## Diffusion Induced Grain Boundary Migration (DIGM): An Atomistic Simulation Study

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#### Abstract

Diffusion-induced grain boundary migration (DIGM) is the phenomenon of normal grain boundary (GB) migration caused by the lateral diffusion of solutes along with it. Despite its technological importance and the fact that DIGM was first observed and studied since 1970, many aspects are still not fully understood. In this study, molecular dynamics (MD) simulations are used to investigate the physical origins of DIGM with a particular focus on the effects of solute-GB interactions. For this purpose, a few binary alloy systems are deliberately selected, e.g., Al-Ti, Al-Ni, and Ni-Cu, in which strong solute-GB interactions, including solute segregation and antisegregation, occur. The simulation results show that strong solute segregation and anti-segregation can both influence DIGM. Furthermore, it is shown that the direction of the GB migration dramatically depends on the type of solute-GB interaction, e.g., segregation or anti-segregation, which cause attraction or repulsion between the GB and solute atoms, respectively. It is thus proven that solute-GB interactions play an important role in driving DIGM. Additionally, the driving forces for DIGM can be quantified by combining two atomistic simulation techniques, i.e., the synthetic driving force (SDF) and interface random walk methods. The second part of the study shows that such a solute-induced driving force can be tuned in both type (i.e. attraction or repulsion) and their magnitude by using different solute types (with varying atomic sizes and cohesive energy). These solute types interact with the GB differently, resulting in solute segregation or anti-segregation. Moreover, it is also found that the lattice strain resulting from atomic size mismatch, which has been proposed as an essential driving force for DIGM, is not always needed to induce GB migration. It is also proposed that the non-equilibrium distribution of solute atoms across GB (e.g., one grain being more enriched with solute atoms than the second grain) can contribute to the driving force for the migration during a typical DIGM. It is anticipated that this study contributes to understanding the phenomenon of DIGM, for which precise physical mechanisms remain elusive after decades of research.

Keywords: DIGM, Grain boundaries, solute-GB interactions, segregation, anti-segregation.

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## Dedication

I dedicate this thesis to "God Almighty my creator" for giving me the courage to face all the challenging situations.

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#### List of Abbreviations

- DIGM Diffusion induced grain boundary migration
- GB Grain Boundary
- CSL Coincidence Site Lattice
- DOF Degrees of Freedom
- EAM Embedded Atom Method
- LJ Lennard Jones Potential
- LAMMPS Large-scale Atomic/Molecular Massively Parallel Simulator
- MD Molecular Dynamics
- NPT Ensemble with constant mass, volume, pressure
- NVE Ensemble with constant mass, volume, and energy
- NVT Ensemble with constant mass, volume, and temperature
- PBC Periodic boundary condition
- CGR- Crack Generation Rate
- LFM- Liquid Film Migration
- HAZ-Heat affected zone
- MC-Monte Carlo
- $k_b$  the Boltzmann constant
- T is temperature
- $U(\vec{R})$  is the inter-particle potential
- 3-dimensional (3D)
- 2-dimensional (2D)
- $\sigma$  and  $\varepsilon$  are the LJ-parameters
- $\sigma_{\alpha\alpha}, \sigma_{\beta\beta}, \varepsilon_{\alpha\alpha}, \varepsilon_{\beta\beta}$ -Parameters representing interactions in the same species
- $\sigma_{\alpha\beta}$ ,  $\varepsilon_{\alpha\beta}$ -Parameters representing interactions in different species
- MPI-Message Passing Interface
- SDF-Synthetic Driving Force

C<sub>GB</sub> - concentration of solutes at the GB C<sub>0</sub>- Concentration of solutes in bulk, Fs-femtoseconds nm-nanometer µm-micrometer at.%-Atomic Percentage

# Chapter 1 Introduction

#### Chapter 1: Introduction

Nature is not always as simple as we are led to believe. Just when it is imagined that we have laws well in hand to predict how a material behaves, something new is discovered that forces us to reevaluate those "laws." Diffusion induced grain boundary migration (DIGM) is such a case in point. DIGM occurs when solute atoms are diffused into (or out of) the grain boundary (GB) in the presence of a solute source (or sink). Such a diffusion process causes the GB to migrate, which creates alloyed, i.e., solute-enriched (or de-alloyed, i.e., solute depleted) zones in its wake. Figure 1.1 shows a schematic of the DIGM phenomenon, where the zig-zag or wavy shape of the GB is characteristic of DIGM.



Figure 1.1. Schematic of DIGM (a) Alloying and (b) De-alloying where solid red lines represented GB position at t=0 and dotted red lines depict GB position at t=t.  $J_{in}$  is the flux of solute atoms entering the system, and  $J_{out}$  is those of leaving.

In polycrystalline materials, DIGM causes various physio-chemical changes of the GB, such as undulation at the interface [1], [2], the formation of misfit dislocations at the original interface [3], and composition fluctuation between the matrix and the migrated region [4]. DIGM has important technological applications in which it can be used to either generate functional properties or deliberately suppressed to avoid detrimental effects [1]. For instance, Hillert and Li [5] suggested that DIGM could be used in surface alloying applications corresponding to carburizing and nitriding. On the other hand, surface de-alloying is a distinctive ability of DIGM, somewhat similar to decarburization. To date, DIGM has been reported in hundreds of binary and multicomponent systems in various materials such as metals, semiconductors, ceramics, and oxides [6], [7].

#### 1.1 Statement of the Problem

DIGM was first identified by Den Broeder in chromium-tungsten (Cr-W) diffusion couple and first recorded in his dissertation in 1970, which was then published in 1972 [8]. From then onwards to 1985, several investigators conducted rigorous research on various aspects of DIGM, which were summarized independently in their respective papers [9]-[13]. Most of those works were experimental, which broadened knowledge about the phenomenon. From 1985 to 1999, researchers conducted critical reviews of experimental data, proposed mathematical models, formulated many theories, and used thermodynamics to explain the mechanism of DIGM [1], [2], [6], [14]–[17]. After 1999, however, not much research was done on this topic. Up to 2005, only two new publications can be found on DIGM. Since 1970, the primary concern that arises from rigorous research on this phenomenon has been the precise origin of the force that moves the GB. The driving force for DIGM has been a topic of considerable controversy. According to the literature, the driving forces for DIGM are classified into four categories: Category (1) the free energy of mixing [13], [18]–[21]; Category (2) changes in energy of the GB with the incorporation of the solute [16], [17]; Category (3) GB Kirkendall effect which leads to the climb of GB dislocations [22]–[24]; and Category (4) the coherency strain arising due to the lattice diffusion ahead of the migrating interface [25]–[28]. However, to date, no single theory can explain all of the aspects of DIGM reported, and a universal picture of DIGM is still absent.

This project stresses the importance of another factor: solute interactions with GB, which result in segregation or anti-segregation. This is highly correlated with the driving forces in Categories (1) and (2) above, i.e., the free energy of mixing and energy changes of the GB with the incorporation

of solute. Meyrick [18] proposed that for alloys in which the solutes tend to segregate at GBs, thereby effectively reducing the GB energy. Reduction in the segregated population due to precipitation can provide the driving force for the grain boundary migration. Brokman et al. [29] discussed relevant solute interactions that can drive DIGM and claimed that segregation plays a crucial role in promoting DIGM by using mathematical formulation. According to Brokman et al. [25], the boundary velocity is proportional to concentration "jumps" across the GB. These jumps depend on the segregation coefficient, and if there is no segregation, diffusion smooths out the difference in concentration across the boundary. So, if there are no segregating solute atoms, there will be no concentration jumps and hence no GB migration. One of the ways to validate the theory proposed by Brokman et al. is to consider a system where the solutes and solvent are isotopes. Such a system will not exhibit DIGM simply because the isotopes do not segregate to the GB. Rabkin and gust [6] observed that DIGM is possible only in systems with a high value of segregation enthalpy. For example, systems like molybdenum nickel (Mo(Ni)) [30] and zinc cadmium (Zn(Cd)) [31] exhibit DIGM due to high values of segregation enthalpy. The low migration rates of the special tilt GBs [32] and immobility of GBs with misorientation close to the twin boundaries [33] in Cu(Zn) during DIGM experiments can also be explained based on the fact that these GBs exhibit a low value of segregation enthalpy.

Nevertheless, no progress has been made in either experimental or theoretical work to further address this issue, according to a recent review on DIGM [34]. One major challenge could be that it is difficult to capture segregation during DIGM using experimental approaches. For example, Pan and Balluffi [35] examined DIGM by using transmission and scanning transmission electron microscopies in the gold (Au)-rich layer of thin-film Au- copper (Cu) and Au-silver (Ag) diffusion couples that have GB structures of controlled geometry. In such experiments, electron microprobe analyzers' beam broadening effect inhibits the possibility of detecting thin segregation layers. Alternatively, Tashiro first proposed that MD simulations can study those aspects of DIGM that are not possible experimentally [36]. However, such a study had been rare, which may be due to the lack of computerized methods to study GB migration at that time. It was not until recent years that various techniques have been developed to simulate and quantify the migration of GBs with arbitrary geometry and under well-controlled driving forces [37]–[43]. Atomistic simulations, particularly MD simulations, have become an essential tool for studying GB migration and

revealing their underlying mechanisms. It is now timely to re-examine DIGM with the use of atomistic simulations.

GB migration specifically inhibited by solute atoms was discussed by John W. Cahn, an American scientist at MITT, as early as 1962, and now the concept of solute drag has been generally accepted in the metallurgy community. However, this work shows via atomistic simulation that solute atoms can also provide the vital driving force to drive (instead of inhibiting) GB migration if they are not distributed in the equilibrium state between the two abutting grains.

Non-equilibrium solute distribution across the GB, e.g., one grain is enriched with solute atoms while the other is depleted of solute atoms, is a common phenomenon during diffusion induced GB migration (DIGM). Therefore, it is proposed here that the driving force provided due to nonequilibrium solute distribution is a crucial factor that maintains a steady-state DIGM. Furthermore, the effects of atomic size mismatch and the cohesive energy can be decoupled by modelling the solute-solvent interactions with a Lennard–Jones (LJ) potential. Results confirm that the popular physical mechanism regarding DIGM based on coherent strain is not the only possible physical origin of DIGM. Instead, the solute-GB interactions are suggested to drive the GB migration. Considering that almost no progress has been made in this field during the past decade, this study contributes to the fundamental understanding of DIGM.

#### 1.2 Objectives of the Dissertation

This dissertation aims to determine the effect of solute-GB interaction on DIGM by utilizing recently developed simulation methods for studying GB migration.

The first objective is to discuss the influence that segregation and anti-segregation resultant of solute-GB interactions have on DIGM.

The second objective is to conduct a parametric study by systematically varying the solute atoms' atomic size and cohesive energy.

This will be achieved using MD, an atomistic simulation technique performed on a computergenerated bicrystal system.

#### **1.3 Dissertation Contributions**

The goals described in the previous section have mainly been achieved. The effect of solute-GB interactions (anti-segregation and segregation) on DIGM by using atomistic simulations based on

a few binary model systems has been explored. This study predicts that systems undergoing a high degree of segregation or anti-segregation can exhibit DIGM due to solute-GB interactions. The migration direction is directly correlated with the type of solute-GB interaction, which is an attraction or repulsion for systems showing a high degree of segregation or anti-segregation, respectively. It is proposed that the non-equilibrium distribution of solute atoms across the GB (e.g., with one grain being more enriched with solute atoms than the second grain) can contribute to the driving forces for the GB migration during a typical DIGM. Furthermore, we find that different solute types (with varying atomic sizes and cohesive energy) interact with the GB differently, thus resulting in solute segregation or anti-segregation. Moreover, the lattice strain that results from atomic size mismatch, which has been proposed to be an important driving force for diffusion-induced GB migration, is not always needed to induce the GB migration.

This study is anticipated to serve as a proof-of-concept for studying DIGM via atomistic simulations, which complements existing experimental and theoretical studies on this topic.

#### 1.4 Structure of the Dissertation

The dissertation is divided into six chapters for ease of reading.

Chapter 1: The "Introduction" gives a small glimpse into the rich world of DIGM in the past and the challenges that have motivated the present, the objective of the research work, and the significant contribution of the dissertation.

Chapter 2: The "Literature Review" is a review of the literature on GBs and an expanded overview of the crucial aspects of DIGM.

Chapter 3: "Research Methodology" provides a detailed description of the MD simulation method, including the use of statistical ensembles, periodic boundary conditions, time integration algorithms, embedded atom method (EAM) and Lennard Jones (LJ) interatomic potentials, and synthetic driving force (SDF) method. The Monte Carlo (MC) simulation method is also discussed, along with the Metropolis algorithm.

Chapters 4 and 5 are the main components of the thesis and contain the details of the results obtained from work done and a discussion of the results. These results are published as follows:

- "Effect of solute segregation on diffusion induced grain boundary migration studied by molecular dynamic simulations" Navjot Kaur, Chuang Deng and Olanrewaju. A. Ojo Computational Material Science, Volume 179,15 June 2020, 109685
- "Atomistic simulation of grain boundary migration induced by non-equilibrium solute distribution" Navjot Kaur, Chuang Deng and Olanrewaju. A. Ojo Materialia, Volume 15, 2021, 101005

Chapter 6 provides the conclusions of the research work and recommendations for future work.

Chapter 2 Literature Review

#### Chapter 2: Literature Review

#### 2.1 Introduction

This chapter summarizes the relevant published literature regarding the GBs and a most critical phenomenon related to diffusion along GBs called DIGM. This chapter intends to provide the reader with a more thorough understanding of this popular topic in materials science. Moreover, this background information helps to understand better the research presented in this dissertation.

#### 2.2 Structure of Grain Boundaries

The GB is a region of a solid crystalline material that separates two crystals (grains) that differ in mutual orientation. They are found in bulk metals, thin films, semiconductors, ceramics, crystalline polymers, and other materials. They form during various processes, i.e., solidification, deposition, and sintering. The mechanical, electrical, and magnetic properties of the materials are greatly affected by the structure and properties of GBs. Therefore, it is essential to understand the thermodynamics and kinetics of the GBs to properly understand the properties of many material systems. Nine parameters describe GB geometry: five are macroscopic parameters, and the remaining four are microscopic or energy parameters [44]. The latter is defined by nature and cannot be controlled, while the former provides information on how to prepare bicrystals from two single crystals. Three of these macroscopic parameters specify the mutual misorientation of the adjoining grains and are defined in terms of the angle of rotation  $\theta$  (one parameter) and directional cosines of the orientation of the interface plane (given by its normal: n) with respect to one of the grains (o: axis of rotation) (Figure 2.1).



Figure 2.1. Various parameters needed to define GB.  $x_A$ ;  $y_A$ ;  $z_A$  and  $x_B$ ,  $y_B$ ,  $z_B$  are the coordinate axes parallel to crystallographic directions in grains A and B, respectively. o is the axis of rotation, and  $\theta$  is the rotation (misorientation) angle necessary to transfer both grains to an identical position. n represents the orientation of the grain boundary plane. (used with permission from Springer, License:5297141487002) [45]

The five degrees of freedom (DOFs) that define the GB crystallography entirely result in many different GBs. These GBs can be categorized into groups according to the relationships among the axis of rotation o denoted as [u v w] and GB plane n, which is denoted by {hkl}. According to these relationships, the GB is said to be the tilt if the axis of rotation [u v w] is in the GB  $(o \parallel n)$  and twist if the axis of rotation [u v w] is perpendicular to the GB plane  $(o \perp n)$  (Figure 2.2). The GB is said to be mixed if the axis of rotation is neither parallel nor perpendicular but inclined instead. The GB is symmetrical if the plane between two grains (Grain 1 and 2) is defined by {hkl}\_1={hkl}\_2. Otherwise, they are asymmetrical (Figure 2.3).



Figure 2.2. Different types of GBs named tilt boundary (a) and a twist boundary (b) between two ideal grains [46] (used from https://www.wikiwand.com/en/Grain\_boundary#/overview)( https://www.tf.uni-kiel.de/matwis/amat/def\_en/kap\_7/backbone/r7\_2\_1.html).

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Figure 2.3. Relative orientation of GBs and rotation axes for different types of GBs. (a) asymmetric tilt boundary; (b) symmetric tilt boundary [44]

To create the bicrystal model, the energy of the structure should be low. The energy achieved is lowest when two adjacent grains have the same orientation, which means no GB. When one crystal is rotated with respect to the other, the energy is expected to increase, but there are some rotations for which the bicrystal achieves the lowest energy [47] (Figure 2.4). The reason is that there are few sites on GB that coincide with both adjacent grains. A boundary with a high density of lattice points in the coincident lattice site (CSL) is expected to have the lowest energy due to a good

atomic fit. These boundaries with unique crystallography are called special GBs and are explained by CSL theory. When a finite fraction of lattice sites coincide between two lattices, then the CSL can be defined. Based on the CSL theory, the parameter to measure the coincidence sites  $\sum$  is defined as:-

$$\Sigma = \frac{volume \ of \ CSL}{volume \ cell \ of \ crystal \ lattice}$$



Figure 2.4. Dependence of the energy of symmetric (110) tilt boundaries in Al on the tilt angle. The indices given in the figure are Miller indices of the corresponding GB planes (used from https://www.tf.uni-kiel.de/matwis/amat/def\_en/kap\_7/backbone/r7\_1\_2.html.) [48].

For instance, Figure 2.5 shows a  $\Sigma$ 5 structure. The blue and green circles are the crystal structure (simple cubic) of the same structure. The lattice formed by large red circles, i.e., coincidence sites, is known as the CSL.  $\Sigma$  is the reciprocal density defined as half of the number of atoms included in one CSL cell. This example contains four green, four blue, and eight coinciding vertices (shared by 4 CSL cells) in one CSL cell. Therefore, the  $\Sigma$  value for the structure is  $(4+4+8\times1/4)/2=5$ .

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Figure 2.5. Illustration of a simple cubic  $\Sigma$ 5 CSL structure [49].

#### 2.3 Grain Boundary Diffusion

GBs are highly disordered and provide a more open medium for atomic movement. Diffusion along the GBs of crystals plays a crucial role in many metallurgical and technological processes. Diffusion along the GB is orders of magnitude larger than through bulk. It is imperative to understand that diffusion can significantly alter the properties and structure of GBs. Thus, it may be possible to use these alterations in GB characteristics to affect the actual structure of polycrystalline materials.

There are changes in the state of GB due to the diffusion of foreign atoms along with them since large internal stresses arise in a diffusion zone. This ultimately results in a new phenomenon called DIGM. To explain the process, consider Figure 2.6, which shows an A/B bicrystal with GBs oriented perpendicular to the interface A/B [50]. No significant bulk diffusion occurs across the A/B interface if the temperature is kept low. However, it is possible to have GB diffusion significantly, e.g. inward diffusion of solute B along the GBs oriented perpendicular to the A/B interface on the A-side of the bicrystal. If the GB is not movable or static, there will be a thin layer (which is deeply penetrating) along the GB composed of mixed A/B material (Figure 2.6 (a)). However, if the GB starts to migrate parallel to the A/B interface, then a diffusionally mixed region is left behind in the wake of the migrating boundary (Figure 2.6 (b)). This diffusional mixing cause decrease in energy of the system, which provides the "driving force" for the migration of the GB. Therefore, this process is called "diffusion-induced grain-boundary migration or DIGM."

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Figure 2.6: Diffusion along a static and migrating grain boundary in an A/B bicrystal. (a) Inward diffusion of B into along static GB. (b) Formation of an alloyed (AB) zone close to the A/B interface by the motion of the grain boundary. The reduction in energy due to diffusional mixing is thought to drive the process of DIGM [50]

#### 2.4 Grain Boundary Migration

The movement of the boundary (separating two grains of the bicrystal) in the direction of the interface normal is called GB migration. Several driving forces cause boundaries to migrate: e.g., chemical, elastic energy, and strain energy (stored as dislocations). The rate of migration of the GB is both a function of this driving force and the mobility of the boundary.

The general relationship between the driving force P and the velocity v of the boundary is:

$$v = MP^n \tag{2.1}$$

where M represents the mobility of the GB. The mobility of the GB is a function of the migration mechanism and depends on the structure of the GB and its solute content. Certain grain misorientations give rise to maximum mobility. Most low angle boundaries and coherent twins, except for certain symmetrical tilt boundaries, are known to have low mobility [51]

The effect of solutes on GB migration has been thoroughly reviewed [50] by Mittemeijer, and the main experimental observations are summarized as follows:

- Solutes generally inhibit the ease of movement of GBs. However, the effects of solute drag on GBs are eliminated at high temperatures.
- Boundaries have high and low mobility regimes that correspond to high and low driving forces. As the solute concentration increases, the mobility decreases (the activation energy for migration increases).
- Different types of solutes have differing effects on mobility for a given system. E.g., faster-moving solutes such as Au and Ag solutes in the lead (Pb) affect mobility to a greater extent than slower-moving solutes such as tin (Sn) solute.
- Solutes affect the migration of high coincidence boundaries more than other (random) boundaries

## 2.5 DIGM Phenomenon2.5.1 Operating conditions and features of DIGM

When a polycrystalline metal is placed in a vapour of another metal, the atoms from the vapour diffuse along the GBs, which leads to the growth of some of the grains and the shrinking of others. The solute atoms that are being diffused are deposited in the newly created parts of the growing crystal. This process which leads to the formation of alloyed zones is considered an alloying case of DIGM. On the contrary, in the de-alloying case, solute atoms are made to diffuse out along the GB, and the migration of the GB produces a de-alloyed region in its wake. These two cases are summarized in Figure 2.7.



Figure 2.7. Schematic illustration of "Diffusion-induced grain boundary migration." (a) solute coming in the sample (Alloying case) (b) solute leaving the sample (De-alloying case) (used with permission, license number 5296801503363) [22].

The GB migration is perpendicular and not uniform throughout the GB. Different boundary segments can move in different directions, thus creating bulges on both sides, as shown in Figure 2.8.



Figure 2.8: Optical micrograph showing the surface relief caused by the zincification of an iron foil heated in Zn vapour for 4 h at 600 °C ) (used with permission, license number 5296820229761) [3]. Interference contrast,  $700 \times$ 

DIGM has been observed and reported in many binary systems, and most of the systems have a substitutional element as the solute [3], [52]. However, DIGM has also been documented in some interstitial alloys, e.g., Ni- carbon (C) systems, where C is the interstitial solute. Some initial reports indicated that DIGM occurs at low temperatures where lattice diffusion is frozen out. However, it was later observed that DIGM could also occur at high temperatures where lattice diffusion is appreciable [53]. DIGM is an important phenomenon because it can cause significant mass transfer through alloying or de-alloying. In polycrystalline materials, DIGM causes various physio-chemical changes of the GB, such as undulation at the interface [1], [2], the formation of misfit dislocations at the original interface [3], and composition fluctuation between the matrix and the migrated region [4]. Furthermore, DIGM is not restricted to diffusion from the vapour phase only, but it takes place in many material processing methods like liquid phase sintering [54]–[56], sputtering of heated alloy targets [57], [58], and irradiation of alloy materials [59].

According to the literature, some of the salient features of DIGM are as follows:

- During the process, the concentration of solutes in a region swept by a moving GB is higher than bulk. As a result, a sharp discontinuity exists across the GB [60].
- The migrated region usually is higher than the bulk and happens due to surface relief [3], [13], [27]; and

The extent of migration is lower in thicker specimens as compared to thinner ones (Figure 2.9) because, in thick samples, GBs migrate in a region close to the initial surface, and deeper areas remain unchanged [61].



Figure 2.9: Schematic representation of DIGM in (a)Thick and (b)Thin samples (used with permission, license number 5296820800037) [61]

#### 2.5.2 DIGM research: an overview

DIGM was first observed in the late 1930s by Rhines and Montgomery [52], who found that GB in bicrystalline Cu moved when exposed to zinc (Zn) vapour. Nevertheless, they lacked understanding of their observation of the disturbed GB of a Cu bicrystal due to inward diffusion of Zn. Although they were the first to discover the phenomenon, they were ignorant of the significance of the findings and neglected to document the details. The next observation was made in the early 1970s in the Cr-W diffusion couple by F.J.A. den Broeder [8], who introduced this new phenomenon to the research community. It is therefore widely acknowledged that F.J.A den Broeder [8] is the pioneering researcher who extensively described the phenomena of DIGM in his experiments. His experiments focussed on interdiffusion in a solid–solid, Cr–W diffusion couple. He observed DIGM by examining the cross-sections taken parallel to the Cr/W interface. From then until the 1980s, investigators conducted rigorous research on various aspects of DIGM summarized independently in their respective papers; see [10]–[12]. Most of these works are experimental, enhancing and broadening knowledge on this phenomenon. After the 1980s and up to the end of the 20<sup>th</sup> century, researchers critically reviewed experimental data, proposed mathematical models, formulated many theories, and used thermodynamics to explain the

mechanisms behind DIGM [1], [15]–[17], [30], [62], [63]. Then in the 21<sup>st</sup> century, interest waned, and one or two new publications on DIGM were produced between 1999-2005. The reason for the absence of interest could be the lack of experimental data to validate the proposed mathematical models. Figure 2.10 summarizes the history of research work on DIGM and its present status.



Figure 2.10: Historical Survey of DIGM

#### 2.5.3 Technological applications of DIGM

DIGM has important technological applications and can either produce functional properties or be intentionally suppressed to avoid detrimental effects [1]. For instance, Hillert and Li [5] proposed that DIGM could be used in surface alloying applications related to carburizing and nitriding processes. With time, the new grains nucleated in the early stages of DIGM can cover the entire surface, which results in a layer of solid solution on the specimen. This process is called "diffusion induced recrystallization" [1]. The new layer formed has a more refined grain structure and thus improves the mechanical properties. Diffusion induced recrystallization can be used to protect materials against corrosion and harden their surface. This mechanism to form surface coatings is more advantageous than alternative technologies involving lasers, electron beams, or ion implantation because the latter three technologies aim to produce non-equilibrium structures to

provide superior properties. The ability of DIGM to create wavy or corrugated boundaries has potential application in enhancing the creep resistance of materials as corrugated boundaries slide less compared to planar ones [64]. Metal silicides are finding extensive applications as contact materials in submicron semiconductor devices. They can be formed through a diffusion-reaction between metal and silicon during DIGM.

On the other hand, surface de-alloying is a unique capability of DIGM, which is related to decarburization. It is interesting to note that DIGM may produce nonhomogeneous stresses (tensile) in surface layers that serve as severe stress concentrators, thus increasing the potential for fatigue cracking. Therefore, DIGM is inhibited to improve fatigue lifetimes. The technology of electrical interconnections is another area where control of DIGM may be necessary. If DIGM is found in these materials, it can provide the mechanism for intermixing of thin layers to form interconnectors, resulting in premature failure of these devices. Shen et al. [65], [66] proposed a new method to evaluate the role of DIGM on the crack generation rate (CGR) of various materials. They found that DIGM can intensify oxidation along migrated GBs. The morphology (tortuous) of migrated GBs can prevent cracking propagation and increase the total crack path, which reduces the CGR. DIGM and liquid film migration (LFM) occur during the processing of materials as they are mechanisms for chemical equilibrium. Owczarski et al. [67] observed LFM in the heat-affected zone (HAZ) during the welding process of Ni-based super alloys (Udimet 700 and Waspaloy). In Ni-based alloys Inconel 718 and Incoloy 903, liquid films result from the constitutional liquefication of carbides in the HAZ [68]–[70]. Migration of these liquid films helps to reduce microfissuring due to equilibration.

#### 2.5.4 Driving Forces of DIGM

The occurrence of DIGM dramatically depends on the presence of a driving force, even though the concept of driving forces for DIGM is not fully understood. Apart from driving forces, certain back-forces or restraining forces oppose the principal driving force. DIGM will stop if these restraining forces become equal to the driving force or the driving force disappears. Several adverse factors that cause restraining forces must be overcome for migration to proceed. The stress build-up in a specimen due to atom size misfit in a solid solution tends to counter DIGM [1]. GB migration causes an increase in the total area of the boundary, which might contribute to the rise in the system's total free energy, which may cause the termination of DIGM. It is also likely that the defects produced by the migrating boundary can affect DIGM adversely [1]. DIGM can also stop if the link between driving force and mechanism is lost. When a solute is applied to the surface of a specimen, there may be a reduction in the system's free energy due to the formation of a solid solution alloy. This decrease in free energy can be considered as a contributing driving force for the GB migration but is not capable of driving the process completely. Balluffi and Cahn [22] pointed out that the nucleation of DIGM by the formation of bulges is not possible by such a driving force. The increase in the free energy due to an increase in the GB area is much higher than a reduction in free energy due to alloying. Therefore, a mechanism that forms a critical nucleus is required to initiate DIGM, although this energy may continue the migration process once initiated. Details of the various mechanisms proposed in the literature are summarized in the following sections.

#### 2.5.5 Coherency Strain Model

The coherency strain model is based on the built-up of strain energy in a crystallized region adjoining the GB. Sulonen [28] was the first to propose the coherency strain theory in 1960 as the driving force for discontinuous precipitation. He stated that GB diffusion forms a zone ahead of the GB, which is either depleted or enriched in a solute concentration. The tensile or compressive lattice misfit stresses arise in this zone depending on the sign of a lattice dimension changes during the formation of the zone. This strain provides a local increase in free energy that produces the driving force of boundary migration because there is no counterpart on the side of the new matrix. Due to the presence of non-symmetrical strain, the system's energy is decreased if the boundary moves through a highly strained layer. This happens because the transfer of atoms across the interface involves the relaxation of stress.

Following Sulonen, Hillert [71] analyzed the effect of the coherency strain energy in a frontal diffusion zone on discontinuous precipitation. He obtained an expression for coherency strain energy by using a parallel tangent construction for equilibrium between the grain and GB. Then Hillert [9] subsequently proposed that the same diffusional coherency strain energy can drive LFM and obtained a similar expression (as obtained for discontinuous precipitation) for coherency strain energy based on the local equilibrium between the liquid and the coherent layer. Hillert suggested that a similar coherency strain energy could also be a driving force for DIGM.

According to Hillert [9], the driving force per unit area of GB in an elastically isotropic material is

$$G = \frac{E\eta^2}{(1-\nu)} (c_+ - c_-)^2, \qquad (2.2)$$

where *E* is Young's modulus,  $\eta$  is the relative change in lattice spacing per unit change in a solute mole fraction, *v* is the Poisson's ratio and  $c_+$  and  $c_-$  are solute mole fractions well in front of and well behind the GB.

According to the coherency strain theory, a GB is treated as a very thin layer of liquid. Both faces of this layer are in equilibrium with the neighbouring crystals. When a film of liquid with different composition is introduced between two solid crystals, local thermodynamic equilibrium is reached through the dissolution of the solid in liquid and/or adsorption of atoms from the liquid surfaces of the solid. The equilibrium compositions at the solid surfaces and in the liquid are found from a common tangent construction between the free energy curves of the solid and liquid phases. These are found to be C<sub>s</sub> and C<sub>l</sub>, respectively. Now consider solid-liquid interface 1. If a solute diffuses from the liquid layer to a small distance into the solid, a strained coherent layer is formed due to elastic misfit. The strain required in a thin alloyed layer to maintain coherency with the bulk material provides a local increase in free energy, as shown in Figure 2.11. The free energy difference between the strained and unstrained solids is directly proportional to the square of atomic misfit and suitable elastic modulus, as shown in Eq. 2.2. Due to this additional strain, a new equilibrium condition arises between strained solid and liquid, as shown in Figure 2.11, and equilibrium compositions can again be obtained using the common tangent construction method. If the same process happens at liquid/solid interface 2, with a different magnitude of the diffusion or different elastic modulus which corresponds to the different orientation, then the free energy curve of this interface will also be different, and a new equilibrium condition is again set up between strained surface 2 and the liquid. In simple terms, it can be said that liquid composition in equilibrium with surface 2 is different from that in equilibrium with the first surface. If local equilibria are sustained at two interfaces, there will be a composition gradient over the liquid film. This causes diffusive flux across the liquid layer and will carry material from more highly stressed solid to less highly stressed solid. This results in the increase of the less highly stressed solid at the expense of the more highly stressed solid and drives the movement of the liquid film.



Figure 2.11: (a) Schematic diagram of LFM showing diffusion of a solute from the liquid into the solid leads to the formation of a strained layer at the surface. (b) Free energy G for solid and liquid phases in a two-component (A and B) system: curve marked  $G_L$  applies to the liquid phase, while  $G_S$  applies to the unstressed solid phase: the usual tangent construction gives the compositions of the solid and liquid in contact with each other at equilibrium as  $C_S$  and  $C_L$ , respectively. For the solid with the initial composition  $C_o$ , diffusion of solute into or out of the surface forms an elastically stressed layer, the free energy of which is increased by an amount  $G_{EI}$  which varies as the square of the difference in a concentration from Co. Because of this stressed layer, new equilibrium compositions at  $C_S'$  and  $C_L'$  are established (used with permission, License: 5297690948584) [1].

Immediately following Hillert [9], Handwerker et al. [50] and Yoon et al. [51] tested this model for liquid film migration. They developed an equation for the migration velocity of the film based on thermodynamics which is given as:

$$v = \frac{D_l V_m}{\lambda_{RT}} \left[ \left( Y(n_A) - Y(n_B) \right) \eta^2 (C^S - C_o)^2 + 2\sigma (K_A - K_B) \right] \times \frac{c^l (1 - c^l)}{(c^l - c^S)^2}$$
(2.3)

 $D_l$  = diffusivity of solute in a liquid

 $C^{l}$  and  $C^{S}$  = compositions of the liquid and solid

 $\lambda =$  film thickness

 $\sigma$ = solid-liquid interfacial energy and

 $K_A$  and  $K_B$  = radii of curvature of the two grains

Therefore, the velocity can be expressed in terms of diffusion across the liquid film initiated due to the mechanism explained above that uses free energy vs composition curves. So, the coherency strain is thus related to the rate of migration.

Motivated by this thermodynamic explanation, the Korea Advanced Institute of Science and Technology (KAIST) group undertook some experiments intending to critically test the coherency strain theory [72]–[75]. The KAIST group conducted experiments on the molybdenum-nickel (Mo-Ni) system, where the coherency strain can be easily varied in both sign and magnitude. The coherency strain can even be reduced to zero by adjusting the concentrations of two solutes (Co and Sn). The KAIST group demonstrated nearly parabolic dependence of the migration distance on the estimated coherency strain (Figure 2.12). The observed zero migration at strain = 0 shows that the coherency strain energy is the driving force for DIGM in their system. The migration distance increases by increasing the strain in either a positive or negative sign. They suggested that the model can be extended to DIGM by simply replacing the liquid film with a GB. Although the exact equations derived for the LFM cannot be used for DIGM, the qualitative predictions are the same.



Figure 2.12. The observed variation of the migration distance for DIGM (labelled CIGM) and LFM for Mo-Ni (Co, Sn) alloys held at 1460 °C for 2 h (embedded into a Mo-Ni-Co-Sn liquid) as a function of coherency strain  $\delta_0$ . The solid and dotted lines are the parabolic fits to the experimental data. (The numbers above the full circles indicate the decimal fraction of Co (used with permission, Licence: 5297350751293) [75].

#### 2.5.6 Solute-grain boundary interaction energy models

Some reports claim that the driving force for DIGM originates from the change in the GB energy with the incorporation of solute. Louat et al. [17] proposed that the might be minimum GB energy at a specific solute concentration. If the solute concentration at the GB is changed, the GB migrates where the solute concentration that produces the minimum energy can be regained. The free energy difference between the boundary at its optimum and instantaneous solute concentrations gives rise to the driving force for DIGM. In an alloying case, the GB concentration increases above the energy minimizing concentration. The only way for a boundary to reduce energy is to dispose of excess solute, which is achieved by migration of the boundary, thereby depositing the extra solute atoms in its wake. In the de-alloying case, boundary concentration falls below the energy minimizing concentration. The boundary moves to absorb solute atoms from nearby grain and creates a solute depleted zone (de-alloyed zone) in its wake. This model, however, has limitations. The reversal of the DIGM direction while the solute source remains constant cannot be explained by this model since the driving force for the forward migration of the GB should always be higher than that for reverse motion.

Kasen [16] proposed a model similar to Louat et al. [17] but with an extra feature of solute-induced structural transformation. He postulated that solute addition or depletion in the GB activates the structural transformation of the boundary, so it moves away (retaining its new structure) until minimization of free energy is achieved. For example, solute addition to GB through the diffusion of solute results in a new boundary structure which is relatively supersaturated in solute; therefore, it moves away to achieve energy minimization and leaves the alloyed zone behind. This model explains the reversal of GB migration. According to this model, during forward migration of supersaturated GB structure, desorption of solute would cause the solute content to fall below equilibrium concentration, which increases GB's energy. This provides a driving force for the reverse migration of GB into the high solute field, where it adsorbs the solute it needs from the matrix and leaves behind the solute-depleted zone. This dynamic process continues until the constant solute source is present. Here, the supersaturated GB structure formed during initial transformation retains its structure during reverse migration. This is the main cause of migration reversal. However, grain boundaries moved due to solute addition and returned to their original position by migration reversal cannot be made to move again by adding solutes. It means that the boundary has become stable during the first DIGM cycle.

One of the challenges of these solute GB interaction energy models is that they cannot be applied at high temperatures. This is because there is a large degree of out-diffusion of solute at high temperatures, and their migration does not significantly change the GB concentration.

Hence, it can be concluded that none of the discussed mechanisms can be universally applicable to all the cases of DIGM. They likely contribute to the initiation and migration of boundaries in varying degrees for different cases. The most favourite among them is the coherency strain energy mechanism, as it explains almost all of the features of DIGM except in a few instances.
# 2.5.7 Role of solute-GB interaction in DIGM

It is well established that the interactions between GBs and chemical impurities play a key role in GB migration [76], [77]. Understanding these interactions helps to explain several important GB-related phenomena like recrystallization kinetics [78], impurity drag effects [78]–[81], GB wetting [82], and DIGM [30], etc. To date, researchers have mostly focussed on one interaction between solutes and GB, which involves the segregation of solute atoms to the boundary. The movement of such a GB can drag segregated impurity atoms along with it. As a result, a massive driving force is needed to move the GB at a matching velocity (compared to the case when no solutes are included). This phenomenon is now known as solute atoms exert a very high drag force to slow down a migrating GB, it has also been widely reported that solute atoms by diffusing into or out of a GB can provide the essential driving force for the GB to migrate, i.e., DIGM [1]–[3]. While there is still debate on the physical origins of DIGM, it is generally accepted that once initiated, DIGM will be sustained in one direction. This causes the solute atoms to accumulate or deplete on one side of the GB, thus resulting in an enlarged alloyed or de-alloyed zone as the GB migrates [1].

# **Chapter 3**

# **Research Methodology**

# Chapter 3: Research Methodology 3.1 Introduction

This chapter presents MD's fundamental principles and procedures as a computational simulation technique. This includes discussing the standard integration techniques, interatomic potential functions, boundary conditions, and various ensembles (NVE, NVT, and NPT). Finally, an introduction and procedure for using a Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) are presented.

## 3.2 Molecular Dynamics

New technologies that can explain the different phenomena in materials science are developing rapidly. Experiments are used to describe much of the phenomena found in materials but are inadequate for studying all aspects of materiFor example, it is impossible to understand the atomistic phenomena in materials through experiments, which has left many technological applications unexplored. This is the reason for the development of simulation and modelling methods.

According to a statement given by Richard Feynman, an American theoretical physicist, the most important scientific knowledge is the awareness that everything is made of atoms. Everything that living things do is understood in terms of the movement of atoms. This means that if there is an understanding of atoms' behaviour, which is then modelled, there will be a subsequent understanding of how materials undergo deformation, phase changes, etc. This concept has led to the development of atomistic simulation tools to explain the movement of atoms that cannot be seen using laboratory experiments/instruments. These tools bridge microscopic molecular understanding and macroscopic continuum engineering. Molecular dynamics (MD) is a powerful computer simulation method [83] that can explain the atomistic behaviour of different materials exposed to situations that are impossible in the laboratory. MD focuses on atoms while observing the behaviour of materials; therefore, this method can be described as a "virtual microscope" with high temporal and spatial resolution. MD can simulate complex systems at the atomic scale. For this purpose, first, a sample was prepared, which consisted of mutually interacting N particles. Then Newton's equations of motion were solved for this system until equilibration, i.e., the system's properties no longer change with time. The actual properties were measured after equilibration. The MD simulations predict the time-dependent trajectories of interreacting particles in a system. These particles might be in the form of a solid, liquid, or gas. All atoms reside in the model, called the simulation cell, as shown in Figure 3.1. A more detailed discussion of MD as a computational technique can be found in the writings of Haile [84], Frenkel and Smit [85], and Leach [86].

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Figure 3.1. A typical molecular dynamics simulation cell containing atoms [87].

# 3.2.1 Advantages of using Molecular Dynamics

Computer simulations aim to provide an understanding of the properties of assemblies of molecules in terms of their structure and the microscopic interactions between them. Simulations facilitate discoveries that cannot be determined experimentally, and as such, they complement experiments. MD and MC simulations are important and widely used techniques. Various branches of science have extensively used MD simulations. Examples of common use include determining the reaction rates in chemistry, formation of solid-state structures and surfaces, defects in materials science, and folding of proteins in biochemistry. Computer simulations bridge theory and experiment, as shown in Figure 3.2. These simulations can test any theory and model and compare the results with experimentally derived findings. One more advantage of simulations is that they can be carried out in extreme environmental conditions: e.g., such as elevated temperature and pressure, where it is impossible to conduct experiments.

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Figure 3.2. Simulations as a bridge between theory and experiments [88].

#### 3.2.2 Molecular Dynamics Algorithm

In general, MD simulations are carried out in a series of steps (Figure 3.3)[85] as follows.

**Step 1**. First, the system that will be simulated is defined, including establishing the dimensions of the system, types of atoms and molecules, and inter-particle potential.

**Step 2.** The model constructed in Step 1 has no physical significance since all atoms are at 0 K, and there is no force between them. So, in this step, a temperature is assigned to the system. The system should reach equilibrium before the simulation and applying any changes.

• Statistical mechanics is used to assign the temperature in which a distribution of velocity is given to particles randomly, and the temperature is calculated by using:

$$3Nk_bT = \sum_{i=1}^{N} \frac{m_i v_i^2}{2}$$
(3.1)

where N is the total number of particles,  $k_b$  is the Boltzmann constant,  $m_i$  is the mass of the *i*<sup>th</sup> particle,  $v_i$  is the velocity of the *i*<sup>th</sup> particle, and T is the temperature assigned to the whole system.

• After assigning the temperature, the next step is to give enough time to the system to reach equilibrium. This is essential as the system needs to be in minimum energy configuration before the simulation.

**Step 3.** Any desired changes are applied to the system, and forces acting on particles are determined using an inter-particle potential. The final position is found by numerically solving Newton's second law equation:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i = -\vec{\nabla} U(\vec{R})$$
 (3.2)

where  $U(\vec{R})$  is the inter-particle potential

**Step 4.** Step 3 is repeated for as many time steps as desired to complete the simulation, and the final properties of the system are calculated.



Figure 3.3.Steps involved in LAMMPS simulation (used from <a href="https://en.wikipedia.org/wiki/Molecular\_dynamics">https://en.wikipedia.org/wiki/Molecular\_dynamics</a>) [89]

## 3.2.3 The time integration algorithm (Verlet algorithm)

MD simulation programs use different kinds of algorithms to solve equations of motion. The Verlet algorithm is most commonly used for integration purposes in MD. Two Taylor expansions are added for position r(t): a forward and backward Taylor expansion. If r(t) is defined until the third order, the velocities, v(t); acceleration, a(t), and third-order derivative of the position b(t) will appear.

$$r(t - \Delta t) = r(t) - v(t)\Delta t + \frac{1}{2}a(t)\Delta t^{2} - \frac{1}{6}b(t)\Delta t^{3} + O$$
(3.3)

$$r(t + \Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^{2} + \frac{1}{6}b(t)\Delta t^{3} + O$$
(3.4)

Adding the two expressions provides a basic form of the Verlet algorithm

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t)\Delta t^{2} + O(\Delta t^{4})$$

$$(3.3)$$

(25)

This algorithm is used to integrate Newton's equations. Therefore, a(t) is the force divided by the mass, and the force is also a function of the positions r(t) [29]:

$$a(t) = -\frac{1}{m}\nabla V(r(t))$$
(3.6)

This algorithm is more robust than the other MD simulators because it is accurate, stable, and easy to implement. The simulation iteratively takes place by calculating the forces and solving the equations of motion alternatively based on accelerations calculated from the new forces.

# 3.2.4 Statistical ensembles

MD simulations generate information at the microscopic level, which includes atomic positions and velocities. Statistical mechanics is required to convert or extrapolate this microscopic information to macroscopic quantities such as pressure, energy, heat capacities, etc. Experiments are done on a macroscopic specimen with a large number of atoms and molecules. It is assumed that the time average is equivalent to ensemble averages. For this purpose, a statistical ensemble is used, composed of many microstates (many replicas of the system). Combining these microstates can lead to the same properties in a macrostate.

The two common types of ensembles are NVE and NVT. The NVE ensemble, also called the microcanonical ensemble, keeps the number of atoms, the volume, and the energy constant during the time integration. However, in most experiments, the temperature is usually the parameter that is generally kept constant. NVE ensemble cannot fix temperature; therefore, the NVT ensemble must be used. The NVT ensemble uses the Nose-Hoover thermostat, which is a deterministic method used to maintain the temperature at around the average. In contrast, the NPT (ensemble) uses a barostat to keep the pressure constant. However, for both the NPT and NVT ensembles, the total system energy is not conserved due to the use of a thermostat and/or barostat [87].

#### 3.2.5 Boundary Conditions

MD simulations provide information on the properties of macroscopic systems, but these are extremely large to be calculated, even by using computers. As such periodic boundary conditions are used to approximate a system that is infinite which is done by using a relatively small part of the system to produce a reasonable representation of the infinite system. This small part of the system is a 3-dimensional (3D) box called a unit cell. A set of boundary conditions controls the particles of this unit cell. During the simulation, the particles are free to move in the central (original) cell. As such, the periodic images of the adjacent cells move identically. In this process, the atom that moves across one cell boundary will show up on the other side of the boundary.

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Figure 3.4. Periodic boundary conditions are shown for a simple 2D system. Note that the simulated system is a sub-ensemble within an in1nite system of identical, small ensembles. [90]

#### 3.2.6 Time step

The most essential parameter in MD simulations is the time step because it determines the total time needed for the simulation and the computational power required. In other words, the time step may help to limit the computational expense. Two criteria should be followed to choose the correct time steps. The first criterion requires the time step to be small enough so that the simulation is realistic and atoms move continuously. The second criterion is that the time step should be large enough so that the simulation is not overly time-consuming.

# 3.2.7 Time and size limitations

MD is limited by the particle size and the time needed to obtain meaningful data. MD simulations work with systems that contain thousands of atoms and capture processes that range from hundreds of nanoseconds to only a few picoseconds.

Due to these limitations, researchers are not able to realize the full power of MD simulation. Improvements are being made in the high-performance computing sector to remove these limitations. It involves using massively parallel processors (MPPs), where 100s or 1000s of processors are used simultaneously to model realistic length scales.

# 3.3 Interatomic Potentials

In MD simulations, the individual particles interact via specific forces described by interatomic potentials. Interatomic potentials represent the potential energy created between two or more atoms when located in a particular configuration. These are usually characterized by using the relative positions of the atoms with respect to each other rather than from the absolute position. The potential function considers the strong repulsion at close distances and weaker attraction at longer distances. The accuracy of these interatomic potentials determines the accuracy of the simulation process.

The simplest way of understanding interatomic potentials is to first look at the electrostatic potential V(r) between two-point charges with a charge separated by a distance (r), which is given by

$$V(r) = \frac{e^2}{r} \tag{3.7}$$

The potential from Eq.3.7 is related to the force F(r), which is given by:

$$F(r) = -\frac{d[V(r)]}{dx}$$
(3.8)

The interatomic potential of a pair of atoms is conceptualized by bringing the atoms from an infinite separation distance to their equilibrium. The total work required to achieve this state is called interatomic potential energy. Many sophisticated interatomic potentials provide accurate explanations for complex systems. They include the embedded atom and LJ potential method.

The embedded atom method (EAM), developed by Daw and Baskes [91], is a multi-body potential to model the bonding in metallic systems. This method was derived from the density functional theory, a method used to determine the properties of systems with many electrons by using functions of another function in its effective-medium [92] and quasi-atom [93] description. The

EAM expresses the potential energy as the sum of two-body (pairwise) interaction between a given atom and its neighbours (within a cutoff distance) and many-body attractive interactions that account for the contribution of a larger group of neighbouring atoms to the electron density of a given atom.

This method considers that each atom is embedded in a host electron gas that is the resultant of the surrounding atoms. The amount of energy required to insert one atom into the electron gas of a given density is called the embedding function. According to this method, in addition to the pair-wise potential, the potential of embedding the atom, i, is given by [EAM][94]

$$E = \sum_{i} F_i\left(\rho_{h,i}\right) + \frac{1}{2} \sum_{\substack{i,j \ i \neq j}} \varphi_{ij}\left(r_{ij}\right)$$
(3.9)

where  $\varphi_{ij}$  is the pair-wise potential between particles i and j,  $F_i$  is the energy of embedding atom i in the host electron density of  $\rho_{h,i}$  and  $r_{ij}$  is the distance between atoms *i* and *j*. The parameters involved are obtained from other fundamental studies, such as *ab initio* simulations or semiempirical methods.

#### 3.3.1 Lennard-Jones Potential

The LJ potential [86] is the most widely used two-body potential in which the energy is approximated by:

$$U(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$
(3.10)

where  $\sigma$  and  $\varepsilon$  are the LJ-parameters that represent the atomic size and cohesive energy, respectively, and  $r_{ij}$  is the interatomic distance.

The first term on the right side of Eq.3.10 represents repulsion and the second term denotes attraction. The force is obtained by the derivative with respect to r<sub>ij</sub>:

$$F_{ij} = -\frac{\partial U(r_{ij})}{\partial r_{ij}} = \frac{24\varepsilon}{r_{ij}} \left[ 2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6 \right]$$
(3.11)

The equilibrium spacing for two atoms (where the force between them is zero) is equal to  $2^{1/6}\sigma$ . Figure 3.5 presents a graphical plot of Eqs 3.10 and 3.11.

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Figure 3.5. The Lennard-Jones potential, along with its derivative [87]

While using LJ potential, the parameters  $\sigma$  and  $\varepsilon$  are chosen as the benchmark unit values for the properties of length and energy parameters. Properties such as mass, temperature, pressure, time, etc., are multiples of these fundamental values. Also, the mass of one atom is taken as unity. With these assumptions, the reduced units for many other properties may be calculated as shown in Table 3.1 (kB is a Boltzmann's constant).

| Table 3.1 L.I. | units for | various | nroperties | used in | simulation | [87] |
|----------------|-----------|---------|------------|---------|------------|------|
| TAULE J.T. LJ  | units 101 | various | properties | useu m  | Simulation |      |

| PROPERTIES  | NON-DIMENSIONAL LJ<br>UNITS     |  |  |
|-------------|---------------------------------|--|--|
| length      | σ                               |  |  |
| energy      | 3                               |  |  |
| time        | $\sigma \sqrt{m  /  arepsilon}$ |  |  |
| force       | ε/σ                             |  |  |
| pressure    | $\epsilon/\sigma^3$             |  |  |
| temperature | $\epsilon/k_{ m B}$             |  |  |

It is always important to consider interactions between two different species of atoms in a system. While using the LJ potential method, it is crucial to determine the interactions of the identical particles among themselves defined by parameters ( $\sigma_{\alpha\alpha}$ ,  $\sigma_{\beta\beta}$ ,  $\epsilon_{\alpha\alpha}$ , and  $\epsilon_{\beta\beta}$ ) for each of material, as well as the parameters for the interspecies interactions ( $\sigma_{\alpha\beta}$  and  $\epsilon_{\alpha\beta}$ ). Here,  $\alpha$  and  $\beta$  refer to different atomic species. The Lorentz-Berthelot combining rules can be used to calculate the parameters that define interspecies interactions [4] by using the following equations:

$$\sigma_{\alpha\beta} = \frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}}{2}$$
 and  $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}$  (3.12)

These represent the arithmetic average for  $\sigma_{\alpha\beta}$  and geometric average for  $\epsilon_{\alpha\beta}$ .

# 3.4 Synthetic Driving Force

Janssens et al. [38] developed a method that applies forces on the GB to move the GB. This is achieved by adding external energy to one grain while keeping the energy of the other grain unchanged. They differentiated between two adjacent grains with an order parameter. The order parameter  $\xi_i$  for each atom *i*, is defined as

$$\xi_i = \sum_j \left| r_j - r_j^I \right| \tag{3.13}$$

where the sum is over N nearest-neighbour atoms *j* of *i* and N is 12 for face-centred cubic (fcc) crystal,  $r_j^I$  is the nearest ideal lattice site of crystal *I* to  $r_j$ . The order parameter is zero if the local orientation is exactly the same as the perfect crystal *I*. If there is any deviation from the perfect orientation, the orientation parameter comes out to be positive.

In the case where atom *i* is in a perfect lattice *j*, the order parameter can be written as:

$$\xi_{IJ} = \sum_{j} \left| r_j^J - r_j^I \right| \tag{3.14}$$

This order parameter is positive since lattices I and J have a different orientation because they belong to two different grains. So, it is easy to differentiate between two grains in terms of the order parameter. Based on the definition of the orientation parameter, orientation-dependent potential energy is added to every atom.

The artificial potential is given as:

$$\mu_{\xi}(r_i) = \begin{cases} 0 & \xi_i < \xi_I \\ \frac{V}{2} (1 - \cos 2\omega_i) & \text{with } \omega_i = \frac{\pi}{2} \frac{\xi_i - \xi_I}{\xi_h - \xi_I} & \xi_I < \xi_i < \xi_h \\ V & \xi_i < \xi_h \end{cases}$$
(3.15)

 $\xi_I = f \xi_{IJ}$ ,  $\xi_h = (1 - f) \xi_{IJ}$ . The value of f is chosen to subtract the error due to thermal fluctuation. Due to this potential, the atoms in one grain would have potential energy larger than

those in the other grain. This causes the GB to move, thus eliminating high-energy grain and the growth of low-energy grain. The extra force that results from the above potential is given by the following expression:

$$F(r_i) = -\frac{\partial \mu_{\xi}}{\partial r_i} = -\frac{\pi V}{2(\xi_h - \xi_l)} \left\{ \left( \sum_j \frac{\delta_{ij}}{|\delta_{ij}|} \right) \sin 2\omega_i + \sum_j \left[ -\frac{\delta_{ji}}{\delta_{ji}} \sin 2\omega_i \right] \right\}$$
(3.16)

This equation is valid for  $\xi_I < \xi_i, \xi_j < \xi_h$  and  $\delta_{ij} = r_i + I_{ij} - r_j$ ,  $I_{ij} = r_j^I - r_i$ . If  $\xi_i, \xi_j$  is outside the given limit,  $F(r_i)$  is zero.

This method is used to perform many simulations. GB displacement is determined by taking the average of those simulations according to the random walk method proposed by Trautt et al. [37]. This method is based on the fact that GB can fluctuate about its equilibrium position at high temperatures in the same way as random walk behaviour. Therefore actual GB displacement is determined by taking the average of the GB displacements obtained from a large number of independent simulations of identical geometry and temperature but with different initializations. Trautt et al. performed MD simulations in crystalline Al at 750K by using LJ and EAM potentials. Figure 3.6 plots the temporal evolution of  $\langle \bar{h} \rangle$  for all 20 runs, for both the LJ and EAM-Al simulations vs time (t).

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Figure 3.6. Temporal variation of the grain boundary profile for all ensemble runs performed in both the LJ and EAM-Al simulations. The profiles are shown for both the upper and lower boundaries within each computational cell [37].

# 3.5 Monte Carlo Simulations

MC simulations are defined as any computational method used to solve problems through random generators. In other words, MC simulations use stochastic methods to generate new configurations of the system under study. The name referred to the Monte Carlo casinos in Monaco. It was first proposed by John von Neumann, Nicholas Metropolis and Stanislaw Ulam while working at the Los Alamos National Laboratory on nuclear weapon related projects in the 1940s [95].

The MC method involves the following steps: (a) an atom is randomly selected, (b) the type of the atom is changed, (c) the change in energy is then calculated, and the trial move with a probability function is accepted as described in the Metropolis algorithm.

#### 3.5.1 Metropolis Algorithm

The Metropolis algorithm is a sampling scheme first proposed by Metropolis et al. [96]. Metropolis sampling involves accepting a new state by probability rather than using fully defined rules and, as a result, can significantly reduce the number of calculations. This is known as the Metropolis criteria and is explained as follows:

If we assume that the previous state is x(n), the system undergoes a certain disturbance, and the state becomes x(n+1),

Correspondingly, the system energy is changed from E(n) to E(n+1)

$$\begin{cases} 1, E(n+1) < E(n) \\ exp\left(-\frac{E(n+1)-E(n)}{T}\right), E(n+1) \ge E(n) \end{cases}$$
(3.17)

If the final energy is decreased by shifting to a new state, then the transfer is accepted (with probability 1). If the energy increases, then it is not immediately abandoned by the algorithm; instead, a probability judgment is conducted. As Chen [97] stated, first, a uniformly distributed random number  $\varepsilon$  is generated in the interval [0,1]. If  $\varepsilon$ <p (p is the probability of acceptance as defined above), this transition will also be accepted; otherwise, it will refuse to move into the next step. This is the Metropolis algorithm, whose core idea is that it receives a certain probability when the energy increases rather than blindly refusing.

#### 3.6 LAMMPS

LAMMPS is a classical MD simulation code initially developed under the Cooperative Research and Development Agreement (CRADA) at the US Department of Energy (DOE) between two DOE labs and 3 companies. The code is distributed by Sandia National Laboratories [98]. It is a free, open-source code written in C++ and distributed under the terms of the GNU Public License. LAMMPS has the flexibility to be used or modified according to the user's requirements. It is used for materials modelling, including solid-state materials (metals, semiconductors, ceramics, oxides), soft materials (biomolecules, polymers), and coarse-grained or mesoscopic systems. LAMMPS models ensembles of particles in a liquid, solid, or gaseous state. It can model millions and billions of particles in 2D or 3D systems. LAMMPS works efficiently on single-processor desktops or laptops and especially parallel computers. LAMMPS requires a compiler that works with C++ and supports the MPI message-passing library on parallel machines. This includes distributed- or shared-memory parallel machines.

LAMMPS works by integrating Newton's equations of motion for collections of atoms, molecules, or microscopic particles. These atoms, molecules, or particles mutually interact via short- or long-range forces with various initial boundary conditions. For computational efficiency, LAMMPS uses neighbour lists to keep track of nearby particles. The lists are optimized for systems with particles that are repulsive at short distances so that the local density of particles never becomes too large.

LAMMPS uses spatial decomposition techniques on parallel machines to divide the simulation domain into small sub-domains, one of which is assigned to each processor, as shown in Figure 3.7. Processors communicate and store "ghost" atom information for atoms that border their sub-domain; see Figure 3.8.

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Figure 3.7. MPI parallelization approach used by LAMMPS: Domain decomposition where each processor owns a portion of the simulation domain and atoms therein [99]

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Figure 3.8. Ghost atoms in the simulation [99]

Files named input, potential, and executable files are used to run MD simulations on LAMMPS. Input files include the initial atom coordinates, types, and force-field coefficients assigned to all atoms and bonds. LAMMPS provides a create\_atoms command which places atoms on solid-state lattices (fcc, body-center cubic (bcc), user-defined, etc.). The force field coefficients are assigned by pair coeff commands. For complex simulation geometries or molecular systems, a separate code can be written, or another type of software can be used to produce the atom coordinates, and the output can be inputted to LAMMPS by using the read\_in command.

LAMMPS generates output files in a simple format. The data in these output files can be postprocessed using various analysis tools, including visualization packages. A detailed explanation of data analysis and visualization is given in section 3.6.2. The output data from LAMMPS can also be reformatted for input into other programs. Moreover, many properties can be determined using LAMMPS and printed using the dump and compute and fix commands.

# 3.6.1 Running LAMMPS

Two essential items are required to run LAMMPS: the input script and the potential file. The input script contains all the instructions needed to run the program. The potential file includes the interatomic potential parameters of a system that is being simulated. The potential files for the most common systems are available from the Interatomic Potentials Repository Project [100]. Every program needs a unique input script that LAMMPS users write. Its structure is as follows:

- 1. Initialization
- 2. Atoms and lattice definition
- 3. Interatomic potential
- 1. Initialization

First, the units that will be used in the simulation are determined. Then the dimensions of the simulation are defined as 2D or 3D. Then the boundary conditions of the simulation are determined. The relevant commands are units, dimension, processors, boundary, atom\_style, and atom\_modify.

2. Atom definition (Atoms and lattice definition and interatomic potential)

There are different ways to define atoms in LAMMPS. The first is to read them from an external data file or restart the file. This is accomplished by using read\_data or read\_restart commands. The other way is to define the lattice type (fcc, bcc, diamond, etc.). Then a simulation box is defined, and atoms are added to it. The following commands are used to give atoms a proper definition: lattice, region, create\_box, and create\_atoms. In this work, the GB structure is created using an Xtal Crystal Maker- tool and then the data are read into the LAMMPS input script.

3. Settings

This step involves specifying various settings, e.g., the force field coefficients, simulation parameters, output options, etc. The most crucial part of this step is to describe the interaction between atoms by selecting the proper interatomic potential function. The force field coefficients are set by using the pair\_coeff command. The fix commands (fix, fix\_modify) are used to set various boundary conditions, time integration, and diagnostic options. Various computations can be performed during a simulation using the compute, compute\_modify, and variable commands. Output options are set by the thermo, dump, and restart commands.

# **Running simulation**

After creating the input script and specifying the desired settings, the simulation can be carried out using the following command

Lammps-daily<inputscript.in

#### 3.6.2 Data Visualization and Analysis

Data visualization is the visual representation of information and data in the form of graphs, charts, maps, or images. Data visualization tools provide an efficient way to understand the data. Visualization is the art of making sense of a large volume of data generated from simulations. Robust analysis and visualization techniques play a crucial role in understanding the data generated by MD. As OVITO, a powerful "3D visualization software designed for post-

processing atomistic data" [101], puts it, "Without the right software tool, key information would remain undiscovered, inaccessible, and unused" [102].

In this research study, OVITO is used to visualize data through the image (.jpg) creation of atomistic configurations. OVITO is a free visualization software (<u>http://ovito.sourceforge.net/</u>) that runs on all major operating systems, including Microsoft Windows and Linux. This software can display several millions of atoms in geometric shapes or animations, thus, allowing the user to enrich atomic data with additional visual aids. OVITO is a robust tool for examining atomic structures and their evolutions with time. Figure 3.9 shows a screenshot of the application's main window. The main window comprises four viewports, each displaying the atomic structure from different view directions. The panel on the right shows the modification parameters to obtain the desired output according to user needs.

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# Figure 3.9. The main window of ovito [101].

All the images presented in this thesis are generated with OVITO. Moreover, all the graphical work was done using the latest version of Origin software. Origin is a complete graphing and data analysis software package that runs on Microsoft Windows.

# **Chapter 4**

# Molecular Dynamics Simulation of Effect of Solute Segregation on Diffusion Induced Grain Boundary Migration

# Chapter 4: Molecular Dynamic Simulation of the effect of solute segregation on diffusion induced grain boundary migration4.1 Introduction

In this study, MD simulations are used to investigate the physical origin of DIGM with a particular focus on the effects of solute-GB interactions. For this purpose, a few binary alloy systems are deliberately selected, e.g., Al-Ti, Al-Ni, and Ni-Cu, in which strong solute-GB interactions, including both solute segregation and anti-segregation, occur. Ti, Ni and Cu were selected as solutes because Ti exhibits anti-segregation on Al grain boundaries while Ni segregates on Al GBS and Cu segregates on Ni grain boundaries. This study aims to present the effect of solute segregation and anti-segregation on DIGM by utilizing the recently developed simulation methods for studying GB migration. The complete methodology to carry out simulations is presented followed by the potential results and discussion section. To confirm the findings of this study, similar simulations are performed on other systems that underwent segregation and anti-segregation, and the results validate the main findings in this study.

# 4.2 Methods

#### 4.2.1 Molecular Dynamics Simulation

The MD simulations were performed by using LAMMPS [103]. Three binary alloys, i.e., Al-Ti, Al-Ni, and Ni-Cu, were used as the model systems in which strong segregation or anti-segregation occurs. The atomic forces between Al-Ti, Al-Ni, and Ni-Cu were described by the embedded atom-type interatomic (EAM) potentials [104]–[106]. Two different models were constructed to simulate the DIGM with either a solute source or sink, denoted as Type I and Type II DIGM, as shown in Figure 4.1. In both models (Type I and Type II), the main component is a bicrystal with symmetric  $\sum 5$  (0 3 1) GB, except in the Ti bicrystal where  $\sum 37$  (610) GB is constructed. To simulate Type I DIGM, thin plates of Ti and Ni were placed on both sides of an Al bicrystal, which served as the solute sources. To simulate Type II DIGM, in contrast, impurity (Ti and Ni) atoms

were added by randomly replacing Al atoms only in one grain at concentrations varying between 0.5-5 at. % before the simulations. Based on the phase diagrams [107], the three alloy systems that were explored all show a single-phase solid solution structure within the temperature (850-1500 K, depending on the alloy system) and concentration (e.g., up to 5% solute) ranges, i.e., the solute atoms are randomly distributed in the alloy system. Therefore, as a reasonable approximation, all initial structures were created by randomly replacing the solvent atoms with solutes at the desired concentration. Figure 4.1(a) shows that the simulation cell is  $28.6 \times 6.1 \times 22.3$  nm in the x, y, and z directions and consists of 210843 atoms. The cell used to study type II DIGM was  $25.95 \times 2.05$  $\times$  21.11 nm in x, y, and z directions (Figure 4.1 (b)) with 64,000 atoms. In this study, the main GB model is a <100>-symmetrically tilted GB ( $\sum 5$  (0 3 1)) with its tilt axis (<100>) along the ydirection. The migration mechanism of the main GB model does not depend on the size of the model along the y-direction. The lattice orientations in Grains 1 and 2 were along x:  $[01\overline{3}]$ , y:  $[\overline{1}00]$ , z: [031] and x:  $[0\overline{1}3]$ , y: [100], z: [031], respectively, for all models. While in the Ti model the, grain 1 and grain 2 were oriented in x: [610], y:  $[00\overline{1}]$ , z:  $[\overline{1}60]$  and x: [610], y: [001], z:  $[1\overline{6}0]$  respectively, in the Ti model. Periodic boundary conditions were applied along the x and y directions while the two surfaces perpendicular to the z-axis were free for both models. The system temperatures for the various systems based on Al, Cu, Ni, and Ti were kept at 850K, 1000K, 1200K, and 1500K, respectively, based on their melting points so that significant GB fluctuation and migration due to interface random walk can be observed. Each model was relaxed at the desired temperature and zero hydrostatic pressure with the isothermal-isobaric ensemble (NPT) during the first 500 ps. As a reference, the interface random walk method proposed by Trautt et al. [37] was also used to investigate the GB migration under zero driving force limit based on purely thermal fluctuations of the GB in Al when no impurities existed. To carry out the quantitative

analysis, 10 independent simulations up to 4 ns with identical geometry but different random velocity initializations were performed. Atomic configurations of each alloy system were visualized by using OVITO [101]. The GB position was determined based on an order parameter that depends on the local lattice orientation [42], [43], [108]. To calculate the driving forces in Type II DIGM, the SDF method developed by Janssens et al. [38] was also used to drive the GB migration in a specific direction. Note that the goal of this work is not to establish a steady-state DIGM process as done so in experiments. The limitations of the models in this study are noted, which were mainly caused by the intrinsic limitations of the short time scale of MD simulations. Therefore, the focus is only on the initiation of the DIGM or the driving force that makes DIGM possible.





### 4.2.2 Hybrid Molecular Dynamics and Monte Carlo Simulations

A new hybrid method that combines MD and MC simulations was used to capture anti-segregation and segregation behaviours in the Al-Ti and Al-Ni systems [109]. This method involves MC swaps of atoms of

one given type with the other based on the Metropolis acceptance criterion. Each swap was performed after every 5000 MD step relaxation at a temperature of 300K for each binary system. To observe each system's segregation or anti-segregation behaviour, the solute atoms were initially placed in either the GB region, as shown by the schematic in Figure 4.1(c) or randomly across the entire model, as shown in Figure 4.1(d).

# 4.3 Results

# 4.3.1 Anti-segregation and segregation tendencies in Al-Ti and Al-Ni

Figure 4.2 shows the strong anti-segregation of Ti and segregation of Ni on the Al GB. For clarity, all Al atoms are removed in the atomistic configurations. In Figure 4.2 (a), the Ti atoms are initially placed around the Al GB. After performing 140,000 MC atom swaps, the Ti atoms moved away from the GB region, indicating strong anti-segregation, as shown in Figure 4.2(b). On the other hand, the initially randomly placed Ni atoms became enriched in the GB area, indicating strong segregation of Ni in the Al GB, as shown in Figures 4.2(c) and 4.2(d).



Figure 4.2. Anti-segregating and segregating behaviour in Al-Ti and Al-Ni systems

## 4.3.2 Type I DIGM with the presence of a solute source

A series of MD simulations were first performed at 850 K based on the Al bicrystal model with Ti as a source, as shown in Figures 4.3(a) to 4.3(c). In this model, the Ti source (red atoms) is placed in contact with the Al bicrystal (green atoms) (Figure 4.3(a)). After 1.8 ns (Figure 4.3(b)), the two ends of the GB moved up first compared to the central part, resulting in a curved GB. At t = 4 ns, the GB moves further, and the center catches up with the ends so that the entire GB is flat again (Figure 4.3(c)). During this process, the solute atoms (Ti, denoted by red dots in Figures 4.3(a) to 4.3(c)) remained in the Al bicrystal, which suggests strong anti-segregation behaviour as observed in Figures 4.2(a) and 4.2(b). It is important to note that the GB migration process shown in Figures 4.3(a) to 4.3(c) is dramatically different from the interface random walk that is mainly caused by thermal fluctuations. For the latter, there is no sequential movement between the ends and the GB centre as observed in Figures 4.3(a) to 4.3(c). More discussion regarding the difference between a purely interface random walk and Type I DIGM as found in Al-Ti can be found in Section 4.3.4.

In contrast, Figures 4.3(d) to 4.3(f) show the results where the solute source was replaced by Ni. Although significant diffusion of the solute (Ni, as represented by red dots) atoms into the Al GB also occurs, the overall migration of the GB is negligible after 4 ns. It is also observed that at t = 4 ns, the solute atoms of Ni mainly stayed in the GB region (Figure 4.3(f)), which implies strong segregation of Ni in the Al GB as found in Figure 4.2(c) to 4.2(d). Nevertheless, Figure 4.3 shows that, even within the short MD timescale, it is possible to simulate a type I DIGM when a solute source is present, although significant DIGM is observed only in Al-Ti where strong antisegregation has occurred.



Figure 4.3. Type1 DIGM in Al bicrystal with Ti (a-c) and Ni (d-f) sources.

# 4.3.3 Type II DIGM with the presence of a solute sink

From the results of Type I DIGM, it can be inferred that the solute interactions with GB play an important role in driving GB migration. To simulate DIGM where de-alloying occurs, as shown in Figure 1.1(b) (Type II DIGM), only one grain was initially doped, and the GB was initially depleted of any solute atoms (Figure 4.1(b)). This setup simulates the condition when the solute atoms in the GB have all moved out due to fast diffusion as if a solute sink exists. As shown in Figure 4.4, in the case of the anti-segregating system (i.e., Ti in Al), the GB moves away from solute atoms (upwards). In contrast, in the segregating system (i.e., Ni in Al), the GB moved toward solute atoms (downwards), during which the GB becomes enriched with solute atoms. The results indicate that when either a high degree of segregation or anti-segregation exists, the GB could move due to strong solute-GB interaction, which is an attraction for the former but repulsion for the latter. However, only the case with segregation (e.g., Ni in Al as shown in Figure 4.4(d)) would create a de-alloyed zone as found in experimentally studied DIGMs when a solute sink is present.



Figure 4.4. Type II DIGM in Al bicrystal with Ti (a, b) Ni (c, d) as solute atoms in Grain 1.

# 4.3.4 Comparison between DIGM and interface random walk

The results above are intended to serve as qualitative proof that it is possible to simulate DIGM via atomistic simulations. However, since relatively high temperatures were used during the simulations, it is essential to exclude the possibility that the GB migration found in Figures 4.3 and 4.4 are just interface random walks due to thermal fluctuations. For this purpose, Figure 4.5(a) plots the GB displacement curves in the pure Al bicrystal obtained from 10 random simulations. The curves represent typical random walk behaviour due to purely thermal fluctuations, which will serve as a reference for analyzing the GB migration behaviours found in both the Al-Ti and Al-Ni systems. Figures 4.5(b) and 4.5(c) plot the GB displacement among the 10 independent simulations for Type I DIGM, where Ti and Ni are the solute sources. First, significant GB migration is observed in the Al-Ti system (Figure 4.5(b), where Ti is present as a solute source.

In contrast, only negligible GB migration is observed in the Al-Ni system (Figure 4.5(c)), where Ni is present as a solute source. Furthermore, it is important to note that, in comparison with the interface random walk behaviour shown in Figure 4.5(a), the GB migration shown in Figure 4.5(b) is significantly faster and, more importantly, at a more or less constant velocity either upwards or downwards in all of the simulations. This suggests that unlike interface random walk due to purely thermal fluctuations, the GB migration is shown in Figure 4.5(b) is driven by forces significantly larger, i.e., the strong solute-GB interactions due to anti-segregation of Ti in Al bicrystal. Figure 4.5(b) thus confirms that the GB migration observed in the Al-Ti system, as shown in Figures 4.3(a) to 4.3(c), was indeed caused by diffusion. Although the original migration direction was random, e.g., the GBs that moved upwards and downwards are about half-half, as shown in Figure 4.5(b), and the GB migration continues in the same direction once started, which is in agreement with experimentally studied DIGM [3], [8], [22], [110]. On the other hand, the negligible GB migration found in the Al-Ni system could be caused by the severe solute drag [79] and the short MD time scale.



Figure 4.5. GB Displacement curves vs time in (a) Pure Al, Type I DIGM in (b) Al-Ti, (c) Al-Ni and Type II DIGM in (d) Al-Ti and (e) Al-Ni systems.

Moreover, in Type II DIGM models, both the Al-Ti and Al-Ni systems showed significant GB migration in directions that are consistent among all the 10 simulations, although there are variations in the migration velocity as shown in Figures 4.5(d) and 4.5(e). While those results are consistent with the findings shown in Figure 4.4, they are in stark contrast to the purely interface random walk where the average GB displacement among the 10 independent simulations is close to zero at any time, as shown in Figure 4.5(a). This thus confirms that driving forces that are different from thermal fluctuation have caused the GB migration based on the Type II DIGM models as presented in Figure 4.4 for both the Al-Ti and Al-Ni systems. Here the solute-GB interactions were proposed to be the main contribution to initiate such directional GB migration, which was a repulsion/attraction for Al-Ti/Al-Ni systems, respectively. Such interactions were also found to be long-range, e.g., without the need for the GB and solute atoms to be in close contact. As shown in Figure 4.6, when the solute atoms (Ni) are initially placed 3 and 10 Å away from the GB region, the GB still migrates in the same direction, as shown in Figure 4.5(e).



Figure 4.6. GB displacement when solute atoms are kept 3Å and 10Å away from the boundary. 4.3.5 Quantification of the driving force for GB migration

The previous results showed that the direction of GB migration due to a solute source or sink depends on the anti-segregation or segregation behaviour of the solute atoms. Specifically, in anti-segregating systems, the GB moves due to repulsive interactions between the solute and GB. On

the other hand, the GB moves in the opposite direction due to the strong attraction between the solute atoms and GB in segregating systems. To validate this observation and quantify this effect, the solute concentrations (e.g., 0.5 - 5 at.% of Ti and Ni in Al-bicrystal) were varied based on the Type-II model, as shown in Figure 4.4. The results in Figure 4.7 show that the degree of GB migration (either in the positive or negative direction) increases with increasing concentration of both the anti-segregating (Ti in Al, see Figure 4.7(a)) and segregating solute atoms (Ni in Al, Figure 4.7(b)). Also emphasized here is that the focus is only on the initiation of the DIGM, or the driving force that makes DIGM possible. In fact, the "initiation" of DIGM has caused many debates in the literature, and all the mechanisms that have been mentioned/reviewed in this thesis, e.g., the coherent strain theory, the free energy of mixing, etc., all focused on this aspect. Therefore, while the displacement vs. time curves have been included for the entire process of the simulation (e.g., those shown in Figure 4.7(a)), in this study, it is the very early stage that is the focus here.

Furthermore, it can be observed that the time-displacement curve is nonlinear, increasing suddenly in the first 0.5 ns and levelling off later, which was observed for all Type-II models. For the antisegregation case (e.g., Al-Ti as in Figure 4.5(d)), the driving force decreases since the solute distribution remains unchanged while the GB-solute distances increase as the GB moves away from the solute atoms. Based on v=MP, the GB velocity (v) should gradually decrease since the GB mobility (M) should be the same as that of pure GB while the driving force (P) decreases. For the segregation case (e.g., Al-Ni as in Figure 4.5(e)), the GB picks up more solute atoms from the grains, which leads to severe solute drag effect on the GB migration. Based on v=MP, M significantly decreases as the solute concentration (and the solute drag) increases in the GB as GB migrates, while P does not change, which causes a sharp decrease in v accordingly.



Figure 4.7. Effect of solute concentration on GB displacement in (a) Al-Ti and (b) Al-Ni system. Two separate methods were used to quantify the driving force due to anti-segregation or segregation. For the anti-segregating system (Al-Ti), a simple method was adopted since the GB remained clean during the migration process. This method is based on the proportionality between the driving force and the GB migration velocity as v = MP. The v at different Ti at. % was extracted by linear fitting the GB displacement with time curves as represented in Figure 4.7(a)(see Figure 4.8 (b)). Only the initial data points when the GB displacement was less than 1 nm were used for the linear fitting since, after that, significant slowing down was observed, as explained earlier. To extract M, a clean Al bicrystal with the same geometry as that used for the Al-Ti model was driven to move at 850 K by applying different SDFs, see Figure 4.8(a). Then the mobility was calculated from the slope of this curve. Based on this mobility and the velocities of the GB in the Al-Ti system under various solute concentrations, as plotted in Figure 4.8(b), the driving forces were calculated in accordance with these concentrations of solute atoms as shown in Figure 4.8(c). Overall, the driving force is linearly increased with increasing concentration of solute atoms up to 5 at.% of Ti.



Figure 4.8. (a) GB velocity of clean Al GB corresponding to applied synthetic driving forces. (b) GB velocity corresponds to varying concentrations of Ti atoms. (c) Driving force obtained as a function of solute concentration.

On the other hand, a relatively more complicated method was adopted to calculate the driving force for the segregating system (Al-Ni), as shown in Figure 4.7(b), since the GB continued to pick up solute atoms during its migration. In order to accurately measure the driving force with the commencement of the GB movement, an SDF was systematically varied and added into the same set of Al bicrystal models in such a way that it acted against the GB migration due to DIGM, as shown in Figure 4.9(a). The intention was to facilitate the GB to retrace its movement, thereby shifting in the opposite direction once the SDF balanced that due to DIGM. Figure 4.9(a) shows this strategy where a GB, which initially moves in the downward direction due to DIGM, can be made to shift in the opposite direction by applying an SDF of 0.002 eV/atom. The corresponding v was measured and is plotted in Figure 4.9(b). The maximum negative velocity represents the GBs that moved purely due to DIGM when no SDF was applied. As the SDF was applied and increased further, the GB velocities gradually crossed the 0 mark and thereby attained positive values. The point where v crosses the 0 mark indicates the driving force needed to balance that induced by DIGM, which is shown with dotted circles for each model containing different concentrations of Ni atoms. The "critical" driving forces that correspond to 0 GB velocities are plotted against the concentration of Ni atoms, as shown in Figure 4.9(c). It can be seen that the

driving force due to solute-GB attraction also monotonically increases with increasing concentrations of solute atoms (see Figure 4.8(c)) due to solute-GB repulsion, although Figure 4.8(c) shows a linear dependence that is not found in Figure 4.9(c).



Figure 4.9. (a) GB displacement vs. time with and without SDF. The inset shows the schematic of the SDF method, (b) variation of GB velocity vs SDF, (c) the driving force vs concentration of solute (Ni) atoms determined by the SDF method (black dots). The solid lines in (b) and (c) are added as guides to the eyes only.

# 4.4 Discussion

The following discussion on the influence of solute-GB interactions on DIGM is based on MD simulation results in this study. The key finding is that the diffusion of solute atoms into or out of a GB due to the presence of a solute source or sink disrupts the thermodynamic equilibrium distribution of solute atoms between the GB and lattice (grain interior) in an alloy. For example, at equilibrium, the concentration of solutes at the GB,  $C_{GB}$ , and in bulk,  $C_0$ , can be described with the following equation for a given alloy [111]:

$$\frac{C_{GB}}{1-C_{GB}} = \frac{C_0}{1-C_0} \exp\left[\frac{-\Delta E^{seg}}{kT}\right]$$
(4.1)

where k is a Boltzmann's constant, T is the temperature and  $\Delta E^{seg}$  is the GB segregation energy. When diffusion occurs preferentially along the GB plane due to the presence of a solute source or sink, equilibrium will be disrupted. To re-establish equilibrium, the solute atoms tend to move away (anti-segregation) or towards (segregation) the GB so that the overall energy in the alloy can be reduced, which results in repulsion or attraction between the GB and solute atoms, respectively; both can contribute to DIGM. As such, all of the DIGM processes that have been studied in this work can be summarized in the schematics in Figure 4.10. For the Type 1 Al-Ti system, the Ti atoms first diffuse into the GB through the ends. Before the Ti atoms can uniformly diffuse along the Al GB plane, the GB moves away from the Ti atoms due to the substantial effects of the antisegregation of Ti in Al GBs. Figure 4.10(a) shows that in Stage 2 of migration, the ends of the GB move earlier than its centre, which forces the GB to curve. Then the GB moves further due to the curvature and flattens again, as shown in stage 3 of Figure 4.10(a), probably due to the small size of the simulation cell and, accordingly, large curvature and surface tension. Curvature-induced GB migration has been well-studied in previous works. For example, Upmanyu et al. [112] examined the dependence of GB migration rate on GB curvature. The results in this study confirm that the vis proportional to the curvature as per the following relation:

$$\upsilon = M\gamma\kappa \tag{4.2}$$

where v and M are the GB velocity and mobility, respectively,  $\gamma$  is the GB energy per unit area, and  $\kappa$  is the mean curvature of the GB. The changes in curvature should affect the average v of GB, although this influence is not clearly reflected by the time-displacement curve for this particular GB, e.g., Figure 4.5(b), which only shows the average GB displacement of the curved GB (see Figure 4.3(b)) during the entire process. In theory, the curvature first develops during the early stage of the GB migration, which creates a force against (in the negative direction to the overall GB migration) the migration of the two ends. Later on, the curved GB will pose a driving force in the positive direction which forces the centre (the curved GB) to flatten. Nevertheless, the non-uniform GB migration and the corresponding mechanisms, as shown in Figure 4.10(a), could shed some light on explaining the experimentally observed curved GBs due to DIGM. In the Al-Ni system in Figure 4.10(b), the degree of GB displacement is negligible because a large solute drag effect pins the GB movement. Given adequate time as under experimental conditions, the solute atoms should be able to diffuse along the GB plane. Eventually, the GB can overcome the solute drag effects and move when the solute concentration in the GB is significantly higher than its segregation limit. However, it is impossible to capture such a process within the MD time scale.



Figure 4.10. Schematics showing (a) the Type I DIGM in anti-segregating alloy system and (b) segregating alloy system, and (c) type II DIGM for both segregating and anti-segregating systems.

Figure 4.10(c) shows a schematic of Type II DIGM models due to solute GB interactions. It can be seen from the schematic in Figure 4.10(c2) that when Ti atoms are present as solutes, they impose repulsive force on GB and intend to move it away. The origin of these repulsive interactions is the anti-segregating behaviour of Ti atoms in Al GBs. On the other hand, the Ni atoms (Figure 4.10(c3)) exert an attractive force on the GB to facilitate the movement of GB towards them. Again, these forces arise due to segregating behaviour of the Ni atoms. These results are confirmed by choosing different systems that exhibit anti-segregation and segregation. Figures 4.11 and 4.12 show the Ti and Ni bicrystal models with Al as a solute. Both of these systems undergo anti-segregation (Figures 4.11(a) and 4.11(b) and Figure 4.12(a) and 4.12(b)) and therefore exhibit Type I and Type II DIGM, which is similar to that shown in Figure 4.10.

Similarly, a Ni-Cu system is examined where Cu tends to segregate into the Ni GBs (Figures 4.13(a) and 4.13(b)). This system exhibits the Type I and Type II DIGM in the same way as found in the Al-Ni system (Figures 4.13(c) and 4.13(d), and Figure 4.13(e) and 4.13 (f), respectively). Though the study was conducted using FCC-based alloys, the same atomic mechanisms would be valid for BCC and HCP alloys. To prove this observation, a similar study was conducted on Ti bicrystal with an HCP crystal structure and containing a different type of GB, i.e.  $\Sigma7$  (6 1 0) (Figure 4.11). Al is used as a source. This system shows Type I and Type II DIGM as shown by FCC-based alloys.



Figure 4.11. (a, b) Anti-Segregation of Al in Ti GB, (c, d) Type I DIGM in Ti bicrystal with Al as a source, (e, f) Type II DIGM in Ti bicrystal with 5 at. % Al atoms as solutes.


Figure 4.12. (a, b) Anti-Segregation of Al in Ni GB, (c, d) Type I DIGM in Ni bicrystal with Al as a source, (e, f) Type II DIGM in Ni bicrystal with 5 at. % Al atoms as solutes.



Figure 4.13. (a, b) Segregation of Cu in Ni GB, (c, d) Type I DIGM in Ni bicrystal with Cu as a source, (e, f) Type II DIGM in Ni bicrystal with 5 at. % Cu atoms as solutes.

Note that similar to GBs, the free surfaces in all of the models in this study can also serve as segregation (or anti-segregation) sites for solute atoms, which suggest possible interactions (attraction or repulsion) between the solutes and free surfaces. Such interactions, however, should not influence how the GB migrates. Moreover, due to the intrinsic limitations on the timescale of the MD simulations, the solute diffusion has not been explicitly considered, especially in our type-II models here. In general, the solute diffusion in the lattice should be orders of magnitude slower than that in the GB. Deng and Schuh [42] also indicated that the GB diffusion and migration share similar activation energies. In this work, solute diffusivity has not been quantified in either the

lattice or the GB, but it is expected that at the high temperature used, the GB migration process is still more rapid than the lattice diffusion process through a vacancy mechanism. The relatively small size of the atomistic model means that only one or two vacancies would cause the entire system to exceed its equilibrium concentration, which makes it challenging to explicitly implement a vacancy-mediated diffusion process in atomistic simulations. Therefore, as a common practice in MD simulations, the possible lattice diffusion has not been taken into consideration here.

Finally, note that the possible contribution of other origins that may have contributed to DIGM, such as coherent strain and dislocation climb, has not been considered here. For example, within the short MD timescale, it is not possible to explore the atomistic process and possible influence of dislocation climb on DIGM. On the other hand, new methods or models may be needed to decouple the possible effect of coherent strain and solute-GB interactions due to possible segregation or anti-segregation. For example, for the Al-Ti and Al-Ni systems of interest here, the solute-GB interactions are so strong that the possible contribution of coherent strain would be hard to evaluate. The ideal systems for explicitly investigating the influence of coherent strain on DIGM would be alloys where the segregation energy is ~ zero. Yet, there exists a large mismatch between the sizes of solute and solvent atoms. Artificial alloy systems described by the LJ potential [113] where the interaction energy and atom size can be tuned separately might be suitable for this purpose, which is currently being explored as a sequel to this study. Nevertheless, the relatively small atom size mismatch between the Ti and Al atoms (and Ni and Cu as well) [114] unambiguously confirms the possible influence of solute-GB interactions on DIGM, which is the primary purpose of this study.

#### 4.5 Conclusions

In summary, the effect of solute-GB interactions (anti-segregation and segregation) on DIGM by using atomistic simulations based on a few binary model systems has been explored in this study. The following main conclusions are made based on the simulation results:

- Although systems with solute anti-segregation have been rarely considered in the previous studies on DIGM through either experimental or theoretical methods, this study predicts that systems undergoing a high degree of segregation or anti-segregation can exhibit DIGM due to the solute-GB interactions. The migration direction is directly correlated with the type of solute-GB interaction, which is attraction or repulsion for systems that show a high degree of segregation or anti-segregation or anti-segregation.
- The findings based on the MD simulations in this study are consistent with those of previous experimental observations that the DIGM could be initiated in a random direction due to thermal fluctuation, but once started, the GB would migrate in the same direction after that.
- When a solute with a high degree of anti-segregation is present, the GB will follow a sequential migration process between its ends and centre, which results in a curved geometry during its migration. This phenomenon and its corresponding mechanism could offer additional insight into the experimentally observed curved GBs due to DIGM.
- By quantifying the driving forces with various solute concentrations, it is found that the driving force required for DIGM is monotonically increased with solute concentration when the solute shows either a high degree of segregation or anti-segregation to the GB plane. This is also consistent with previous reports based on analytical models that DIGM cannot exist in systems with no solute segregation, e.g., a system with an isotopic solute.

It is anticipated that this study can serve as a proof of concept for studying DIGM via atomistic simulations, complementing existing experimental and theoretical studies on this topic. Furthermore, this study might inspire new experimental designs on DIGM, e.g., based on alloy systems where a high degree of anti-segregation occurs.

# **Chapter 5**

# Atomistic simulation of grain boundary migration induced by non-equilibrium solute distribution

# Chapter 5: Atomistic simulation of grain boundary migration induced by non-equilibrium solute distribution

#### 5.1 Introduction

The results in Chapter 4 indicated that solute-GB interactions play a vital role in the driving forces for DIGM. It has also been widely reported that the diffusion of solute atoms into or out of a GB can provide the essential driving force for the GB to migrate, i.e., DIGM [1]-[3]. While there is still debate regarding the physical origin of DIGM, it is generally accepted that once initiated, DIGM will be sustained in one direction such that the solute atoms are accumulated or depleted on one side of the GB, thus resulting in an enlarged alloyed or de-alloyed zone as the GB migrates [1]. Diffusion-induced grain boundary migration has been reported in about a hundred binary and multicomponent systems in various materials such as metals, semiconductors, ceramics, and oxides [1], [30]. Hillert et al. [115] present experimental evidence showing that grain boundary motion can be induced in Fe-Zn alloys by changing the composition through grain boundary diffusion. Cahn et al. [110] documented the non-equilibrium distribution of solute atoms caused by diffusion in various diffusion couples such as Cu-Zn, Cu-Au and Ag-Au. Therefore, in this study, the non-equilibrium distribution of solute atoms across the GB (e.g., with one grain being more enriched with solute atoms than the others) is hypothesized to contribute to important driving forces for the GB migration during a typical DIGM. Based on this hypothesis, it is also proposed that the unbalanced free energy between two grains due to non-equilibrium solute distribution can be used as a new physical driving force for investigating GB migration in general in atomistic simulations. This is in contrast to the popular SDF method [38] for studying GB migration in atomistic simulations, which is based on selectively adding so-called artificial energy to one of the two grains across the GB plane. While atomistic methods for investigating GB migration based on physical driving forces have been previously proposed, they all have severe limitations. For example, the method based on curvature can only be used to study curved GBs [112], [116].

Additionally, while the method based on an elastic strain can only be applied to study planar GBs, it is limited to non-symmetrical GBs [117]. Therefore, to date, atomistic methods for studying GB migration based on physical driving forces that can be applied to general GBs are still elusive. Moreover, the study highlights that it is possible to tune both the type (e.g., attraction or repulsion)

and the magnitude of the driving force. Furthermore, the atomic size mismatch and cohesive energy effects can be decoupled by modelling the solute-solvent interactions with an LJ potential. Results show that the popular physical mechanism regarding DIGM based on coherent strain is not the only possible physical origin of DIGM.

This study seeks an understanding of the role of different solute types on DIGM, which is challenging to do experimentally. In particular, both the direction and magnitude of the driving force for GB migration can be systematically tuned by varying the solute atoms' atomic size, cohesive energy, and concentration.

It is anticipated that while this study proposes a new atomistic method for simulating GB migration, the results also contribute to a better understanding of the phenomenon of DIGM, for which precise physical mechanisms remain elusive after decades of research.

### 5.2 Methods



Figure 5.1. (a) Schematic of the model used in this study. (b) An Al-bicrystals model with only one grain doped with solute atoms (Al atoms-Coloured green, Solutes-coloured red). (c) The initial random distribution of solute atoms in an Al bicrystal and (d) the distribution of solute atoms after 140,000 Monte Carlo swaps in e same system. The Al atoms in (c) and (d) have been removed for clarity.

To prove the concept that physical GB migration can be induced in atomistic simulations through a non-equilibrium solute distribution, a bicrystal model of Al that contains a symmetric  $\Sigma 5$  (310) GB was constructed and systematically investigated to determine how the GB migrates by using

MD simulations when solute atoms of different atomic radii, cohesive energies, and concentrations are purposely added to only one grain of the bicrystal. A schematic is shown in Figure 5.1(a).

All simulations were conducted by using LAMMPS [103] with a pairwise LJ potential [86] so that the properties of the solute atoms (e.g., the atomic size and cohesive energy) can be varied with comparable ease:

$$U(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$
(5.1)

where  $\sigma$  and  $\varepsilon$  are the LJ-parameters that represent the atomic size and cohesive energy, respectively, and  $r_{ij}$  is the interatomic distance. For Al,  $\sigma$  and  $\varepsilon$  are set to 2.5 (Å) and 0.5072 (eV) [118], respectively. With solute atoms, a total of six LJ-parameters are needed, namely: $\sigma_{\alpha\alpha}$ ,  $\sigma_{\beta\beta}$ ,  $\sigma_{\alpha\beta}$ ,  $\varepsilon_{\alpha\alpha}$ ,  $\varepsilon_{\beta\beta}$ , and  $\varepsilon_{\alpha\beta}$  where the subscripts  $\alpha$  and  $\beta$  refer to the atom type ( $\alpha$ : Al, and  $\beta$ : solute atom). The interactions between the solute and solvent atoms are determined by using the following rules:

$$\sigma_{\alpha\beta} = \frac{\sigma_{\alpha\alpha} + \sigma_{\beta\beta}}{2}$$
 and  $\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}$  (5.2)

where  $\sigma_{\alpha\beta}$  and  $\varepsilon_{\alpha\beta}$  are the arithmetic and geometric averages of the two parameters, respectively.

The present study required to gradually vary the atomic diameter and bond energies (sigma & epsilon) of the solute atoms. In other words, it was desired to conduct a general study that was not material specific. This was easiest with an LJ potential.

Table 5.1 summarizes the different LJ parameters used in this study.

| Table 5.1 | L Various LJ | parameters |
|-----------|--------------|------------|
|-----------|--------------|------------|

| Atomic type           | $\sigma_{\beta\beta}$ | ε <sub>ββ</sub> | $\sigma_{lphaeta}$ | ε <sub>αβ</sub> |
|-----------------------|-----------------------|-----------------|--------------------|-----------------|
| Varying $\sigma$      | 2.2                   | 0.5             | 2.35               | 0.5             |
|                       | 2.3                   | 0.5             | 2.40               | 0.5             |
|                       | 2.4                   | 0.5             | 2.45               | 0.5             |
|                       | 2.5                   | 0.5             | 2.50               | 0.5             |
|                       | 2.5                   | 0.5             | 2.50               | 0.5             |
|                       | 2.6                   | 0.5             | 2.55               | 0.5             |
|                       | 2.7                   | 0.5             | 2.60               | 0.5             |
|                       | 2.8                   | 0.5             | 2.65               | 0.5             |
| Varying $\varepsilon$ | 2.5                   | 0.25            | 2.5                | 0.35            |
|                       | 2.5                   | 0.42            | 2.5                | 0.46            |
|                       | 2.5                   | 0.64            | 2.5                | 0.56            |
|                       | 2.5                   | 1.05            | 2.5                | 0.72            |
|                       | 2.5                   | 2.0             | 2.5                | 1.00            |

The effects from  $\sigma$  and  $\varepsilon$  of the solute atoms were decoupled by keeping one of the parameters constant while varying the other. Each simulation consisted of 800,000 time steps with a time step size equal to 5 fs which represents a total time of 4 ns. The x, y, and z dimensions of the simulation cell are  $25.3 \times 2.0 \times 20.4$  nm, which contain ~ 63800 atoms. The boundaries were kept periodic in all three directions. Solute atoms were added to Grain 1 of the bicrystal by randomly replacing a certain percentage (e.g., 1- 5%) of the host atoms; an example is shown in Figure 5.1(b). All simulations were performed at a temperature of  $0.30\varepsilon/k_B$ . Relaxation was performed in each model for the first 500 ps using the isothermal-isobaric ensemble (NPT). To minimize the influences from possible thermal fluctuations, 5 separate simulations with different random velocity initializations were performed for each model, and the results were based on the average among the 5 simulations. OVITO was used for the visualization [101], and the GB position was tracked based on the changes in the local lattice order parameters in the bicrystal as used in [35] and [108].

The MC approach was used to randomly swap the solute and solvent atoms based on the Metropolis acceptance criterion to estimate the segregation capacity of the GB. A maximum of

800,000 MC swaps was performed for each type of solute atom. To investigate the segregation in the bicrystal system, the solute atoms were initially added to the entire bicrystal model with a global concentration of 1 at. % in a random manner. Figure 5.1(c) shows one example of the initial model with solute atoms with  $\sigma_{\beta\beta} = 2.8$  and  $\varepsilon_{\beta\beta} = 0.5072$ . The solute atoms are coloured blue, and the Al atoms are removed for clarity. The solute atoms are enriched towards the GB region after conducting 140,000 MC atom swaps, thus indicating a large degree of solute segregation, as depicted in Figure 5.1(d). Since periodic boundary conditions are used, there is also segregation at the top, and bottom edges of the bicrystal, as shown in Figure 5.1(d), but those regions are cropped to show only segregation at the central GB. To obtain the solute concentration profile, the bicrystal was divided into 20 bins of equal thickness. Then the concentration of solute atoms was evaluated for each bin and plotted.

## 5.3 Results and Discussion

#### 5.3.1 Effects of atomic size mismatch

The influence of atomic strain caused by the atomic mismatch between the solute and the solvent/host atoms was first investigated. In Figures 5.2(a) and 5.2(b),  $\sigma_{\beta\beta}$  is varied between 2.2 and 2.8 while  $\varepsilon_{\beta\beta}$  is fixed at the same value as  $\sigma_{\alpha\alpha}$ (i.e., 0.5). This represents the case where the solute atoms have the same cohesive energy as Al but different atomic sizes. Figures 5.2(a) and 5.2(b) show the GB displacement of the migrating GB by varying the atomic size  $\sigma$  of the solute atoms from 2.2 to 2.5 (Figure 5.2(a), i.e. when the solute atoms are smaller than the Al atoms with  $\sigma_{\alpha\alpha} = 2.5$ ) and from 2.5 to 2.8 (Figure 5.2(b), i.e., when the solute atom is larger than Al). Figures 5.2(a) and 5.2(b) clearly show that when the atomic size of the solute atoms is varied in either the positive or negative direction, the displacement of GB increases, and the migration of GB is in the same direction toward Grain 1. This migration of the GB can be explained by the unbalanced strain energy between the two grains such that the GB migrates to minimize the overall strain energy.

This observation is consistent with previous studies where GB migration was induced by applying an elastic strain [119], [120], which nevertheless can only be applied to asymmetric GBs.



Figure 5.2. (a, b) GB displacement vs time curves. The LJ parameter  $\sigma_{\beta\beta}$  is varied, (c,d) Concentration of solutes in different regions of bicrystal showing solute enrichment at GB (segregation).

The energy that arises as a result of the elastic stress field encircling the solute atoms can be reduced by shrinking the grain with doped solute atoms (e.g., Grain 1, as shown in Figures 5.1(a) and 5.1(b)) and segregating the solute atoms into the GB. Reducing the elastic energy causes the GB to move, thereby picking up the solute atoms as the GB moves. The stress field around the solute atoms, and therefore, the elastic strain energy, should be zero when the solvent and solute atoms are identical in size and increase when the difference in atomic radius between the solute atoms increases. These analyses are supported by the MC simulation results that the

GB shows a high degree of segregation (indicated by the peak at the GB region) of the solute atoms, which increases as the atomic mismatch (either positive or negative) increases, as shown in Figures 5.2(c) and 5.2(d).

#### 5.3.2 Effects of cohesive energy



Figure 5.3. (a) GB Displacement vs time. Concentration of solutes in different regions of bicrystal showing (b) solute enrichment (segregation) and (c) solute depletion in the GB region (anti-segregation).

In Figure 5.3, the size of the solute atoms is fixed, while the cohesive energy  $\varepsilon_{\beta\beta}$  is varied between 0.25 and 2.0 (Table 5.1), with 0.5072 being that for the solvent Al atoms. This implies changing the cohesive energy of the solute relative to the Al host atoms without introducing atomic strain. It appears that this cohesive energy (i.e.,  $\varepsilon_{\beta\beta}$ ) alters the direction of GB migration. When  $\varepsilon_{\beta\beta}$  is less (or greater) than 0.5, the GB moves in the downward (or upward) direction, as shown in Figure 5.3(a).

It is interesting to note that when  $\varepsilon_{\beta\beta}$  is lower than 0.5 (e.g., 0.25 and 0.42), the GB and solutes have attractive interactions, as shown by the segregation peak in Figure 5.3(b). However, when  $\varepsilon_{\beta\beta}$  is higher than 0.5 (e.g., 1.05 and 2.0), the solutes repel the GB, which is confirmed by a dip in the segregation curve (Figure 5.3(c)).

These results support the study conducted by Machlin and Levy [121] on GBs with impurities for a model f.c.c. System. They investigated the effect of the difference in atomic diameter and cohesive energies between the host and solute upon the segregation energy. They concluded that segregation is favoured when there is a difference in the atomic diameter of the solute and host and/or when the cohesive energy of the solute is lower than that of the host.



#### 5.3.3 Effects of solute concentration

Figure 5.4. Effects of solute concentration on GB displacement vs. time for (a)  $\sigma_{\beta\beta}=2.2$ , (b)  $\sigma_{\beta\beta}=2.8$ , (c)  $\varepsilon_{\beta\beta}=0.25$  and (d) $\varepsilon_{\beta\beta}=2.0$ . For (a) and (b),  $\varepsilon_{\beta\beta}$  is fixed at 0.5 while in (c) and (d),  $\sigma_{\beta\beta}$  is fixed at 2.5.

In Figures 5.4(a) and 5.4(b), the concentration of the solute atoms in the lower grain of the bicrystal is varied, and the GB displacement for the impurity type with  $\sigma_{\beta\beta} = 2.2$  and 2.8 are calculated while maintaining their cohesive energy at  $\varepsilon_{\beta\beta}=0.25$ . It can be seen that when the solute atoms are either smaller or larger than the solvents, the GB migrates and the displacement of the GB increases with increased concentration of solutes. This observation is consistent with Figure 5.2: greater lattice mismatch (and accordingly larger strain energy difference between the two grains) means a higher driving force for GB migration. Similar effects of the solute concentration can be observed

when the atomic size is fixed while the cohesive energy is varied, as shown in Figures 5.4(c)  $(\varepsilon_{\beta\beta}=0.25)$  and 5.4(d)  $(\varepsilon_{\beta\beta}=2.0)$ ; a higher solute concentration denotes a more rapid GB migration.

In principle, there is no critical value of the heterogeneity in the neighbouring grains to induce GB migration. As long as the impurity concentration and free energy are not balanced between the two grains separated by the GB, GB migration should take place. The magnitude of migration can be determined as v=MP; here, v is GB migration velocity, M is GB mobility, and P is the driving force due to the unbalanced free energy. This study shows that a minimum of 1 at.% of solute concentration present in one grain of the bicrystal is enough to induce observable GB migration within the short MD timescale. The GB migration increases with increasing concentration of the solues, i.e., by increasing the heterogeneity.

It is now clear, based on the results shown in Figures 5.2 to 5.4, that a non-equilibrium solute distribution can indeed induce strong GB migration that is observable within the short MD time scale. However, it is worth noting that although the physical driving force due to the non-equilibrium solute distribution can be easily tuned by varying both the atomic size and cohesive energy, as shown in Figures 5.2 and 5.3, respectively, the possible solute drag due to segregation as shown in Figure 5.2 will severely impact the mobility the GB. Therefore, it is recommended that the case in which solutes have minimal size mismatch but significantly different cohesive energy as opposed to host atoms is applied to investigate the intrinsic mobility of a GB. As shown in Figure 5.3, anti-segregation occurs in this case, and the GB remains in a clean state while migrating away from the enriched grain. Alternatively, it is possible to dope the grain in such a way that the GB is initially away from the enriched region so that there is a range that the GB can migrate without picking up solute atoms even if it migrates towards the doped grain. Kaur et al. [122] showed that GB migration can still be induced when the GB is 1 nm away from the doped region.

It needs to be clarified that the systems used in this study were not equilibrated so that the chemical elements (impurities) were segregated in the GB for models where GB migration was studied. The GB segregation that we have presented in Figures 5.1(d) Figures 5.2(c) to 5.2(d), and Figures 5.3(b)-5.3(c) are all based on the initially uniform distribution of solutes among the whole model, in which no DIGM occurred. However, in the models where DIGM occurs, e.g., when the

impurities are initially placed in only one grain, as shown in Figures 5.1(a) and 5.1(b), the GB did pick up the solute atoms and became enriched with impurities when the GB migrated towards the grain with doped impurities. The GB migration will slow down when the GB is enriched with solute atoms due to the well-known solute drag effects.

Based on a visual inspection of the atomic configurations, we did not notice any short-range order or clustering of the chemical elements that are picked up in the GB during the migration process. In other words, the distribution of the impurity appears to be random along the GB. This is mainly due to the short time scale of molecular dynamics and the periodic boundary conditions that we have applied in the x- and y- directions so that no concentration gradient exists along the GB plane. Therefore, it is very important to clarify that the atomistic simulations presented here are not a reproduction of the steady-state DIGM that has been observed and studied in experiments.

It is also important to clarify that although in principle, the method proposed in this study can be potentially applied to investigate the migration of any GB, some limitations should be taken into consideration in practice. First, the types of solute atoms that can be added to induce the migration of a GB for a certain type of material are limited by the availability of potentials. Secondly, quantifying the exact driving force by using this method is not as straightforward as the other methods, e.g., the SDF method. However, it is possible to determine the magnitude of the driving force induced by the solute-GBs by applying the synthetic driving force method in the opposite direction and varying its magnitude systematically until a balance is reached. This method has been previously applied in [122] to determine the magnitude of the solute-induced driving force in an Al-Ni alloy. Additionally, it is difficult to maintain a constant driving force since it is expected that the solute-induced driving force decreases as the GB migrates away or towards the solute region.

Despite these limitations, solute-induced migration of GB still stands out as a general method that can be potentially applied to any GB. This method is particularly useful for comparing the relative mobility among a series of GBs, which can be used to investigate the possible structure-mobility correlation in GBs. Furthermore, this method can be used to investigate the physical mechanisms of GB migration. For example, the popular SDF method can cause some non-physical translation of the entire simulation cell during the GB migration process [123]. By comparing the migration

of the same GB induced by the SDF and the solute-induced migration proposed in this study, it is possible to reveal if such translation of the entire model would impact how a GB migrates.

#### 5.3.4 Implications on the understanding of DIGM

Due to the intrinsically short time scale of MD (i.e., on the order of ns), the results reported in this study should not be directly compared with the experimentally observed steady-state DIGM, which is based on a different time scale (i.e., on the order of  $\mu s$ ). However, it is still possible to extrapolate the results based on the current theoretical models to real systems by focusing on the physical origin and driving forces involved during the DIGM.

For example, one result from this study can be correlated with the experimental tests performed by Yoon and co-workers at the Korea Advanced Institute of Science and technology back in 1985, i.e., the presence of lattice mismatch (strain energy) either in positive or negative direction can cause GB migration as reported in Section 5.3.1 and Figures 5.2(a) and 5.2(b). This is in qualitative agreement with the DIGM research performed by Yoon [30], Yoon et al. [72] and Rhee and Yoon [75]. Specifically, Yoon and colleagues conducted experiments on the Mo-Ni system where the coherency strain can be easily altered in both sign and magnitude and, particularly, can be reduced to zero by adjusting the concentration of the two solutes (Co and Sn). Yoon and colleagues indicated that the variation of the GB migration rate with the coherency strain shows parabolic behaviour (as shown in Figure 2.12 in Section 2.5.5) and that the migration increases by increasing the strain with either positive or negative signs. Moreover, the observed zero migration at zero strain shows that the coherency strain energy plays a dominant role in driving DIGM. The simulation results in this study, as shown in Figures 5.2(a) and 5.2(b), generally support the findings of Yoon and colleagues regarding the role of the coherency strain on DIGM.

Apart from Yoon [30], Yoon et al.[72] and Rhee and Yoon [75], there are also other researchers who claim that coherency strain energy contributes to the driving force for DIGM. For example, according to Hillert [25], the driving force (P) per unit area of the GB in an elastically isotropic material is

$$P = \frac{E\eta^2}{(1-\vartheta)} (c_+ - c_-)^2$$
 (5.3)

where E is Young's modulus,  $\eta$  is the change in the lattice spacing per unit change in solute mole fraction,  $\vartheta$  is the Poisson's ratio, and  $c_+$  and  $c_-$  are solute mole fractions in front of and behind the GB. Such a driving force tends to change the microscopic structure of the atoms around the GB region, which causes them to fit the lattice of the growing grain at the expense of the shrinking one. Another common explanation of the coherency strain model for DIGM is provided by Penrose [124], who predicted that the boundary tends to approach the grain with the larger strain energy to consume it. Moreover, Tashiro and Purdy [125] claimed that a considerable elastic misfit is required to initiate DIGM in a system as no DIGM is observed in systems where elastic misfit is not present. The simulation results in this study (e.g., Figure 5.2 and Figures 5.4(a) and 5.4(b)) thus support all of the findings of previous studies in the literature that the contrasting strain energy stored in two neighbouring grains provides an important driving force for GB migration in DIGM.

Nevertheless, the results shown in Figure 5.3 suggest that the coherency strain is not the only source of a driving force that can induce DIGM, which is consistent with the literature that there could be multiple physical origins of DIGM in real materials systems. For example, it has been proposed that the driving force for DIGM can also result from the free energy of mixing [13], [15]–[18], [126], the GB energy changes with solute inclusion [16], [17] and the GB Kirkendall effect [22], [24], [127]. Due to the limitations of length and time scales in MD, it is impractical to explore all the other origins of driving forces for DIGM in this study. However, the simulation results in this study further support a previous atomistic investigation on DIGM [122] that the solute-GB interaction, i.e., attraction or repulsion as evidenced by solute segregation or anti-segregation, seems to be a more fundamental cause of DIGM than the coherency strain (or similarly, elastic energy); ultimately it is the unbalanced solute-GB interaction between the two grains that leads to GB migration. The lattice mismatch (or coherency strain) is just one possible source resulting in strong solute-GB interaction.

#### 5.4 Conclusions

In summary, the concept of simulating GB migration by taking advantage of the unbalanced free energy induced by a non-equilibrium solute distribution between two abutting grains has been proven. Based on a model system of Al bicrystal with LJ potentials, it is shown here that the solute-GB interaction resulting from the non-equilibrium solute distribution is strong enough to enable observable GB migration in atomistic simulations within a short MD timescale, which offers a new method of simulating general GB migration with physical and tunable driving-forces. Both the direction and magnitude of the driving force can be systematically tuned by varying the atomic size, cohesive energy, and concentration of solute atoms. Since the non-equilibrium distribution of solute atoms occurs frequently during DIGM, this study also provides important atomistic insights into the physical origins of DIGM.

Chapter 6

# **Conclusions and Future Work**

## Chapter 6: Conclusions and Future Work

#### 6.1 Conclusions

The work in this thesis has explored the physical origins of the driving force responsible for the migration of GBs in DIGM through atomistic simulations. Earlier experiments show the alloy systems undergoing DIGM and conclude that DIGM is found to occur in hundreds of binary systems. Few of them have formulated theories and used thermodynamics to explain the mechanism behind DIGM. Moreover, only one or two publications on DIGM were produced between 1999-2005. The reason for this could be the lack of experimental data to validate the proposed mathematical models. No progress has been made experimentally or theoretically further to explore the origins of the driving force for DIGM. After an extensive literature review, I realized that observing the phenomenon at the atomic level is essential to understand it better.

Nevertheless, this task cannot be experimentally realized, so modern atomistic simulation methods are used in lieu. Experimental techniques are challenging to carry out, as DIGM operates in layers of few microns, so that it is difficult and imprecise to conduct experiments in this range; therefore, atomistic modelling is used as an alternative approach. The next challenge is to build a model system as there are no attempts in the literature to used use MD to understand DIGM, and hence no studies can be referenced. Therefore, a model is constructed from scratch, and atomistic simulations are performed to understand DIGM. The details are provided in Chapters 4 and 5 of this dissertation. This study is limited to a few nanoseconds and hence cannot be used for comparison purposes with experimental DIGM of micrometres in scale.

The first study in Chapter 4 of the thesis concluded that solute-GB interactions play an important role in driving DIGM. Systems that demonstrate solute segregation and anti-segregation undergo DIGM. Furthermore, it is concluded that the direction of GB migration greatly depends on the type of solute-GB interaction, e.g., segregation or anti-segregation. The driving force for DIGM is also quantified. The results show that the driving force required for DIGM monotonically increases with solute concentration when the solute shows either a high degree of segregation or anti-segregation towards the GB plane.

The results of this study have raised more questions. For example, it is concluded that solute-GB interactions have an important role in driving DIGM. At the same time, many reports in the literature indicate that coherency strain is the main source of the driving force for DIGM. Therefore, it was necessary to decouple the effects of solute-GB interactions and coherency strain on the driving force for DIGM. Secondly, is it possible to vary the magnitude of the driving force for DIGM?

To further research DIGM regarding these issues, various alloy systems are selected using an LJ potential because it provides availability to choose solute types with varying solute sizes and cohesive energy. Furthermore, it is found that different solute types (with varying atomic size and cohesive energy) interact with the GB in different ways, thus resulting in solute segregation or anti-segregation. The driving force is also tuned by varying the type of solute. Moreover, it is also concluded that the lattice strain that results from atomic size mismatch, which has been proposed to be an important driving force for DIGM, is not always essential for inducing GB migration.

While researching DIGM, a new general atomistic method for simulating GB migration based on a tunable physical driving force induced by a non-equilibrium solute distribution emerged, which has been fully explained in Chapter 5.

#### 6.2 Future Prospects

This study has only modelled the initiation stage of DIGM and not steady-state DIGM. It is not possible to model the complete DIGM reaction due to the timescale limitation of MD. The experimental DIGM reaction is at a microseconds scale, and MD can capture the timescales of nanoseconds. The results reported in this study can not be directly compared with the experimentally observed steady-state DIGM. Work can be done in the future to improve MD methods to capture the experimentally observed DIGM phenomenon (in the orders of microseconds). The recent developments of accelerated molecular dynamics (MD) [128] and precision atomistic modelling [129], [130] push atomistic simulations even closer to experimental conditions. These methods can reach simulation times several orders of magnitude longer than direct molecular dynamics while retaining full atomistic detail.

Moreover, this research can be extended to study DIGM in polycrystalline materials. The different types of grain boundaries, misorientations and triple junctions in polycrystalline materials will

have different GB energy. This would influence the extent of solute-GB interactions, but the major conclusions and atomic mechanism will be valid. Different types of GBs in polycrystalline materials may affect the results quantitatively, but qualitative findings would remain the same. In other words, it is possible to tune the occurrence of DIGM quantitatively. This study would be highly informative as it will help in designing new materials where it is possible to control DIGM.

Recently, it has been possible to realize the real-time atomistic observation of GB migration by insitu transmission electron microscopy (TEM) technologies [131][132][133], [134]. In situ TEM results of GB migration provide atomic information of the phenomenon that can be reproduced using MD simulations. Li et al. published a paper in January 2022 [135] where they used a combination of experiment and simulation to examine GB migration. Experimental results are used as input to the simulations, allowing one to interpret the experimentally observed migration unambiguously. Both in-situ experiments and simulations compliment each other and can be combined to explore many aspects which cannot be studied by conducting experiments or simulations independently. This method makes it possible to interlink results from experiments with simulations. In regard to the present research, in situ experiments would validate the simulation results regarding solute-GB interactions in DIGM.

It is desirable to conduct advanced research to understand DIGM and operating atomistic mechanisms for scientific interest as well as for industrial application.

# Chapter 7 References

## Chapter 7: REFERENCES

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