



ELSEVIER

Physica D 124 (1998) 271–284

PHYSICA D

The interface response-functions in multi-componental alloy solidification

A. Ludwig¹

Foundry Institute of the Technical University Aachen, 52056 Aachen, Germany

Received 30 March 1998; accepted 3 July 1998

Communicated by H. Müller-Krumbhaar

Abstract

Usually during solidification of alloys solute is redistributed at the solid/liquid interface. For high solidification velocities a deviation from local thermodynamic equilibrium at the interface reduces the tendency for redistribution. This effect is known as solute trapping. Based on the model for binary systems presented in M.J. Aziz, T. Kaplan [Acta Metall. 36 (1988) 2335], we have developed a theory for multi-componental solute trapping. It enables the determination of the n solid concentrations by solving an n -dimensional nonlinear system of equations, called first response-functions. In addition we derived a relation between the growth velocity and the driving force for crystallisation for both planar and non-planar solid/liquid interfaces, called second response-function. Our model shows that the usual concept to calculate the interface temperature by reducing the actual “interface liquidus temperature” by a curvature and a kinetic undercooling term cannot be applied with non-dilute binary and arbitrary multi-componental alloys. © 1998 Elsevier Science B.V.

1. Introduction

To describe the interface motion during phase transformation, shape interface models assume that: (i) long range transport of atoms (or molecules) and heat towards and/or away from the interface occurs, and (ii) an “interface reaction” takes place, which is responsible for the incorporation of atoms (or molecules) into the growing solid. The long range heat and mass transport can be described by the differential equations of classical continuum mechanics. The “interface reaction” is formally described by response-functions and is still subject of on-going research.

To move a solid/liquid interface, a driving force and therefore a deviation from thermodynamic equilibrium must be present at the interface. This deviation from equilibrium is discussed in the rate theory [1,2,3]. For pure materials an undercooling at the interface drives the interface movement. With alloys the different solubility of solute in liquid and solid results in a redistribution at the interface. Here the deviation from equilibrium produces concentrations at the interface which are variant to the phase diagram prediction.

¹ E-mail: ludwig@gi.rwth-aachen.de

On atomic scale, the redistribution at the interface can be regarded as taking place by hopping processes across the interface. Due to rate theory this produces a relation between the growth velocity V , the interface temperature T , and the concentration in liquid C_L and solid C_S as

$$C_S = f_1(T, V, C_L, C_S). \quad (1)$$

This relation is called first response-function [4,5]. For small growth velocity, where the interface is at thermodynamic equilibrium, the first response-function can be expressed by the distribution coefficient of the system as $C_S = k(T) \cdot C_L$.

With increasing growth velocity a deviation from thermodynamic equilibrium increases (for $k < 1$) or decreases (for $k > 1$) the solute content in the solid, a phenomenon which is known as solute trapping. For given interface temperature and liquid concentration, solute trapping can be described by a velocity-dependent distribution coefficient $k_V(T)$. The model of Baker gave the basic ideas for a quantitative description of $k_V(T)$ [5,6]. Jackson et al. [7] suggest a model, wherein k increases with V , but it does not predict a total solute trapping ($k = 1$). This was first described theoretically by the continuous growth model (CGM) of Aziz [8]. With dilute alloys his model gives

$$k_V(T) = \frac{k(T) + (V/V_D)}{1 + (V/V_D)}, \quad (2)$$

where V_D is the diffusion velocity across the interface, which is often approximated by $V_D = D_L/\delta_i$. Here δ_i is the “thickness” of the interface and D_L the diffusion coefficient in the liquid. The validity of Eq. (2) was tested in many studies and proved, especially for slidely doped Si-alloys, to be correct [9,10,11].

In addition to the above mentioned model of Baker [5], Hillert and Sundman [12], Jönsson and Agren [13,14], and Aziz and Kaplan [4] developed further models for describing solute trapping in non-dilute binary alloy systems. Recent investigations on rapid solidification of Si-9at% As showed that Baker, Hillert–Sundman and Aziz–Kaplan models can correctly predict the experimental k – V relation. However, the measured T – V relation can only be adequately described by the Aziz–Kaplan model [15,16]. In their model the following expression is derived:

$$k_V(T, V) = \frac{\kappa_e + (V/V_D)}{1 + (V/V_D) - (1 - \kappa_e)C_L} \quad (3)$$

with the so-called partitioning parameter $\kappa_e := \exp[(\Delta\tilde{\mu}^2 - \Delta\tilde{\mu}^1)/RT]$. For the definition of the redistribution potentials $\Delta\tilde{\mu}^1$ and $\Delta\tilde{\mu}^2$ see Eq. (16). In dilute binary systems it is $\kappa_e \cong k$. In this case the third term in the denominator is small compared to one and can thus be ignored. Therefore Eq. (2) is an approximation of Eq. (3).

As the rate theory describes not only individual hopping processes, but also the sum of rates of atoms incorporated in the growing solid (and hence the motion of the interface), it yields a relation between growth velocity and driving force, i.e. the difference of free energy between liquid and solid at the interface. This relation is called the second response-function [4,5]. If this difference in free energy is expressed by the concentration in liquid and solid at the interface, the second response-function can be expressed as

$$V = f_2(T, C_L, C_S). \quad (4)$$

For dilute binary systems Boettinger and Corriell derived the following expression for the second response-function [17]:

$$T = T_f + m_V C_L + \frac{m}{(1-k)} \frac{V}{V_0}, \quad (5)$$

with

$$m_V := m \cdot \left(1 + \frac{k - k_V(1 - \ln(k_V/k))}{1 - k} \right).$$

Here $m = m(T)$ is the slope of the (equilibrium) liquidus line, T_f is the melting point of the pure solvent and V_0 is the maximum possible growth rate. m_V is sometimes called the “kinetic liquidus slope”. With pure materials Eq. (5) together with the Van’t Hoff rule [18] gives

$$(T_f - T) = V/\mu \quad \text{with} \quad \mu := -\Delta H_f V_0 / (RT_f^2). \quad (6)$$

Thus the expression derived by Boettinger and Corriell includes the linear approximation for the growth kinetics of pure substances.

In this paper we present a theoretical model for the first and the second response-functions in the general case of a multi-componental alloy system. Based on the continuous growth model of Aziz and Kaplan [4], we have derived the n first response-functions for an n -componental system in Section 2.1. The second response-function for an n -componental system is given for a flat solid/liquid interface in Section 2.2 and for a curved interface in Section 2.3. Our theoretical investigation showed that for non-dilute binary and any arbitrary multi-componental system it is essentially not possible to derive an analytical expression for the T – V relation. Thus the expressions for kinetic and capillary undercooling, which are known for dilute binary alloys, are not applicable in these more general cases. In Section 3 we apply the present model for (i) the movement of the solid/liquid interface for different velocities and to (ii) a spherical crystal with different stationary sizes within the melt ($V = 0$). In Section 4 the main results of the present work are summarised.

2. Rate theory in multi-componental systems

2.1. First response-functions

We consider an n -componental system with a flat solid/liquid interface which grows with a constant velocity V at a temperature T . For the sake of simplicity we assume that all componentals have the same atomic volume, Ω , both in solid state and in liquid state. We denote the concentration (in mole fraction) as (C_S^1, \dots, C_S^n) for the solid (S) at the interface and (C_L^1, \dots, C_L^n) for the liquid (L) at the interface. Then the number of atoms of the i th component per unit area and unit time incorporated into the solid is given as

$$J^i = C_S^i \cdot V/\Omega. \quad (7)$$

J^i is the physical flux of atoms of the i th component across the interface measured in a frame of reference fixed with the interface. With $C_S^1 + \dots + C_S^n = 1$, the total number of atoms per unit area and unit time incorporated into the solid, $J_C := J^1 + \dots + J^n$, the so-called crystallisation flux, is simply given as

$$J_C = V/\Omega. \quad (8)$$

For a co-ordinate system fixed on the lattice of the crystal the so-called diffusive flux J_D^i is given as the difference between the actual flux J^i and the flux on growth of the solid with the composition of the liquid at the interface. Thus it is determined by

$$J_D^i := C_L^i \cdot V/\Omega - J^i = (C_L^i - C_S^i) \cdot V/\Omega. \quad (9)$$

Note that with $C_L^1 + \dots + C_L^n = 1$ and $C_S^1 + \dots + C_S^n = 1$ the sum of the diffusive fluxes $J_D := J_D^1 + \dots + J_D^n$ vanishes. The diffusive flux J_D^i describes the number of atoms of the i th component per unit area and unit time which are rejected from the interface due to the different solubility between solid and liquid. Phenomenologically, this rejection is carried by redistribution processes between the i th and the j th component, where $j = 1, \dots, n$ and $i \neq j$.

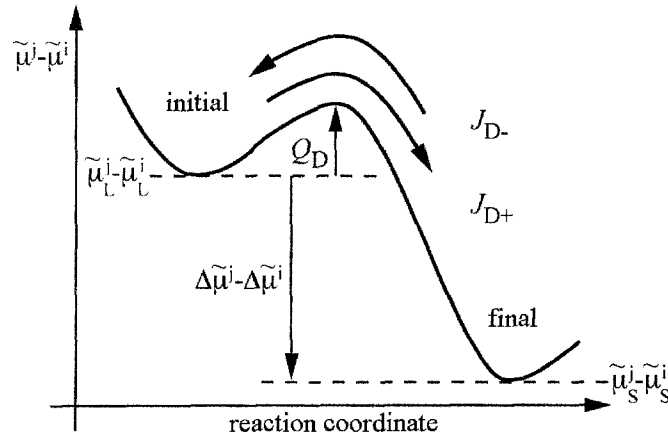


Fig. 1. Reaction co-ordinate diagram for the redistribution reaction $i \leftrightarrow j$. Initial state: i in the liquid and j in the solid. Final state: i in the solid and j in the liquid (according to [4]).

Fig. 1 illustrates the redistribution process in the free enthalpy/reaction co-ordinate diagram. Here we have defined the initial stage of the redistribution process $i \leftrightarrow j$ by

- i th component in the liquid,
- j th component in the solid,

and the final state by the corresponding change of places. For the reaction to occur, the activation barrier for interdiffusion across the interface Q_D has to be overcome. According to the kinetic rate theory, the diffusive flux caused by the redistribution process $i \leftrightarrow j$ is given as the difference between the forward [$i : (L) \rightarrow (S)$, $j : (S) \rightarrow (L)$] and the backward [$i : (S) \rightarrow (L)$, $j : (L) \rightarrow (S)$] reaction

$$J_D^{i,j} := J_{D+}^{i,j} - J_{D-}^{i,j}. \quad (10)$$

The forward reaction is given as [4]

$$J_{D+}^{i,j} = \frac{f\nu\delta}{\Omega} C_L^i C_S^j \exp\left(-\frac{Q_D}{RT}\right), \quad (11)$$

where f is a geometrical factor, ν is an attempt frequency,² δ an interatomic distance and R the gas constant. It is assumed that f , ν and δ are equal for the different redistribution processes. The activation barrier Q_D depends on the energetic situation locally at the interface and is therefore affected by all components present. Thus for a first approximation, it can be assumed that Q_D is equal for each individual redistribution process. We will discuss the consequence of this assumption in Section 3. The factor $C_L^i C_S^j$ reflects the fact that the forward reaction of i – j exchange is proportional to the concentration of the i th component in the liquid and the j th component in the solid. The final factor is the fraction of attempted successful interchanges.

The rate of reverse reaction is

$$J_{D-}^{i,j} = \frac{f\nu\delta}{\Omega} C_S^i C_L^j \exp\left(-\frac{Q_D + (\Delta\tilde{\mu}^j - \Delta\tilde{\mu}^i)}{RT}\right). \quad (12)$$

Here the convention used is that differences in quantities across the interface, expressed by the symbol Δ , are the values of these quantities in the solid minus those in the liquid.

² According to [19] ν is in the order of the atomic vibrational frequency (Debye frequency).

The redistribution potential $\tilde{\mu}^i$ of the i th component is given as the difference between the chemical potential and the contribution from the ideal mixing entropy

$$\tilde{\mu}^i(T, C^1, \dots, C^n) := \mu^i(T, C^1, \dots, C^n) - RT \ln(C^i) \quad (13)$$

and thus

$$\Delta \tilde{\mu}^i = \Delta \mu^i - RT \ln(C_S^i/C_L^i). \quad (14)$$

As Aziz and Kaplan pointed out [4], the reason for taking the redistribution potential rather than the actual chemical potential is that any local entropic effects are included in weighting the rates of individual atomic hops, whereas the ideal mixing entropy is already accounted for by the $C_L^i C_S^j$ and $C_S^i C_L^j$ factors in Eqs. (11) and (12). If the interface is at equilibrium, this results in equal rates for the forward and the backward reaction $J_{D+}^{i,j} = J_{D-}^{i,j}$ and thus no net reaction rate occurs $J_D^{i,j} = 0$.

Using

$$\mu^i = \mu_0^i + RT \ln(C^i) + RT \ln(\gamma^i) \quad (15)$$

we can further write

$$\Delta \tilde{\mu}^i = \Delta \mu_0^i + RT \ln\left(\frac{\gamma_S^i}{\gamma_L^i}\right) = -RT \ln(k^i) - RT \ln\left(\frac{\gamma_{S,e}^i \gamma_L^i}{\gamma_{L,e}^i \gamma_S^i}\right). \quad (16)$$

To distinguish the actual quantities at the interface from the equilibrium values we have introduced the index e. Thus the equilibrium distribution coefficient of the i th component is $k^i = C_{S,e}^i/C_{L,e}^i$ and the actual one is $k_V^i = C_S^i/C_L^i$.

The net diffusive flux of the j th component, J_D^j , is given by the sum of all possible redistribution processes with every component present in the system ($i = 1, \dots, n$). Redistribution processes with same components result in a zero contribution to the sum ($J_D^{j,j} \equiv 0$). Thus the summation can be carried out over $i = 1, \dots, n$. With Eqs. (10)–(12) we obtain

$$J_D^j = \sum_{i=1}^n J_{D+}^{i,j} = \sum_{i=1}^n (J_{D+}^{i,j} - J_{D-}^{i,j}) = \frac{V_D}{\Omega} \cdot \sum_{i=1}^n (C_L^i C_S^j - \kappa^{i,j} C_S^i C_L^j), \quad (17)$$

with $V_D := f v \delta \exp(-Q_D/RT)$. $\kappa^{i,j}$ are the so-called partitioning parameters [4] and they are defined by

$$\kappa^{i,j} := \exp\left(-\frac{\Delta \tilde{\mu}^j - \Delta \tilde{\mu}^i}{RT}\right). \quad (18)$$

With Eq. (16) these parameters can be written as

$$\kappa^{i,j} = \frac{k^j}{k^i} \left\{ \frac{\gamma_{S,e}^j \gamma_L^j \gamma_{L,e}^i \gamma_S^i}{\gamma_{L,e}^j \gamma_S^j \gamma_{S,e}^i \gamma_L^i} \right\}. \quad (19)$$

For ideal solutions and for dilute non-ideal solutions (where the laws of Raoult and Henry apply) Eq. (19) reduces to $\kappa^{i,j} = k^j/k^i$. This is also true for equilibrium where the forward reaction of the redistribution $i \leftrightarrow j$ is equal to the backward reaction of the redistribution $j \leftrightarrow i$: $J_D^{i,j} = -J_D^{j,i}$.

Combining Eqs. (9) and (17) results in

$$(C_L^j - C_S^j) \frac{V}{V_D} = \sum_{i=1}^n (C_L^i C_S^j - \kappa^{i,j} C_S^i C_L^j) \quad \text{with } j = 1, \dots, n. \quad (20)$$

These are the n first response-functions of an n -componental system. For $V = 0$ these equations are redundant. Adding these gives $C_S^1 + \dots + C_S^n = 1$. Knowing the compositions in the liquid at the interface (C_L^1, \dots, C_L^n) as well as V and T , the first response-functions form a (nonlinear) system of equations for the n unknown solid concentrations at the interface (C_S^1, \dots, C_S^n).

$C_L^1 + \dots + C_L^n = 1$ and rearranging the equations in (20) after dividing them with C_S^j result in the velocity dependent distribution coefficient of the j th component

$$k_V^j = \frac{V/V_D + \sum_{i=1}^n \kappa^{i,j} C_S^i}{V/V_D + 1}. \quad (21)$$

For binary systems ($n = 2$) this can be reduced to

$$k_V^2 = \frac{V/V_D + \kappa^{1,2} + (1 - \kappa^{1,2})C_S^2}{V/V_D + 1} = \frac{V/V_D + \kappa^{1,2}}{V/V_D + 1 - (1 - \kappa^{1,2})C_L^2}. \quad (22)$$

With $\kappa_e = \kappa^{1,2}$ this equation is equal to Eq. (11) in [4]. For ideal solutions or dilute non-ideal solutions ($\kappa^{i,j} = k^j/k^i$) Eq. (21) with $C_L^1 + \dots + C_L^n = 1$ results in

$$k_V^j = \frac{V/V_D + k^j}{V/V_D + 1}. \quad (23)$$

2.2. Second response-function

Chemical rate theory for one componental systems describes the interface movement by assuming thermally activating individual hopping processes of atoms across the interface as in Section 2.1. The theory yields for the growth velocity

$$V = V_0(T) \cdot [1 - \exp(\Delta G/RT)], \quad (24)$$

where V_0 is the maximal growth velocity when the driving force is infinite (no backward hopping) and ΔG is the (negative for solidification) difference between the free energy of solid and liquid responsible for interface motion.

In classical papers on interface kinetics [2,3,20,21] it is assumed that the attachment to the interface is caused by a diffusion process. In this case, which is known as “diffusion-limited” growth, the prefactor in Eq. (24) is given by the diffusion rate $V_0 = V_D$. In pure systems the attachment to the interface according to Turnbull [21], only requires impingement processes. This case is known as “collision-limited” growth and the maximal solidification velocity is given by the speed of sound $V_0 = V_S$. Evidence of “diffusion-limited” growth was found for: (i) alloys with different solubility of solvents in the solid and liquid; (ii) alloys with a chemically ordered solid (e.g. intermetallic phases); (iii) systems consisting of molecules which form mainly directed bonds in the solid (e.g. SiO_2) and (iv) systems consisting of molecules which differ considerably from a spherical geometry. In all cases mentioned above a diffusion (or similar) process is needed to incorporate particles in the growing solid. In all other cases “collision-limited” growth can be assumed [22].

For pure substances ΔG results from an undercooling of the interface ΔT . Assuming the linear approximation $\Delta G = \Delta G_0 = \Delta S_f \Delta T$ [23], and $\Delta G \ll RT$, Eq. (24) gives a linear relation between V and ΔT . For pure metals this linear relation is reasonable [18] and has been experimentally proved [24].

Aziz and Kaplan assumed [4] that even for alloys the kinetics of interface displacement can be described by thermally activated hopping processes across the interface. The driving forces for these hopping processes

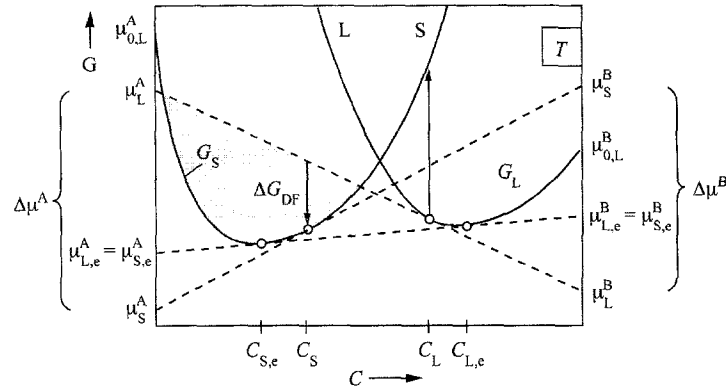


Fig. 2. The common tangent construction can be applied for a liquid with concentration $C_{L,e}$ in equilibrium with a solid with concentration $C_{S,e}$. For a liquid and a solid with concentration C_L and C_S , which are not in equilibrium with each other, a difference in the free energy ΔG_{DF} can be calculated according to Eq. (25) (after [5]). For solidification ΔG_{DF} must be negative, which restricts the range of possible C_S to the shaded region.

are the differences in chemical potentials between the solid and liquid of the different components, $\Delta\mu^i$ ($i = 1, \dots, n$).

The total difference of the free energy between the solid and liquid is given as [5]

$$\Delta G_{DF} = \sum_{i=1}^n C_S^i \cdot \Delta\mu^i, \tag{25}$$

with $\Delta\mu^i := \mu_S^i - \mu_L^i$. For the binary case the range of solid concentration for which ΔG_{DF} is less than zero, is shown in Fig. 2. With $\Delta G = \Delta G_{DF}$ Eq. (24) gives

$$V = V_0 \left(1 - \exp \left(\frac{1}{RT} \sum_{i=1}^n C_S^i \cdot \Delta\mu^i(T, C_S^i, C_L^i) \right) \right) \tag{26}$$

for the growth velocity. Eq. (26) is the second response-function of n -componental systems.

If the driving forces for solidification are small, i.e. if the linear approximation $\Delta G_{DF}/RT = -V/V_0$ can be applied, the second response-function gives

$$\frac{V}{V_0} = -\frac{1}{RT} \sum_{i=1}^n C_S^i \cdot \Delta\mu^i. \tag{27}$$

For a dilute solution which contains mainly the \hat{i} th component, the temperature of the interface T can be estimated from the corresponding equilibrium concentrations $C_{L,e}^j$ by

$$T = T_f^{\hat{i}} + \sum_{j=1, j \neq \hat{i}}^n m^j C_{L,e}^j. \tag{28}$$

This equation shows that without further approximation for the temperature dependence of the $\Delta\mu^i$'s, neither the second response-function (Eq. (26)) nor the linear approximation (27) can be solved to give an analytical expression for T .

Theoretically it is not clear whether ΔG_{DF} is consumed completely by moving the interface (without solute-drag) or whether a ΔG_{DF} is partly consumed by the redistribution processes at the interface (with solute-drag). From [4] it is conceivable that the crystallisation rate should be determined by the driving force for crystallisation averaged over all of the atoms that actually crystallise. This argument supports the absence of solute-drag. On the other hand, if some of the overall driving free energy is consumed in driving the redistribution reactions, and is therefore unavailable to drive interface motion, solute-drag should be considered. That amount can be evaluated by $\Delta G_{\text{D}} = \sum (C_{\text{S}}^i - C_{\text{L}}^i) \Delta \mu^i$, leading to $\Delta G = \Delta G_{\text{DF}} - \Delta G_{\text{D}} = \sum C_{\text{L}}^i \Delta \mu^i$ in Eq. (24). An argument in support of solute-drag is that the liquid atoms should crystallise at a rate determined by the driving force of crystallisation averaged over all the atoms on the liquid at the interface [4]. This opinion is also hold in [30]. However experimental work on Si-9at% As alloys [15,16] indicates that at least in this system, solute-drag does not play an important role. Thus in this paper we consider only the case without solute-drag.

We now give an approximate expression of the second response-function for dilute solutions. Applying basic thermodynamics, Eq. (25) can be transformed into

$$\Delta G_{\text{DF}} = RT \sum_{i=1}^n C_{\text{S}}^i \ln \left(\frac{k_{\text{V}}^i}{k^i} \right) + \sum_{i=1}^n C_{\text{S}}^i \ln \left(\frac{\gamma_{\text{S}}^i(T, C_{\text{S}}^i) \gamma_{\text{L}}^i(T, C_{\text{L},e}^i)}{\gamma_{\text{L}}^i(T, C_{\text{L}}^i) \cdot \gamma_{\text{S}}^i(T, C_{\text{S},e}^i)} \right). \quad (29)$$

For a dilute solution which contains mainly the \hat{i} th component, Eq. (29) gives

$$\Delta G_{\text{DF}}/RT = C_{\text{S}}^{\hat{i}} \ln \left(\frac{k_{\text{V}}^{\hat{i}}}{k^{\hat{i}}} \right) + \sum_{j=1, j \neq \hat{i}}^n C_{\text{S}}^j \ln \left(\frac{k_{\text{V}}^j}{k^j} \right). \quad (30)$$

This expression was formulated for a binary system in 1971 by Baker and Cahn [5]. As the sum of components is equal to one and as $\ln(z) \rightarrow (z - 1)$ for $z \rightarrow 1$, the following approximation gives

$$C_{\text{S}}^{\hat{i}} \ln \left(\frac{k_{\text{V}}^{\hat{i}}}{k^{\hat{i}}} \right) \approx \sum_{j=1, j \neq \hat{i}}^n (C_{\text{L},e}^j (k^j - 1) + C_{\text{L}}^j (1 - k_{\text{V}}^j)). \quad (31)$$

Here we have disregarded the second order terms by setting the prefactor of the logarithm, $C_{\text{S}}^{\hat{i}}$, equal to one. With this approximation Eq. (30) gives

$$\Delta G_{\text{DF}}/RT \approx \sum_{j=1, j \neq \hat{i}}^n \frac{(1 - k^j)}{m^j} (m_{\text{V}}^j C_{\text{L}}^j - m^j C_{\text{L},e}^j), \quad (32)$$

where

$$m_{\text{V}}^j := m^j \cdot \frac{1 - k_{\text{V}}^j + k_{\text{V}}^j \ln(k_{\text{V}}^j/k^j)}{(1 - k^j)} \quad (33)$$

is called the “kinetic” slope of the liquidus plane in the “ j -direction”. Applying the linear approximation of Eq. (26) $\Delta G_{\text{DF}}/RT = -V/V_0$, together with Eq. (32) results in

$$V/V_0 \approx \sum_{j=1, j \neq \hat{i}}^n \frac{(1 - k^j)}{m^j} (m^j C_{\text{L},e}^j - m_{\text{V}}^j C_{\text{L}}^j). \quad (34)$$

A comparison of Eqs. (28) and (34) shows that for n components, despite considering a dilute system, T and V cannot be coupled analytically. This is only possible for binary systems ($n = 2$) where the following relation results from this comparison

$$T = T_f + m v C_L + \frac{m}{1-k} \frac{V}{V_0}. \quad (35)$$

This equation was derived by Boettinger and Coriell in 1986 [17].

Notice that for $C_L \rightarrow 0$ Eq. (35) gives $V = \mu \cdot (T_f - T)$ with $\mu = -m / ((1-k) V_0) = -RT_f / (\Delta S_f V_0)$. In the last equation the Van't Hoff law was used. $\Delta T_k =: (T_f - T) = V / \mu$ is known as kinetic undercooling. Eq. (35) states that the interface temperature can be calculated by reducing the “actual” liquidus temperature at the interface by kinetic undercooling. Following the argumentation given above, this statement is not correct for non-dilute binary and arbitrary n -componental systems.

2.3. Response-functions for curved interfaces

We now turn to n -componental systems with curved solid/liquid interfaces. According to Mullins [25] and Trivedi [26] the chemical potential of the i th component in the solid at the interface is given as

$$\mu_S^i|_{K \neq 0} = \mu_S^i|_{K=0} + v_{\text{mol}}^i \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \varphi^2} \right) K_2 \right]. \quad (36)$$

Here γ is the anisotrope solid/liquid surface tension which depends on two independent angles θ and φ . v_{mol}^i is the molar volume of the i th component. K_1 and K_2 are the two main curvatures at the considered interface position. The difference in chemical potential of the i th component between the solid and liquid in this case is

$$\Delta \mu^i|_{K \neq 0} = \Delta \mu^i|_{K=0} + v_{\text{mol}}^i \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \varphi^2} \right) K_2 \right] \quad (37)$$

and thus the difference in the corresponding redistribution potentials is

$$\Delta \tilde{\mu}^i|_{K \neq 0} = \Delta \tilde{\mu}^i|_{K=0} + v_{\text{mol}}^i \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \varphi^2} \right) K_2 \right]. \quad (38)$$

With this equation the partitioning parameters defined by Eq. (18) changed to

$$\kappa^{i,j}|_{K \neq 0} = \kappa^{i,j}|_{K=0} \cdot \exp \left(- \frac{(v_{\text{mol}}^j - v_{\text{mol}}^i) \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \varphi^2} \right) K_2 \right]}{RT} \right). \quad (39)$$

In this paper it is assumed that the atomic volume is approximately equal for all components, and therefore the argument of the exponential function in Eq. (39) is zero. Thus the partitioning parameters, and with this the first response-functions, are equal for systems with flat and curved solid/liquid interfaces.

For the total difference of the free energy between the solid and liquid we obtain with Eq. (37)

$$\begin{aligned} \Delta G_{\text{DF}}|_{K \neq 0} &= \sum_{i=1}^n C_S^i \cdot \Delta \mu^i|_{K \neq 0} \\ &= \sum_{i=1}^n C_S^i \cdot \Delta \mu^i|_{K=0} + \left[\left(\gamma + \frac{\partial^2 \gamma}{\partial \theta^2} \right) K_1 + \left(\gamma + \frac{\partial^2 \gamma}{\partial \varphi^2} \right) K_2 \right] \sum_{i=1}^n C_S^i \cdot v_{\text{mol}}^i. \end{aligned} \quad (40)$$

With the assumption of equal atomic volumes and with $C_S^1 + \dots + C_S^n = 1$ this equation gives

$$\Delta G_{\text{DF}}|_{K \neq 0} = \Delta G_{\text{DF}}|_{K=0} + \Delta G_K \quad (41)$$

with $\Delta G_K := [(\gamma + \partial^2\gamma/\partial\theta^2)K_1 + (\gamma + \partial^2\gamma/\partial\varphi^2)K_2]v_{\text{mol}}$. Hence, we obtain for the growth rate

$$V = V_0 \cdot [1 - \exp(\Delta G_{\text{DF}}|_{K=0} + \Delta G_K)/RT]. \quad (42)$$

This is the second response-function of n -componental systems with curved solid/liquid interfaces.

The total difference in free energy between the solid and liquid in a system with curved solid/liquid interface is given as Eq. (41) and has been assumed previously by Brunco et al. [27,28] for dilute binary systems. Aziz commented upon this assumption in [29].

For $(\Delta G_{\text{DF}} + \Delta G_K) \ll RT$ the linear approximation of Eq. (42) holds and we thus obtain

$$V/V_0 = -\frac{1}{RT} \left(\Delta G_K + \sum_{j=1, j \neq \hat{i}}^n \Delta G_{\text{DF}}^j \right), \quad (43)$$

where

$$\Delta G_{\text{DF}}^j/RT := C_S^j \cdot \Delta\mu^j|_{K \neq 0} \quad (44)$$

represents the “weighted” driving force for interface motion due to the deviation from equilibrium of the j th component.

For a dilute n -componental system, Eq. (43) with Eq. (32) results in

$$V/V_0 = \frac{1}{RT} \left(-\Delta G_K + \sum_{j=1, j \neq \hat{i}}^n \frac{(1-k^j)}{m^j} (m^j C_{L,e}^j - m_V^j C_L^j) \right). \quad (45)$$

As in the case of a flat solid/liquid interface (Eq. (34)), it is not possible to combine this equation with Eq. (28) to obtain an analytical relation between T and V . This is only possible for dilute binary systems. Considering only one curvature $K_1 = K_2 = K$ and applying the Van't Hoff rule, Eq. (45) gives for binary systems

$$V/V_0 \approx \frac{\gamma + \partial^2\gamma/\partial\theta^2 + \partial^2\gamma/\partial\varphi^2}{RT} K v_{\text{mol}} + \frac{\Delta S_f}{RT} (T - (T_f + m_V C_L)) \quad (46)$$

and with Eq. (28)

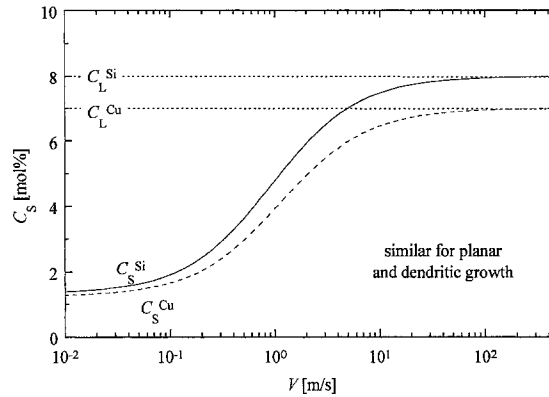
$$T = T_f + m_V C_L - V/\mu - \Gamma_{\theta,\varphi} K \quad (47)$$

with $\Gamma_{\theta,\varphi} := \Gamma + (\partial^2\gamma/\partial\theta^2 + \partial^2\gamma/\partial\varphi^2)v_{\text{mol}}/\Delta S_f$ [25]. $\Gamma := \gamma v_{\text{mol}}/\Delta S_f$ is the Gibbs–Thomson coefficient. $\Delta T_R := \Gamma K$ is called capillary or curvature undercooling [18].

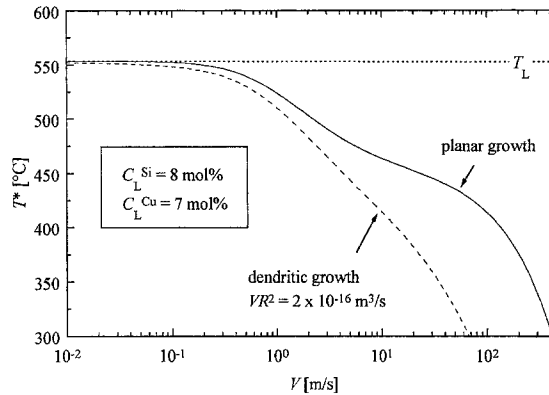
From Eq. (47) it is often assumed that for arbitrary alloy systems the actual interface temperature is given as the liquidus temperature at the interface minus “kinetic undercooling” and “curvature undercooling”. The derivation presented above shows that this assumption is not valid for non-dilute binary and arbitrary n -componental systems.

3. Results and discussion

Using the commercial thermodynamic software tool ChemAppTM, which allows the evaluation of $\mu_S^i(T, C_S^1, \dots, C_S^n)$ and $\mu_L^i(T, C_L^1, \dots, C_L^n)$ (as subroutine library in FORTRAN), we have solved the four-dimensional non-linear system of equations consisting of the three first response-functions (Eq. (20)) and the second response-function (Eq. (26) and/or Eq. (42)) for the ternary AlSiCu system. We have focused our attention especially on (i) the movement of the solid/liquid interface for different velocities, and (ii) a spherical crystal with different stationary



(a)



(b)

Fig. 3. (a) Solid concentrations at the interface as a function of growth velocity for an alloy in the ternary AlSiCu system. The shape of the curves is similar for planar and dendritic growth. (b) Interface temperature as a function of growth velocity for a planar interface (full line) and a dendrite tip (broken line).

sizes within the melt ($V = 0$). We have performed our calculation for $C_L^{Si} = 8 \text{ mol\%}$ and $C_L^{Cu} = 7 \text{ mol\%}$ and used $V_D = 1 \text{ m/s}$ and $V_0 = 10^3 \text{ m/s}$.

The movement of the solid/liquid interface for different velocities was calculated for a planar front and for the tip of a dendrite. In the latter case we have assumed that: (i) the tip has the shape of a paraboloid of revolution; (ii) anisotropy of surface tension can be disregarded; and (iii) $V^2 \cdot R$ is constant with $V \cdot R^2 = 10^{-14} \text{ m}^3/\text{s}$. Solving the diffusion problem around a growing dendrite tip in the considered ternary alloy system exactly is beyond the scope of this paper. On the other hand, the scaling law of the constancy of $V \cdot R^2$ is well established [18]. The assumed nominal value of $10^{-14} \text{ m}^3/\text{s}$ for this constant is correct for Al 0.165wt.% Cu and may only give an order of magnitude approximation for the considered ternary alloy. However, we believe that the basic differences in the prediction of the presented model for the growth of a flat and a dendritic interface shape will be covered by this value. From the three assumptions for dendritic growth we obtain $\Delta G_K = (2\gamma v_{\text{mol}} V^{1/2}/10^{-7}) \text{ s}^{1/2}/\text{m}^{3/2}$,³ which was used in the second response-function (Eq. (42)).

³ Here we used $\gamma = 9.3 \cdot 10^{-2} \text{ J/m}^2$ and $v_{\text{mol}} = 1.1 \cdot 10^{-5} \text{ m}^3/\text{mol}$ [18].

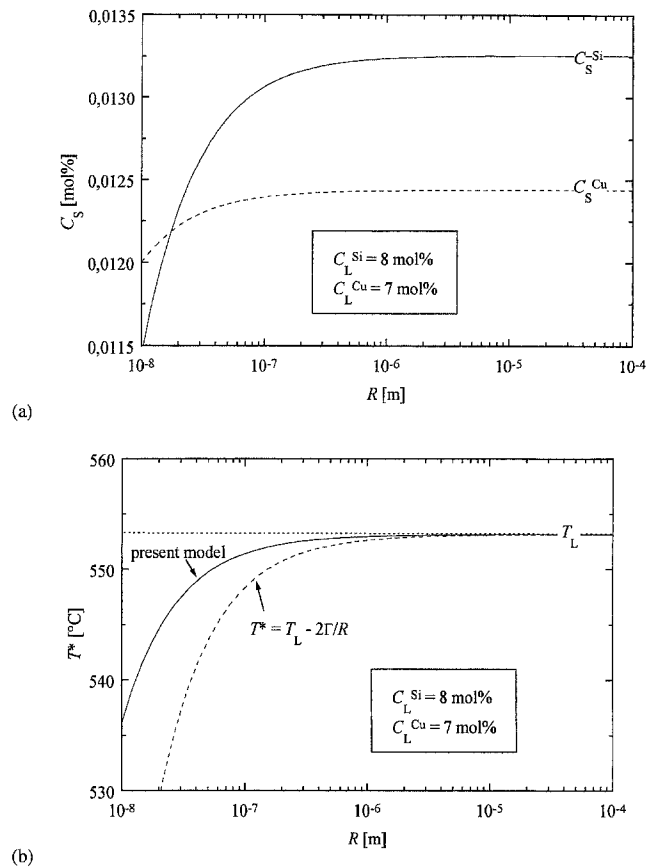


Fig. 4. (a) Concentrations in the solid at the interface as a function of the radius of a spherical crystal with $V = 0$ ("equilibrium") for an alloy in the ternary AlSiCu system. (b) Interface temperature as a function of the radius calculated from the present model (full line). The interface temperature resulting from applying the curvature undercooling expression is shown for comparison (broken line).

Fig. 3(a) shows the velocity dependence of C_S^{Si} , C_S^{Cu} and Fig. 3(b) that of T . For large V the solid concentration at the interface increases until the nominal liquidus concentration is reached. Thus the model predicts full solute trapping for sufficiently large growth velocities. The reason for both curves in Fig. 3(a) having a similar shape is the use of the same V_D for both components. This is, in fact, a result of the assumption that the activation barrier Q_D is equal for each redistribution process across the interface. Although it is not clear what determines different Q_D 's, it is conceivable that different alloy components can be trapped at different growth velocities. This could formally be represented by different V_D 's. Considering the diffusion theory for multi-componental systems for the evaluation of the Q_D 's, the present model can probably be refined.

Fig. 3(b) shows that the interface temperature decreases as the concentrations increase. For full solute trapping a change in the slope of the T - V relation can be seen. The decrease of the interface temperature with velocity is so high for the considered alloy that a change in the diffusivity is expected and thus temperature-dependent V_D 's should be considered to describe the process realistically (which is not done in the presented example).

The curvature effect taken into consideration for the growing dendrite tip does not influence the solid concentration, and affects the interface temperature (tip temperature) clearly, as can be seen in Fig. 3. The tip temperature, represented by the broken line in Fig. 3(b), is below the interface temperature for the planar front, as expected from the dilute binary alloy.

To evaluate the interface response-functions for spherical crystals with different stationary sizes within the melt ($V = 0$), we have assumed that the curvature is simply given as $K = 2/R$. Fig. 4 shows the solid concentration and the interface temperature as a function of R . The model predicts that the presence of a curved solid/liquid interface affects C_L^{Si} , C_L^{Cu} and T simultaneously. Applying the widely used Gibbs–Thomson formulation, the concentrations at the interface should not be influenced and the interface temperature should be given as $T_R = T_L - 2\Gamma/R$. Δs_f is the entropy of fusion per volume. For comparison the “Gibbs–Thomson” interface temperature is also given in Fig. 4(b).⁴ Obviously, as the Gibbs–Thomson formulation describes the deviation from equilibrium (flat interface) only by a temperature reduction, it overestimates the real “curvature undercooling”. Instead, curvatures lead to a deviation from equilibrium by affecting “all available” quantities.

4. Conclusions

For an n -componental alloy system the solid/liquid interface reacts to a deviation from thermodynamic equilibrium by a displacement of the interface position accompanied by a redistribution of solute across the interface. This reaction is expressed by $(n + 1)$ response-functions, which correspond to the general form

$$C_S^i = f_1^i(T, V, C_L^1, \dots, C_L^n, C_S^1, \dots, C_S^n), \quad \text{where } i = 1, \dots, n \quad (48)$$

and

$$V = f_2(T, C_L^1, \dots, C_L^n, C_S^1, \dots, C_S^n, K). \quad (49)$$

Analogue to the binary case, we have named Eq. (48) first response-functions and Eq. (49) second response-function.

In the present paper we have derived analytical expressions for these response-functions with and without curvature effects (Eqs. (20), (26) and (42)). It is shown that for dilute binary alloys, the first response-function gives the $k_V(T)$ -expression from the model of Aziz and Kaplan [4]. The second response-function gives for dilute binary alloys in case of flat interfaces the expression for the interface temperature derived by Boettinger and Corriell [17] and in case of a curved interface to the same expression combined with $\Delta T_R = 2\Gamma/R$.

For non-dilute binary and any arbitrary multi-componental alloy systems it is not possible to resolve the response-functions to yield an analytical expression for the T – V relation. Thus, it is not appropriate to use a kinetic undercooling term ($T_k = V/\mu$) and a curvature undercooling term ($\Delta T_R = 2\Gamma/R$) in these general cases.

Instead the T – V relation and the C_S^i – V relations ($i = 1, \dots, n$) can only be evaluated by solving an $(n + 1)$ -dimensional nonlinear system of equations whereby on-line use of thermodynamic information is necessary. Examples of such calculations are given for an alloy of the AlSiCu system. The presented model describes partially and fully solute trapping for flat interface growth and for dendritic growth. In addition for a stationary spherical crystal, the curvature of the solid/liquid interface affects not only the interface temperature, but also the solid concentration of the different components.

Acknowledgements

The author is grateful to K. Greven for his assistance in programming the thermodynamic subroutines.

⁴ We have used $\Gamma = 2.4 \cdot 10^{-7}$ Km [18].

References

- [1] J.W. Christian, *Theory of Transformation in Metals and Alloys*, Pergamon Press, Oxford, 1975.
- [2] J. Frenkel, *Phys. Z. Sowjet.* 1 (1932) 498.
- [3] H.A. Wilson, *Phil. Mag.* 50 (1900) 328.
- [4] M.J. Aziz, T. Kaplan, *Acta Metall.* 36 (1988) 2335.
- [5] J.C. Baker, J.W. Cahn, in: *Solidification*, ASM, Metals Park, Ohio, 1971, p. 23.
- [6] J.W. Cahn, S.R. Coriell, W.J. Boettinger, in: C.W. White, P.S. Peercy (Eds.), *Laser and Electron Beam Processing of Materials*, Academic Press, New York, 1980, p. 89.
- [7] K.A. Jackson, G.H. Gilmer, H.J. Leamy, in: C.W. White, P.S. Peercy (Eds.), *Laser and Electron Beam Processing of Materials*, Academic Press, New York, 1980, p. 104.
- [8] M.J. Aziz, *J. Appl. Phys.* 53 (1982) 1158.
- [9] M.J. Aziz, J.Y. Tsao, M.O. Thompson, P.S. Peercy, C.W. White, *Phys. Rev. Lett.* 56 (1986) 2489.
- [10] M.J. Aziz, C.W. White, *Phys. Rev. Lett.* 57 (1986) 2675.
- [11] P.M. Smith, R. Reitano, M.J. Aziz, *Mater. Res. Soc. Symp. Proc.* 279 (1993) 749.
- [12] M. Hillert, B. Sundman, *Acta. Metall.* 24 (1976) 731.
- [13] J. Agren, *Acta. Metall.* 37 (1989) 181.
- [14] B. Jönsson, J. Agren, J. Less, *Common Metals* 145 (1988) 153.
- [15] J.A. Kittl, M.J. Aziz, D.P. Brunco, M.O. Thompson, *Appl. Phys. Lett.* 64 (1994) 2359.
- [16] J.A. Kittl, M.J. Aziz, D.P. Brunco, M.O. Thompson, *Mat. Res. Soc. Symp. Proc.* 398 (1996) 119.
- [17] W.J. Boettinger, S.R. Coriell, in: P.R. Sahm, H. Jones, C.M. Adams (Hrsg.), *Science and Technology of Undercooled Melt Martinus*, Nijhoff Publications, Dordrecht, 1986, p. 81.
- [18] W. Kurz, D. Fisher, *Fundamentals of Solidification (3. Auflage)*, Trans Tech Publications, Aedermannsdorf, Schweiz, 1992.
- [19] D.H. Vineyard, *J. Phys. Chem. Solids* 3 (1957) 121.
- [20] K.A. Jackson, in: N.B. Hannay (Hrsg.), *Treatise on Solid State Chemistry*, Bd. 5, Plenum, New York, 1975, p. 233.
- [21] D. Turnbull, *J. Phys. Chem.* 66 (1962) 609.
- [22] M.J. Aziz, W.J. Boettinger, *Acta. Metall.* 42 (1994) 527.
- [23] D. Turnbull, *J. Appl. Phys.* 21 (1950) 1022.
- [24] R. Willnecker, D.M. Herlach, B. Feuerbacher, *Phys. Rev. Lett.* 62 (1989) 2707.
- [25] W.W. Mullins, in: *Metal Surfaces: Structure, Energetics and Kinetics*, ASM, Metals Park, OH, 1963, p. 44.
- [26] R. Trivedi, in: H.I. Aaronson (Hrsg.), *Lectures on the Theory of Phase Transformations*, Trans. Metall. Soc. of AIME, New York, 1975, p. 51.
- [27] D.P. Brunco, Thesis, Cornell University, Ithaca, New York, 1995.
- [28] D.P. Brunco, M.O. Thomson, D.E. Hogle, M.J. Aziz, *Mater. Res. Soc. Symp. Proc.* 1995, p. 354.
- [29] M.J. Aziz, *Metall. Trans. A* 27 (1996) 671.
- [30] B. Caroli, C. Caroli, B. Roulet, *Acta. Metall.* 34 (1986) 1867.