} \begin{bmatrix} B_{11} & -B_{21} & B_{31} \\ -B_{12} & B_{22} & -B_{32} \\ B_{13} & -B_{23} & B_{33} \end{bmatrix} \tag{87}$$

where

$$B_{11} = \begin{vmatrix} \mu_{2,3}^{\phi} & \Delta S_2^{\phi} \\ \mu_{3,3}^{\phi} & \Delta S_3^{\phi} \end{vmatrix} \quad B_{21} = \begin{vmatrix} \mu_{1,3}^{\phi} & \Delta S_1^{\phi} \\ \mu_{3,3}^{\phi} & \Delta S_3^{\phi} \end{vmatrix} \quad B_{31} = \begin{vmatrix} \mu_{1,3}^{\phi} & \Delta S_1^{\phi} \\ \mu_{2,3}^{\phi} & \Delta S_2^{\phi} \end{vmatrix}$$

$$B_{12} = \begin{vmatrix} \mu_{22}^{\phi} & \Delta S_2^{\phi} \\ \mu_{32}^{\phi} & \Delta S_3^{\phi} \end{vmatrix} \quad B_{22} = \begin{vmatrix} \mu_{12}^{\phi} & \Delta S_1^{\phi} \\ \mu_{32}^{\phi} & \Delta S_3^{\phi} \end{vmatrix} \quad B_{32} = \begin{vmatrix} \mu_{12}^{\phi} & \Delta S_1^{\phi} \\ \mu_{22}^{\phi} & \Delta S_2^{\phi} \end{vmatrix}$$

$$B_{13} = \begin{vmatrix} \mu_{22}^{\phi} & \mu_{23}^{\phi} \\ \mu_{32}^{\phi} & \mu_{33}^{\phi} \end{vmatrix} \quad B_{23} = \begin{vmatrix} \mu_{33}^{\phi} & \mu_{32}^{\phi} \\ \mu_{13}^{\phi} & \mu_{12}^{\phi} \end{vmatrix} \quad B_{33} = \begin{vmatrix} \mu_{12}^{\phi} & \mu_{13}^{\phi} \\ \mu_{22}^{\phi} & \mu_{23}^{\phi} \end{vmatrix}$$

We thus obtain that

$$\Lambda_{ij}^{\phi} = \frac{\sum_{k=1}^{3}(-1)^{k+i-1}B_{k(i-1)}\mu_{kj}^{l}}{\sum_{k=1}^{3}(-1)^{k+i-1}B_{k(i-1)}\mu_{ki}^{\phi}} \tag{88}$$

$$m_i^{\phi} = \frac{\sum_{k=1}^{3}(-1)^{k+3}B_{k3}\mu_{ki}^{l}}{\sum_{k=1}^{3}(-1)^{k+3}B_{k3}\Delta S_k^{\phi}} \tag{89}$$

B. Approximations of the model

Approximation of Δ' as independent of growth conditions

In this appendix, we analyze the hypotheses that $-\Delta' = \frac{\partial\overline{\Delta T}^{\beta}}{\partial f_\alpha}\Big|_{f_\alpha^E} - \frac{\partial\overline{\Delta T}^{\alpha}}{\partial f_\alpha}\Big|_{f_\alpha^E}$ can be approximated to $-\Delta'_0$ where Δ'_0 is independent of λ and V. The expression of Δ' is obtained from expressions of $\overline{\Delta T}^{\alpha}$ (Eq. (30)) and $\overline{\Delta T}^{\beta}$ (Eq. (31)) and from mean liquid concentration of independent elements on each solid phase interface (Eq. (27) and (28)). From these expressions, the derivation of $\overline{\Delta T}^{\alpha}$ and $\overline{\Delta T}^{\beta}$ according to f_α induce that Δ' can be written:

$$\Delta' = \Delta'_0 + V\lambda\xi_C + \frac{\xi_R}{\lambda} \tag{90}$$

where Δ'_0, ξ_C and ξ_R are coefficients independent on λ and V.

As Δ'_0 is a zero order term in Peclet numbers and $V\lambda\xi_C$ is at first order term in Peclet numbers, if the interface grows at low Peclet numbers, then we can assume that $V\lambda\xi_C \ll \Delta'_0$. Moreover, by analyzing the expressions of $\overline{\Delta T}^{\beta}$ and $\overline{\Delta T}^{\alpha}$ we find:

$$\Delta'_0 = \sum_{i=2}^{N}\Delta m_i \sum_{j=2}^{N}\left[\overline{\Lambda}\right]_{ij}^{-1}\Delta C_j \tag{91}$$

In the general case, the order of parameters involved in this expression are: $\Delta m_i \sim (10 - 10^3)\, K/(\text{at}\%)$, $\Delta C_j \sim 10\,\text{at}\%$ and $[\Lambda]_{ij}^{-1} \sim 0.1 - 10$, so $\Delta_0' \sim 10 - 10^5\, K$. We also get that

$$\frac{\xi_R}{\lambda} = \frac{2}{\lambda}\left[\frac{\Gamma_{\beta/l}\sin(\mid \theta_\beta \mid)}{f_\beta^2} + \frac{\Gamma_{\alpha/l}\sin(\mid \theta_\alpha \mid)}{f_\alpha^2}\right] \tag{92}$$

The order of parameters involved in this expression are: $\Gamma_{(\alpha/\beta)/l} \sim 10^{-7}\, K.m$, $\sin(\mid \theta_{(\alpha/\beta)} \mid) \sim 10^{-1}$, $f_{(\alpha/\beta)} \sim 10^{-1}$ and $\lambda \sim 10^{-6}\, m$. So $\frac{\xi_R}{\lambda} \sim 1\, K$ and so, in the general case, $\frac{\xi_R}{\lambda} \ll \Delta_0'$.

We verify now that $(\xi_C V\lambda_m, \xi_R/\lambda_m) \ll \Delta_0'$ (where λ_m is the eutectic spacing of minimum undercooling for a given velocity) on 4 binary alloys: $Fe - Fe_3C$, $Al - Si$, $Al - Al_2Cu$ and $Sn - Pb$. Parameters used for this study are taken from Ref [3]. For $V = 100 \times 10^{-6}\,\text{m/s}$ we obtain that for all systems, $V\lambda_m\xi_C$ and $\frac{\xi_R}{\lambda_m}$ are three orders of magnitude smaller than Δ_0'. So the approximation $\Delta' \approx \Delta_0'$ is relevant for all these systems.

Is Δf_α^{iso} a first order term in Pe_i?

We supposed in section 2.2.3 that the term $\left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E}$ could be approximated at zero order in Peclet number in the expression of the mean undercooling of an isothermal interface (see Eq. 41). This assumption is justified if Δf_α^{iso} is a term at first order in Peclet numbers and so if the α_R/λ_m term in Eq (34) is in the order of $\alpha_C V\lambda_m$. We analyze this hypotheses on the 4 binary systems used in the first part of appendix B. We observe that α_R/λ_m is of the same range as $\alpha_C V\lambda_m$ for all systems except for $Sn - Pb$ where $\alpha_C V\lambda_m = -0.17\frac{\alpha_R}{\lambda_m}$. This induces that, for $Sn - Pb$, $\Delta f_\alpha^{\text{iso}}$ is a variation at a lower order than Pe_i and that, for this system, $\left.\frac{\partial \overline{\Delta T}_C}{\partial f_\alpha}\right|_{f_\alpha^E}$ could be developed at first order in Peclet number in eq. (38).

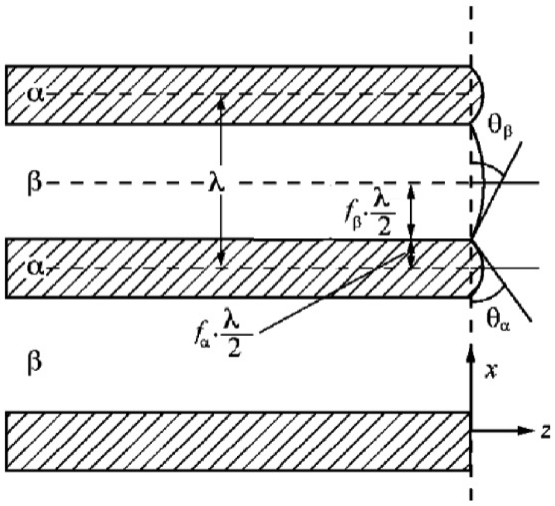

Figure 1: Schematic representation of steady state directional growth with a lamellar morphology. Quantities reported on the figure are: eutectic spacing λ, solid fraction of α phase (f_α) and β phase (f_β), angles of curvature of α phase (θ_α) and β phase (θ_β) at the tri-junction. (After Ludwig et al. [30])

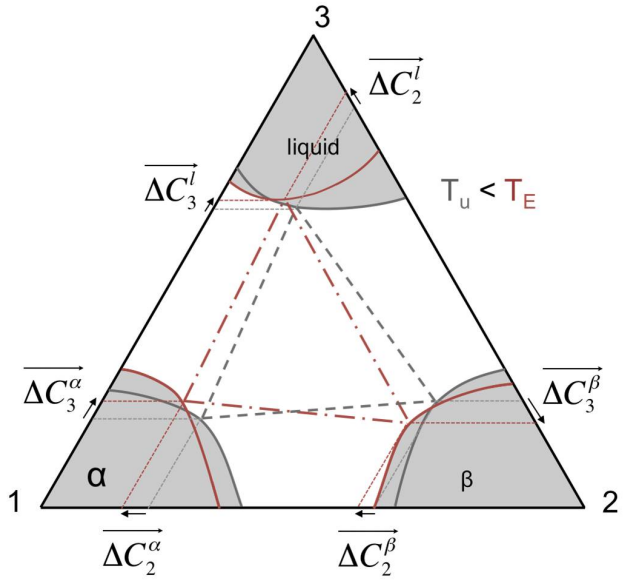

Figure 2: Sketch of the evolution of equilibrium tie lines with temperature in a ternary two-phase eutectic. The arrows represent the concentration of elements 2 and 3 evolution in the different phases with the temperature evolution from T_E to T_u

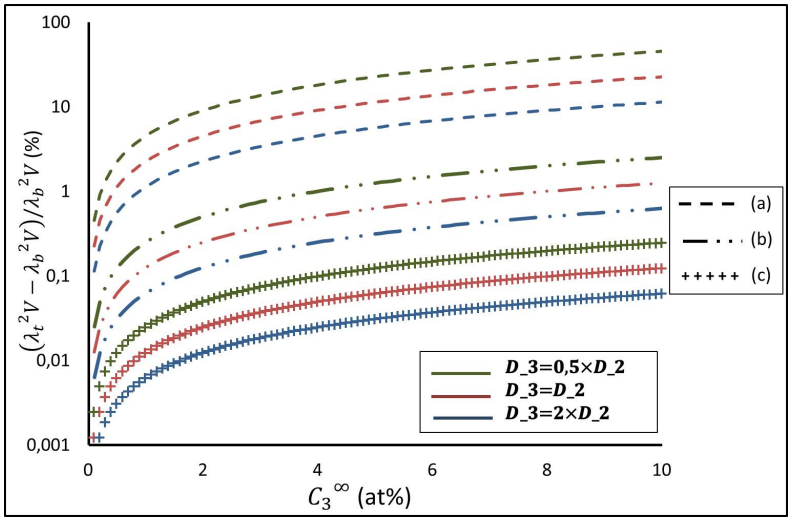

Figure 3: Variation of the $\lambda_m^2 V$ law with the addition of element 3 compared to the $\lambda_m^2 V$ law of the symmetrical binary alloy (in %) according to C_3^{∞}. Lines (a) correspond to: $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E = 1.9$ and $m_3^{\beta} = -9\,K/(at\%)$, lines (b) correspond to $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E = 0.1$ and $m_3^{\beta} = 10\,K/(at\%)$, and lines (c) correspond to: $\Delta\Lambda_{33}/\overline{\Lambda_{33}}^E = 0.1$ and $m_3^{\beta} = -9\,K/(at\%)$