Simulation Based Study of Solidification in Aluminum-Silicon System

SIMULATION BASED STUDY OF SOLIDIFICATION IN ALUMINUM-SILICON SYSTEM

BY

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A Thesis

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Abstract

Using molecular dynamics (MD) and boundary element method (BEM), different aspects of solidification in the aluminum silicon system are studied. The angular embedding atom model (AEAM) was implemented on LAMMPS, and the necessary potentials are developed. Firstly, a modified version of the Stillinger-Weber (SW) interatomic potential for pure Si is proposed. The advantage of this potential is that, in contrast to the original SW form, the modified version allows one to grow diamond cubic crystal structures from the melt at high temperatures. Additionally, an Al-Si binary potential of the AEAM type is able to accurately predict the experimental enthalpy of mixing. It is also able to predict an Al-Si phase diagram with a eutectic concentration for the liquid that agrees with experiment within 4 at% and a eutectic temperature that differs from experiment by only 13 K.

Considering the importance of step mobility and step free energy on the solidification growth rate, chapters 3 and 4 are devoted to calculation of these concepts using MD simulations. In chapter 3 the step mobility, which is the proportionality constant between the velocity and driving force, was determined for the alloy with melt composition of Al-90%Si as a function of temperature and composition. It was found that mobility decreases fairly rapidly with the addition of Al solute. Also, from the variation with temperature, it appears the mobility is proportional to the interdiffusion coefficient in the liquid. It is observed that for the Al-60%Si alloy diffusion-controlled growth is the dominant scenario, even for a few degrees of undercooling.

In chapter 4 equilibrium molecular dynamics (MD) simulations and the capillaryfluctuations method (CFM) are employed to calculate crystal-melt step free energies at three different melt compositions. Anisotropy of steps are investigated by setting up the systems with different crystal orientations of steps on the high-symmetry interface plane, (111) in this case. A complete isotropy of step free energy is observed for Al-60%Si and Al-90%Si alloying systems, while CFM failed in determining step free energy in Al-30%Si due to lack of step roughness.

In chapter 5 the BEM is utilized to numerically compute the concentration profile in a fluid phase in contact with an infinite array of equally spaced surface steps. In addition, under the assumption that step motion is controlled by diffusion through the fluid phase, the growth rate is computed and the effect of step spacing, supersaturation and boundary layer width is studied. BEM calculations were also used to study the phenomenon of step bunching during crystal growth and it is found that, in the absence of elastic strain energy, a sufficiently large perturbation in the position of a step from its regular spacing will lead to a step bunching instability.

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Chapter 1

Introduction

Continually rising energy prices have inspired increased interest in weight reduction in the automotive and aerospace industries, opening the door for the widespread use and development of lightweight structural materials. Chief among these materials are cast Al-Si alloys which represent over 80 percent of all Al cast alloys and are used extensively in pistons, cylinders and engine blocks in automotive and aerospace applications [12]. Utilization of Al-Si alloys depends on obtaining a modified fibrous microstructure instead of the intrinsic flake structure of silicon dendrites. Recent experiments show unanticipated new behaviours in the modified alloying system [4], and the relevance and interest in understanding the underlying physics has increased with these events. It has been reported that in cast Al-Si alloys the morphology of the nearly pure Si phase has a dramatic effect on the mechanical properties [4]. For slow cooled products a needle or plate shaped Si morphology is produced, which results in low ductility and low tensile strength. By contrast, for fast cooled directionally solidified material or for cast products with the addition of small amounts of certain

elements, most notably Na and Sr, the Si phase adopts a fibrous form and the toughness, strength and ductility is increased substantially [13]. Although the plate to fibre transition has been studied for several decades the exact mechanisms controlling the morphology are not fully understood and several nucleation based and growth based models have been proposed. The objective of the this work is to utilize classical molecular dynamics (MD) and boundary integral method (BEM) simulations, to investigate, for the first time, the atomic processes taking place at a solidifying Si-liquid alloy interface. A quantitative description of the crystallization process derived from MD simulations will provide important insights into the flake to fibre transition and will help to reconcile the many models of the morphological transition that have been proposed. To reach this goal an interatomic potential that can explain interactions between atoms is developed. In the next step the atomic mechanisms taking place at the Si-liquid interface in Al-Si, mainly step kinetic coefficient and step free energy, are investigated. Classical molecular dynamics simulations will examine growth processes of Si crystals from the melt and the results will shed light on the phenomenon of quench modification.

1.1 Literature Review

Aluminum is known for having high corrosion resistance, low density, and high relative abundance. Although extremely soft and ductile as pure metal, aluminum can achieve significant strength levels when alloyed.

Aluminum-Silicon alloy is one of the most important aluminum based systems, forming the irregular eutectic at 12.6 wt% Si at 577°C. Irregular eutectics such as Fe-C and Al-Si grow with non-isothermal solid-liquid interfaces. In other words, solubility of aluminium in silicon phase is almost zero and pure silicon dendrites form during solidification process. Products of irregular eutectic transformation exhibit large spacings and under coolings [14]. Aluminum-Silicon alloy, with the composition range of 3-20% Silicon, is commonly used in the as-cast condition, eliminating the need for extensive post-cast processing. They are desirable for their superior castability, excellent corrosion resistance, low density, and good mechanical properties. The superior castability attributed to eutectic alloys are related to their relatively low solidification temperatures, high fluidity and small or nonexistent mushy zones. The excellent corrosion resistance is from surface passivation due to the strongly adherent oxide layers inherent to both aluminum and silicon. However, machinability and mechanical properties of this allow depend strongly on the mechanisms occurring during the solidification process. While the traditional flake morphology observed in pure Al-Si castings causes poor mechanical properties, a significant improvement in strength and ductility is obtained with microstructural modification. Microstructural modification techniques for Al-Si system can be classified into two main categories: i) Quench modification transition, ii) Trace elements addition. Both methods result in transition from bulky flake morphology to a more desirable fine fibrous morphology.

For better understanding the modification mechanisms it is necessary to understand the formation and growth of silicon dendrites in an unmodified system. It is considered in the first part of literature review (1.1.1). In the section 1.1.2, the branching phenomenon, which plays a crucial roll in Al-Si system, will be explained. Proposed mechanisms for explaining morphological modification will be reviewed for both quench modified and chemical modified systems in section 1.1.3 and 1.1.4. brief explanation about simulation techniques including MD and BEM will be presented in sections 1.2 and 1.3

1.1.1 Unmodified Silicon flakes formation and growth mechanism

Silicon has a diamond crystal lattice structure, which is due to the hybridization of s and p electrons and causes each atom to have four neighbours in order to form a tetrahedron [15]. (001) and (111) faces of semifical ductor including silicon, are used for growth. For such faces in specific directions, *terraces* separated by *steps* of atomic hight are observable. This type of separation is more observable for (111) planes. As it is shown in figure 1.1 these steps are not straight. They consist of straight parts separated by *kinks*. There are some surface vacancies known as *advacancies* which represent missing surface atoms. Crystal growth in diamond cubic structure



Figure 1.1: Schematic illustration of steps, kinks and advacancies in (111) faces.

is completely anisotropic. The growth rate in the normal direction to the closest packed (111) planes is slowest. Therefore, there is a strong tendency for the other less close-packed planes to grow until the crystal surface consists only of (111) facets

[16]. Growth of relatively long lath-like dendrites of silicon from undercooled melt, presence of a (111) twinned structure, appearance of well developed $\{111\}$ habit faces, the unlimited propagation of the lattice in the $\langle 211 \rangle$ direction and the tendency for branching in other coplanar $\langle 211 \rangle$ directions have been observed decades ago [17]. At a very early steps of crystal growth, silicon tetrahedra which is shown in figure 1.2(a) forms in the melt [18]. These tetrahedrons start aggregating and the subsequent crystal form depends on the participation of these tetrahedrons. Aggregation results in formation of embryos. An appropriate form of embryo is an assembly of two tetrahedra, as in figure 1.2(b). If this grows to critical nucleus size by attachment of single silicon atoms to the surfaces the faces can develop into favourable low energy $\{111\}$ facets while the central mirror plane becomes a $\{111\}$ twin plane. If many embryos such as figure 1.2(b) exist in the melt near the liquidus temperature, it can be expected that some will attach to nucleant particles in the melt and grow to critical size. The double tetrahedron shape is not ideal for minimizing surface area and the surface-to-volume ratio can be further reduced as the nucleus grows if the two apices are truncated to produce a more nearly spheroidal shape. As in figure 1.2(c), planes parallel to the central twin plane would form readily, preserving the advantage of low energy facets.

These new surfaces form suitable points of attachment for additional silicon tetrahedra from the melt, forming twin planes parallel to the first.

If two or more twin planes form in this way the condition is established for formation of a twin plane re-entrant edge, which was considered as the fundamental concept for explaining the growth mechanism of facetted crystal in crystal-melt interface. This mechanism was first proposed by Hamilton in 1960, identified in the crystal growth of



Figure 1.2: a) Individual silicon tetrahedron form in liquid. b) Silicon tetrahedra with {111} mirror plane. c) Truncated tetrahedra at later stage growth

germanium [1]. Regarding to structural similarities between germanium and silicon, this mechanism was expanded to silicon as well. According to this mechanism, two {111} planes of Si intersecting at a twin form a corner, which acts as a heterogeneous nucleation site for the subsequent formation of new atomic planes. It results in rapid growth along <211> directions within the twin plane. This mechanism is known as Twin Plane Re-entrant Edge (TPRE). Based on this mechanism at least two twin planes must be present in order to growth from these leads to a preferred directions of continuous propagation and branching. Figure 1.3 shows how this mechanism can explain preferred nucleation sites and crystal growth.

Another aspect that was the subject of discussion has been the effect of inclusions and impurities. Shankar et al. [19] proposed that, in commercial aluminium-silicon foundry alloys invariably contain some amounts of iron, which play an important role in the nucleation of the eutectic phases in these alloys. Relatively high iron contents promote formation of the iron containing $\beta(Al, Si, Fe)$ phase [2]. In unmodified hypoeutectic AlSi alloys, eutectic silicon nucleates on these $\beta(Al, Si, Fe)$ particles before the nucleation of eutectic Al, and this results in free growth of silicon into the eutectic liquid with its typical plate like morphology. They proposed that nucleation of the



Figure 1.3: a) A crystal containing two twin planes is found to have six of the favourable reentrant sites. b) The growth cycle in part (a) at the original re-entrant corners is completed by growth from the new re-entrant corner. c) Nucleation events (I) at two of the six reentrant corners. Growth from there has resulted in the development of the new corners marked (II). d) By allowed an increased nucleation rate, a solid is obtained in which many steps are growing at once [1].

eutectic phases in Al-Si hypoeutectic alloys proceeds as illustrated schematically in figure 1.4a-d. During solidification, the primary aluminium phase forms as dendrites at the liquidus temperature of the alloy. This is followed by the evolution of a secondary β (Al, Si, Fe) phase at some temperature between the liquidus temperature and the eutectic temperature of the alloy depending on the concentration of Fe in the alloy. At the eutectic temperature, and at an undercooling of $0.4 - 0.8^{\circ}C$, eutectic silicon nucleates on the secondary β (Al, Si, Fe) phase in the solute field ahead of the growing aluminium dendrites. Once nucleated, the eutectic silicon grows as flakes into the eutectic liquid. The liquid surrounding the eutectic silicon flakes become enriched with aluminium as it is being depleted of silicon; consequently, eutectic aluminium



nucleates and grows on the edges and tips of the eutectic.

Figure 1.4: Sequence of events during nucleation of eutectic phases in AlSi hypoeutectic alloys: (a) growth of Al dendrites, (b) Nucleation of β (Al, Si, Fe) phase, (c) nucleation of eutectic Si on the β (Al, Si, Fe) phase in the solute field ahead of the primary aluminum, nucleation of eutectic Al on eutectic Si, and growth of eutectic Al; (d) impingement of dendrites and eutectic Al grains resulting in arrest of the growth of dendrites and further nucleation and growth of the eutectic phases. [2].

1.1.2 Branching phenomenon

Branching phenomenon was another concept which was first explained by Kobayashi and Hogan [3]. They did one of the most comprehensive crystallographical studies on modified and unmodified silicon crystals in Al-Si alloy. It has been observed that a given silicon plate usually grows straight for some distance, then may branch or change direction through a large angle, in response to local conditions at the growth interface which occur by multiple twinning. Figure 1.5(a) shows all the possible crystal growth directions for a specific crystal plane. Figure 1.5(b) illustrates $\{111\}$ which have formed due to special attachment of tetrahedrons. The geometry of tetrahedra dictates the form at the edges and angle between the crystal layers. if {111} planes are exposed at the growing tip, they would necessarily form the 141° re-entrant angle shown, which is the condition for TPRE growth in the <121> direction. Base on Hogan research, the plates tend to thicken in places by addition of a further twinned layer, which would form the 109.5° growth step shown in figure 1.5(c). The original crystal with alternate twins A and B branches by twinning at a {111} plane to give a 70.5° direction change. The branch contains two crystal B and C in twin relationship. Branching might start by nucleation of twinned crystal B on A and subsequent formation of the crystal C in twin relationship with B. Branching cause the space between crystal tips to increase, therefore diffusion distance between silicon growth tips increase and they claimed that this is the driving force of Branching phenomenon. In addition, regarding to the fact that growth direction of silicon fibers in impurity modified alloy is (100) and (110) but rarely (121), they concluded that growth is unlikely to be by the TPRE mechanism.

Experimental observations and scientific explanations, clarified that twin density has a significant role in crystal growth and final morphology of the dendrites. Therefore, establishing methods for increasing twin density, modification of microstructure and more sophisticate explanation of the mechanisms were aimed subsequently.



Figure 1.5: Schematic drawings of growth mechanisms in flake-type eutectic silicon. Possible nucleation points for the eutectic aluminium phase are indicated [3].

1.1.3 Quench modification transition

Modification of Al-Si eutectic promotes change from coarse flake eutectic silicon to a fine fibrous form by fast cooling exceeding above 400 $\mu m s^{-1}$. Figure 1.6 illustrates the transition from flake to fibrous morphology by increasing the cooling rate, observed by Hosch. et al. [4]. Microstructural modification results in improved mechanical properties and as they reported in table 1.1, the ultimate tensile strength (UTS) increases by 37% with solidification rate over the full range of experiment. Additionally, they found that elongation reaches rapidly to a maximum although a sudden decrease is observed at very high cooling rates. Base on their study, influence of solidification velocity on mechanical property is directly correlated with the average eutectic spacing.



Figure 1.6: Al-Si eutectic structures after directional solidification at velocities of 20, 250, and 950 μ m/s. These structures represent flake (left), mixed flake/fibre (center), and fibre (right) morphologies, respectively [4].

Table 1.1: Tension tests performed on Al-Si eutectic samples solidified at different velocities [4].

V ($\mu m/s$)	UTS (MPa)	El (%)
20	162	8.7
80	179	15
250	190	17.6
600	207	23.8
1000	222	12.5

Early modification studies [20, 21] concluded that course-fine transition is related to massive increase in the density of twins in the silicon phase with progressive refinement of the eutectic. However, another set of studies [22, 23] revealed that this is not the case when Al-Si eutectic is quenched modified. Transmission electron microscopy observations indicates that the density of twins in quenched-modified silicon dendrites is very low and even some of them are twin free. Another theory proposed by Jackson [24] suggested that in quench modification the transition in shape occurred because isotropic growth is dominant at high undercoolings. This is probably due to transition from faceted to non-faceted behaviour. Khan and Elliot [25] performed directional solidification experiments on Al-Si at growth velocities as high as 1000 μ m/s. The authors observed that the flake to fibre transition was accompanied by a drop in undercooling and the measured velocity vs spacing relationship was similar to that of normal eutectics. It was concluded that the flake to fibre transition is associated with a change from faceted to non-faceted behaviour of the crystal-melt interface. They proposed that quench-modified fibres retain the characteristics of flakes refined by a large undercooling. However, the twin density is slightly higher than for flakes.

1.1.4 Chemical Modification mechanisms

The other modification method, that has been used extensively industrially since about the 1970's, is addition of some elements, most notably strontium (Sr), sodium (Na) and antimony (Sb), to Al-Si alloys. Sr known as the most effective addition. Figure 1.7 illustrates the effect of Sr on microstructure of the alloy [5].

Kazuhiro et al. [26] reported that morphology of silicon dendrites in alloys contain 50-150 ppm Sr changes from course plate-like structure to fine fibrous rod-like one. They observed a significant improvement of mechanical properties of modified alloy as a result of eutectic structure refining. However, they mentioned that for high Sr level (Sr>700ppm), porosity characteristics alter and mechanical properties can not improve furthermore.

Several theories have been proposed to explain the chemical modification mechanism. Basically there are six classes of theories about the mechanism of chemical


Figure 1.7: Optical micrographs of Al-10 wt.% Si alloy showing a eutectic microstructure: (a and b) unmodified alloy, (c and d) alloy modified by 200 ppm Sr [5]. A clear change in the size of pure silicon dendrite and transition from plate-like to fibrous one is observed as a result of adding a trace of Sr.

modification as follows;

1) restricted growth theory: In a classic model of chemical modification, Lu and Hellawell [27] observed that normal flake silicon grows anisotropically and has low twin density while quench modified fibrous silicon is essentially twin free and grows isotropically which cause a non-faceted dendritic growth. in addition, for the case of a sodium modified silicon, which contains a very high twin density and faceted fibres, TPRE is the dominant growth mechanism. They claimed that the impurity modifiers poison steps by accumulation of add-atoms at sufficient density to create a "traffic problem", which cause the step sources being temporarily halted. However, a question arises that why continued propagation should be in a twin configuration after reactivation of a pinned step? In another research they [28] explained that impurities with a large atomic size relative to the radius of a Si atom that has segregated to the growth interface can force newly deposited Si atoms onto unfavourable sites on the (111) plane. In particular, a large Sr or Na atom will push, for example, C type atoms onto A sites in the normal ABCABC stacking of (111) planes and, therefore, will trigger the formation of a new twin variant. Lu and Hellawell argue that the most favourable radius ratio of impurity to Si is 1.65 and qualitatively the model is consistent with experiment as the potent modifiers Sr and Na are close to the ideal ratio.

In 2004 Nogita, McDonald and Dahle [29] studied the solidification of Al-Si with the separate addition of 14 rare earth elements, each with an atomic size ratio close to the ideal value. In only one instance (Eu) was Si modification observed. Based on their observation that elements within the range of radii, mentioned by Lu-Hellawell, behave differently they concluded that the criterion is insufficient on its own to determine and predict the effectiveness of a modified element and further developments of the modification mechanism are required.

2) Ternary eutectic theory: Hedge [30] considered this problem as a complete thermodynamic problem. He showed that sodium forms a ternary alloy with aluminum and silicon and hypothisised that the regular morphology of this ternary eutectic is the morphology that is observed in modified system.

3) Restricted nucleation theory: In 1991, Qiyang and co-workers [31] proposed that conventional Na additions enhance the activity of aluminum, causing it to nucleate at a higher temperature and to develop into primary phase. Eutectic aluminum grows epitaxially from Al without need for re-nucleation. Na adsorbs on the twin reentrant groove or growing surfaces of eutectic Si. By neutralizing part of the hanging bonds on the Si surface and causing structural discontinuity of the Si crystal lattice, the adsorption of Na will decrease the activity of the growing surface of Si. Thus, Na will poison the Si embryos during eutectic nucleation and restrict the Si growth during eutectic growth.

In another study, Nogita and Dahle [26] employed electron backscattered diffraction (EBSD) to examine crystallographic orientation relationships in unmodified Al-Si and alloys modified with 70ppm Sr. They compared the orientation of the aluminum in the eutectic to that of the surrounding primary aluminum dendrites and determined the growth mode of eutectic. Based on mapping results, they claimed that in unmodified alloys the eutectic grows from the primary phase and thus have the same orientation as the surrounding primary dendrite. It means that, in this case, aluminum dendrites are preferred sites for nucleation of eutectic aluminum. However, when the eutectic is modified by strontium, eutectic grains nucleate separately from the primary dendrites and there is no orientation relationship between the aluminum and the surrounding dendrites. In other words, the role of Sr lies in the nucleation mechanism and not in twin formation during growth. The authors argue that eutectic grains in Sr modified alloys are nucleated and grow in the interdendritic channels, totally independent of the primary phase where delayed nucleation will cause the Si to grow along the tortuous paths characteristic of the interdendritic region and to do so will require twin formation, whereas under rapid nucleation conditions the Si is allowed to grow freely in the melt. They believed that it is the only mechanism which can explain the porosity formation in Sr- modified alloy. In addition, they claimed that the other effect of modifying elements include Sr, Na and Eu is significant depression of the eutectic nucleation and growth temperatures. They counted this effect as the other reason of morphology variation in chemically modified Al-Si alloys.

4) Surface energy theory: Based on this theory, surface energy of aluminum-silicon changes in presence of modifier results in change in morphology of silicon eutectic dendrites. It was suggested that crystal growth rate depends on a balance between the rate of heat flow from the liquid to the solid through the interface and the latent heat of fusion released during solidification. For chemical modification, a decrease in surface energy of the aluminum-silicon solid interface upon the addition of the chemical modifier increases the interface angle. This in turn suppresses growth of the silicon crystal and causes modification of the eutectic structure and undercooling.

5) Diffusion control theory: This theory is based in the observation that solubility of sodium in solid aluminum and silicon are low [3]. This in turn, implies that sodium would segregate ahead of the growing interface, which could restrict the diffusion of silicon in the melt. Sodium reduces the diffusion rate of silicon, results in change in morphology of silicon.

6) Multi effect theory: In 2012 Timpel et al. [5] conducted very accurate APT(atom probe tomography is used for determination of concentration and phase distribution) and TEM observations in order to investigate the role of strontium in modifying Al-Si alloys. They claimed that contrary to main assumption of previous mechanisms include TPRE and impurity induced twinning mechanisms, modifying atoms can not be considered as individual atoms which have distributed homogeneously interacting with twins and dendrites. Therefore, they tried to determine strontium distribution and characterize its form and influence on microstructure of the alloy. They observed heterogeneous distribution of Sr that forms two types of co-segregations of Sr with Al or Si in eutectic silicon phase. Nano size segregations that form due to high density twinning during crystal growth in different crystallographic directions and courser segregations that restrict Si crystal growth and controls branching phenomenon. Earlier published results reported homogenous distribution of modifiers in the structure[26]. In addition, according to this study, geometrical size factor (atomic radius of impurity elements) which is known as the dominant parameter, does not play a major role and chemistry of co-segregation determines how effective a modifier is. Figure 1.8 illustrates size and position of segregations schematically.



Figure 1.8: Schematic representation of (011) plane projection of eutectic Si phase: (a) type I SrAlSi co- segregation which promotes twinning by changing the stacking sequence. (b) locations of type II Sr AlSi co-segregations within the eutectic Si phase at the re-entrant edges or growing surfaces [5].

7) Poisoning the inclusions: As it was mentioned in section 1.1.1 inclusions in a commercial Al-Si alloy play an important role on the nucleation of eutectic phase. Therefore, some researches focus on the interaction between the inclusions and modifiers. In chemically modified hypoeutectic Al-Si alloys, at the temperature near the end of solidification of the mushy zone, the modifier concentration in the eutectic liquid within the interdendritic regions reaches relatively high levels. The chemical modifier increases the viscosity of the eutectic liquid, therefore its surface tension, ahead of the Al dendrites. Thus, the growth of eutectic phase on the β (Al, Fe, Si) inclusion is halted resulting in a large number of equiaxed eutectic Al grains nucleating before nucleation of eutectic silicon, and hence, silicon is forced to grow in between the eutectic Al grains acquiring a fibrous, broom like morphology. This growth pattern is aided by silicons ability to twin easily and growth proceeds with the twin plane re-entrant edge mechanism [19]. However, Nogita et al. [32] questioned this theory and pointed out that apart from β phase other potent nuclei like AlP will be present for the silicon nucleation. To support their arguments Shankar et al. [33] performed experiments on low phosphorus containing alloys with different Fe content and observed that the solidification morphology changed with the Fe content.

In another research McDonald et al. [34] showed that the grain size in modified Al-Si is increased dramatically from the unmodified alloy and this observation is also consistent with the notion of fewer nucleation events. The authors suggest that Sr poisons the phosphorous based nucleants (AlP) present in the melt.

1.2 Molecular Dynamics

1.2.1 Theory of Molecular Dynamics

Molecular dynamics (MD) is a computer simulation of physical movements of atoms and molecules. The atoms are allowed to interact for a period of time, giving a view of the motion of the atoms. New positions of the atoms are determined with respect to Newton equation of motion with an interaction specified within a cutoff distance around each atom. For a system of N particles with coordinates x and mass of m, the following pair of first order differential equations may be written in Newton's notation as follows:

$$F(\vec{r}) = -\nabla E(\vec{r}) = m\ddot{x}(t) \tag{1.1}$$

where F is the force between the interacting atoms at distance r, E is the interatomic potential. For every timestep, each particle's position and velocity may be calculated. Based on Eq.1.1, as long as the interatomic potential field, the initial positions (e.g. from theoretical knowledge) and velocities (e.g. randomized Gaussian) are available, we can calculate all future (or past) positions and velocities. Therefore, the potential energy function is the basic and fundamental necessity of each MD simulation. Any potential energy function describing interactions among N analytical particles can be written in general as Eq.1.2, which includes 1-body two-body 3-body and higher order interactions.

$$E(1,\dots,N) = \sum_{i=1}^{N} \phi_1(i) + \sum_{i < j} \phi_2(i,j) + \sum_{i < j < k} \phi_3(i,j,k) + \dots + \phi_N(1,\dots,N) \quad (1.2)$$

where the first term represents the effect of external forces that for periodic boundary condition is zero and the higher orders interactions converge to zero very fast. According to the type of components of a system and the nature of bonding the global potential energy equation simplifies. A brief description of two major methods relevant to this study is given below.

1.2.2 Embedding Atom Method

Daw and Baskes introduced a semi-empirical, many-atom potential for computing the total energy of a metallic system in 1984 [35]. In this approach, they viewed the energy of the metal as the energy obtained by embedding an atom into the local electron density provided by the remaining atoms of the system. This method has enabled a semi quantitative and, in some cases, even quantitative investigation of many phenomena including point defects, melting, alloying, fracture, crystal growth and many others [36]. The energy of atom i in EAM method is given by Eq.1.3.

$$E_i = \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) + F_\alpha(\sum_{j \neq i} f_\beta(r_{ij}))$$
(1.3)

where F is the embedding energy which is a function of the partial electron density contribution f, ϕ is a pair potential interaction, and α and β are the element types of atoms i and j. The multi-body nature of the EAM potential is a result of the embedding energy term. Both summations in the formula are over all neighbors j of atom i within the cutoff distance.

1.2.3 Stillinger-Weber Potential

In 1984 Stillinger and Weber proposed a potential energy function comprising both two and three atom contributions to describe interactions in solid and liquid forms of Silicon [37]. Considering the fact that the Si crystal consists of atoms held in place by strong and directional bonds, their model approximated by the combination of pair and triple potentials as:

$$E_{i} = \frac{1}{2} \sum_{j \neq i} \phi_{2}(r_{ij}) + \sum_{j \neq i} \sum_{k>j} \phi_{3}(r_{ij}, r_{ik}, \theta_{ijk})$$
(1.4)

$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)$$
(1.5)

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \exp(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}}) \exp(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}})$$
(1.6)

where λ , ϵ , γ , σ and a are parameters. θ_0 is the ideal tetrahedral angle and $\cos \theta_0 = -\frac{1}{3}$, ϕ_2 is a two-body term and ϕ_3 is a three-body term. The summations in the formula are over all neighbours j and k of atom i within a cutoff distance equal to $a_{ij}\sigma_{ij}$. Figure 1.9 illustrates the variation of these potentials at different atomic distances and bond angles.



Figure 1.9: (a) Pair potential vs distance. (b) Three body potential with respect to distance and angle between bonds.

As is shown in figure 1.10, based on the SW potential, diamond structure is the preferred one in comparison with BCC, FCC and SC crystal structures and the lattice parameter is exactly the same as what is expected.

So far many simulations have been conducted using Stillinger-Weber potential which verified good agreement of the results of this potential with experimental results. For example Xu et al. [38] studied $Si_{(1-x)}Ge_{(x)}$ epitaxial growth on Si(100)



Figure 1.10: Lattice energy (per atom) vs number density in reduced unit base on Si potential for different crystal structures (simple cubic (SC), body-centred cubic (BCC), face-centred cubic (FCC) and diamond (DIA) crystal structure).

substrate and in a similar study Lampinen [39] and Zhang [40] studied Molecular beam epitaxy on a Si(100) substrate and determined the effects of substrate temperature and atomic species flux ratios on epilayer morphology utilizing the StillingerWeber potential. Buta et al. [8, 41], used classical MD and Stillinger-Weber potential to study the interface between the liquid and the (111) faceted, as well as vicinal, surface in pure Si. The simulations yielded an accurate value of the step kinetic coefficient, the growth rate vs undercooling for the step nucleation controlled growth of (111) and the atomic structure vs position through the interface. In a very recent study Hale et al. [42] simulated compression of silicon nanospheres with the Stillinger-Weber potential and observed several defects that cause the yielding, including dislocations, stacking faults and phase transformations [43]. Timonova [44] used the Stillinger-Weber potential to identify the atomistic details of relaxation and crystallization dynamics. This potential has been used to determine the heat conduction in silicon by Srinivasan [45] and in a similar study, Skye et al. [46] elucidate thermal transport in SiGe alloys. As an example of two component simulation Li et al. [47] employed the StillingerWeber three-body potential to simulate the silicon substrate and the Born-Mayer-Higgins potential to compute the interactions between Aluminum cluster and Silicon substrate and found interesting results about changing substrate temperature, cluster energy and cluster size.

1.2.4 Angular-EAM

Since the bonding in pure Al and pure Si is governed by very different mathematical formulation, it is not immediately obvious how the two approaches can be combined to develop an Al-Si alloy potential. However, in 2009, Dongare et al. [48] developed the angular-EAM (AEAM) interatomic potential model, which is specifically designed to model alloys of a metal species combined with a semiconductor (Si, Ge, etc). The lack of an explicit three body term in EAM, makes this model inappropriate for covalently bonded materials. Therefore, rewriting the equations in order to extract three-body term from the original EAM and retaining all the properties of the pure components as predicted by SW and EAM potentials was the main goal of this method. For this purpose, a linear sum of partial electron density contributions is used and is expressed through the sum of products of partial electron densities as below:

$$\rho_i = \left[\left[\sum_{j \neq i} f_j(r_{ij}) \right]^2 \right]^{\frac{1}{2}} = \left[\sum_{k \neq i} \sum_{j \neq i} f_j(r_{ij}) f_k(r_{ik}) \right]^{\frac{1}{2}}$$
(1.7)

The sum on the right-hand side of the above equation includes two-body terms with identical pairs of atoms (j=k) and three-body terms $(j\neq k)$ that was separated from each other. And finally they wrote the three-body terms in forms of a sum over unique triplets of atoms (i, j, k):

$$\rho_i = \left[\sum_{j \neq i} [f_j(r_{ij})]^2 + 2\sum_{j,k \in T_i} f_j(r_{ij}) f_k(r_{ik})\right]^{\frac{1}{2}}$$
(1.8)

where in the first(two-body) term under the square root the summation is over all atoms interacting with atom i and in the second (three-body) term the summation is over all pair of atom j and k that form unique triplets with atom i. Therefore, for an alloy system containing both metal and Si atoms, they formulated a combined potential that reduces to the conventional SW and EAM potentials for pure components as follows:

$$E_{i} = \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) + F_{\alpha}[[(1 - \delta_{i}) \sum_{j \neq i} f_{\alpha\beta}(r_{ij}) + c_{i} \sum_{j,k \in T_{i}} f_{j}(r_{ij}) f_{k}(r_{ik}) (\cos \theta_{ijk} - \cos \theta_{0ijk})^{2}]^{n_{i}}]$$
(1.9)

where δ_i , c_i and n_i are constants and depend on type of atom *i*. With respect to this formulation, they determined a number of properties of Au-Si alloy like ground state energy, cohesive energy, bulk modulus, enthalpy of mixing and phase diagram and the values predicted by the model agrees quite well with experiment. In addition, in 2012 Dongare et al. [6] proposed a potential for Al-Si system where all the calculated terms except the phase diagram are close to experimental measurements.

Considering the time and size scale of the simulation in Molecular Dynamics, which is nano second and nano meter respectively, simulations are very expensive computationally. Thus the first step of this project was implementing the AEAM method into the LAMMPS code. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is an open source classical molecular dynamics code and runs on single processors or in parallel using message-passing techniques and a spatial-decomposition of the simulation domain. Figure 1.11(a) shows simplified and basic algorithm that LAMMPS follows. Necessary codes for making crystal structure, determination of velocities, temperature, pressure and new position of atoms and printing the output are common for all potentials. Therefore, we needed to focus on calculation of forces and potentials regarding to AEAM potential that can be seen in figure 1.11(b). It was tried to develop LAMMPS very sophisticatedly and design in a way to minimize the computation costs. Forming the neighbour list and dividing the domain between the processors (link-cell binning) are two main issues that are considered in LAMMPS code. Therefore, developers of LAMMPS believe they have one of the fastest MD algorithms [49, 50]. In the combined method, atoms are only binned once every few timesteps for the purpose of forming neighbour lists. A shell around the interacting sphere is assumed and the new neighbour list forms when the movement of the atoms is more than the shell thickness. The other time saving method in many of MD codes including LAMMPS is based on Newton's third law by only computing a force once for each pair of atom rather than once for each atom in the pair. Since the cutoff distance of different atom types are not equal and partial density contribution equations are not the same for atoms in cross interactions, taking advantage of Newton's third law is not possible in AEAM method.

1.3 Boundary integral method

The time scale of the MD simulations is in the range of nano second and simulations of system larger than a few hundred nano meter is computationally very expensive. Therefore, it is necessary to use an alternative for the cases that bigger system size or longer simulation time is needed.

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Figure 1.11: a) Simplified algorithm of Molecular Dynamics. b) Simplified algorithm of interaction calculation part.

The alternative that we have used is the boundary element method (BEM), which is a numerical computational method of solving linear partial differential equations. During the last few decades, BEM has gradually evolved to become one of the few widely used numerical techniques for solving boundary value problems in engineering and physical sciences. This method have been formulated as integral equations. The integral equation is the exact solution of the governing partial differential equation. The boundary element method attempts to use the given boundary conditions to fit boundary values into the integral equation. Once this is done, in the post-processing stage, the integral equation can then be used again to calculate numerically the solution directly at any desired point in the interior of the solution domain. This method is applicable to problems for which Green's functions can be calculated [51].

The convection-diffusion mass transfer problem is a basic phenomenon in many physical processes, such as crystal growth that can govern by a partial differential equation. The approach that is explained in chapter 3 uses a variable transformation to reduce the diffusion problem to a Helmholtz equation. In this case the exact integral solution and corresponding Green's functions can be calculated. Therefore, for this case we can take advantage of low computational cost and accuracy of this method.

1.4 Goals of this research

Despite numerous studies of solidification of Al-Si alloys the precise mechanism of modification due to impurity additions has not been identified. Some of proposed mechanisms such as surface energy theory and diffusion control theory related to information about these terms in unmodified Al-Si system to be compared with the same terms in chemically modified system. In addition, if one considers the modification that occurs at high growth rates, then the origin of the flake to fibre transition becomes even more unsettled.

The so-called microscopic solvability theory of dendrite growth predicts that a dendrite tip radius and growth velocity are sensitive functions of two crucial materials parameters, the crystal-melt interfacial free energy and the kinetic coefficient. Therefore, in this study we employed MD to calculate mobility of steps (chapter 3) and step free energy (chapter 4). In order to do so, AEAM model implemented on open source MD code (lammps) and an appropriate potential for describing the interatomic forces in Al-Si system is developed (chapter 2). For the case of diffusioncontrolled scenario BEM employed to investigate the effect of geometrical parameters of this system on the growth rate of steps. In addition, step bunching phenomenon is studied in this system. Furthermore, a mathematical model for solving diffusion equation in the stagnant case is proposed (chapter 5).

Chapter 2

An Angular Embedded Atom Method Interatomic Potential for the Aluminum-Silicon System

A modified version of the Stillinger-Weber (SW) interatomic potential for pure Si has been developed. In contrast to the original SW form, the modified version allows one to grow diamond cubic crystal structures from the melt at high temperatures. The modified SW potential has been then combined with an embedded atom (EAM) description of pure Al developed by Mendelev et al. to formulate an Al-Si binary potential of the angular EAM type. The Al-Si potential reproduces quite well the experimental enthalpy of mixing in the liquid. It also predicts an Al-Si phase diagram with a eutectic concentration for the liquid that agrees with experiment within 4 at% and a eutectic temperature that differs from experiment by just 13 K.

2.1 Introduction

Lightweight structural materials such as cast Al-Si alloys are used extensively in high technology applications. Several studies have investigated various structureproperties relationships in cast Al-Si alloys including, the mechanical properties of Al-Si alloys as a function of the size, form and distribution of second phase silicon particles, dendrite arm spacing, eutectic morphology and grain structure [4, 52]; nucleation of the eutectic phase [19]; crystallographic orientation relationships [23, 3]; the effect of quench modification on Si morphology [25, 34]; and the mechanism of Si morphology transition in the presence of modifier agent [29, 26, 27, 5, 32]. It is now firmly established that superior mechanical properties are observed in Al-Si alloys that exhibit a fibrous Si phase morphology, rather than a flake-like form [30]. However, despite the importance and widespread use of cast Al-Si, the factors controlling the flake to fibrous transition remain elusive and a detailed investigation for the atomic processes taking place at the solid-liquid interface may provide important insights into the mechanism.

Atomistic scale simulation methods, such as molecular dynamics (MD) and Monte Carlo, can provide important insights into interfacial properties and atomistic kinetic processes, such as the excess free energy and mobility of solid-liquid interfaces [53, 54, 55], grain boundaries [56, 57] and interphase boundaries [58, 59]; the structure and kinetics of faceted crystal-melt interfaces [8, 41]; and equilibrium solute segregation to interfaces [60, 54, 61]. However, the results of classical MD simulations rely on the quality of the employed models for the interatomic potentials. Central force Embedded Atom Method (EAM) potentials have been used extensively for studying metallic systems [35] whereas, covalently bonded systems, described by pair and three body terms, have been simulated using the SW potential [37], the Tersoff potential [62, 63] and Lenosky potential [64]. To date many simulations have been conducted using the SW potential. The SW description has been successful in studies of epitaxial growth of $Si_{(1-x)}Ge_{(x)}$ on Si(100) substrate[38]; the effect of dislocations, stacking faults and phase transformations on yielding of Si[43], liquid-liquid phase transition[65], the homogeneous nucleation and crystallization process of silicon [66], defects and plasticity of silicon [67], crystal-melt interface stresses in the Si-Ni system [68], etc.

In a recent study of the step energy of (111) facets on the crystal-melt interface, Frolov and Asta [69] concluded that, at high temperatures, SW solidifies into *wurtzite*, rather than the experimentally observed diamond cubic phase. Starting with MD simulation cells consisting of circular diamond cubic islands at the (111) crystal melt interface, the authors observed consumption of the preexisting islands by wurtzite islands. In addition, other MD simulations reported random mixture of stacking sequences during solidification with (111) oriented solid-liquid interfaces using SW Si potential[70, 18]. Thus, despite the success of previous MD studies, it appears the SW potential is not optimal for the study of solidification phenomena.

For MD simulations of the Al-Si binary system, an interatomic potential that can capture accurately both metallic and covalent bonding is needed. One option is the modified embedded atom method (MEAM) developed by Baskes [71]. The MEAM formulation has been employed successfully in modelling several metal-semiconductor systems such as Mo-Si[72], Ni-Si[73], Au-Si-O[74], Au-Si [75] and Al-Si [76]. However, MEAM potentials are computationally rather expensive because of the many body angular screening function, which is used to limit the interaction range in MEAM. An alternative potential scheme for systems with mixed type of bonding has been developed by Dongare and co-workers [48] and is known as the angular EAM (AEAM). A distinct advantage of the AEAM method is the fact that existing EAM potentials for the metallic component and the SW description of pure Si (or Ge) can be implemented and only the cross species interaction needs to be formulated. The AEAM has been used to develop interatomic potentials for Au-Si, Au-Ge [48] and Al-Si [6]. In the case of Al-Si, the Dongare et al. potential reproduces quite accurately the enthalpy of mixing for different compositions and ground state energies of the L1₂ and B1 structures compared with the results of GGA and LDA methods. However the predicted phase diagram exhibits some deviation from the experimental Al-Si phase diagram. For example the eutectic composition and temperature are 9 at% Si and 38K larger than the experimental measurements, respectively.

The purpose of the present study is twofold. First, we propose a slight modification of the SW potential for pure Si that reproduces the ground state cohesive energy difference between wurtzite and diamond cubic as computed from first principles density functional theory. Furthermore, from MD simulations of crystallization along the (111) direction, it is shown that the diamond cubic structure is also the favoured phase at high temperatures. Second, we construct an interatomic potential of the AEAM type for the Al-Si system where the pure Al EAM potential developed by Mendelev et al. [77] is used. It will be shown that the new potential accurately predicts the enthalpy of mixing vs composition for the liquid, the formation energies for the L1₂ and B1 ordered compounds and the eutectic temperature and composition.

2.2 Potentials

2.2.1 Formulation of modified SW

Considering the fact that the Si crystal exhibits strong and directional bonds, Stllinger and Weber described the energy of an atom as a combination of pair and three body potentials:

$$E_{i} = \frac{1}{2} \sum_{j \neq i} \phi_{2}(r_{ij}) + \sum_{j \neq i} \sum_{k>j} \phi_{3}(r_{ij}, r_{ik}, \theta_{ijk})$$
(2.1)

$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)$$
(2.2)

$$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \exp(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}}) \exp(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}})$$
(2.3)

where λ , ϵ , γ , σ and a are parameters. θ_0 is the ideal tetrahedral angle and $\cos \theta_0 = -\frac{1}{3}$, ϕ_2 is a two-body term and ϕ_3 is a three-body term. The summations in the formula are over all neighbours j and k of atom i within a cutoff distance equal to $a_{ij}\sigma_{ij}$ and in the original SW formulation the cutoff range, for both the two-body and triplet interactions, extends to first neighbour only. The wurtzite and diamond cubic crystal structures have identical first and second neighbour configurations. As a result of the short range SW cutoff the ground state energy of the two structures is degenerate. The results of Frolov and Asta [69] indicate that either the bulk free energy or the step free energy of wurtzite is lower in comparison to the diamond

cubic phase, leading to the formation of wurtzite in layer-by-layer solidification simulations starting with a seed of the diamond cubic structure with solid-liquid interfaces oriented normal to [111].



Figure 2.1: Coordination number and distance of neighbouring atoms in the a) diamond cubic crystal structure and b) wurtzite crystal structure. The atomic coordination is identical for the first and second neighbour shells.

As shown in fig.2.1 the wurtzite structure (shown in b) is characterized by a third neighbour shell consisting of one Si atom located at findiatorystal to the second neighbour shell. Furthermore, the fourth neighbour of wurtzite and the third neighbour shell of diamond cubic correspond to the same distance, but the coordination for diamond cubic is larger. Therefore we propose a modification to the SW pair interaction term that exhibits a shallow minimum at the position of the third neighbour diamond cubic shell, ie. approximately 4.5Å. The form of the modified potential is given by:

$$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right) + d_{ij}\exp\left(-\left(Z_{ij}(r_{ij})\right)^2\right) \quad (2.4)$$

where d_{ij} is a constant that represents the depth of the well located at the distance determined by Z_{ij} . Notice the added potential is of a Gaussian type. However, in order to allow more flexibility in the potential description the term Z_{ij} was considered as a cubic polynomial in the distance variable r_{ij} . Thus:

$$Z(r_{ij}) = c_1(r_{ij} - D)^3 + c_2(r_{ij} - D)^2 + c_3(r_{ij} - D)$$
(2.5)

where c_1 , c_2 and c_3 are constants that determine the level of asymmetry of the well and D that represents the location of the well centre.

A limited search over six parameters ϵ_{ij} , A_{ij} , p_{ij} , c_1 , c_2 and c_3 was carried out to identify an acceptable choice of $\phi_2(r_{ij})$. Three main components of this search were considered. Firstly, ground state lattice energies were evaluated to ensure that the diamond structure is more stable than other crystal structures for a reasonable range of pressure, among most probable alternatives including wurtzite. In particular the energy difference between wurtzite and diamond cubic as predicted by density functional theory [78, 79] was used as a fit parameter. Secondly, the melting temperature of silicon obtained with the new potential should be at least as accurate as the melting temperature derived from the original SW potential. Finally, the first component of elastic constants tensor (C_{11}) was another target parameter.

Although only C_{11} was used as a fit parameter in the potential optimization, the three independent elastic constants C_{11} , C_{12} and C_{44} were computed using a procedure described by Clancy et al. [80]. First note that in general an element of the elastic constant tensor, C_{ijkl} , can be written as a partial derivative of a stress component with respect to strain as:

$$C_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}|_{T,\dot{\varepsilon}}$$
(2.6)

and, from a prescription described by Karimi et al.[81], one can write $C_{11} = C_{1111}$, $C_{12} = C_{1122}$ and $C_{44} = C_{2323}/4$. In this work, for the calculation of C_{11} , a uniaxial positive deformation is applied in the [100] direction of the periodic boundary cell in a canonical ensemble (NVT). The two other cell dimensions remain unchanged during the simulation. A 24 × 6 × 6 unit cells system of silicon in the diamond structure containing 6912 atoms at 1K was used to conduct this simulation. Tensile deformation was applied over a simulation period of 1ns with a relative deformation rate of $1 \times 10^6 \text{s}^{-1}$. As indicated in the stress tensor equation, the slope of a given component of stress tensor plot vs corresponding relative strain will yield the elastic constant in that specific direction. From the same simulation, we extracted the normal strain in the [0 1 0] direction, which was then used for the calculation of C_{12} . For the calculation of C_{44} , we used the same strain rate, ensemble, temperature and system size. However, a shear deformation was applied to the (1 0 0) plane instead of a normal deformation and the corresponding shear stress was calculated.

The melting point of pure Si was computed using the coexistence method first proposed by Morris and Song [82]. In the present application of this technique a system with the size of $30 \times 5 \times 5$ unit cells, containing both a solid and liquid phase is equilibrated at the estimated melting temperature, which, for the present study is the melting point of the original SW potential. Subsequently, simulations for 400ps in an isoenthaplic or the NP_zAH ensemble were performed. The ensemble maintains zero normal pressure along the direction normal to the two crystal-melt interfaces; while the dimensions in the two directions parallel to the interfaces remain unchanged. In an isoenthaplic ensemble, if the temperature of the system is initially higher (lower) than the melting temperature, then a fraction of the solid phase will melt (solidify) and due to latent heat absorbtion (release) the temperature will decrease (increase). Thus the system will eventually approach and stabilize at the actual melting temperature. The coexistence method relies on a crystal-melt interface that is mobile for very small departures from the melting point, that is, a rough interface. Therefore, the simulation cells used for the melting point computation were oriented with the (100) crystallographic direction perpendicular to the interface.

2.2.2 The Al-Si AEAM potential

In 2009, Dongare et al. [48] developed the AEAM interatomic potential model, which is specifically designed to model alloys of a metal species combined with a semiconductor (Si, Ge, etc). The lack of an explicit three body term in EAM, makes this model inappropriate for covalently bonded materials. Therefore, rewriting EAM potential to include three-body interactions and retaining all the properties of the pure components as predicted by the SW and EAM potentials were the main goals of the AEAM method.

In the AEAM description the density contribution is written as:

$$\rho_i = \left[\sum_{j \neq i} \left[f_{ij}(r_{ij})\right]^2 + 2\sum_{j,k \in T_i} f_{ij}(r_{ij})f_{ik}(r_{ik})\right]^{\frac{1}{2}}$$
(2.7)

where in the first(two-body) term under the square root the summation is over all

atoms interacting with atom i and in the second (three-body) term the summation is over all pairs of atoms j and k that form unique triplets with atom i. Therefore, for an alloy system containing both metal and Si atoms, the AEAM formulation uses a combined potential that reduces to the conventional SW and EAM potentials for pure components as follows:

$$E_{i} = \frac{1}{2} \sum_{j \neq i} \phi_{ij}(r_{ij}) + F_{i} \left\{ \left[(1 - \delta_{i}) \sum_{j \neq i} f_{ij}(r_{ij}) + c_{i} \sum_{j,k \in T_{i}} f_{ij}(r_{ij}) f_{ik}(r_{ik}) (\cos \theta_{ijk} - \cos \theta_{0ijk})^{2} \right]^{n_{i}} \right\}$$
(2.8)

where δ_i , c_i and n_i are constants and depend on type of atom *i*.

With the AEAM formulation, a number of properties of the Au-Si system, such as ground state energies, cohesive energies, bulk modulus, enthalpy of mixing and phase diagram were reported and the values predicted by the model agree quite well with experiment. In addition, in 2012 Dongare et al. [6] proposed a potential for the Al-Si system where all the predicted terms except the phase diagram are predicted well. However, a suitable potential for the simulation of solid-liquid interface properties should predict critical compositions and temperatures (e.g. melting temperatures, eutectic composition and temperature) as accurately as possible. Therefore, in the current work we have developed a new interatomic potential for the Al-Si system the phase diagram over the entire range of composition was defined as a target value. In addition, we used the potential for pure silicon. These choices ensured that, on the one hand, the calculated melting temperature of the pure components is close to the experimental values and, on the other hand, the stable crystal structures are FCC and diamond cubic for aluminum and silicon respectively.

One problem of using the Mendelev et al. aluminum potential was the different scaling of the electron density contribution in comparison with the formulation of Dongare. For solving this problem we used the scale invariance of the embedding functional in the EAM scheme, which has been applied in previous works for developing potentials in binary systems [84]. It has been shown [85] that the energy and forces in an EAM system are invariant to the following transformations:

$$f_{ij}(r_{ij}) \to g f_{ij}(r_{ij}) \tag{2.9}$$

$$F(\rho) \to F\left(\frac{\rho}{g}\right)$$
 (2.10)

where f_{ij} is the partial density contribution, F is the embedding contribution of the total energy, g is an arbitrary scale factor. It should be noted that this transformation does not affect the properties of the pure element. However, it does effect the behaviour of the alloy. Therefore, the parameter g is treated as a fitting variable, in the Al-Si potential development procedure, which can be varied without changing the Al potential.

For the next step we focused on the potential functions for Al-Si cross interactions. The pair energy term is defined as:

$$\phi_{ij}(r_{ij}) = f_{\phi}(r_{ij}) \left[A_C \exp\left(-\alpha_C \left(\frac{R_M}{r_{ij} - R_M}\right)\right) \left(\frac{r_{ij}}{\sigma_C}\right)^{-P_C} \right] - f_{\phi}(r_{ij}) \left[B_C \exp\left(-\beta_C \left(\frac{R_M}{r_{ij} - R_M}\right)\right) \left(\frac{r_{ij}}{\sigma_C}\right)^{-Q_C} \right]$$
(2.11)

where A_C , B_C , σ_C , β_C , σ_C , P_C , Q_C and R_M are fitting parameters. The formalism for pair energy is similar to the one defined by Dongare et. al. [6] with an extra coefficient $f_{\phi}(r_{ij})$. This function is used to apply a local and smooth increase in the pair potential to avoid interstitial solubility of Silicon in solid Al in the FCC crystal structure and is defined as,

$$f_{\phi}(r_{ij}) = \begin{cases} 1 & r_{ij} < R_{\phi_1} \\ 1 + C_{\phi} \left(1 - \cos \left(2\pi \left(\frac{r_{ij} - R_{\phi_1}}{R_{\phi_2} - R_{\phi_1}} \right) \right) \right) & R_{\phi_1} < r_{ij} < R_{\phi_2} \\ 1 & r_{ij} > R_{\phi_2} \end{cases}$$
(2.12)

where C_{ϕ} , R_{ϕ_1} and R_{ϕ_2} are constants. The partial electron density contributions from Si to Al and Al to Si are defined as,

$$f_{ij}^{Si \to Al}(r_{ij}) = f_e^{Al} \exp\left(-\gamma_C^{Al}\left(\frac{R_M}{r_{ij} - R_M}\right)\right)$$
(2.13)

$$f_{ij}^{Al \to Si}(r_{ij}) = \left[f_e^{Si} \exp\left(-\gamma_C^{Si}\left(\frac{R_M}{r_{ij} - R_M}\right)\right) \right] f_f(r_{ij}) \tag{2.14}$$

where f_e^{Al} , γ_e^{Al} , f_e^{Si} and γ_e^{Si} are fitting parameters. The density contribution of an Al atom on a neighbouring Si atom (eq.2.14) is very close to the density contribution of a Si atom on an Al neighbouring atom(eq.2.13). A slight difference in the current formulation is the function $f_f(r_{ij})$ which is introduced to avoid substitutional solubility

of Si in Al in the solid state. The function is given by:

$$f_f(r_{ij}) = \begin{cases} 1 & r_{ij} < R_{f_1} \\ 1 - C_f \left(1 - \cos \left(2\pi \left(\frac{r_{ij} - R_{f_1}}{R_{f_2} - R_{f_1}} \right) \right) \right) & R_{f_1} < r_{ij} < R_{f_2} \\ 1 & r_{ij} > R_{f_2} \end{cases}$$
(2.15)

where C_f , R_{f_1} and R_{f_2} are constants. Therefore, according to this formulation, the partial electron density contribution is based on the type of the neighbouring atom and not the type of bonds. A primary goal of this work is the development of a potential that accurately reproduces the Al-Si phase diagram. Determination of a phase diagram using MD is a three step procedure. For the first step the melting temperatures of the pure components, in this case Al and Si are calculated. The next step is the calculation of the free energy difference between solid and liquid phases of pure Al and Si. For this purpose, we used the Gibbs-Helmholtz equation, which defines a thermodynamic relation between the enthalpy and free energy of the solid and liquid phases at different temperatures:

$$\Delta G = T \int_{T_M}^T \frac{H^L(T') - H^S(T')}{{T'}^2} dT'$$
(2.16)

where $\Delta G = G^L - G^S$. G^L and G^S denotes the free energy of liquid and solid and H is the enthalpy. The enthalpy of both the solid and liquid phases were computed using simulations in the (NPT) ensemble on $10 \times 10 \times 5$ unit cells system for a series of eleven temperatures in the range of $T_M \pm 400$ K for Al and Si. Since liquid and solid were not stable at high supercoolings, we assumed that heat capacity is constant in the relevant range of temperature. In other words the enthalpy difference was least

squares fit to a straight line vs temperature.

The last step in the phase diagram determination is the calculation of the Gibbs free energy of mixing for the whole range of compositions at a specific temperature and zero pressure. This calculation involves the use of MD simulations and the Semi-Grand-Canonical technique [86, 87]. Based on this technique, at fixed temperature, pressure, total number of atoms and composition the chemical potential difference between the species, $\Delta \mu(x_{Si}, T) = \mu^{Al} - \mu^{Si}$, is calculated. For calculations of $\Delta \mu(x_{Si}, T)$, we carried out a series of virtual switches in the species type of a randomly selected Si atom to Al. The switch results in a change in the potential energy of the system and after a large number of switches, and assuring that the change in the potential energy $\Delta U_{Si \to Al}$ and average of the corresponding Boltzmann factor $\exp\left(-\frac{\Delta U_{Si \to Al}}{k_B T}\right)$ is converged, we used the following equation to calculate the chemical potential difference between Al and Si.

$$\Delta\mu(x_{Si},T) = -k_B T \ln\left\langle \frac{N_{Si}}{N_{Al}+1} \exp\left(-\frac{\Delta U_{Si\to Al}}{k_B T}\right)\right\rangle$$
(2.17)

where k_B is the Boltzmann constant, N_{Al} and N_{Si} are the number of Al and Si atoms and $\Delta U_{Si \to Al}$ is the potential energy changes due to the virtual switch in the atom type. Eq.3.9 includes the term $-k_BT \ln \left(\frac{N_{Si}}{N_{Al}+1}\right)$ which is the ideal mixing contribution to the chemical potential and $\ln \left\langle \exp \left(\frac{-\Delta U_{Si \to Al}}{k_BT}\right) \right\rangle$ is the excess chemical potential [87].

From the knowledge of $\Delta \mu$ at different compositions and temperatures, the free energy vs composition can be determined by using the Gibbs-Duhem equation and integrating the chemical potential function,

$$\left(\frac{\partial G}{\partial x_{Si}}\right)_{P,T} = \Delta \mu(x_{Si},T) \tag{2.18}$$

where G is the Gibbs free energy and x_{Si} is the atomic percent of Si atom in the system. For sufficiently small concentrations the chemical potential difference will approach negative infinity (for $x_{Si} \rightarrow 0$) or positive infinity (for $x_{Si} \rightarrow 1$). Therefore, for integration of the Gibbs free energy, we followed the method discussed by Ramalingam [60] and separated the ideal and excess part of the chemical potential and fitted eq.3.9 to the following form:

$$\Delta\mu(x_{Si},T) = -k_B T \ln\left(\frac{N_{Si}}{N_{Al}+1}\right) + \sum_{i=0}^{n} A_i x_{Si}^i$$
(2.19)

where the second term on the right-hand side is a polynomial fit in concentration with coefficients A_i .

The Gibbs free energy of the liquid phase was calculated by integrating eq.3.11 as:

$$G(x_{Si},T) = G(x_{Si} = 0,T) + k_B T[x_{Si} \ln x_{Si} + x_{Al} \ln x_{Al}] + \sum_{i=0}^{n} \frac{A_i x_{Si}^{i+1}}{i+1}$$
(2.20)

where $G(x_{Si} = 0, T)$ is the reference state and is taken as zero for the liquid state. An important feature of the Al-Si system is a near zero solubility of Al in diamond cubic Si and a small solubility (about 1.5%) of Si in FCC Al at the eutectic temperature. Therefore, one of the main assumptions in developing this potential and the one developed by Dongare et al. [6] is lack of solubility in the solid state. Therefore

we defined solubility level as one of the target values in developing this potential. Two $10 \times 10 \times 10$ unit cells systems of silicon in the diamond structure and Al in the FCC structure at 850K was used to verify a low solubility. A random Al/Si atom was substituted with a Si/Al atom and the change in energy of the system was calculated. This process repeated for all atoms in the system. The average energy change represents the enthalpy of mixing in the solid state. Summation of the ideal free energy and the enthalpy of mixing represents the Gibbs free energy of mixing. It was found that the energy change on adding a single Al impurity to diamond cubic Si increases the energy by 1.698eV/atom for the new interatomic potential and therefore the solubility is essentially zero. For Si added to FCC Al the increase in energy is 0.497 eV/atom and the G vs x_{Si} curve exhibits a minimum at less than 1%. However, for the potential developed by Dongare et al. [6], although adding an Al to Si in diamond cubic structure increases the energy by 2.28eV/atom, which guarantees zero solubility in solid silicon, adding a Si impurity to Al in the FCC crystal structure decreases the energy by 0.72eV/atom. Therefore, the solubility of Si in Al in FCC appears to overestimate the experimental value. In fig. 2.2 variation in free energy on adding a Si impurity to Al at 850K for the present potential and the one in reference [6] are compared.

In the results to follow we assumed zero solubility of Si in Al (and vice versa) in the solid state for the whole range of temperature. Based on this approximation we constructed the common tangent between the Gibbs free energy of the pure Al and Si phases and the $G - x_{Si}$ curve for the liquid at a given temperature. By repeating the above procedure at several temperatures, the phase diagram was constructed.



Figure 2.2: Effect of adding a Si atom to Al in the FCC crystal structure at 850K on the free energy of the system using (a) present potential and (b) potential developed in reference [6]

The accuracy of a potential in the prediction of properties depends upon the potential parameters which establish the interaction between atoms. Modification of the AEAM potential refers to changes in those parameters which will optimize the properties of the Al-Si alloy. To modify this potential, six AEAM parameters describing the pair and embedding functions were targeted. The chosen parameters were A_C , B_C , σ_C , R_M , C_{ϕ} and C_f . A small change in any of the six parameters will vary all of the resulting material properties of the AEAM Al-Si. The properties chosen to be evaluated where enthalpy of mixing in the liquid state for the Al – 50%Si and Al – 40%Si systems ($\Delta H_{50\%}^{mix}/\Delta H_{40\%}^{mix}$), eutectic composition (C^{Eu}), eutectic temperature (T^{Eu}) and the composition in which ΔG^{mix} for solution of Si in FCC Al and Al in diamond Si is minimum ($\Delta G_{Si \to Al}^{mix}/\Delta G_{Al \to Si}^{mix}$). To assess the property changes a series of simulations were performed where one parameter is altered by a small amount (approximately 5%) and the resulting property changes were computed. Changes in the six materials parameters just described are related to the six target AEAM parameters by the following six by six matrix:



The matrix is then inverted to obtain any desired change in the properties.

2.3 Results

2.3.1 Pure Silicon

To confirm that the modified SW potential proposed here predicts a stable diamond cubic phase at high temperatures, we first observed coexistence of diamond and wurtzite crystal structures by running a simulation of solidification using the original SW potential at 1660 K in the NP_zT ensemble, under fully periodic boundary conditions. The simulation box size was $5 \times 5 \times 18$ unit cells with zero pressure in the direction normal to the liquid-solid interface and the growth direction was (111).

After completion of solidification the system temperature was cooled down to zero Kelvin to avoid atomic vibrations and allowed for an accurate determination of the neighbors of a given atom up to the fourth neighbour shell. An analysis of the local atomic configuration verified that both diamond and wurtzite crystal structures existed in the final solid that had crystallized from the liquid. Fig.2.3 shows the distribution of the two stacking sequences with green(red) lines represents layers of the wurtzite(diamond cubic) structure. The results indicate that the wurtzite crystal structure is dominant. However atom planes exhibiting the diamond cubic structure are formed random by, too. The results structure is dominant. However atom planes exhibiting the diamond cubic structure are formed random by, too. The results structure is dominant. However atom planes exhibiting the diamond cubic structure are formed random by, too. The results structure is dominant. However atom planes exhibiting the diamond cubic structure are formed random by, too. The results structure is dominant. However atom planes are structure is dominant. However atom planes exhibiting the diamond cubic structure are formed random by, too. The results structure is a structure is dominant. However atom planes are structure is dominant. However atom planes exhibiting the diamond cubic structure are formed random by, too. The results structure is a structure is a structure in the results of Frolov and Asta [69] where simulations were performed at T=1670K (smaller undercooling) and a most pure wurtzite was observed. Instance (A) and the structure is dominant.



Figure 2.3: The distribution of two crystal structures forming during MD solidification of pure Si using the original SW potential. Green lines represent regions exhibiting the wurtzite crystal structure and the red lines represent the diamond cubic crystal structure.

The crystallization simulation described above was repeated using the modified SW potential. Fig.2.4 shows the potential energy vs time during the solidification process. Clearly evident is a series of nearly equal potential energy plateaus separated by abrupt decreases in energy. The step like pattern is indicative of a crystallization process characterized by the nucleation, and subsequent rapid spreading, of islands of the emerging solid. The behaviour seen in fig.2.4 therefore confirms that, as with the original SW, the (111) interface is facetted.

Analyzing the distance and number of neighbouring atoms shows that diamond cubic is the stable phase and the results are shown in fig.2.5. The top panel of the fig.2.5 (a) represents a view along the $[\bar{1}10]$ direction whereas (b) shows a view along $[11\bar{2}]$. Panel (c) is coloured to illustrate the different crystal structures formed and it is clear that diamond cubic is preferred. It should be noted that small wurtzite regions



Figure 2.4: The potential energy variation during the solidification process using the modified SW potential.

have been detected at the very final stages of crystallization. From the inset however,

it is concluded that the structure is actually a twinned diamond cubic structure.

Table 2.1: Optimal parameters for the modified SW potential and a comparison, where applicable, with the original SW potential.

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potential	ϵ	A	В	p	q	a	d	c_1	c_2	c_3	D
SW	2.1672	7.0496	0.6022	4	0	1.80	—	—	—	—	—
MSW	2.1428	7.3835	0.6140	3.5496	0	1.80	0.0081	5	-1	2.4259	4.5014

Overall, the most satisfactory parameter set for the modified SW is listed in table 2.1 and a comparison with the original SW is provided. The cohesive energy per atom versus number density (in reduced units) is compared for several crystal structures, including wurtzite, in fig.2.6.

The minimum of the ground state energy curve for the diamond lattice occurs at $\rho\sigma^3 = 0.46$ where the length unit, σ , was introduced by Stillinger and Weber for computational convenience [37]. From the minimum of the curve the lattice parameter



Figure 2.5: Atomic arrangement after crystallization using the modified SW potential. a) The view along the $[\bar{1}10]$ direction. b) The $[11\bar{2}]$ direction. Panel (c) is coloured as in fig.2.3 to show the distribution of crystal structures and the inset to (b) shows two twins of the diamond cubic structure that formed late in the solidification process.

corresponds to a = 5.431Å, which is exactly the same as the experimentally determined value [88]. At this lattice parameter the binding energy per atom in diamond cubic is 0.0122eV more negative than the wurtzite structure, which is the same as the value calculated using density functional theory [79]. Fig.2.7 plots the pair potential part of the interatomic potential as a function of distance for both the original and modified SW potentials. The inset depicts the very shallow minimum, described by eq.2.4, added to the modified potential.

In addition to stabilizing the diamond cubic structure, the modified SW form proposed here exhibits a melting temperature that is as accurate as the original SW model, within the statistical uncertainties of the simulation. In table 2.2 the melting point of the modified potential, 1686 K, is compared with the original SW and experimental value. Also, shown in table 2.2 is a comparison of the elastic constants predicted by the two Si potentials. Although the C_{12} value is overestimated and C_{44}


Figure 2.6: Ground state lattice energy (per atom) vs density base on modified Si potential for different crystal structures.

is underestimated for both potentials, an improvement in the C_{11} value has been achieved with the modified form.

Table 2.2: Comparison with experiment of the melting temperature and elastic constants from the Stillinger-Weber and modified Stillinger-Weber. Elastic constants are in units of $(10^{11} \frac{dyn}{cm^2})$ Simulations temperature is 1K and the experimental results are calculated by extrapolation of values from [10].

Method	Melting Temperature	C_{11}	C_{12}	C_{44}
MSW	$1686\pm10^{\circ}\mathrm{C}$	16.47	7.39	5.20
SW	$1691\pm10^{\circ}\mathrm{C}$	14.98	7.47	5.23
Experiment	$1686^{\circ}\mathrm{C}$	16.7	6.4	8.2

2.3.2 Aluminum-Silicon

Fig.2.8 shows the embedding energy functional vs. density contribution for Al and Si. The form of the embedding energy term for Si is the same as the one introduced by Dongare et al. [6].

The embedding energy of Al, which is based on the EAM formulation by Mendelev [83], is more negative in comparison with embedding energy used by Dongare [6] and,



Figure 2.7: The pair potential vs distance for the modified SW potential (blue) compared to the original SW (red). The inset shows a magnified portion of the modified potential in the vicinity of the distance of the third neighbour in the diamond cubic structure. The pair potential contribution is zero beyond a cutoff of r = 3.77Å.

the density contribution corresponding to the minimum embedded energy is skewed to higher values of density. Fig.2.9 shows the two body terms and partial electron density contribution terms for the pure and cross interactions. As was mentioned above, we applied modifications to both pair interaction term and partial electron density. The pair potential for the Al-Si cross interaction is less negative in comparison with the one proposed by Dongare et al. [6]. The values of the constants which yield the optimized Al-Si potential are given in table 2.3.

Table 2.3: Constants of Al-Si potential					
Parameter	Value	Parameter	Value		
$A_C(eV)$	2.4	$R_{\phi_1}(\text{\AA})$	1.65		
$B_C(eV)$	4.17	$R_{\phi_2}(\text{\AA})$	2.6		
$lpha_C$	-0.555	f_e^{Al}	1		
eta_C	-0.555	f_e^{Si}	1		
$\sigma_C(\text{\AA})$	2.2	$\gamma_C^{Al \to Si}$	0.86		
$R_M(m \AA)$	4.28	$\gamma_C^{Si \to Si}$	0.86		
P_C	4	C_{f}	0.11		
Q_C	0	$R_{f_1}(\text{\AA})$	2.45		
C_{ϕ}	0.18	$R_{f_2}(\text{\AA})$	3.5		



Figure 2.8: Embedding energy functionals for Al (EAM) and Si (SW).



Figure 2.9: a) The pair potentials and b) Partial electron density functions for Al-Al, Al-Si and Si-Si of the modified AEAM potential.

Representative results for the semi-grand canonical technique using MD for determining $\Delta \mu$ vs composition are shown in fig.2.10. The data refers to the liquid phase and two temperatures, 837 K and 1400 K, are depicted.

In fig.2.11 the enthalpy of mixing vs composition results from the model is compared to the experimental values. It should be stressed, however, that the experimental curve depicted in the figure is an assessment of several experiments [7], but in fact there is a considerable variation in the experimental values [89]. For example comparison of the results reported from reference [90] with [91] shows that, using the same experimental technique, and only a 4K difference between temperature, ΔH^{mix} is 3.1kJ/mol more negative in reference [91]. Even a positive enthalpy of mixing has been reported [92, 93]. Therefore, we conclude that the potential, despite predicting and overestimate of ΔH^{mix} by over 1kJ/mol (at $x_{Si} = 0.5$) provides an adequate description of ΔH^{mix} . In addition, similar to experimental observations this potential predicts a reduction in the enthalpy of mixing and a shift in the minimum to the Al-rich side with decreasing temperature [7].

It should be emphasized that the main target value of this study has been the phase diagram of Al-Si in the whole range of composition. Despite the fact that enthalpy of fusion of Si, calculated by modified SW, is closer to the experimental measurements, in comparison with the original SW, it is still 0.185eV/atom less than the experimental values. Therefore, we had to accept a less negative enthalpy of mixing in order to obtain a more accurate phase diagram.



Figure 2.10: Chemical potential difference vs composition for the liquid phase determined using the semi-grand canonical technique. Two temperatures are shown: a) 837K and b)1400K

Fig.2.12 illustrates the common tangent procedure for determining the Al-Si phase diagram from atomistic simulations. Panel (b) shows the free energy of mixing vs



Figure 2.11: Comparison between the calculated enthalpy of mixing at 1700K with experimental results [7].

composition, as determined from the integration of the chemical potential functions of fig.2.10, for the liquid curve at a temperature of 1400 K. Also shown are the free energy differences between solid and liquid for pure Si and Al. As mentioned above the solubility in either solid phase is very low. At this high temperature the solid Al phase is not stable for any composition, whereas a two phase mixture of liquid plus pure solid Si is found for Si compositions greater than 68 at% Si. The left hand panel of fig.2.12 shows the common tangent construction at a temperature of 837K. The common tangent now intersects all three phase and hence 837 K is our best estimate for the eutectic temperature in the model Al-Si system.

The Al-Si phase diagram computed for the AEAM Al-Si potential is shown in fig.2.13. Consistent with experiment [11], the model system exhibits a eutectic and as discussed above, almost complete lack of solubility of the two pure components. In addition, the experimental value of the eutectic composition is 12.2 at% Si whereas the new potential predicts a composition of 16.1 at% Si (see fig.2.13). The eutectic temperature is also in good agreement. Experiment reports a eutectic temperature of 850 K as compared to the 837 K found here. A summary of the experimental vs model Al-Si eutectic and melting points is provided in table 2.4. Notice the considerable



Figure 2.12: Free energy of mixing vs. composition in the Al-Si system at two temperatures a) 837 K and b) 1400 K. The common tangent construction is indicated in each plot. In (a) three phases are in equilibrium and therefore T=837 K represents the best estimate of the eutectic point.

improvement over the previous AEAM formulation. Because the heat of mixing behaviour is similar for the current and Dongare et al. potential it can be concluded that the improvement shown here arises primarily due the more accurate melting point for pure Al provided by the Mendelev et al. potential.

In order to assess the stability of the diamond structure in presence of Al atoms in the melt, we ran a simulation at 1570 K for a system with a crystal in the diamond cubic structure in contact with a liquid of composition Si10%Al. The amount of undercooling is small so the effect of kinetics on formation of new phase is minimized. The results are shown in fig. 2.14. Since the composition of liquid changes during the simulation, the driving force of the transformation decreases and solidification stops after formation of a few layers of solid. Based on these results we can conclude that the diamond crystal structure has stabilized using the present potential while a wurtzite crystal structure is still dominant using the previous potential. The very good agreement with the experimental results suggests that the new potential function should be a reliable one for studying solidification and related phenomenon, such as nucleation, interface properties etc, in the entire range of compositions and temperatures.



Figure 2.13: Phase diagram of the Al-Si system calculated by the AEAM potential.

Table 2.4: The melting temperatures of the pure components, the eutectic composition and temperature in the Al-Si system obtained experimentally [11], calculated using the AEAM potential [6] and the results of this study.

	AEAM[6]	Experiment[11]	Present Study
T_M^{Al} (K)	1100	926	929
$\mathbf{T}_{M}^{Si}\left(\mathbf{K}\right)$	1691	1686	1686
$T_{Eu}(K)$	887	850	837
\mathbf{x}_{Si}^{Eu}	0.21	0.121	0.161

In the original AEAM study of Al-Si, Dongare et al. compared ground state energies for $L1_2$ and B1 structures with those predicted from first principles calculations. In this work we have chosen not to carry out such a comparison. A more reliable test of the accuracy of a classical MD interatomic potential is the compound formation energy, rather than the ground state energy itself, and the ab-inito computed formation energies have not been reported for these compounds.



Figure 2.14: Simulation of solidification at T=1570 K. a) Initially the simulation box contains a crystal in the diamond structure in contact with Al-90%Si liquid. b) newly formed crystal layers are in diamond crystal structure while c) the wurtzite crystal structure is dominant (green part) using Al-Si potential from ref. [6]

2.4 Conclusion

A modification was applied to the three body SW Si potential such that the correct diamond cubic crystal structure was found to form at high temperatures. Recent simulations have shown that the wurtzite structure forms at temperatures in the vicinity of the melting point and thus the modified SW represents an important improvement for atomistic simulations of crystallization processes. In addition the modified SW predicts a more accurate melting temperature and elastic constants.

A potential for the Al-Si binary system was developed using the Angular-EAM method where the potential for pure Al was taken from the work of Mendelev et al. and the modified SW potential was used to describe pure Si. The new Al-Si model predicts a phase diagram in very good agreement with experiment. The eutectic temperature is within 13K of experiment and the eutectic composition agrees to within 4 at % Si.

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Chapter 3

Atomistic simulation of the step mobility at the Al-Si(111) crystal-melt interface using molecular dynamics

Molecular dynamics simulations and an angular Embedded Atom Method description of interatomic forces have been utilized to compute the mobility of steps on the facetted (111) crystal-melt interface in the binary alloy Al-Si. Two systems were studied: an Al-90%Si alloy in the temperature range of 1560-1580 K and Al-60%Si at T=1190-1220 K. It was determined that the higher Si content alloy exhibited attachment controlled growth of steps whereas for the lower temperature, higher Al concentration alloy step growth is characterized by a diffusion controlled or mixed mode mechanism. The step mobility, which is the proportionality constant between the velocity and driving force, was determined for the Al-90%Si alloy as a function of temperature and composition. It was found that mobility decreases fairly rapidly with the additional of Al solute. Also, from the variation with temperature, it appears the mobility is proportional to the interdiffusion coefficient in the liquid.

3.1 Introduction

In the quantitative morphological modelling of solidification, one of the crucial materials parameters is the mobility of interface crystalline. Theories of interface motion in crystal growth classify the rate controlling parameter according to two systems: diffusion-controlled, and/or interface-controlled. In the case of a diffusion-controlled system, solute transfer to the surface may be limited by mass transfer or diffusion through the bulk solution. For such systems many analytical solutions are available [94, 95, 96, 97, 98, 99]. However, in the case of an interface-controlled system, some rate-controlling events occur on the surface which control the mobility of the interface during solidification [100, 101, 102], and thus it is essential to investigate different properties of crystal-melt interfaces. Predictions of the so-called microscopic solvability theory of dendritic growth shows that the anisotropy of interfacial free energies and kinetic coefficients has a significant effect on growth velocity and dendrite tip radius [103, 104].

Despite the importance of the kinetic coefficient in the modelling of solidification microstructures, very few experiments have successfully measured this term in metals and alloys [105]. Most of our knowledge about the physics of crystallization kinetics has been obtained from molecular dynamics simulations [106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 8] using Lennard-Jones, hard-sphere, repulsive power-law and embedded atom method potentials, as well as Stillinger-Weber for pure Silicon. Of the different methods, free-solidification is known as the most convenient technique [111]. In nearly all these studies the interface is rough, and atom attachment to the growing phase occurs readily at any point on the boundary. Central force Embedded Atom Method (EAM) [35] potentials have been used extensively in the study of metallic systems. However, in some systems a crystal will grow with a faceted interface from its melt, which means atomic attachment occurs at steps which are energetically favourable. Thermodynamic, structure and kinetic properties of steps at crystalvapor interfaces[118] and crystal-melt interfaces[119, 8] have been considered in some studies.

More specifically for the case of silicon, Landman et. al. [120] observed the formation of {111} faceted planes and short range ordering in the melt close to the interfaces using MD simulations. In a different study, Luedtke [121] observed discontinuous growth of {111} layers in Si. In a related field of research Jackson [122] investigated the growth of silicon crystals from the amorphous phase. In addition, Buta et al. [8] used non equilibrium MD simulations of crystal growth to calculate the step kinetic coefficient at crystal melt interfaces, as well as the effect of step separation on the kinetic coefficient. In all these studies, the Stillinger-Weber (SW) potential [37] has been used to approximate the interactions between silicon atoms.

Although a detailed understanding of the properties of solid-liquid interfaces between chemically dissimilar materials is important for the description of a number of technologically important phenomena, relatively few fundamental studies have been carried out on alloying systems [123, 124]. Furthermore, to the knowledge of the authors, there have been no molecular dynamics study of the kinetic coefficient for

a mixed type bonding system, such as a metallic species alloyed with a covalently bonded element. The main reason for the lack of data in such systems is that the classical MD interatomic potentials for mixed systems are difficult to model. However, in 2009, Dongare et al. [48] developed the angular-EAM (AEAM) interatomic potential model, which is specifically designed to model alloys of a metal species combined with covalently bonded materials such as silicon. In 2014 Saidi et al. used this model for the case of Al-Si to develop a potential which reproduces quite accurately the enthalpy of mixing for different compositions and ground state energies of the L12 and B1 structures. Moreover, the predicted phase diagram is very close to the experimental Al-Si phase diagram. For example, the eutectic concentration for the liquid agrees with experiment within 4 at% and the eutectic temperature differs from experiment by just 13 K. Another important feature of this potential is zero solubility of Si in Al (and vice versa) in the solid state for the whole range of temperature. An advantage of this potential is that, in contrast to the original Stillinger-Weber (SW) potential where pure silicon stabilizes in the correct diamond cubic structure, a recent MD simulation of nucleation of solid circular islands on a liquid terrace frolov[69] showed the formation of the wurtzite crystal structure.

The current work is devoted to the study of the structure and kinetic properties of steps using an AEAM potential for Al-Si. However, in the first part of this paper we reproduce the results of Buta et al, [8] for pure silicon to assure that, despite the modification of SW potential, the satisfying capabilities of the original SW potential in reproducing silicon properties are preserved. For this purpose, the magnitude of the step kinetic coefficient, M_{step} , is defined as the proportionality constant between crystal growth rate and undercooling determines for silicon. In the remainder of the paper, we change the composition of the melt in contact with the silicon crystal. Some important features such as the diffusivity of components in the Al-Si melt and the range of undercooling in which a reaction-controlled scenario is dominant are investigated. The nonequilibrium MD simulations are employed to calculate the effect of composition and step separation on the step kinetic coefficient from interfaces vicinal to the (111) plane. In this case the driving force of the transformation is the difference in chemical potential of Si between the solid and liquid [125], where the chemical potential change due to changes in liquid concentration in the liquid must be accounted for. At each temperature, the driving force as a function of composition is calculated using the Semi-Grand-Canonical technique, whereas the interface velocity during transformation is determined at each composition. The computed kinetic coefficients and related results are presented, followed by a discussion and conclusion.

3.2 Methodology of atomistic simulation

By definition, the step kinetic coefficient, M_{step} , of a crystal-melt interface is the constant of proportionality between the growth velocity, and the driving force of the transformation. Driving force for the solidification in pure systems is typically expressed in terms of the undercooling $\Delta T = T_m - T$ and for alloying systems it is the difference between the chemical potential at each component from the equilibrium chemical potential $\Delta \mu = \mu_{Eq} - \mu$ [126]. The step velocity, then, can be written as:

$$v_{step}\left(T,C\right) = M_{step}\Delta\mu\left(T,C\right) \tag{3.1}$$

where both driving force and velocity are dependent on the temperature and composition of transformation. Thus, to determined the mobility, the interface velocity and driving force of solidification should be calculated at each point during the transformation.

The interactions between the components of this system are approximated by the angular embedding atom method (AEAM) empirical potential [127]. Morris' coexistence technique [128, 82] was employed to prepare systems with coexistence of a pure silicon crystal in contact with a pure or alloying liquid. Since the crystal orientations are high index directions the size of the the system should be calculated accurately to avoid very small distances between atoms under periodic boundary conditions. In order to prepare steps with different terrace lengths the crystal is rotated around the $[\bar{1}2\bar{1}]$ or $[10\bar{1}]$ directions, which results in the formation of steps along the $[\bar{1}2\bar{1}]$ and $[10\bar{1}]$, respectively. Table 3.1 shows the list of the vicinal orientations used in this study.

Table 3.1: Dimensions and orientations of the MD simulation systems. L_T is the length of terraces, L_y is the length of simulation cell in the direction perpendicular to the steps. $L_{[111]}$ is the initial length of the simulation box in the [111] direction, which changes during solidification. The minimum possible size of the system for the corresponding crystal orientation specified in the column " N_{atoms} ". In the column "system" P stands for the pure system and A stands for an alloying system.

	10					
Vicinal plane	Step direction	$L_T\left({A} ight)$	$L_{y}\left(\mathring{A} ight)$	$L_{\left[111 ight] }\left(\AA ight)$	N_{atoms}	System
(321)	$[\overline{1}2\overline{1}]$	7.8	53.50	122.58	16128	Р
(543)	$[\overline{1}2\overline{1}]$	15.5	53.50	135.13	16800	Р
(765)	$[\overline{1}2\overline{1}]$	23.16	53.50	114.52	16220	P-A
(987)	$[\overline{1}2\overline{1}]$	30.89	93.14	152.10	65184	P-A
(787)	$[10\overline{1}]$	49.04	50.19	104.24	12636	P-A

System preparation starts with the equilibration of pure silicon in the solid state using an NPT ensemble at the desired temperature T and pressure P = 0. The output of this level of simulation is used as the initial condition for the subsequent step. However, in the case of alloying systems, the type of some atoms changes to reach the corresponding composition of the liquid in contact with solid silicon crystal. The melt-solid system is prepared by employing the $NA_{yz}P_xT$ ensemble. This means that the system size is fixed in the y and z directions, and the pressure is controlled by changes in the x direction, which is perpendicular to the vicinal plane. The portion of the system that is melted increases to a temperature well above the melting temperature, then the temperature decreases gradually to the temperature of interest and is held constant until equilibration is established. Subsequently the system is quenched and the progress of solidification is captured. The amount of undercooling is determined with respect to the liquidus line in the phase diagram of Al-Si, whereas for the pure silicon system it is the melting temperature of silicon $(T_M = 1682 \pm 1K)$. Snapshots of the system were saved every 50 ps during this simulation. The snapshots contained positions of atoms, energies, and stresses, and were used for post processing.

Based on Eq. 3.1 the interface velocity and the driving force of transformation should be calculated for all independent snapshots. In the case of a pure silicon system, the crystal growth rate in the vicinal direction $(v_{vicinal})$ is proportional to the rate of energy release, $\left(\frac{dE}{dt}\right)$, during solidification:

$$v_{vicinal} = \frac{1}{2A_{yz}\Delta H_m} \frac{dE}{dt}$$
(3.2)

where ΔH_m is the latent heat of melting per volume in the silicon diamond crystal structure and A_{yz} is the fixed cross sectional area of the simulation box perpendicular to the crystal/melt interface. According to the geometry of the periodic system there are two solid-melt interfaces, and therefore the denominator will carry a factor of 2.

However, in the case of alloying systems, the average velocity of interfaces in the vicinal direction is calculated from the rate of conversion of silicon atoms from liquid state to the solid state by passing through the interface $\left(\frac{dN_{Si}^{L\to S}}{dt}\right)$ [129].

$$v_{vicinal} = \frac{\Omega}{2A_{yz}} \left(\frac{dN_{Si}^{L \to S}}{dt}\right)$$
(3.3)

where Ω is the atomic volume of silicon atoms in the solid state at the corresponding temperature. Converting $\left(\frac{dN_{Si}^{L\to S}}{dt}\right)$ using the mass conservation principle for a closed system, $v_{vicinal}$ can be reformulated as:

$$v_{vicinal} = \frac{\Omega N_{Al}}{2A_{yz}} \left(\frac{1}{1-C}\right)^2 \left(\frac{dC}{dt}\right)$$
(3.4)

where C is the composition in the liquid $\left(C = \frac{N_{S_i}^l}{N_{S_i}^l + N_{Al}}\right)$, N_{Al} is the number of Aluminum atoms in the system and $\left(\frac{dC}{dt}\right)$ is the rate of composition variation in the liquid. Considering the assumption of complete solute rejection from the silicon crystal, N_{Al} is a constant for each system. However, $N_{S_i}^l$ decreases by attachment of Si atoms to the crystal, thus, the composition decreases until equilibrium is achieved and solidification stops.

An exponential equation with the form of $C = (C_0 - C_{Eq}) \exp(-Bt) + C_{Eq}$ is fitted to the liquid C vs solidification time, t, where C_{Eq} is the equilibrium melt concentration at the corresponding temperature, C_0 is the initial liquid composition and B is a positive fitting parameter. The form of this equation comes from the knowledge that the $C = C_0$ at t = 0 and $C = C_{Eq}$ at $t \to \infty$. Therefore, the rate of composition variation would be $dC/dt = B(C - C_{Eq})$, which shows a linear trend with respect to $\Delta C = C - C_{Eq}$, which is very useful in simplifying further analysis.

We should point out that the term B, which represents the frequency of atom attachment from the melt to crystal, is dependent to the geometry of the system. Therefore, we rescale B in a way to be independent of geometry. These geometry parameters are i) the length of steps in the system (l_{step}) : steps are sinks of Si atoms from the melt. The longer the steps, the higher the frequency of attachment. ii) the length of the liquid region (l_{liq}) . The longer the melt region the lower the rate of composition variation. iii): the cross sectional area of liquid region (A_{liq}) : The bigger the cross section, the more atoms need to be attached, thus, the lower the rate of composition variation. Therefore, we define $B = \beta \frac{l_{step}}{A_{liq}l_{liq}} = f\beta$ where f is the geometry factor and β is the rescaled attachment frequency term.

Growth velocity along the faceted interface direction $v_{[111]}$ and the average velocity of the step is geometrically related to the vicinal velocity as follows:

$$v_{[111]} = \frac{v_{vicinal}}{\cos \theta}$$

$$v_{step} = \frac{v_{vicinal}}{\sin \theta}$$
(3.5)

where θ is the angle between the vicinal direction and the high symmetric direction, here [111]. Therefore the final from of the step velocity is:

$$v_{step}(C,T) = \frac{\Omega \rho_{Al} \rho_{step}}{2\sin\theta} \left(\frac{1}{1-C}\right)^2 \beta \left(C - C_{Eq}(T)\right)$$
(3.6)

where $\rho_{Al} = \frac{N_{Al}}{A_{liq}l_{liq}}$ is the density of Al atoms in the melt and $\rho_{step} = \frac{l_{step}}{A_{yz}}$ is planar density of the steps at the interface.

In order to calculate the composition of melt during solidification and capturing the crystal growth velocity, the state of all atoms in the system are determined using the order parameter proposed by Buta [8] for diamond crystal structures. Once the discriminator values are calculated for each atom, the position of the crystal-melt interface can be calculated accurately. This criterion is based on the symmetry of the second neighbour atoms of each individual atom and four first nearest neighbours. The discrimination function $\psi(i)$ of atom *i* defined as:

$$\psi(i) = \left| \frac{1}{ZN_{\mathbf{q}}} \sum_{\mathbf{q}_{i}} \sum_{j=1}^{Z} \exp\left(-i\mathbf{q}_{i} \cdot \mathbf{r}_{j}\right) \right|^{2}$$
(3.7)

where Z is the number of neighbouring atoms found in a sphere of radius 2.8Å surrounding atom i. \mathbf{r}_j is the vector from atom i to the immediate $N_{\mathbf{q}} = 12$ atoms out of the cut of distance of first nearest neighbours, and \mathbf{q}_i are the reciprocal lattice vectors in a perfect diamond cubic crystal structure. By design, $\psi(i) = 1$ for a perfect diamond crystal structure and $\psi(i) \approx 0$ for an atom in a liquid phase. The accuracy of the discrimination factor is improved by calculating the average order parameter $\bar{\psi}$ for each atom with the order parameter of the Z nearest neighbours:

$$\bar{\psi}(i) = \frac{1}{Z+1} \left(\psi(i) + \sum_{j=1}^{Z} \psi(j) \right)$$
 (3.8)

Based on eq. 3.1 the other term that should be calculated is the driving force of crystal growth from the melt, which for pure systems is the undercooling. However, for alloying closed systems, the composition of the liquid changes, thus the driving force, which depends on composition as well as temperature, varies. The driving force at any composition is the difference between the chemical potential of the solidifying component from the equilibrium chemical potential ($\Delta \mu = \mu_{Eq} - \mu$).

 $\Delta \mu$ is calculated using the Gibbs free energy of mixing for the whole range of

compositions at the temperature of interest and zero pressure. This calculation involves the use of MD simulations and the Semi-Grand-Canonical technique [86, 87]. Details of this method are explained in some studies (read refs. [127, 48]). However, as a brief explanation, at fixed temperature, pressure, total number of atoms and composition, the chemical potential difference between species $\mu_{Si} - \mu_{Al}$ is calculated. For calculations of $\mu_{Si} - \mu_{Al}$, a series of virtual switches in the species type of a randomly selected Si atom to Al are carried out. The switch results in a change in the potential energy of the system and after a large number of switches, ensuring that the change in potential energy $\Delta U_{Si \to Al}$ and average of the corresponding Boltzmann factor $\exp\left(-\frac{\Delta U_{Si \to Al}}{k_BT}\right)$ have converged, the following equation was used to calculate the chemical potential difference between Al and Si:

$$\mu_{Si}(C_{Si},T) - \mu_{Al}(C_{Si},T) = -k_B T \ln\left\langle \frac{N_{Si}}{N_{Al}+1} \exp\left(-\frac{\Delta U_{Si\to Al}}{k_B T}\right)\right\rangle$$
(3.9)

where k_B is the Boltzmann constant, N_{Al} and N_{Si} are the number of Al and Si atoms and $\Delta U_{Si \to Al}$ is the potential energy changes due to the virtual switch in the atom type. Eq.3.9 includes the term $-k_BT \ln\left(\frac{N_{Si}}{N_{Al}+1}\right)$ which is the ideal mixing contribution to the chemical potential and $\ln\left\langle \exp\left(\frac{-\Delta U_{Si \to Al}}{k_BT}\right)\right\rangle$ is the excess chemical potential [87]. It is shown in [127] that the solubility of Si in Al (and vice versa) in the solid state is zero for the entire range of temperature. Therefore, the semi grand canonical method was applied only to the liquid system to calculate the Gibbs free energy of mixing, while for the pure components in solid state chemical potential was calculated using the Gibbs-Helmholtz equation, which defines a thermodynamic relation between the enthalpy and free energy of the solid and liquid phases at different temperatures.

From the knowledge of $\mu_{Si} - \mu_{Al}$ at different compositions and temperatures, the free energy vs composition can be determined by using the Gibbs-Duhem equation and integrating the chemical potential function,

$$\left(\frac{\partial G}{\partial C_{Si}}\right)_{P,T} = \mu_{Si}(C_{Si},T) - \mu_{Al}(C_{Si},T)$$
(3.10)

where G is the Gibbs free energy. For sufficiently small concentrations the chemical potential difference will approach negative infinity (for $C_{Si} \rightarrow 0$) or positive infinity (for $C_{Si} \rightarrow 1$). Therefore, for integration of the Gibbs free energy, we followed the method discussed by Ramalingam [60] and separated the ideal and excess part of the chemical potential and fitted eq.3.9 to the following form:

$$\mu_{Si}(C_{Si},T) - \mu_{Al}(C_{Si},T) = -k_B T \ln\left(\frac{N_{Si}}{N_{Al}+1}\right) + \sum_{i=0}^n A_i C_{Si}^i$$
(3.11)

where the second term on the right-hand side is a polynomial fit in concentration with coefficients A_i .

The Gibbs free energy of the liquid phase was calculated by integrating eq.3.11 as:

$$G(C_{Si},T) = G(C_{Si} = 0,T) + k_B T[C_{Si} \ln C_{Si} + C_{Al} \ln C_{Al}] + \sum_{i=0}^{n} \frac{A_i C_{Si}^{i+1}}{i+1}$$
(3.12)

where $G(C_{Si} = 0, T)$ is the reference state and is taken as zero for the liquid state.

For determining the form of $\Delta \mu$ for fitting the numerical values we use the form that can be resulted from the ideal binary solution. In this case the variation of chemical potential from an initial non-equilibrium to equilibrium composition follows the form of $\Delta \mu = k_B T \left[\ln \left(C_{Eq} / (1 - C_{Eq}) - \ln \left(C / (1 - C) \right) \right] \right]$. Considering the fact that the system is not dilute and the range of composition variation is not wide, after taylor expansion of the logarithms it can be simplifies to the form of $\Delta \mu = k_B T \left(C - C_{Eq} \right) / C \left(1 - C \right)$. Therefore the driving force is fit to the equation in the form of

$$\Delta \mu = \frac{S_{DF} k_B T \left(C - C_{Eq} \right)}{C \left(1 - C \right)}$$
(3.13)

where S_{DF} represents the deviation of the solution from the ideal behaviour. Substituting $\Delta \mu$ and eq. 3.6 in eq. 3.1, the mobility of step is:

$$M_{step} = \frac{\Omega \rho_{Al} \rho_{step}}{2 \sin \theta} \frac{\beta}{S_{DF} k_B T} \left(\frac{C}{1-C}\right)$$
(3.14)

3.3 Results and discussions

3.3.1 Calculation of driving force

Calculation of the driving force for solidification is one aspect of step mobility calculation. The driving force of step mobility in a pure system is $\frac{\Delta H_m \Delta T}{T_m}$, proportional to undercooling, whereas for an alloying system is the chemical potential difference at each composition from the equilibrium chemical potential.

Fig. 3.1 illustrates the free energy of mixing vs composition, as determined from the integration of the chemical potential functions resulting from the Semi-Grand-Canonical technique for the liquid curve at a temperature of 1190 K. Based on both the experimental phase diagram of the Al-Si system and the AEAM potential used



Figure 3.1: Free energy of mixing vs. composition in the Al-Si system at T=1190 K. The common tangent construction is indicated for determining the equilibrium composition, and another dashed line indicates the chemical potential corresponding to the initial composition. The driving force for transformation is the difference between these two chemical potentials, which is zero at equilibrium.

in this study [127], the solubility in silicon crystal is almost zero. Therefore, for each temperature the equilibrium composition is calculated from the common tangent procedure between the liquid free energy curve and chemical potential of pure silicon in the solid state. The direction of chemical potential and corresponding composition variation is determined using the red arrows.

Fig. 3.2 shows the driving force as a function of composition deviation from equilibrium at three temperatures of interest. Considering the narrow range of composition variation, and the fact that the liquid composition is not dilute, $\Delta \mu$ can be estimated with Eq.3.13. For all cases the driving force is zero at equilibrium and is higher for the higher deviation of composition from the equilibrium. The rate of variation is larger for higher temperatures. However, based on the phase diagram of Al-Si for hypo-eutectic compositions, the lower the temperature, the wider the range of allowed composition variation in the two phase solid-liquid region. As noted in section 4.2 the driving force of these systems are fit to the equation of form Eq.3.13. The advantage of this formulation is that the term $(C - C_{Eq})$ cancels out from two sides of eq. 3.1, thus, the step kinetic coefficient will be independent of C_{Eq} and ΔC in eq. 3.14.



Figure 3.2: Diving force for step mobility vs the deviation of the liquid concentration from equilibrium. Over the range of temperatures studied the trend is approximately linear

3.3.2 Structure of the interface

The range of initial step separation L changes from 7.8 Å to 49 Å and from 23 Å to 49 Å for pure and alloying systems, respectively. The longer terrace lengths were chosen for the alloy system to avoid interaction between steps and to consider the net effect of the rate controlling parameter in simulations. Fig. 3.3 illustrates three different views of the crystal-melt system from a snapshot in the MD simulation. The vicinal direction is [987] and the step is along [$\bar{1}2\bar{1}$]. The solid silicon particles (blue) in contact with Si (yellow) and Al (red) in the melt. Panel (a) depicts a large scale view of the system, whereas panel (b) shows an individual layer where the rough step separating the crystal and liquid can be clearly seen. Fig. 3.3 (c) is a cross section of the system showing only the crystalline atoms and the array of steps along the interface is indicated by the red line. The sequence of silicon planes in the crystal is (A AB BC CA) and the bilayer nature of the steps is observable in all simulation systems.



Figure 3.3: a) The coexistence of crystal and melt in the Al-Si system. The vicinal direction is [987] and the step is along $[\bar{1}2\bar{1}]$. Atoms are coloured based on their type and state. Blue for Si in solid, yellow for silicon in liquid and red for Al atoms. b) An individual bilayer step with a rough crystal-melt interface. c) Cross section of the system showing only atoms in solid state.

3.3.3 Interaction of crystal/melt, solute trapping and interdiffusion coefficient

Before calculating the step kinetic coefficient, it is helpful to understand the structure of an equilibrium interaction and the interaction of aluminum atoms with a silicon crystal. In order to assess the interaction of the diamond cubic structure and the liquid in the presence of Al atoms in the melt, a simulation was run with a system size of $10 \times 5 \times 5$ unit cells, with a faceted (111) silicon crystal interface in contact with liquid of composition Al-90at.%Si, equilibrated at 1570 K. The amount of undercooling is small so the driving force is not high enough to overcome the nucleation energy barrier for crystallization in the time frame of the simulation.



Figure 3.4: Concentration profile at the crystal-melt interface for coexistence of the (111) silicon crystal with a liquid of composition Al-90at.%Si equilibrated at 1570 K. The range of repulsive interaction is shown by arrows in front of the silicon layers.

The concentration profile of 128 snapshots were averaged for time intervals of 100 ps and the results are shown in Fig. 3.4. A region of Al atom depletion is observed at both solidification fronts, which represents a repulsive interaction between the silicon crystal and Al atoms. The range of repulsive interaction is about 4Å, which is greater than the first nearest neighbour distance but less than the second nearest.

When choosing an appropriate driving force to apply during the MD simulations it is tempting to choose a large driving force since the total time of the simulation will be relatively short. However, at large driving forces a complicating factor is the observation of solute trapping (see for example [124]). It has been observed that by increasing the transformation driving force and deviation from the equilibrium condition, the concentration of the Al in silicon in the solid state increases. Fig. 3.5, shows a system of (321)silicon/Al-90at.%Si melt at 1350K using an undercooling of $\Delta T = 240$ K. The top figure is the initial configuration and the bottom panel shows the same system after 64ps. At this high undercooling the system shows a very fast progress of solidification and a substantial level of solute trapping. In the results to follow the driving force was chosen to be sufficiently small such that solute trapping was avoided.



Figure 3.5: Solute trapping effect for a (321)silicon/Al-90at.%Si melt at 1350K.

The other effect of increasing the undercooling is that the driving force of transformation increases whereas the diffusion rate decreases. Therefore, gradually a transition from reaction-controlled to diffusion-controlled systems occurs. There is a specific undercooling beyond which the transition will be diffusion-controlled. However, one of the main assumptions of reaction-controlled transformations is that the undercooling is small enough so that there is no composition gradient in the melt, thus, the transformation is not controlled by diffusion of solute atoms in the melt. For a more comprehensive understanding of the dominant mechanism of transformation, the interdiffusion coefficient in the liquid was calculated for four alloying systems Al-90at.%Si, Al-80at.%Si, Al-70at.%Si and Al-60at.%Si. Simulation systems of the size $10 \times 10 \times 10$ unit cells were equilibrated at the temperature of interest using the NPT ensemble. The mean-squared displacement of similar atoms were summed and averaged, where all effects due to atoms passing through periodic boundaries was included and the effect of any drift in the centre-of-mass of atoms was subtracted out before the displacement of each atom was calculated. The link between the mean square displacement (R_n^2) and the diffusion coefficient of individual species is well established ([130]) as $R_n^2 = qDt$, where R_n is the mean distance from the starting point that an atom will have diffused in time, t and q is a numerical constant depending on a dimensionality equal to 6 for three dimensional diffusion. The interdiffusion coefficient, \hat{D} , is then calculated using $\hat{D} = X_{Al}D_{Si} + X_{Si}D_{Al}$ where X_{Al} and X_{Si} are the mole fraction of Al and Si.



Figure 3.6: Natural logarithm of diffusion coefficient vs inverse of temperature for Al-90at.%Si (1560K $\leq T \leq 1860$ K) and Al-60at.%Si (1410K $\leq T \leq 1710$ K) in the liquid state. At a constant temperature the diffusivity is higher for compositions where the atom is more likely to be surrounded with dissimilar atoms.

The diffusion coefficient was calculated at three different temperatures over a range of 300 K starting from 1560K, 1510K, 1460K and 1410K for Al-90at.%Si, Al-80at.%Si, Al-70at.%Si and Al-60at.%Si, respectively. The results are presented in Fig. 3.6. As expected, the natural logarithm of the diffusion coefficient shows a linear trend with respect to inverse of temperature. In all cases the diffusivity of Al in the Al-Si melt is faster than Si. However, the difference between the diffusion coefficient of two components is the most for Al-90at.%Si and it is the least for Al-60at.%Si. In addition, at a specific temperature, the diffusivity increases by increasing the amount of aluminum atoms in the system. In other words, the higher the probability of coordination by a dissimilar atom, the higher the diffusivity of the atom in the liquid. For the Arrhenius-type equation $\hat{D}^{Al-Si} = D_0 \exp\left(-\frac{Q}{RT}\right)$ the values of D_0 and $\frac{Q}{R}$ are reported in table 3.2.

Table 3.2: Activation energy and diffusion constant results from gradient and intercept of $\ln \hat{D}$ vs 1/T graph.

Composition	Al - 90at.%Si	Al - 80at.%Si	Al - 70at.%Si	Al - 60at.%Si
$D_0(m^2s^{-1})$	$1.38 imes 10^{-7}$	1.06×10^{-7}	1.16×10^{-7}	1.27×10^{-7}
Q/R(K)	4316.6	3633.8	3592.1	3572.7

3.3.4 Mobility of Pure Silicon

As mentioned in the introduction the interatomic potential used in this study involves a slight modification of the pure Si SW potential. Therefore, to check if the modification produces a significant change in the step mobility we have repeated the step mobility computation for pure Si. Fig. 3.7 illustrates the variation of potential energy vs solidification time for five different step separations. Although deviation from linearity is observable in some cases, the trend of variation is mostly linear. Therefore, for a specific undercooling the rate of energy release is the highest and lowest for the [321] and [787] vicinal directions, respectively.



Figure 3.7: Potential energy during crystal growth for MD simulations of pure Si. Results for all 5 systems, which correspond to differing step separations, are shown and the undercooling used is 22 K.

Using the slope of line fitted to the graphs in Fig.3.7 and eq.3.5, the crystal growth rate in the high symmetry direction, here [111], is plotted in Fig. 3.8. A clear linear dependance of the growth rate on undercooling for $\Delta T < 32$ K is observable and the kinetic coefficient can be determined from the slope. The results for all simulations are summarized in Fig. 3.9, which is a plot of the step kinetic coefficient vs. the step separation. The results are compared with those reported by Buta [8], using the original SW and it is clear that the modified Si potential is in excellent agreement with the original SW formulation.

3.3.5 Mobility of steps in Al-90at.%Si

Al-90at.%Si is the first set alloying system beyond the pure silicon system we considered to study the effect of composition on the mobility of the steps on the



Figure 3.8: Solidification rates in the [111] direction for 5 solid-melt interfaces and for 12, 22 and 32 K undercoolings.

reaction controlled scenario. Fig. 3.10 shows the non-linear potential energy variation during solidification for a system including silicon crystal with a vicinal interface in contact with melt of initial composition Al-90at.%Si. Release of energy is fastest at the beginning of the transformation and converges to a specific value which is dictated by the undercooling applied to the system.

Based on eq. 3.6 the final step velocity equation is a function of composition. Composition variation during transformation is shown in Fig. 3.11 where again the results correspond to (787) Si-Al with initial melt composition of Al-90at.%Si¹. The composition variation follows a nonlinear trend and, depending on the amount of undercooling applied to the system, the composition in the melt converges to the corresponding equilibrium composition. Since there exists local fluctuations in the composition over short time intervals we are unable to determine the instaneous variation in composition. Therefore, as explained in the previous section, the results are fit to an exponential function of the form $C = (C_0 - C_{Eq}) \exp(-f\beta t) + C_{Eq}$ where

¹Since the composition is determined by a random number generation algorithm implemented on the molecular dynamics code, the initial composition might deviate from the target value.



Figure 3.9: Step kinetic coefficient vs average terrace length for 5 vicinal orientations. The results are compared with the results of Buta et al. [8].

 $f = \frac{l_{step}}{A_{liq}l_{liq}}$ is the geometry factor and the values of C_{Eq} and C_0 are determined by the phase diagram and are reflected in the graph directly. An alternative method for calculating the equilibrium composition beside the composition that the curves in Fig. 3.11 are converging to, is using SGC method. As it was explained in section 3.3.1, the equilibrium composition was calculated from the common tangent between the free energy curve of melt and chemical potential of solid at the temperature of interest. The results of both techniques are very close to each other. The fitting parameter β , which represents the rate of composition variation with time, is determined for each case, as well as the composition difference from the equilibrium composition, $(C - C_{Eq}(T))$.

Using eqs. 3.4 and 3.5 the growth velocity along the high symmetry direction, [111], as a function of composition deviation from equilibrium for Al-90at.%Si alloy at 1572K, is presented in Fig. 3.12. The velocity converges to zero as composition in the liquid side of the interface reaches equilibrium. As expected, the velocity in [111] direction depends on the step separation and decreases by increasing the terrace



Figure 3.10: Total potential energy vs. time for an Al-Si alloy with initial liquid concentration of Al-90at.%Si. The vicinal interface is (787) and three different temperatures are shown.

length. This pattern was observed all undercoolings.

The velocity of the steps as a function of composition deviation from equilibrium is calculated using eq.3.6 at three different temperatures and three solid-melt interfaces. The results are shown in Figs. 3.13. It was observed that at a specific composition and temperature, the calculated v_{step} for different vicinal directions are very close to each other. In addition, there is no consistency in the order of the curves depicted in the three graphs of Fig. 3.13.

Considering these results it was concluded that for this alloying system, the minimum step separation is large enough to avoid the interaction between steps, thus, the assumption was made that the step velocity is independent of solid-melt interface direction in the range of step separation of this study. Therefore, the averaged step velocities over different interface orientations vs ΔC is calculated for mobility calculations. The step velocity is maximized at the initial composition and decreases while silicon atoms attach to the crystal. The molecular dynamic system is closed,



Figure 3.11: Melt composition variation during solidification for the (787) vicinal direction for three undercoolings in the Al-90%Si alloy. An exponential decay, dashed lines, is fitted to the results.

therefore, the composition in the liquid becomes more rich with Al atoms by progress of solidification. Thus, the composition variation in the melt results in a gradual decrease in the step velocity until solidification ceases at equilibrium composition. Deviation of initial composition from the equilibrium composition (ΔC) depends on the temperature of transformation or the amount of undercooling. Thus, as it is observed in the graph for a certain initial composition, the range of ΔC is wider at lower temperatures. The summary of the constants related to the velocity, the driving force constant, averaged for all orientations and corresponding temperatures are tabulated in table 3.3.

The main results of this study are the kinetic coefficient of steps shown in Fig. 3.14 for Al-90at.%Si. Both the crystal growth rate and driving force are decreasing as the melt composition approaches equilibrium. However, for an isothermal curve, variation of melt composition affects the rate of velocity more than driving force, thus, the mobility of steps decreases gradually. The variation of mobility with respect to Al concentration is fairly strong, for instance, for a 3% change in composition during



Figure 3.13: Step velocity vs composition deviation from equilibrium, for three solid-melt interfaces and three undercoolings. The initial liquid composition Al-90at.%Si.

solidification, mobility decreases 25%. Influence of composition on the mobility is more significant at more Si-rich composition. This dependency on composition can explain why mobility in the alloying system is one order of magnitude smaller than pure case.

The other parameter which affects the mobility of the system is temperature of transformation. For a similar deviation of composition from equilibrium, the mobility of steps increases with increasing temperature. There are several analytical models

Table 3.3: Driving force and average velocity parameters for the Al-90at.%Si alloy at temperatures of the simulated systems. Velocities are calculated from the composition equation with the form of $C = A \exp(-f\beta t) + C_{Eq}^{Sim}$ where constant A is equivalent to $C_0 - C_{Eq}$, f is the geometry factor and C_{Eq}^{Sim} is the equilibrium composition results from simulations. \hat{D} is the interdiffusion coefficient at the corresponding temperature and initial composition.

T (K)	$A\times 10^{-2}$	$\beta \times 10^{-9} \left(\frac{m^2}{s}\right)$	$C_{Eq}^{Sim} \times 10^{-2}$	S_{DF}	$\hat{D} \times 10^{-9} \left(\frac{m^2}{s}\right)$
1560	4.5	13.3	85.7	1.110	8.70
1572	2.8	13.7	87.1	1.119	8.90
1580	1.8	14.0	88.0	1.125	9.02



Figure 3.14: Kinetic coefficients for steps at initial melt compositions Al-90at.%Si at three different undercoolings.

[106, 111, 115]. for the crystal/melt interface migration suggesting that the kinetic coefficient is a function of temperature and, more specifically, the diffusion coefficient [131, 132]. Based on the results in table 3.3 the terms β and S_{DF} are temperature dependent and can reflect the effect of temperature. Constant β represents the frequency of atom attachment to the interface from the melt to the crystal at the interface. It has the same units as the interdiffusion coefficient. The trend of β with temperature is the same as the diffusion coefficient for Al-90at.%Si. If we fit β to an Arrhenius-type equation $\beta = \beta_0 \exp\left(-\frac{Q_\beta}{RT}\right)$ we find $Q_\beta/R = 6360K$. This value
is higher than the Q/R = 4316K results from the interdiffusion coefficient for Al-90at.%Si but of the same order of magnitude. Thus, we tentatively conclude that the solid-liquid interface mobility in the case of an alloy also depends on the diffusivity in the liquid.



Figure 3.15: Composition profile in the liquid side of the crystal/melt interface for a Al-90at.%Si alloy. The bin spacing used in the averaging procedure corresponds to 3.5Å.

The mobility results quoted above assume that the growth is reaction controlled and it is important to validate this assumption. The first piece of evidence is the observation that the interface velocity is independent of the step spacing (for large enough spacings). In a purely diffusion controlled growth mechanism it is know that the velocity will depend on terrace length [99]. To further justify the assumption of reaction control, the composition profile in the melt side of the interface was determined. The average composition profile regardless of interface fluctuations does not capture the exact composition profile. Therefore, the crystal/melt interface is descretized within the y - z plane and the position of the interface. In the next timestep the position of the discretized interface is shifted so that the interface has the same position for all slices. Finally, the concentration profile is averaged over all descritized regions. In addition, the composition profiles are averaged over the snapshots from initial composition until it reaches to $(C_0 - C_{Eq})/2$. Results are presented in Fig. 3.15. The width of each bin is $3.5\mathring{A}$ and by increase of bin number the distance from the interface increases.

The concentration of aluminum in each bin is normalized by the average concentration of Al at the corresponding composition. Therefore, for a complete homogeneous distribution of atoms in the melt, C^{Al}/C^{Al}_{ave} is equal to unity. For the case that there is accumulation of Al atoms this ratio will be more than one. As Fig. 3.4 suggests, the normal interaction between Si crystal with the melt results in a depletion of melt from Al atoms at the interface. Using the method explained above in Fig. 3.15 a concentration profile is plotted for Al-90at.%Si and as can be seen a slight increase in the Al concentration is observed at the interface. Nevertheless the percentage increase in C^{Al} is relatively small (see below) and the absolute Al composition at the interface remains low. The difference between Q_{β}/R and activation energy of interdiffusion can be explained using this small deviation of composition at the interface.

3.3.6 Mobility of steps in Al-60at.%Si

The second set of alloying system we have studied is Al-60at.%Si. Similar to Al-90at.%Si, the variation of potential energy as well as composition of melt is non-linear during solidification. Figs. 3.16 illustrates the velocity of the steps as a function of composition deviation from equilibrium for Al-60at.%Si at three different temperatures and for three solid-melt interfaces. In contrast with the Al-90at.%Si alloy independence of v_{step} and terrace length can not be concluded and it is observed that



Figure 3-16: Step velocity vs composition deviation from equilibrium, at three solid-melt interfactor and three undercoolings. The initial fiduid composition of the solid of

Table 3.4: Drfving³ force⁴ and ⁵ average verochy³ parameters⁵ for Al-60 av 5 Si and or ⁵ average verochy³ parameters⁵ for Al-60 av 5 Si and veroperatures of the simulated systems. The constants are the same as table 3.3.

0.

Orientation	T(K)	$A\times 10^{-2}$	$\beta \times 10^{-9} \left(\frac{m^2}{s}\right)$	$C_{Eq}^{Sim} \times 10^{-2}$	S_{DF}	$\hat{D} \times 10^{-9} \left(\frac{m^2}{s}\right)$
(787)	1190	4.8	7.6	55.2	1.06	6.26
(787)	1205	4.2	11.4	56.3	1.07	6.51
(787)	1220	1.8	13.2	57.8	1.08	6.75
(987)	1190	4.7	7.2	55.9	1.06	6.26
(987)	1205	3.9	11.2	57.0	1.07	6.51
(987)	1220	1.8	13.1	57.7	1.08	6.75
(765)	1190	5.2	7.0	55.0	1.06	6.26
(765)	1205	4.1	10.9	56.6	1.07	6.51
(765)	1220	2.2	12.7	57.3	1.08	6.75

Based on these the term β , which represents the frequency of atom attachment to the crystal, increases by increasing the temperature, as well as step separation. However, the rate of variation of the constant β with temperature is much faster than the variation of interdiffusion coefficient. In other words if we fit the β values to an Arrhenius-type equation, related activation energy is one order of magnitude higher than the activation energy of interdiffusion coefficient. This also suggests that the change of temperature has influenced the mechanism of transformation. In addition, as was shown In a previous study [99] for diffusion-controlled crystal growth, the solidification velocity depends significantly on the step separation and consistent with the results found here the velocity increases with increasing step separation.



Figure 3.17: Composition profile in the liquid side on crystal/melt interface for Al-60at.%Si.

Using the same approach explained in section 3.3.5 composition profile at the melt side of the interface calculated which illustrated in fig. 3.17. It is observed that for Al-60at.%Si, the concentration of Al atoms at the interface is much higher than average and more pronounce than the Al-90%Si alloy. It can be concluded that the dominant mechanism of the transformation is not complete reaction-controlled growth and it is instead the mixed scenario. This effect is more significant at higher undercoolings in which the initial driving force of transformation is higher.

3.4 Conclusion

Molecular dynamics simulations have been proven to be an effective tool for computing the mobility of rough solid-liquid interfaces in both pure metals and alloys and for obtaining the mobility of steps at facetted crystal-melt interfaces in the case of pure Si. In this work we have extended the use of MD to determine the step mobility for the case of a facetted interface in an alloy system. In the two compositions and temperature ranges studied we have determined that the lower temperature, higher Al content Al-Si alloy exhibits diffusion or mixed controlled growth of the steps on the (111) interface. Therefore, we have determined the mobility at lower concentrations of Al and at higher temperatures. We find that the mobility decreases fairly rapidly with increasing Al content and the mobility follows the same trend with temperature as the interdiffuion coefficient in the liquid. Finally, the mobility for Al-90%Si in the range T=1560-1580 K is roughly an order of magnitude less than that computed for pure Si.

Chapter 4

Atomistic computation of step free energy in Al-Si

Molecular-dynamics simulations using interatomic potentials of the angular embedded atom method have been performed on Al-Si to compute step free energy which is necessary for continuum modeling of dendritic solidification. The solid-liquid step free energy was obtained by monitoring equilibrium fluctuations in the interface position for Al - 87.4at.%Si and Al - 59.4at.%Si at two step orientations. No anisotropy was observed for these two alloying systems. For the case of Al - 30at.%Si the capillary fluctuation method could not capture the step free energy due to smoothness of the steps.

4.1 Introduction

Mechanical properties of casting and welding products depend significantly on the dendritic microstructure and morphology. Interface motion of crystal-melt is a key process in microstructural evolution, and therefore the thermodynamics and kinetics of interface are of both fundamental and practical importance. As microscopic solvability theory of dendrite growth predicts [104, 103], a dendrite tip radius and growth velocity are sensitive functions of the anisotropy in the crystal-melt interfacial free energy, γ , as well as the kinetic coefficient. The crystal-melt interfacial free energy, defined as the reversible work required to form a unit area of interface between a crystal and a coexisting fluid, has been the subject of many studies for rough interfaces.

Direct experimental measurements of crystal-melt free energy are quite difficult and relatively few in number[133]. They typically involve contact angle studies and, with the exception of a small number of studies on transparent organic materials[134, 135], are not precise enough to capture anisotropy. This inherent difficulty associated with direct experimental measurements motivated the development of a variety of novel computational methods to determine γ via molecular simulation. These methods include ab initio method, [136], classical nucleation theory based models [137], free energy integration method [138, 139], cleaving wall molecular dynamics simulation method [140, 141, 142] and analysis of equilibrium capillary fluctuations in interfacial position for complicated molecules[143], grain boundaries [144] pure metals[145, 146, 147, 117, 114, 148], binary [149, 150, 151, 152] and ternary [153] alloying systems.

In classification of interfaces, beside the rough interface, where atom attachment to the growing phase occurs readily at any point on the boundary, faceted interfaces form some energetically favourable sites for *adatoms*. These smooth interfaces are identified by the presence of immobile terraces separated by steps of roughly atomic height. This kind of system has addressed in a very few studies [8, 69]. In these studies, Buta et al. [8] used non equilibrium MD simulations of crystal growth to calculate the step kinetic coefficient at crystal melt interfaces, as well as the effect of step separation on the kinetic coefficient and Frolov and Asta [69] used classical nucleation theory based model for two dimensional nucleation of silicon liquid pools to calculate the step free energies , γ_{step} at faceted crystal-melt interfaces from equilibrium MD simulations. In both of these studies, the Stillinger-Webr (SW) [37] potential has been used to approximate the interactions between silicon atoms. However, Frolov and Asta [69] observed that SW Si potential solidifies in wurtzite crystal structure, rather than the diamond cubic structure. They predicted that it might be due to the lower step free energy of wurtzite crystal structure compare to the diamond cubic crystal structure. Beaucage and Mousseau [66] had been reported formation of random mixture of stacking sequences of silicon layers using SW as well. In order to solve this problem Saidi et al. [127] extended the cut off distance of pair interaction in original SW up to the second nearest neighbour and stabilized the diamond crystal structure in compete with wurtzite crystal structure.

Systems that include chemically dissimilar components are another class of systems that despite their technologically importance, in relatively few fundamental studies have been considered [123, 124]. This gap of investigation is more significant for a mixed type bonding alloying systems. The main reason is the lack of a reliable model to include all types of interactions in such a system as well as an authentic interatomic potentials. in 2009, Dongare et al. [48] developed the angular-EAM (AEAM) interatomic potential model, which is specifically designed to model alloys of a metal species combined with covalently bonded materials such as silicon. Using this model, Saidi et al. [127] developed a potential for the case of Al-Si, which reproduces quite accurately the phased diagram with almost zero solubility of components into each other in solid state, which is an important feature of this alloying system. Using this potential they predicted the kinetic coefficient of silicon steps [99].

In the present study we employ equilibrium molecular dynamics (MD) simulations, AEAM based Al-Si potential and the capillary-fluctuations method (CFM) to calculate crystal-melt step free energies at three different melt compositions. Anisotropy of steps investigates by setting up the systems with different crystal orientations of steps on the high-symmetry interface plane, (111) in this case. Using these results, will discuss the range of composition and temperature that level of crystallinity and fluctuations of steps is not in the range to use CFM to calculate the step free energy.

4.2 Methodology of atomistic simulation

In the CFM, step free energies are derived through an analysis of equilibrium stepheight fluctuations obtained from MD simulations for coexisting crystal-melt system that includes an active step. This method is based on the relationship between the static height-fluctuation spectrum of a rough step and its effective Hamiltonian [154].

$$\left\langle \left| A\left(k_{\rm n}\right) \right|^2 \right\rangle = \frac{k_{\rm B} T_{\rm Eq}}{l_{\rm step} \left(\gamma_{\rm step} + \gamma_{\rm step}''\right) k_{\rm n}^2} \tag{4.1}$$

where $A(k_n)$ is the Fourier amplitude of the step height fluctuation with wave number $k_n = \frac{2\pi n}{l_{\text{step}}}$ where $n = -N/2 + 1, -N/2, \dots, -1, 0, 1, \dots, N/2$, k_B is Boltzmann constant, T_{Eq} is the equilibrium temperature of coexistence of crystal and melt at the composition of interest and l_{step} is the length of the fluctuating step. The term $(\gamma_{\text{step}} + \gamma_{\text{step}}'')$ corresponds to the step stiffness, where γ_{step}'' is the second derivative of step effective Hamiltonian as a function of the angle between the instantaneous and average step normal.

Equation 4.1 is derived starting from an effective Hamiltonian for the step and by applying equipartition of energy. strictly speaking it does not include entropic contributions to the true step free energy. This subtle point has been discussed in previous studies (Fisher). recently, Freitas et al have derived a correction to the CFM formulation that captures the true step free energy. Assuming lack of crystal orientation dependancy (isotropy) for the step, the authors calculated the step free energy per unit length as

$$\gamma_{\text{step}}^{\text{Modified}} = \gamma_{\text{step}} \left[1 + \left(\frac{k_B T_{\text{Eq}}}{\gamma_{\text{step}} l_{\text{step}}} \right) \sum_{n=1}^{n=(N-1)/2} \ln \left[\left(\frac{\gamma_{\text{step}} l_{\text{step}}}{\pi k_B T_{\text{Eq}}} \right) \left(\frac{2\pi n}{N} \right)^2 \right] \right]$$
(4.2)

In the subsequent section we will present results for the step energy using both eqs. 4.1 and 4.2

In this study the interactions between the components of the Al-Si system are approximated by the (AEAM) empirical potential developed by Saidi et al[127]. In order to prepare systems with an active step at coexistence of a pure silicon crystal in contact with an alloying liquid, a non-orthogonal box is considered which is periodic in three dimensions. A non-orthogonal coordinate system allows us to prepare the system in such a way that the component of stress in the step plane remains zero and thus does not affect the fluctuation of the step. Fig. 4.1 shows the crystal and melt and two interfaces, each one including one active step. The xz plane of simulation box is tilted around the step axes in a way that guarantees a displacement at the periodic image is equal to the height of the step (h). System preparation starts with the equilibration of pure silicon in the solid state using the NPT ensemble at the desired temperature T and pressure P = 0. After equilibration of the system, the identity of some atoms, which are meant to be in the liquid state, changes to reach the corresponding composition of the liquid in contact with solid silicon crystal. The liquid region develops in a way that two steps form. The output of this level of simulation is used as the initial condition for the subsequent simulations. In the next level an $NA_{xz}P_yT$ ensemble is employed, which means that the system size is fixed in the x and z directions, and the pressure is controlled by changes in the y, ([111]), direction.



Figure 4.1: Illustration of the geometry of the simulation cells employed in CFM calculations of the step free energies. Si atoms are colored blue and Al atoms, which appear in the liquid only, are red.

Table 4.1 shows the list of the systems which were considered in this study. Three liquid compositions at three temperatures dictated by the phase diagram were selected. For each temperature, steps are designed in two orientations, $[\bar{1}10]$ and $[11\bar{2}]$. The time step of the simulations were 1 fs and snapshots of the systems were saved every 50 ps during this simulation. 200 snapshots were saves for each system, which contained positions of atoms, energies, and stresses, and used for post processing.

In order to capture the fluctuations of the step, we need to determine the position

Table 4.1: Compositions, dimensions, temperature and orientations of the MD simulation systems. l_{step} is the length of the system along the steps, l_z is the length of simulation cell in the direction of the step fluctuations. $l_{[111]}$ is the initial length of the simulation box in the [111] direction perpendicular to the interface plane, which changes during solidification. The number of the atoms in each system is " N_{atoms} ". The composition of the liquid and the temperature of interest are chosen based on the Al-Si phase diagram for the AEAM potential.

Composition	Step direction	$l_{ m step}\left({A} ight)$	$l_{z}\left(\mathring{A} ight)$	$l_{\left[111 ight]}\left(\mathring{A} ight)$	N_{atoms}	Temperature (K)
Al-87.4at.%Si	$[\bar{1}10]$	92.65	142.66	113.48	73704	1570
Al-87.4at. $\%$ Si	$[11\bar{2}]$	133.74	92.65	113.48	69120	1570
Al-59.4at. $\%$ Si	$[\bar{1}10]$	92.65	142.66	113.48	73704	1230
Al-59.4at. $\%$ Si	$[11\overline{2}]$	133.74	92.65	113.48	69120	1230
Al-30at. $\%$ Si	$[\bar{1}10]$	92.65	142.66	113.48	73704	920
Al- $30at.\%Si$	$[11\bar{2}]$	133.74	92.65	113.48	69120	920

of the interface between crystal and melt. Therefore the state of all atoms in the system are determined using the order parameter proposed by Buta [8] for diamond crystal structures. This criterion is based on the symmetry of the second neighbour atoms of each individual atom and four first nearest neighbours. The discrimination function $\psi(i)$ of an atom *i* defined as [8] :

$$\psi(i) = \left| \frac{1}{ZN_{\mathbf{q}}} \sum_{\mathbf{q}_{i}} \sum_{j=1}^{Z} \exp\left(-i\mathbf{q}_{i} \cdot \mathbf{r}_{j}\right) \right|^{2}$$
(4.3)

where Z is the number of neighbouring atoms found in a sphere of radius 2.8Å surrounding atom i. \mathbf{r}_j is the vector from atom i to the immediate $N_{\mathbf{q}} = 12$ atoms found within the cut-off distance of first nearest neighbours, and \mathbf{q}_i are the vectors where we expect to observe the neighbouring atoms in a perfect diamond cubic crystal structure. By design, $\psi(i) = 1$ for a perfect diamond crystal structure and $\psi(i) \approx 0$ for an atom in a liquid phase. The accuracy of the discrimination factor is improved by calculating the average order parameter $\bar{\psi}$ for each atom with the order parameter of the Z nearest neighbours. Fig. 4.2 shows the atoms coloured based on their state

and type. 4.2 (a) is the illustration of a simulation box where a silicon crystal (blue part) is in contact with the melt on two sides where yellow particles represent silicon in liquid state and red particles are aluminum. 4.2 (b), (c) and (d) are snapshots of atomic planes containing individual steps in contact with melt with compositions Al-30at.%Si, Al-59.4at.%Si and Al-87.4at.%Si respectively.



Figure 4.2: a) Results of applying discrimination factor to the atoms of a simulation box. Blue particles are Si in solid state. Yellow atoms are Si in liquid state and red ones are Al atoms. (b), (c) and (d) are showing individual steps where the melt includes 30%, 59.4% and 87.4% silicon, respectively.

Results of the order parameter calculation during fluctuation of steps shows that small solid islands on the melt side of $_{(t)}$ he interface and $_{(t)}$ puddles of liquid in the crystalline step are identified. These local regions are not stable for more than 1 ps. The solid islands remelt very quickly while the liquid puddles solidify. Therefore, in a subsequent step in the post processing analysis, the bilayer active steps are separated and the state of these local parts modifies in order to avoid the errors associated to these local defects in calculation of interface position. Different steps of this procedure are depicted in Fig. 4.3.

Fig. 4.3(a) shows the view perpendicular to a step after applying the discrimination factor to each atom. The domain is divided into discrete counterparts. Discrete



Figure 4.3: Different steps of state modification for discretized domain. a) Colouring the atoms according to their state. b) Discretizing the domain and determining the state of each counterpart based on the average order parameter of the involved atoms. c) Changing the state of the liquid puddles according to the state of the neighbouring counterparts in a way that a continuous solid part without liquid puddles forms. d) Changing the state of the solid islands according to the state of the neighbouring counterparts so that a continuous liquid part without solid islands forms. e) Utilizing the continuous parts of last two steps as the liquid and the solid parts f) Altering the state of the horizontal branches in each column of counterparts and determining the exact position of the interface in the corresponding column.

domains are rectangles with the side size of 0.8a and 0.5a along and perpendicular to the step, respectively, where a is the lattice parameter of silicon in diamond crystal structures. This size guarantees that there is at least one atom in each domain and that it is smaller perpendicular to the step direction, which allows a more precise determination of interface position. As shown in Fig. 4.3(b) the state of each domain is determined based on the average order parameters of all atoms contained in the domain. Starting from the solid side of the system (lower left corner of the system), an ID is assigned to each region and the state of the regions are checked. If it is in liquid state but the neighbouring regions with smaller IDs are in solid state, the state of the respective region is changed to solid. The result of this modification is shown in Fig. 4.3(c), eliminating liquid puddles within the continuous solid. The algorithm then assigns new IDs, starting in the top-right corner, and eliminates solid islands from the continuous liquid region; solid islands are changed based on neighbouring liquid regions with lower IDs. The results are shown in Fig. 4.3(d). Fig. 4.3(e) shows the merged output of the algorithm. If there was no state change in b, c, and d then the state did not change. If liquid became solid from b to c solid was assigned to that region for part e. Similarly, if solid became liquid from b to d liquid was assigned to that region for part e. In the final step, each column of domains is descended until crossing the liquid to solid boundary, establishing the interfacial position. In this way all horizontal branches are eliminated. The position of the interface mapped from the original atoms position and atoms state is shown in Fig. 4.3(f).

After calculating the position of the interface, the amplitudes $A(k_n)$ are obtained through a Fourier transform of the interface location. This is performed for each snapshot and the results are time averaged to obtain $\langle |A(k_n)|^2 \rangle$. A fit of $\langle |A(k_n)|^2 \rangle$, versus $\frac{1}{k_n^2}$ is then used to derive values for the step free energy.

4.3 **Results and discussions**

Fig. 4.4 shows the fluctuation spectra, $\langle |A(k_n)|^2 \rangle l_{\text{step}}$ vs k_n , on a log-log scale for (a) Al - 59.4at.%Si and (b) Al - 87.4at.%Si. Results include both [$\bar{1}10$] and [$11\bar{2}$] step orientations. Standard errors for the quantity $\langle |A(k_n)|^2 \rangle$ are also shown by the error bars in the graphs. The solid lines in these graphs represent slopes of -2, which is the value predicted by Eq.4.1. For almost all cases the curves show a levelling off for small values of k_n .

One of the advantages of the CFM is its application to determine the anisotropy in γ_{step} to a higher precision than is possible in other methods, including cleaving. This is due to the fact that the CFM determines directly the interfacial stiffness, $\gamma_{\text{step}} + \gamma_{\text{step}}''$, which is much more anisotropic than γ_{step} itself. For a weakly anisotropic system and steps with a six fold symmetry, the relationship between the stiffness with θ follows $\gamma_{\text{step}} + \gamma_{\text{step}}'' = \gamma_0 (1 - \alpha \cos 6\theta)$. In this study two independent stiffness value are measured to parameterize γ . The calculated stiffness are presented in table4.2. Using these results we find $\alpha < 0.03$. Considering the standard deviation in the calculation, which is about 6%, the values calculated for different orientations are equal within statistical uncertainty. In other words, the step free energy is invariant with respect to direction.



Figure 4.4: Log-Log plot of the fluctuation spectra, $\langle |A(k_n)|^2 \rangle l_{\text{step}}$ vs k_n , for (a) Al - 59.4at.%Si and (b) Al - 87.4at.%Si alloys in the [$\overline{1}10$] and [$11\overline{2}$] step orientations. The solid line indicates a slope of -2. These graphs illustrate the effect of crystal orientation on the stiffness of steps. The predict of 1.59.6 at %Si cFM is the same for both step orientation Al - 59.6 at %Si indicates the steps are isotropic in 1.59.6 at %Si em.



on the step-effective Hamiltonian. A full statistical mechanics treatment of the fluctuation problem results in a modified step free energy given in Eq. 4.2. The only assumption of this equation is the isotropy of step free energy. Using this assumption the modified value of step free energy per unit length is reported in the last column of table 4.2. This correction coefficient can be up to 30% for the results in this study.

Table 4.2: Calculated stiffness values before and after modification as a function of interface orientation for a Al-87.4at.%Si and Al-59.4at.%Si alloy. Error bars represent estimated 95% confidence levels associated with statistical sampling.

			1 0	
Composition	Step direction	$T_{\mathrm{Eq}}\left(k ight)$	$\left(\gamma_{\text{step}} + \gamma_{\text{step}}''\right) \times 10^{-11} \left(\frac{J}{m}\right)$	$\gamma_{\text{step}}^{\text{Modified}} \times 10^{-11} \left(\frac{J}{m}\right)$
Al-87.4at.%Si	$[\bar{1}10]$	1570	1.78 ± 0.12	2.12
Al-87.4at. $\%$ Si	$[11\overline{2}]$	1570	1.67 ± 0.11	2.18
Al-59.4at. $\%$ Si	$[\bar{1}10]$	1230	2.61 ± 0.13	3.29
Al-59.4at.%Si	$[11\bar{2}]$	1230	2.60 ± 0.16	3.35

Fig. 4.5 illustrates the effect of composition on the slope of the fit and the fluctuation spectra. The results indicate that the CFM can predict successfully the stiffness of the steps in the Al - 59.4at.%Si and Al - 87.4at.%Si alloys. Using classical nucleation theory, Frolov and Asta computed the value of $\gamma_{\text{step}} = 1.03 \pm 0.05 \times 10^{-11} (J/m)$ for the step free energy of pure silicon. Based on the results of this study we conclude that the step free energy increases with decreasing temperature and/or increasing concentration of Al in the liquid. Previous studies have indicated that the excess free energy of rough solid-liquid interfaces (Spaepen) increases with increasing temperatures, that is, the opposite as that observed here. This suggests that the role of Al additions is playing a crucial role in the step free energy of steps.

However, for the low temperature, high Al content alloy (Al - 30at.%Si), a line with slope -2 can not be fitted to the $\langle |A(k_n)|^2 \rangle l_{\text{step}}$ vs k_n results. This behaviour develops gradually. For the case of Al - 87.4at.%Si the best fit line agrees well with a slope of -2, however for the Al - 594at.%Si alloying system, the slope of the best fit to





Figure 4.5: Log-Log plot of the fluctuation spectra, $\langle |A(k_n)|^2 \rangle l_{\text{step}}$ vs k_n , for (a) [$\overline{110}$] and (b) [$11\overline{2}$] for Al - 87.6at.%Si, Al - 59.4at.%Si and Al - 30at.%Si alloying systems at 1570 K, 1230K and 920K, respectively. For the last system the results do not follow the predicted slope of -2.

the amplitude vs wave number results is less than -2. As a fundamental assumption, the CFM can be used only for cases where the step is rough. Based on the Al-Si phase diagram, this alloy shows a single eutectic point at 12.6 at% Si. Therefore, the liquidus line decreases by adding Al to the melt and the equilibrium temperature decreases for more Al-rich compositions. Based on these results it can be concluded that at lower temperatures or higher Al concentrations, the step behavior can no longer be considered rough. However, this observation does not necessarily imply the step is undergoing a roughening transition. Results from previous theoretical studies [119] indicate that in the solid on solid model a roughening transition cannot occur, but the equilibrium kink density can decrease significantly with decreasing temperature. Chernov concluded high surface energies and low temperatures lead to a low density of kinks on steps, which is the case, e.g., in low-temperature epitaxy. A decreasing kink density may also account for the results shown in Fig. 4.5.

4.4 Conclusion

Through an analysis of capillary fluctuations in the interfacial position, we have determined the step free energy for a binary Al-Si mixture at three compositions and two crystal orientations. In addition, a recent correction to the calculation of step free energy was applied to the results as well. Our results for the anisotropy in γ_{step} show complete isotropy of step free energy. The CFM could not lay on the appropriate slope in the fluctuation spectra, vs k_n graphs for Al - 30at.%Si. We concluded that the steps are no loner rough at 920 K, which is the liquidus temperature of the Al - 30at.%Si system.

Chapter 5

Diffusion Controlled Growth Rate of Stepped interfaces

For many materials, the structure of crystalline surfaces or solid-solid interphase boundaries is characterized by an array of mobile steps separated by immobile terraces. Despite the prevalence of step-terraced interfaces a theoretical description of the growth rate has not been completely solved. In this work the boundary element method (BEM) has been utilized to numerically compute the concentration profile in a fluid phase in contact with an infinite array of equally spaced surface steps and, under the assumption that step motion is controlled by diffusion through the fluid phase, the growth rate is computed. It is also assumed that a boundary layer exists between the growing surface and a point in the liquid where complete convective mixing occurs. The BEM results are presented for varying step spacing, supersaturation and boundary layer width. BEM calculations were also used to study the phenomenon of step bunching during crystal growth and it is found that, in the absence of elastic strain energy, a sufficiently large perturbation in the position of a step from its regular spacing will lead to a step bunching instability. Finally, an approximate analytic solution using a matched asymptotic expansion technique is presented for the case of a stagnant liquid or equivalently a solid-solid stepped interface.

5.1 Introduction

The mobility of interphase boundaries plays a crucial role in the description of many important processes, from the growth of protein crystals to the heat treatment of alloys. In studying the motion of interfaces, the first level of classification is the distinction between rough and faceted (smooth) interfaces. For a rough interface atom attachment to the growing phase occurs readily at any point on the boundary and rough interfaces are characteristic of solid-liquid interfaces in most metals and alloys. On the other hand faceted interfaces are identified by the presence of immobile terraces separated by steps of roughly atomic height. The description of crystal growth from the vapor as the lateral motion of steps across the surface was first introduced by Frankel [94] and Burton, Cabrera and Frank [95]. In many alloy systems the interface between a precipitate and the matrix phase can also be described by a series of mobile steps. Thus Aaronson [155] extended the ideas of Burton et al and proposed the so-called ledge mechanism in solid-solid systems. To date, electron microscopy studies, most notably, those employing the scanning tunnelling microscopy (STM) technique [156] confirmed the ledge mechanism in many systems such as pure Si [157] grown from the vapour, and alloying systems [158, 159] including steels [160, 161] and Aluminum alloys [162, 163, 164, 165, 166, 167, 168].

The other set of classification in crystal growth theories are diffusion-controlled

and/or interface-controlled systems. In the latter case, most theories assume some rate-controlling event to occur on the surface, either as a result of nucleation rates or some process such as adsorption, surface diffusion, step incorporation, etc [102, 101, 100]. Another real possibility is that the solute transfer to the surface may be limited by mass transfer or diffusion through the bulk solution. Despite the importance of diffusion controlled growth only a limited number of analytic solutions are available. For a planar, rough interface growing in an infinite system the concentration profile can be obtained and the solution has been utilized in the well known Mullins and Serkerka instability theory [169, 170]. The diffusion controlled growth of a paraboidal shaped dendrite has been solved exactly by Ivantsov [171] under the assumption of no capillarity effects. The more general case has been the subject of many theoretical studies and has lead to the solvability criterion of velocity selection for dendritic solidification. In many alloy systems plate-like precipitates with approximately parabolic tips are observed and several studies have been conducted to predict the precipitate growth rate from the Ivantsov approach [96, 97, 98]. In these studies the relationship between the velocity of the plate tip and supersaturation at a specific tip curvature was predicted. However, the predictions of these models usually show a significant deviation from experimental results [172]. In order to explain this discrepancy several authors examined factors such as anisotropy of the surface energy [173], non-ideal solution [174] and, most importantly, inability of a smooth parabola to represent the step-terrace geometry [175].

For faceted interfaces, reliable modelling of the diffusion controlled ledge mechanism needs a geometry in which mobile steps, as sinks of solute, are positioned at discrete locations along the interphase boundary. This geometry differs from classical models where a uniform flux along the rough interface is assumed. For the case of smooth interfaces, the most general form of the diffusion equation would be the following:

$$D\nabla^2 c - v_K \frac{\partial c}{\partial x} - v_S \frac{\partial c}{\partial y} - v_D \frac{\partial c}{\partial z} = 0$$
(5.1)

where v_K , v_S and v_D are kink, step and surface velocities, respectively, D is the diffusion coefficient in the matrix phase and c is the concentration. The solution of Eq. 5.1 with different simplifying assumptions has been considered in the literature. One of the first models developed by Burton et al. [95], known as the BCF model, assumed that steady growth occurs only at energetically favourable kinks. In addition, it was assumed that the relative motion of any sinks such as kinks or steps is negligible when compared with the bulk diffusion fluxes. Therefore they solved $D\nabla^2 c = 0$. Using a set of geometric approximations, and defining the influence region for kinks, steps and the solidification front, they calculated the interface velocity for systems with equally spaced steps.

When the ledge mechanism is dominant, attachment of the adatom can happen anywhere along the step, which is itself rough. Therefore, in this case, kink formation is unnecessary for the progress of crystal growth. Thus, the term in Eq. 5.1 that includes the kink velocity can be eliminated. Chernov [176] modified the BCF diffusion model. He made the simplifying assumption that the distance between two successive kinks is so small that one can consider a step as a long sink, and thus the concentration profile is merely dependent on two dimensions perpendicular to the step line. Instead of using an approximate solution by a geometrical division of the domain (as was done by BCF), $D\nabla^2 c = 0$ was solved analytically, using a conformal mapping technique, in two dimensions for an infinite and periodic array of steps. However, Chernov used an attachment limited boundary condition at the steps, rather than a diffusion controlled condition. In the Chernov approach each step is a source point and the height of the step is negligible in comparison with the length of the terraces. Besides simple mass transfer limitations, Ohara [171] considered the effect of heat evolution (or absorption) at the crystal interface and derived an equation to account for the simultaneous transfer of heat and mass and they concluded that simultaneous heat transfer effects are negligible. In another study by Jones and Trivedi [9], the height of the step was considered explicitly and diffusion control was assumed. The analytic solution was obtained in the limit of zero Peclet number and is valid for a single isolated step. Atkinson further improved the previous method by calculating the concentration profile in the case of small Peclet numbers by utilizing Fourier transformations, multiple scale analyses and a singular perturbation method for an isolated step [177], multiple steps [178] and steps close to an external surface [179]. In addition, a finite-difference based diffusional growth model has been used for numerical modelling of the ledge density effects, ledge nucleation kinetics and the presence of multiple precipitates on solute buildup in the matrix. [180, 181, 182, 183, 184, 185]

The other phenomenon that can be addressed by solving the diffusion equation is step bunching, which refers to the tendency of a regular spaced step train to become unstable and to form regions of closely spaced steps separated by long terraces. For the case of crystals grown from deposition through a vaopr phase step bunching has been well studied. In an early treatment of step bunching, Frank explained this phenomenon using an impurity mechanism [186]. A more recent stability analysis [187] has shown that step bunching can occur due to an asymmetric flux to a step arising from the Ehrlich-Schwoebel barrier [188, 189].

For crystals grown from the melt the asymmetry in flux and hence step bunching can be provided by flow in the liquid. For a far field liquid flow in the direction of step motion the regular array is stabilized against bunching, whereas flow in the direction counter to the step growth direction acts to destabilize the interface. In several studies Bredikhin and co-workers [190, 191, 192, 193] have studied step bunching and they conclude that, even in the absence of liquid flow, a regular train of steps is inherently unstable due to the interaction between traveling inhomogeneities of step density and diffusion in the solution. The BEM computations performed here will help address step bunching during diffusion controlled growth.

The purpose of the present work is to provide numerical and analytic solutions to a growth process of facetted interfaces not yet considered, that is, the diffusion controlled growth of an infinite train of equally spaced steps. We begin by introducing the boundary element technique for the case where a boundary layer is assumed in the liquid adjacent to the crystal-melt interface and determine the concentration field and growth velocity as a function of step separation and boundary layer width. In addition, we examine the instability of equally spaces train of arrays by apply a perturbation to a single step and calculating the velocity of the neighbouring steps to determine the final stable arrangement of a train of steps. Finally, we present an approximate analytic solution based on a matched asymptotic technique for the case of no boundary layer, which is valid for the case of growing precipitates in alloys.

5.2 Boundary Integral Formulation

Consider a coordinate system in which the steps are moving at constant velocity in the direction x and the interface as a whole migrates in the y direction. If the step spacing is large it is reasonable to neglect the velocity in y and the diffusion equation can be rewritten as:

$$D\nabla^2 c + v_x \frac{\partial c}{\partial x} = 0 \tag{5.2}$$

where v_x is the step velocity, D is the diffusivity in the matrix, liquid or vapour phase, and c is the concentration. The 2D geometry also assumes that the steps are straight. Further we assume that the steps are energetically favourable sites for atom attachment and no surface adsorption at the terraces is allowed.

For convenience we can re-write Eq. 5.2 in a dimensionless form by defining a Peclet number $p_x = \frac{v_x h}{D}$ which is scaled by the step height h and a scaled concentration given by the form used by Atkinson: $u = \frac{c-c_0}{c_e-c_0}$. The scaled variables yields the following:

$$\nabla^2 u + p_x \frac{\partial u}{\partial \tilde{x}} = 0 \tag{5.3}$$

The value of scaled concentration varies between zero for the far field limit and unity for the equilibrium condition. For developing the boundary element formulation, we employed the method used by several authors [194, 195, 196, 175], which relies on a variable transformation in order to reduce the problem to a Helmholtz equation. The variable transformation has the form $u = \phi e^{-\frac{p_x}{2}\tilde{x}}$. After substituting the final Helmholtz equation obtains as

$$\nabla^2 \phi - \left(\frac{p_x}{2}\right)^2 \phi = 0 \tag{5.4}$$

The fundamental solution corresponding to Eq. 5.4 should satisfy the equation:

$$\nabla^2 G\left(\mathbf{r}, \mathbf{r}'\right) - \left(\frac{p_x}{2}\right)^2 G\left(\mathbf{r}, \mathbf{r}'\right) = -\delta\left(\mathbf{r}, \mathbf{r}'\right)$$
(5.5)

where \mathbf{r} and $\mathbf{r'}$ are vectors representing field and boundary points respectively, δ is the Dirac delta function and $G(\mathbf{r}, \mathbf{r'})$ is the Greens function for the corresponding Helmholtz equation and is expressible as a function of K_0 , the modified Bessel function of the second kind of order zero i,e.:

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{2\pi} K_0\left(\left(\frac{p_x}{2}\right)|\mathbf{r} - \mathbf{r}'|\right)$$
(5.6)

where the Peclet number is defined as a positive quantity.

From Greens theorem, the boundary integral formulation is established:

$$\alpha u\left(\mathbf{r}\right) - \int u\left(\mathbf{r}'\right) \frac{\partial G\left(\mathbf{r},\mathbf{r}'\right)}{\partial n'} e^{\frac{p_{x}}{2}\left(r'_{x}-r_{x}\right)} d\Gamma\left(\mathbf{r}'\right) + \frac{p_{x}}{2} \int G\left(\mathbf{r},\mathbf{r}'\right) u\left(\mathbf{r}'\right) \frac{\partial r'_{x}}{\partial n'} e^{\frac{p_{x}}{2}\left(r'_{x}-r_{x}\right)} d\Gamma\left(\mathbf{r}'\right) = -\int G\left(\mathbf{r},\mathbf{r}'\right) \frac{\partial u\left(\mathbf{r}'\right)}{\partial n'} e^{\frac{p_{x}}{2}\left(r'_{x}-r_{x}\right)} d\Gamma\left(\mathbf{r}'\right)$$
(5.7)

where the parameter α is a constant and its value depends on the location of **r**. When **r** lies inside the domain α takes the value of unity and when **r** lies on a smooth boundary α takes the value $\frac{1}{2}$. In the above equation $\frac{\partial}{\partial n'}$ is the directional derivative of the corresponding function in the direction of the outward pointing normal n' to the surface element $d\Gamma$. The derivative of the fundamental solution appearing in the first integral is:

$$\frac{\partial G}{\partial n'} = \frac{p_x}{4\pi} K_1 \left(\frac{p_x}{2} \left| \mathbf{r} - \mathbf{r}' \right| \right) \cdot \frac{(\mathbf{r} - \mathbf{r}') \cdot n'}{\left| \mathbf{r} - \mathbf{r}' \right|}$$
(5.8)

where K_1 is the modified Bessel function of the second kind of order one.

For boundary integral implementation we follow the procedure explained in detail in [51] and used in several studies [194, 196]. Equation 5.7 can be rewritten as

$$\alpha u + \int_{\Gamma} uq^* d\Gamma - \int_{\Gamma} qu^* d\Gamma = 0$$
(5.9)

where we have taken q^* as the coefficients of u and u^* is the coefficients of $q = \frac{\partial u(\mathbf{r}')}{\partial n'}$. The boundary Γ is discretized into N straight line segments where u_j and q_j are respectively approximated as constants, such that they can be removed from the integrals. This yields:

$$\frac{1}{2}u_i + \sum_{j=1}^N \left(\int_{\Gamma} q^* d\Gamma\right) u_j - \sum_{j=1}^N \left(\int_{\Gamma} u^* d\Gamma\right) q_j = 0$$
(5.10)

After integration the whole set of equations can be expressed in matrix form as:

$$[\mathbf{A}] \{ \mathbf{Y} \} = [\mathbf{F}] \tag{5.11}$$

where \mathbf{Y} is the vector of unknowns *u*'s or *q*'s. For each case the total number of unknowns should be equal to the number of the possible equations for the whole domain. Therefore, we can find the value of scaled concentration and flux for every element on the boundary of the domain. In a post processing step one can calculate the concentration at any point in the interior from the known boundary terms.

It is common to employ numerical methods such as Gaussian quadrature for the integrals appearing in Eq. 5.10 and the matrix elements of [A] [175]. However, singularities occur when $\mathbf{r} = \mathbf{r}'$. The singularity problem is usually solved by estimating the Bessel functions in the limit of small $\mathbf{r} = \mathbf{r}'$, which results in integrable functions. However, In order to avoid this difficulty we utilized the analytical integration results developed by Ang [197]. Here the integral over any element, including the singular elements, cane computed without resorting to the more expensive Gaussian quadrature or similar numerical integration schemes.

Using the mass conservation principle for the step element we can calculate the relationship between flux, concentration and velocity as:

$$D\frac{\partial c}{\partial x} = v_x \left(c - c_s\right) \tag{5.12}$$

where x is perpendicular to the step element and c_s is the concentration in the solid. After scaling x with the step height h and using the dimensionless concentration in equilibrium condition we have:

$$\left. \frac{\partial u}{\partial n'} \right|_{step} = p_x \left(1 - \frac{1}{\Delta} \right) - p_x u \tag{5.13}$$

where $\frac{\partial u}{\partial n'}\Big|_{step}$ is the flux at the step and $\Delta = \frac{c_e - c_0}{c_e - c_s}$ is the supersaturation. Therefore, since scaled concentration is unity under equilibrium conditions, $\frac{\partial u}{\partial n'}\Big|_{step} = -\frac{p_x}{\Delta}$ represents the linear relationship between supersaturation and Peclet number under the assumption of local equilibrium at the step face.

5.3 Results and discussions

Fig. 5.1 shows the geometry of the domain we consider in this study. The interface consists of a series of steps of uniform height as well as terraces, which is the characteristic geometry of the ledge mechanism. Fig. 5.1 is a snapshot from a molecular dynamics simulation [198] of pure Si (the red atoms) solidifying into an Al-Si liquid. The faceted interface is a vicinal 111 boundary.



Figure 5.1: The geometry of the computational domain and the boundary conditions used in the boundary integral formulation. The periodicty in the x direction is given by λ and the length along y is boundary layer thickness δ . The equilibrium concentration is assumed along the step face and a zero flux condition is applied at the immobile terraces.

In this study we assumed that steps are equally spaced. Therefore a domain whose bottom boundary includes a single step and has a length equal to the half distance of neighbouring terraces can represent the whole system. The computational domain in the vertical direction extends up to the length (δ) . By setting the scaled concentration to zero all along the top boundary we are assuming that there exists a boundary layer of dimension δ after which convective mixing fixes the liquid composition at its average value. Clearly, the effect of convection limits the solution to solid-liquid or solid-vapor systems and the stagnant case, valid for alloys, will be treated in a subsequent section. Since the height of the step is on the order of atomic height, we assume the concentration along the step is constant and the step is in equilibrium (u = 1). In the previous conformal mapping solution by Jones and Trivedi the concentration along the step varies considerably and an advantage of the BEM is the ability to maintain a fixed value of u = 1 along the step face.

To set the boundary conditions along the two sides of the computational domain we exploit the fact that the system is periodic in x. Therefore, we solve the Helmholtz equation subject to the following:

$$\begin{aligned} u\left(-\frac{\lambda}{2}, y\right) &= u\left(\frac{\lambda}{2}, y\right) \\ \frac{\partial u}{\partial n'}\Big|_{x=-\frac{\lambda}{2}} &= -\frac{\partial u}{\partial n'}\Big|_{x=\frac{\lambda}{2}} \end{aligned}$$
(5.14)

Here we must distinguish the actual step spacing λ with the *x* dimension of the computational domain, which has been denoted by *T*. A simple geometric expression relates the two quantities: $\lambda = T \cos \theta + \frac{h}{2} \sin \theta$ where θ is the angle between the terrace and periodicity direction. There are several different ways to apply the above boundary condition in a boundary integral code. We followed the method explained in detail by Ang [197], which requires the addition of two sets of unknowns, rather than one, for each element at the sides of the domain, and at the same time two sets of constraint equations based on periodic boundary conditions given above.

In the results to follow all elements were the same length, which was set equal to the length of the step face. Thus, the total number of nodes is in proportion to the terrace length and δ . That is, T/h + 1 and T/h along the bottom and the top boundaries of the domain respectively and δ/h on the two vertical sides. As mentioned above, all integrals in the BEM procedure were evaluated analytically.

The value of the Peclet number for solidification where the diffusion coefficient in liquid phase is in the order of $10^{-5} \frac{cm^2}{s}$ and for a system like Al-Si, with step height of $h = 3.15 \times 10^{-8} cm$, would be in the order of 10^{-6} . Therefore the velocity of the step is negligible when compared with the bulk diffusion flux and the term including Peclet number in Eq. 5.2 could be ignored. Thus, Helmholtz equation reduces to Laplace equation. The equivalent boundary condition would be zero flux for side boundaries, which is similar to the boundary condition used in other studies [95, 176]. The range of validity of the Laplace equation assumption will be investigated below.

The scaled concentration and flux along the boundary of the domain are shown in Figs. 5.2 and 5.3, respectively, for a domain with terrace length of $T = 10 \times h$ and diffusion length of $\delta = 10 \times h$. A range of Peclet numbers are summarized in the plots.

The origin of the domain is the upper left corner, therefore regions (I) to (IV) represent the left, bottom, right and top sides of the domain, respectively. Therefore, region (II) includes two half size terraces and the step. We can observe a nearly linear variation of concentration along the side edges, from zero to a value between zero and unity. However, the concentration profile along terraces is neither linear nor symmetric. For Peclet numbers less than 10^{-3} the effect of velocity can be ignored. However, for higher Peclet numbers the concentration difference along the terraces



Figure 5.2: Concentration profile along the four boundaries for a system with dimensions $T = 10 \times h$ and $\delta = 10 \times h$. The position of the step is the centre of domain II.

decreases. Fig. 5.3 shows that the flux along the left and right boundaries is almost zero and across the step the flux decreases for higher Peclet numbers.

Fig. 5.4 shows the concentration profile in the liquid surrounding the step where $T = 10 \times h$, $\delta = 80 \times h$ and $p_x = 10^{-3}$.

In these results we can see the asymmetry of the concentration profile with respect to the step. The asymmetry is a result of treating the step explicitly in the computation. In cases where the step is considered as a source point [95, 176] the concentration field is radially symmetric about the step. In addition, a fast drop in concentration with increasing distance normal to the step is captured and again we did not make the assumption of variable concentration along the step as was done in previous studies [9, 178].

Fig. 5.5 Shows the concentration profile for a case where $T = 10 \times h$ and $\delta = 50 \times h$ and a Peclet number an order of magnitude than that shown in Fig. 5.4, $p_x = 10^{-2}$. As expected, at higher velocities concentration profile is closer to equilibrium along the terraces. It should be noted that we ignored the solute trapping during transformation



Figure 5.3: Flux across for all boundary nodes boundary for a system characterized by $T = 10 \times h$ and $\delta = 10 \times h$.



Figure 5.4: Concentration profile for an isolated step with $p_x = 10^{-3}$. The dimension of the domain are: $T = 10 \times h$, $\delta = 80 \times h$.

in this study and assumed that concentration along the step is in equilibrium. In addition, comparison between concentration isolines shows that asymmetry of the concentration profile increases by increasing the velocity.

As was shown in Eq. 5.13 we can define a relationship between Peclet number, supersaturation and flux at the step where under the assumption of equilibrium concentration along the step face it simplifies to the relationship $\frac{\partial u}{\partial n'}\Big|_{step} = -\frac{p_x}{\Delta}$. If the step velocity is sufficiently low and the dimensions of the domain are such that Laplaces



Figure 5.5: Concentration profile for an isolated step with $p_x = 10^{-2}$. $(T = 10 \times h \text{ and } \delta = 50 \times h)$

equation is a good description of the concentration profile, then the derivative $\frac{\partial u}{\partial n'}\Big|_{step}$ is a constant and a linear relationship is predicted between the Peclet number and the supersaturation. In the results of Figs. 5.6 and 5.7 the BEM computed velocities are compared with this linear prediction.

In Fig. 5.6 we show the effect of terrace length on the relationship between supersaturation and scaled velocity. At a constant supersaturation, the scaled velocity is higher for larger step spacing. However, the effect of terrace length can be ignored when the terrace length is more than a critical value, which is roughly $T = 40 \times h$. However, this critical value is a function of boundary layer dimension and for a system with longer δ this critical value increases. It is also evident from Fig. 5.6 that the linear relationship between step velocity and supersaturation is obeyed for small Δ , but deviates sub-linearly for higher Δ . The value of the supersaturation where the departure from linearly begins appears to decrease slightly with increasing step spacing.

The other geometric parameter affecting the relationship between scaled velocity and supersaturation is boundary layer width, the relationship of which is shown in



Figure 5.6: The Peclet number vs step spacing showing the effect of step separation on the kinetics of the transformation. The width of the boundary layer for all simulations is constant and equal to $50 \times h$

Fig. 5.7. This graph suggests that for a certain supersaturation, the scaled velocity is higher for the systems with smaller layer widths. In addition, deviation from linearity occurs at lower Peclet numbers, for the systems with longer δ . For a system with a very small boundary layer, even at a Peclet number around 0.04, the linear relation between p_x and Δ is still valid.



Figure 5.7: Effect of boundary layer size on the growth kinetics of transformation. Step separation for all simulations is constant and equal to $10 \times h$
5.4 Step bunching

In this part we are use the technique and results we obtained in the previous section in order to test whether the step bunching phenomenon can occur in diffusion controlled crystal growth. From experimental observations It has been suggested that equally spaced steps are inherently not stable and step trains tend to form bunches of steps close to each other, where each of these bunches are separated with a long terrace. The problem of bunching in crystals is very important, since it is closely related to the problem of defect formation. A rigorous treatment of the step bunching problem would entail a linear stability of the equal step spacing geometry. That is, the step spacing is perturbed by an infinitesimally small amplitude perturbation with some prescribed wavelength. The change with time is then formulated and if the amplitude increases with time the interface is unstable. However, since the base state of the problem cannot be solved analytically, the linear stability investigation is difficult. Therefore, in this study we will take a simplified approach which will yield the increase of flux to each step after a after a single step is repositioned by some amount along the interface. Although the procedure is not able to determine if the step array is linearly stable or not, it will show that perturbations of sufficient size can lead to step bunching.

The procedure adopted can be illustrated with reference to Fig. 5.8, which shows the central portion of three separate systems. The total number of steps in each computation is 25, the diffusion boundary length is taken as $\delta = 50 \times h$ and all other boundary conditions are the same as described above. The top portion of Fig. 5.8 shows the step separation when all steps are equally spaced by $T = 8 \times h$. The middle figure shows a perturbation, equal to h, of the center step in the negative x direction and the bottom figure shows, the case of a 2h perturbation. In each case the BEM calculation provides the flux, and hence velocity, of each step. If the center step and those trailing it exhibits a velocity that is lower than the equally spaced case and the steps leading the center step show an increased velocity, then the interface is unstable with respect to step bunching.



Figure 5.8: Geometry of the system in the vicinity of central step. Top figure corresponds to no perturbation, whereas the middle and bottom figures correspond to perturbations of the central step equal to 1h and 2h respectively.

Fig. 5.9 shows the result of the analysis. The left plot corresponds to the case where the unpertuined system consists of steps spaced by 8 the addition in the legend lists the length of the leading terrace used in each calculation. As expected the step velocity is equal for the equally spaced steps. However, the results clearly show a tendency to step bunching with the trailing steps slowing down and the leading steps speeding up after the perturbation is introduced. In this case the influence of the perturbation extends over roughly five steps to either side of the central step. Furthermore, as the perturbation increases in magnitude the effect is amplified, which implies the step bunching will grow after the initial perturbation. The right plot of Fig. 5.8 shows the same procedure for the case of an initial $12 \times h$ spacing of steps. The qualitative trend is equivalent to $T = 8 \times h$ result.

For a better comparison of the effect of a perturbation on step bunching behavior for different terrace lengths, we perform a series of BEM calculations in which the



perturbation is kept fixed at 10% of total terrace length. In other words, for the T_{max}=63h Г_{___}=100h 42 systems with terrace length of $10 x_{max}^{max}$ for the perturbation is $1 \times h$ and fort_theo10ase of T = 100 ×ah perturbation is $10 \times h_{\text{max}}^{-61h}$ in order to accurately $\tau_{\text{max}}^{-102h}$ the change in step velociter Number computation, the flux at step velociter is normalized by the baseline flux obtained from the case of equally spaced steps. As above, in each computation the total number of steps is 25 and $\delta = 50 \times h$. The results are presented in Fig.5.10 and the data show that for equal percentage of perturbation, the change in flux of steps is increased for smaller terrace lengths. The numerical results suggest that an interface with closely spaced steps is more susceptible to step bunching than interfaces with longer terraces. In the long wavelength limit, i.e. infinitely spaced steps, the interface appears to be neutrally stable. It is important to note that the computations presented here neglect any elastic interaction between steps, which will effect the equilibrium concentration at the step face [199]. It is expected that the inclusion of elastic energy will tend to stabilize the system for small wavelength perturbations (small step spacings).



Figure 5.10: Comparison of the normalized step velocity for equal percentage of perturbation at the terrace length range of $T = 10 \times h$ to $T = 200 \times h$. J is the scaled flux for a perturbed system and J_0 is the scaled flux of steps in an equally spaced system.

5.5 Analytic solution, stagnant case

As mentioned in the proceeding section, the assumption of a boundary layer implies convective mixing occurs in the liquid phase. In this section we formulate an analytic solution to the diffusion controlled growth of a step-terraced interface for the case of no convection. The solution will be applicable to the growth of stepped interfaces in solid-solid systems.

To proceed we note that as the boundary layer width δ increases the concentration gradient at the step decreases linearly with the distance y and eventually the growth rate will approach zero. However, in the computation we have neglected the velocity of the interface in the y direction. Inclusion of a v_y term, no matter how small, will guarantee a finite flux and growth rate in the limit $\delta \to \infty$ [200, 201]. The above discussion implies that an approximate solution can be developed using a matched asymptotic expansion. A similar approach has been employed by Atkinson [177].

Now we can consider the more complicated case where the velocity in any x

or y direction cannot be ignored. Therefore the diffusion equation in the unscaled coordinates would be:

$$D\nabla^2 u + v_x \frac{\partial u}{\partial x} + v_y \frac{\partial u}{\partial y} = 0$$
(5.15)

To obtain an "outer" solution note that sufficiently far from the interface $(y \sim T)$ all variations of u in the x direction become vanishingly small. The diffusion equation reduces to $\frac{\partial^2 u}{\partial y^2} + v_y \frac{\partial u}{\partial y} = 0$ and the outer solution is given by:

$$u_{out}\left(\tilde{x},\tilde{y}\right) = A' \exp\left(-p_y \tilde{y}\right) + B' \tag{5.16}$$

where, anticipating the inner solution, we have rescaled all lengths by $\tilde{x} = x/h$, $\tilde{y} = y/h$ and $\tilde{\lambda} = \lambda/h$. In the above solution, the boundary condition $u(\tilde{x}, \tilde{y} \to \infty) = 0$ forces B' to be zero.

To formulate the inner solution we identify a small parameter as h the step height and rescale all length variables in the diffusion equation. The result is simply $\nabla^2 u = 0$ where all terms of order of the Peclet number have been neglected. An approximate general solution to Laplaces equation for a periodic step train has been derived by Chernov using a conformal mapping procedure. Assuming a step spacing much larger than the step height, the general solution is given by:

$$u_{in}\left(\tilde{x},\tilde{y}\right) = \frac{A}{2}\ln\left(\sin^2\left(\frac{\pi}{\tilde{\lambda}}\tilde{x}\right) + \sinh^2\left(\frac{\pi}{\tilde{\lambda}}\tilde{y}\right)\right) + B$$
(5.17)

Chernov completed the problem by applying a kinetically limited boundary condition at the step. Here we apply a diffusion controlled condition. Noting that the solution assumes the steps are represented by point sources of solute, we apply the boundary condition u(1,0) = u(0,1) = 1, which means, on the surface of a half cylinder surrounding the step with radius equal to the height of the step, the composition is equal to the equilibrium composition. Applying this boundary condition, the constant *B* can be obtained as:

$$B = 1 - A \ln \left(\frac{\pi}{\tilde{\lambda}}\right) \tag{5.18}$$

So far we have determined the solution of the diffusion equation for the inner and the outer regions. However, there are two constants remaining in Eqs. 5.17 and 5.16. To complete the problem we apply a formal matching procedure, which is given by $u_{out}(\tilde{y} \to 0) = u_{in}(\tilde{y} \to \infty)$. For the inner region (Eq.5.17) the sin term can be neglected relative to the sinh term and, using the definition of $\sinh\left(\frac{\pi}{\lambda}\tilde{y}\right) = \frac{exp(\frac{\pi}{\lambda}\tilde{y}) - \exp(-\frac{\pi}{\lambda}\tilde{y})}{2}$, the limits become:

$$u_{in}\left(\tilde{x},\tilde{y}\right) = A\left[\left(\frac{\pi}{\tilde{\lambda}}\right)\tilde{y} - \ln\left(\frac{2\pi}{\tilde{\lambda}}\right)\right] + 1$$
(5.19)

$$u_{out}\left(\tilde{x},\tilde{y}\right) = A'\left(1 - p_y\tilde{y}\right) \tag{5.20}$$

A solution for the concentration field, valid over the entire domain, can be obtained via $u(\tilde{x}, \tilde{y}) = u_{in} + u_{out} - u_{match}$, where u_{match} is the value of the field under the matching procedure. Therefore the final result reads:

$$u\left(\tilde{x},\tilde{y}\right) = \frac{A}{2}\ln\left(\sin^2\left(\frac{\pi}{\tilde{\lambda}}\tilde{x}\right) + \sinh^2\left(\frac{\pi}{\tilde{\lambda}}\tilde{y}\right)\right) + B + A'\exp\left(-p_y\tilde{y}\right) - A'\left(1 - p_y\tilde{y}\right) \quad (5.21)$$

where $A = -\frac{p_y \tilde{\lambda}}{\pi - p_y \tilde{\lambda} \ln\left(\frac{2\pi}{\tilde{\lambda}}\right)}$, $A' = \frac{\pi}{\pi - p_y \tilde{\lambda} \ln\left(\frac{2\pi}{\tilde{\lambda}}\right)}$ and B is determined based on Eq 5.18.

The concentration profile resulting from Eq. 5.21 for $\tilde{x} = 0$, which represents the profile from the step into the liquid, is shown in Fig. 5.11. Notice, the inner solution decreases linearly and without bound as \tilde{y} tends to infinity, whereas the matched asymptotic solution exhibits the correct exponential decay for large \tilde{y} .



Figure 5.11: Results of the matched asymptotic analysis showing the inner and outer regions, and the final composition profile. The profile is shown as a function of \tilde{y} and \tilde{x} is set equal to the step position, i.e., $\tilde{x} = 0$.

Our ultimate goal is to determine the growth rate from the analytic solution to the concentration field. Recall the step is treated as a semicircle with radius equal to the step height. Thus, for calculation of the flux it is easier to transform Eq. 5.21 to cylindrical coordinates, which is given by:

$$u(r,\phi) = \frac{A}{2} \ln\left(\sin^2\left(\frac{\pi}{\tilde{\lambda}}r\cos\phi\right) + \sinh^2\left(\frac{\pi}{\tilde{\lambda}}r\sin\phi\right)\right) + B + A'\exp\left(-p_yr\sin\phi\right) - A'\left(1 - p_yr\sin\phi\right)$$
(5.22)

For sufficiently small r, that is in the vicinity of the step, the next to last term can be expanded in a Taylor series and, when combined with the last term, leads to a contribution of order p_y^2 , which will be neglected. With this simplification, the concentration does not vary with ϕ in the region near the step. In other words, $\frac{\partial u}{\partial \phi}\Big|_{r \to 1} = 0$. In addition, the gradient of the concentration in the radial direction is equal at all angles including $\phi = \frac{\pi}{2}$. Using these assumptions we obtain:

$$\frac{\partial u}{\partial r}\Big|_{r=1,\,\mathrm{any}\,\phi} = \left.\frac{\partial u}{\partial r}\right|_{r=1,\,\phi=\frac{\pi}{2}} = \frac{A\pi}{\tilde{\lambda}} \left(\frac{\cosh\left(\frac{\pi}{\tilde{\lambda}}\right)}{\sinh\left(\frac{\pi}{\tilde{\lambda}}\right)}\right) - A'p_y\left(\exp\left(-p_y\right) + 1\right)$$
(5.23)

Applying the mass conservation principle, the flux into the inner semicircle with the area of πh , is equal to the flux at the step with height of h. In scaled coordinates, $\pi \frac{\partial u}{\partial r} = \frac{\partial u}{\partial n'}$. Combining Eqs. 5.13 and 5.23 and noting that u = 1 at the step, the step velocity is then given by:

$$p_x = \frac{\pi \Delta \tilde{\lambda}}{2\pi^2 \Delta - \tilde{\lambda} \pi \ln\left(\frac{2\pi}{\tilde{\lambda}}\right)} \tag{5.24}$$

where the p_y term appearing in the constant A was converted using $p_y = p_x \sin(h/\lambda) \approx p_x/\tilde{\lambda}$. Also, the terms involving the hyperbolic functions were simplified under the assumption of large $\tilde{\lambda}$.

The above approximate result predicts that the step velocity in the x direction decays to zero as the inter step spacing $\tilde{\lambda}$ increases. Unfortunately, this behavior contrasts with the analytic results obtained by Jones and Trivedi and Atkinson for the case of an isolated step. However, the decrease in p_x with spacing predicted by the above result is characterized by a slowly varying logarithmic dependence. Fig. 5.12 shows the scaled velocity vs. supersaturation for different step spacing values computed using Eq. 5.24. Based on this model, for a specific supersaturation, the step velocity is higher for a smaller step spacing. The variation with $\tilde{\lambda}$ is large for step spacings that are relatively small, as is evident from the curves labeled $\tilde{\lambda} = 10$ to 50. For larger spacings the variation is much slower with a small difference observed for the order of magnitude change from $\tilde{\lambda} = 100$ to 1000. For comparison the Jones and Trivedi result is shown by the open circles and the two results compare favorably in the vicinity of $\tilde{\lambda} = 100$.



Figure 5.12: Scaled velocity of the step vs. supersaturation for different λ s. The results of Jones and Trivedi [9] are compared with the calculation of the present study.

5.6 Conclusion

The boundary element method has been used to compute the growth rate and concentration profile for the case of an infinite and periodic array of mobile interface steps separated by immobile terraces. An important assumption in the numerical study is the existence of a boundary layer at the interface, beyond which there exists complete mixing in the fluid. The BEM results therefore describe the case of vicinal surfaces growing into a liquid or vapor. Growth rates have been computed as a function of two important variables: the step spacing and the boundary width. The computations indicate that the step velocity varies linearly with supersaturation for low supersaturation and deviates below linear at high Δ . The departure from linear behavior occurs at lower supersaturation for increasing boundary layer width. The BEM computations were also used to study the effect of geometry of the system on the tendency for step bunching. We have investigated the special case where the position of one central step is perturbed. It was concluded that the equally spaced steps are not stable to sufficiently large perturbations and the system tends to form separated bunches of steps.

For the case of a stagnant liquid or a step-terraced interface separating two crystalline phases, an approximate analytic solution has been derived. The solution is based on a matched asymptotic expansion technique and the solution valid in the vicinity of the step is formulated from a conformal mapping procedure. The results predict that for a given supersaturation the step velocity decreases with increasing step spacing.

Chapter 6

Conclusions

In this dissertation we simulated several related solidification phenomena using Molecular Dynamics (MD) and Boundary Element Method (BEM). Using MD requires implementing the appropriate model which represents all the interactions in the system. For this purpose we implemented the Angular-EAM model on Lammps, which is the MD code we used in this study. This model is capable of considering both metallic and covalent bonds, as well as cross-interactions between Al and Si.

In the next step, corresponding potentials based on the AEAM model were developed. First, a modification was applied to the three-body SW Si potential such that the correct diamond cubic crystal structure was found to form at high temperatures. This modification improved the classical SW potential which solidifies into the wurtzite structure at temperatures in the vicinity of the melting point, and thus the modified SW represents an important improvement to atomistic simulations of crystallization processes. In addition, the modified SW predicts a more accurate melting temperature and elastic constants. A potential for the Al-Si binary system was also developed using the Angular-EAM method where the potential for pure Al was taken from the work of Mendelev et al. [77] and the modified SW potential was used to describe pure Si. The advantage of new Al-Si model is the relatively accurate prediction of phase diagrams and the close to zero solubility of aluminum in silicon crystal.

Considering the importance of the step kinetic coefficient and the step free energy on the crystal growth rate, we devoted two chapters of this study to these two concepts.

In addition to the mobility of steps at faceted crystal-melt interfaces in the case of pure Si we also extended the use of MD to determine the step mobility for the case of a faceted interface in an alloy system. In the two compositions and temperature ranges studied we have determined that the lower temperature, higher Al content Al-Si alloys exhibit diffusion or mixed controlled growth of the steps on the (111) interface. Therefore, we have determined the mobility at lower concentrations of Al and at higher temperatures. We find that the mobility decreases fairly rapidly with increasing Al content and the mobility follows the same trend with temperature as the interdiffuion coefficient in the liquid. Finally, the mobility for Al-90%Si in the range T=1560-1580 K is roughly an order of magnitude less than that computed for pure Si.

Based on the results of chapter 3 it can be concluded that the dominant scenario of crystal growth for eutectic reaction of Al-Si system is diffusion-controlled crystal growth. Based on Al-Si phase diagram, eutectic transformation happens at 850 K. This temperature is much lower than the liquidus temperature of Si-rich alloys. For the reaction-controlled scenario interdiffusion should be fast enough that the composition all over the melt, including the melt part of the interface, remain constant. For this to happen, activation energy of the interdiffusion coefficient should decrease with the increase of Al atoms in the system in order to have faster transportation of solute atoms to the interface. However, it is observed that the rate of decrease of activation energy from 90% to 60% has not been fast enough. Therefore, a significant pile up of Al atoms at the interface, even for small undercoolings around 10K, results in the growth scenario change from reaction-controlled for 90% to mixed case for 60%. Considering the trend of interdiffusion coefficient and the eutectic temperature it can be concluded that the interdiffusion in the system with eutectic composition will not be fast enough to form a melt with zero composition gradient from the interface to the melt and. Therefore, the diffusion-controlled scenario is more probable for eutectic composition.

Utilizing molecular dynamics (MD) simulations and the capillary-fluctuations method (CFM), the crystal-melt step free energies at three different melt compositions were calculated. The anisotropy of steps was investigated by setting up the systems with different crystal orientations of steps on the (111) interface plane. A complete isotropy of step free energy is observed for Al-60%Si and Al-90%Si alloying systems, while the CFM failed to determine step free energy in Al-30%Si due to lack of step roughness. Using these results a clear transition from rough steps to smooth (faceted) step was observed. In other words, for the alloying systems with eutectic composition, we predict that the steps are not rough.

Despite the applications of the MD in calculation of micro state terms, the simulation time and system size scale is limited to nano second and a few hundred nano metres, respectively. Therefore, diffusion-controlled crystal growth cannot be examined using MD. However, the BEM is a fast and accurate simulation method which was used to compute the growth rate and concentration profile for the case of an infinite and periodic array of mobile interface steps separated by immobile terraces. Growth rates were computed as a function of two important variables: the step spacing and the boundary width. The computations indicate that the step velocity varies linearly with supersaturation for low supersaturation and deviates below linear at high Δ . The departure from linear behavior occurs at lower supersaturation for increasing boundary layer width. The BEM computations were also used to study the effect of system geometry on the tendency for step bunching. We have investigated the special case where the position of one central step is perturbed. It was concluded that the equally spaced steps are not stable at sufficiently large perturbations, and the system tends to form separated bunches of steps.

For the case of a stagnant liquid or a step-terraced interface separating two crystalline phases, an approximate analytic solution has been derived. The solution is based on a matched asymptotic expansion technique and the solution valid in the vicinity of the step is formulated from a conformal mapping procedure. The results predict that for a given supersaturation the step velocity decreases with increasing step spacing.

Chapter 7

Future Work

Considering the importance of twins on the crystal growth of silicon dendrites in the Al-Si system, calculation of mobility and step free energy at the presence of twins could be considered as a next step to this research. In addition, the effect of twins on the critical nucleation size could also be studied.

As mentioned in the introduction, one of the chemical modification theories is the complete geometrical effect of Sr on the active Si steps. Since this mechanism ignores the interaction between Sr atoms with other components of the system, validity of the mechanism can be examined by defining a noninteracting particle at the interface to observe possible passivation of the step or formation of twins.

In addition, the validity of surface energy theory can be examined by calculating the surface energy at the presence of the modifier.

Appendix A

Semi Grand Canonical Method Formulation

For a binary solution at constant temperature an pressure the separate contributions of components A and B on total free energy can be summed:

$$\Delta G'|_{T,P} = \mu_A \Delta n_A + \mu_B \Delta n_B \tag{A.1}$$

In the Semi Grand Canonical Method the type of a B atom switches to A type. Therefore, $\Delta n_A = 1$ and $\Delta n_B = -1$. Thus:

$$\Delta G'|_{T,P} = \mu_A - \mu_B \tag{A.2}$$

On the other hand total free energy change can be written based on internal energy and entropy of the system.

$$\Delta G'|_{T,P} = \mu_A - \mu_B = \Delta H' - T\Delta S' \tag{A.3}$$

The total change of enthalpy of the system at P = 0 is $\Delta H' = \Delta U' + P\Delta V + V\Delta P = \Delta U'$, which is the total variation of internal energy of the system.

The other term is total variation of entropy of the system due to the switch of type of an atom. By definition

$$\Delta S'|_{T,P} = k_B \left(\ln \omega_2 - \ln \omega_1 \right)$$

= $k_B \left(\ln \frac{(n_A + n_B)!}{n_A! n_B!} - \ln \frac{(n_A + 1 + n_B - 1)!}{(n_A + 1)! (n_B - 1)!} \right)$ (A.4)
= $k_B \ln \left(\frac{n_B}{1 + n_A} \right)$

Substituting Eq. A.4 in Eq. A.3, the difference between the chemical potential of components is:

$$\mu_A - \mu_B = \Delta U' - Tk_B \ln \frac{n_B}{n_A + 1} \tag{A.5}$$

For calculating this term using molecular dynamics we need to statistically average results of Eq. A.5:

$$\mu_A - \mu_B = -Tk_B \ln \left\langle \frac{n_B}{n_A + 1} \exp\left(\frac{\Delta U'}{k_B T}\right) \right\rangle \tag{A.6}$$

Appendix B

Step Free Energy modification

B.1 Step Excess Free Energy

Consider the free energy of the system with a flat surface $F_{\text{surf}} = -k_{\text{B}}T \ln Z_{\text{surf}}$ an the free energy of the system with a surface with a step on it is $F_{\text{step}} = -k_{\text{B}}T \ln Z_{\text{step}}$. The step excess energy can be defined as

$$[F] \equiv F_{\text{step}} - F_{\text{surf}} = -k_{\text{B}}T\ln\left(\frac{Z_{\text{step}}}{Z_{\text{surf}}}\right) = -k_{\text{B}}T\ln Q_{\text{step}} \Rightarrow [F] = -k_{\text{B}}T\ln Q_{\text{step}}$$
(B.7)

where $Q_{\text{step}} = Z_{\text{step}}/Z_{\text{surf}}$. Alternatively, we can also write the excess step free energy as

$$[F] \equiv \gamma_{\text{step}} L_0 \tag{B.8}$$

where γ_{step} is the free energy per unit box length, and extensive thermodynamic variable. In thermodynamic integration (TI) we compute $[F] \equiv F_{step} - F_{surf}$. Thus, if we want to obtain γ_{step} we have to divide the TI method result by the box length L_0 , as shown in Eq. B.8.

B.2 Step Partition Function Coarse Graining

We are going to separate (in Z_{step}) the step degrees of freedom from the bulk and surface degrees of freedom. Denoting $\mathbf{R} \equiv \{R_i\}$ with i = 1, ..., N the step degrees of freedom and $\mathbf{r} \equiv \{r_j\}$ with j = 1, ..., M the non important degrees of freedom (build and surface) we can write

$$Z_{\text{step}} = \int d^{N} R d^{M} r \exp\left[-\beta H\left(\mathbf{R},\mathbf{r}\right)\right] = \int d^{N} R \exp\left[-\beta H_{\text{cg}}\left(\mathbf{R}\right)\right]$$
(B.9)

where

$$H_{\rm cg} = -k_{\rm B}T \ln\left\{\int \mathrm{d}^M r \exp\left[-\beta H\left(\mathbf{R},\mathbf{r}\right)\right]\right\}$$
(B.10)

This equation, as written in Eq. B.10, can be interpreted as the free energy of the non important degrees of freedom **r**. Alternatively, it is also the Hamiltonian that generates the step dynamics on the system, as seen clearly by Eq. B.10. Because of this, H_{cg} is also known as the potential of mean force, *i.e.*, it is the potential acting on the step that arises from the mean contribution of the bulk and surface degrees of freedom.

Our next goal is to define the excess step free energy within this coarse-graining formalism. If we now substitute Eq. B.9 in the equation for Q_{step} we obtain

$$Q_{\text{step}} = \frac{Z_{\text{step}}}{Z_{\text{surf}}}$$

$$= \frac{1}{Z_{\text{surf}}} \int d^{N}R \exp\left[-\beta H_{\text{cg}}\left(\mathbf{R}\right)\right]$$

$$= e^{+\beta F_{\text{surf}}} \int d^{N}R \exp\left[-\beta H_{\text{cg}}\left(\mathbf{R}\right)\right] \qquad (B.11)$$

$$= \int d^{N}R \exp\left[-\beta \left[H_{\text{cg}}\left(\mathbf{R}\right) - F_{\text{surf}}\right]\right]$$

$$= \int d^{N}R \exp\left[-\beta H_{\text{step}}\left(\mathbf{R}\right)\right]$$

where we have defined a step effective Hamiltonian $H_{\text{step}} \equiv H_{\text{cg}} - F_{\text{step}}$. The excess free energy can now be obtained from Eq.B.7.

$$[F] = -k_{\rm B}T \ln\left\{\int d^N R \exp\left[-\beta H_{\rm step}\left(\mathbf{R}\right)\right]\right\}$$
(B.12)

from where it becomes clear that H_{step} is the Hamiltonian describing the step dynamics, removing the mean contribution due the bulk and surface.

B.3 Step Effective Hamiltonian

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Everything we have done so far is exact, thus Eq.B.12 is exact. The only thing we have done is interpreted specific parts of the step partition function. It is possible now, using our interpretation of the equations above, to introduce a model for the step effective Hamiltonian, H_{step} , according to something we think should describe the forces on the step. A reasonable model is to assume

$$H_{\text{step}} = \int_{\zeta} \alpha\left(\theta\right) \mathrm{d}s \tag{B.13}$$

where $\alpha(\theta)$ is the step tension and the integral is over the curve ζ describing the step physical length.

In Eq. B.13 the step length as function of the position along the x axis can be expressed as

$$ds = \sqrt{dx^2 + dy^2} = \sqrt{1 + y'(x)^2} dx$$
 (B.14)

and we can rewrite the step Hamiltonian as

$$H_{\text{step}} = \int_{0}^{L_{0}} \alpha\left(\theta\right) \sqrt{1 + y'\left(x\right)^{2}} \mathrm{d}x \qquad (B.15)$$

In the small slope approximation we have $y'(x) = \tan \theta \approx \theta$. Using this approximation we can expand the terms inside the integral of Eq. B.15 in powers of θ :

$$\alpha(\theta)\sqrt{1+y'(x)^2} = \left[\alpha_0 + \alpha'_0\theta + \frac{1}{2}\alpha''_0\theta^2 + \dots\right] \left[1 + \frac{1}{2}\theta^2 + \dots\right]$$
$$= \alpha_0 + \alpha'_0\theta + \frac{1}{2}(\alpha_0 + \alpha''_0)\theta^2 + \mathcal{O}(\theta^3)$$
(B.16)

where the zero subscript like in α'_0 denotes a function evaluated at $\theta = 0$. Using this expression in Eq. B.15 we obtain

$$H_{\text{step}} = \int_{0}^{L_{0}} \alpha(\theta) \sqrt{1 + y'(x)^{2}} dx$$

= $\alpha_{0} \int_{0}^{L_{0}} dx + \alpha'_{0} \int_{0}^{L_{0}} \theta dx + \frac{1}{2} (\alpha_{0} + \alpha''_{0}) \int_{0}^{L_{0}} \theta^{2} dx$ (B.17)
= $\alpha_{0} L_{0} + \frac{1}{2} (\alpha_{0} + \alpha''_{0}) \int_{0}^{L_{0}} y'(x)^{2} dx$

where $\alpha_0 L_0$ is the contribution due to a flat interface, and we have defined the step stiffness as $(\alpha_0 + \alpha_0'')$. We have also used that $\int_0^{L_0} \theta dx = y(0) - y(L_0) = 0$ due to the periodic boundary conditions. with this result we can finally rewrite the step effective Hamiltonians as

$$H_{\text{step}} = \alpha_0 L_0 + \frac{1}{2} \left(\alpha_0 + \alpha_0'' \right) \int_0^{L_0} y' \left(x \right)^2 \mathrm{d}x \tag{B.18}$$

We now expand the height of the interface, y(x), in a Fourier expansion. The wave vectors are given by $k_n = n\left(\frac{2\pi}{L_0}\right)$ with $n = -N/2 + 1, -N/2, \ldots, -1, 0, 1, \ldots, N/2$ and the expansion in written as

$$y(x) = \sum_{n=-N/2+1}^{N/2} A_n \exp(ik_n x)$$
(B.19)

where the amplitude of the mode is found as usual by multiplying both sides by

 $\exp(ik_m x)$ and integrating over x:

$$\int_{0}^{L_{0}} y(x) \exp(ik_{m}x) dx = \int_{0}^{L_{0}} \sum_{n=-N/2+1}^{N/2} A_{n} \exp\left[i(k_{n}-k_{m})x\right] dx$$
$$= \sum_{n=-N/2+1}^{N/2} \int_{0}^{L_{0}} A_{n} \exp\left[i(k_{n}-k_{m})x\right] dx = \sum_{n=-N/2+1}^{N/2} A_{n}L_{0}\delta_{nm} = A_{m}L_{0}$$
(B.20)

$$\Rightarrow A_n = \frac{1}{L_0} \int_0^{L_0} y(x) \exp(ik_n x) \,\mathrm{d}x \tag{B.21}$$

Using Eq.B.20 we can compute the integral in Eq. B.19. We start by computing the derivative of Eq. B.20

$$\frac{\mathrm{d}y}{\mathrm{d}x} = i \sum_{n=-N/2+1}^{N/2} A_n k_n \exp\left(ik_n x\right) \tag{B.22}$$

Now we compute the squire of y'(x)

$$y'(x)^{2} = y'(x) \left[y'(x)\right]^{*} = \sum_{n=-N/2+1}^{N/2} \sum_{m=-N/2+1}^{N/2} A_{n} A_{m}^{*} k_{n} k_{m} \exp\left[i\left(k_{n}-k_{m}\right)x\right] \quad (B.23)$$

and integrate over x

$$\int_{0}^{L_{0}} y'(x)^{2} dx = \sum_{n=-N/2+1}^{N/2} \sum_{m=-N/2+1}^{N/2} A_{n} A_{m}^{*} k_{n} k_{m} \int_{0}^{L_{0}} \exp\left[i\left(k_{n}-k_{m}\right)x\right] dx$$
$$= \sum_{n=-N/2+1}^{N/2} \sum_{m=-N/2+1}^{N/2} A_{n} A_{m}^{*} k_{n} k_{m} L_{0} \delta_{nm} \qquad (B.24)$$
$$= L_{0} \sum_{m=-N/2+1}^{N/2} k_{n}^{2} |A_{n}|^{2}$$

and we can finally rewrite the step effective Hamiltonian as

$$H_{\text{step}} = \alpha_0 L_0 + \frac{1}{2} \left(\alpha_0 + \alpha_0'' \right) L_0 \sum_{n=-N/2+1}^{N/2} k_n^2 |A_n|^2$$
(B.25)

where A_n are the step degrees of freedom (*i.e.*, amplitudes of the Fourier modes).

B.4 Capillary Wave Fluctuation Method

Computing the complex conjugate of Eq.B.21 results in $A_0^* = A_{-n}$ and thus $|A_n| = |A_{-n}|$. Using these results we can write Eq. B.25 as

$$H_{\text{step}} = \alpha_0 L_0 + (\alpha_0 + \alpha_0'') L_0 \sum_{n=1}^{N/2-1} k_n^2 |A_n|^2 + \frac{1}{2} (\alpha_0 + \alpha_0'') L_0 k_{N/2}^2 |A_{N/2}|^2$$

= $\alpha_0 L_0 + (\alpha_0 + \alpha_0'') L_0 \sum_{n=1}^{N/2-1} k_n^2 \Re (A_n)^2 + (\alpha_0 + \alpha_0'') L_0 \sum_{n=1}^{N/2-1} k_n^2 \Im (A_n)^2$ (B.26)
+ $\frac{1}{2} (\alpha_0 + \alpha_0'') L_0 k_{N/2}^2 \Re (A_{N/2})^2$

where we have used that $\Im (A_{N/2})^2 = 0$, which is a result of y(x) being real, but which can also be seen in Eq. B.21 by using $k_{N/2} = (N/2)(2\pi/L_0)$ and $x = L_0m/N$ with $m = 0, 1, \ldots, N - 1$.

The theorem of the equipartition of energy says that each quadratic degree of freedom in the Hamiltonian of a system at constant temperature T contributes $k_B T/2$ to the average energy. We now apply this theorem to the equation above. Notice that each mode amplitude A_n appears quadratically in the Hamiltonian, and that the real and imaginary parts of A_n are independent. Therefore

$$\left(\alpha_{0} + \alpha_{0}^{\prime\prime}\right)L_{0}k_{n}^{2}\left[\left\langle\Re\left(A_{n}\right)^{2}\right\rangle + \left\langle\Im\left(A_{n}\right)^{2}\right\rangle\right] = \left(\alpha_{0} + \alpha_{0}^{\prime\prime}\right)L_{0}k_{n}^{2}\left\langle\left|A_{n}\right|^{2}\right\rangle = k_{B}T \quad (B.27)$$

$$\left\langle \left|A_{n}\right|^{2}\right\rangle = \left(\frac{k_{B}T}{\left(\alpha_{0} + \alpha_{0}^{\prime\prime}\right)L_{0}}\right)\frac{1}{k_{n}^{2}} \tag{B.28}$$

where $\langle \ldots \rangle$ indicated a canonical ensemble average.

B.4.1 Step Free energy

if we substitute the effective step Hamiltonian, Eq.B.25, in the expression for the excess free energy of the step, Eq. B.12, we can compute the excess free energy. To simplify the notation we denote $\Re(A_n) \equiv x_n$ and $\Im(A_n) \equiv y_n$. The effective step Hamiltonian can be written as

$$H_{\text{step}} = \alpha_0 L_0 + (\alpha_0 + \alpha_0'') L_0 \sum_{n=1}^{N/2-1} k_n^2 (x_n^2 + y_n^2) + \frac{1}{2} (\alpha_0 + \alpha_0'') L_0 k_{N/2}^2 x_{N/2}^2$$

$$= \alpha_0 L_0 + \sum_{n=1}^{N/2-1} B_n (x_n^2 + y_n^2) + \frac{1}{2} B_n x_{N/2}^2$$
(B.29)

with $(\alpha_0 + \alpha_0'') L_0 k_n^2$. The step partition function is

$$\begin{aligned} Q_{\text{step}} &= \int d^{N}R \exp\left[-\beta H_{\text{step}}\left(\mathbf{R}\right)\right] + \frac{1}{L_{0}^{N}} \int d^{N}A_{n} \exp\left[-\beta H_{\text{step}}\left(\mathbf{A}\right)\right] \\ &= e^{-\beta\alpha_{0}L_{0}} \left\{ \prod_{n=1}^{N/2-1} \left[\frac{1}{L_{0}} \int_{-\infty}^{\infty} dx_{n} e^{-\beta B_{n}x_{n}^{2}}\right] \right\} \\ &\left\{ \prod_{n=1}^{N/2-1} \left[\frac{1}{L_{0}} \int_{-\infty}^{\infty} dy_{n} e^{-\beta B_{n}y_{n}^{2}}\right] \right\} \left\{ \left[\frac{1}{L_{0}} \int_{-\infty}^{-\infty} dx_{N/2} e^{-\beta B_{N/2}x_{N/2}^{2}}\right] \right\} \\ &= e^{-\beta\alpha_{0}L_{0}} \left\{ \prod_{n=1}^{N/2-1} \left[\frac{1}{L_{0}} \sqrt{\frac{\pi k_{B}T}{B_{n}}}\right] \right\} \left\{ \left[\frac{\sqrt{2}}{L_{0}} \sqrt{\frac{\pi k_{B}T}{B_{n}}}\right] \right\} \left\{ \left[\frac{\sqrt{2}}{L_{0}} \sqrt{\frac{\pi k_{B}T}{B_{N/2}}}\right] \right\} \\ &= e^{-\beta\alpha_{0}L_{0}} \left\{ \prod_{n=1}^{N/2-1} \left[\frac{\pi k_{B}T}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{(L_{0}k_{n})^{2}}\right] \right\} \sqrt{2} \sqrt{\frac{\pi k_{B}T}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{\alpha_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{\alpha_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{\alpha_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{\alpha_{0}}\frac{1}{(\alpha_{0} + \alpha_{0}^{\prime\prime})L_{0}}\frac{1}{\alpha_{0}}\frac{1$$

and the free energy is

$$[F] = -k_{\rm B}T \ln Q_{\rm step}$$

$$= \alpha_0 L_0 - k_B T \sum_{n=1}^{N/2-1} \ln \left[\left(\frac{\pi k_B T}{(\alpha_0 + \alpha_0'') L_0} \right) \left(\frac{N}{2\pi n} \right)^2 \right]$$

$$= \alpha_0 L_0 + k_B T \sum_{n=1}^{N/2-1} \ln \left[\left(\frac{(\alpha_0 + \alpha_0'') L_0}{\pi k_B T} \right) \left(\frac{N}{2\pi n} \right)^2 \right]$$

$$= \alpha_0 L_0 \left[1 + \left(\frac{k_B T}{\alpha_0 L_0} \right) \sum_{n=1}^{N/2-1} \ln \left[\left(\frac{(\alpha_0 + \alpha_0'') L_0}{\pi k_B T} \right) \left(\frac{2\pi n}{N} \right)^2 \right] \right]$$
(B.31)

Now we divide everything by L_0 to obtain γ_{step} .

$$\gamma_{\text{step}} = \alpha_0 \left[1 + \left(\frac{k_B T}{\alpha_0 L_0}\right) \sum_{n=1}^{N/2-1} \ln \left[\left(\frac{(\alpha_0 + \alpha_0'') L_0}{\pi k_B T}\right) \left(\frac{2\pi n}{N}\right)^2 \right] \right]$$
(B.32)

Finally, assuming isotropy we have $(\alpha_0 + \alpha_0'') = \alpha_0$ and the step free energy per unit length is

$$\gamma_{\text{step}} = \alpha_0 \left[1 + \left(\frac{k_B T}{\alpha_0 L_0}\right) \sum_{n=1}^{N/2-1} \ln\left[\left(\frac{\alpha_0 L_0}{\pi k_B T}\right) \left(\frac{2\pi n}{N}\right)^2 \right] \right]$$
(B.33)

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