Molecular dynamics simulation study of grain boundary migration in nanocrystalline Pd

Shengyu Wang
Louisiana State University and Agricultural and Mechanical College, swang8@lsu.edu

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

Part of the Mechanical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_theses/3687

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master’s Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
MOLECULAR DYNAMICS SIMULATION STUDY OF GRAIN BOUNDARY MIGRATION IN NANOCRYSTALLINE Pd

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
In partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

By
Shengyu Wang
B.S., University of Science and Technology, Beijing, China, 1998
May 2006
To my father, Guocai Wang
ACKNOWLEDGEMENTS

First, I would like to express my sincere gratitude to Dr. Dorel Moldovan, my advisor, for his valuable guidance and encouragement throughout my study at Louisiana State University. His tenacious supervision, helpful suggestions, patience and time deserve a special attention. I have learnt the basics of Molecular Dynamics Simulation under his guidance.

I would like to express my appreciation to my committee members Dr. Wenjin Meng and Dr. Harris Wong for their support and suggestions.

I would like to thank my colleagues and friends at LSU for their constant help and valuable suggestions throughout the study. Special thanks are extended to my friends Mr. Dinesh Pinisetty, Mr. Jijun Lao, Mr. Kanishk Rastogi, Mr. Rakesh Behera, Ms. Donghong Min and Ms. Yiping Lu for their constant help and encouragement.

I would like to express my gratitude towards my husband, Yanfei Ding, my parents, Guocai Wang and Lanying Song and my sisters, Shaoyu Wang, Guangyu Wang. Their encouragement and support has been a constant source of inspiration during my stay at LSU.

Last but not the least, I would like to gratefully acknowledge the project support from Louisiana Board of Regents and Louisiana State University, Department of Mechanical Engineering.
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS .......................................................................................... iii

ABSTRACT .............................................................................................................. vi

CHAPTER 1. INTRODUCTION ................................................................. 1
  1.1. Overview ........................................................................................................ 1
  1.2. Objectives ....................................................................................................... 4

CHAPTER 2. BACKGROUND AND LITERATURE REVIEW ............... 5
  2.1 General Review of Grain Boundaries .......................................................... 5
    2.1.1 Grain Boundary Energy ....................................................................... 7
    2.1.2 Grain Boundary Mobility ................................................................... 9
  2.2 Theoretical Investigations of Grain Boundary Migration ......................... 9
    2.2.1 Fundamentals ...................................................................................... 10
    2.2.2 Driving Forces for Grain Boundary Migration ................................... 13
      2.2.2.1 Dislocations and External Shear Stress ................................... 14
      2.2.2.2 Capillarity Pressure ................................................................. 15
      2.2.2.3 High Magnetic Field ............................................................... 16
      2.2.2.4 Elastic Strain Field ................................................................... 17
  2.3 Models for Grain Boundary Migration ....................................................... 18
    2.3.1 Single-process Models ......................................................................... 19
    2.3.2 Step Models ......................................................................................... 22
    2.3.3 Boundary Defect Models .................................................................... 23
  2.4 Measurement of Grain Boundary Mobility ................................................ 23
    2.4.1 Bicrystal Methods ................................................................................ 24
    2.4.2 Polycrystal Methods ............................................................................. 25

CHAPTER 3. THE MODEL AND SIMULATION METHODOLOGY ........ 27
  3.1 Molecular Dynamics Simulation of Grain Boundary Migration ............. 27
    3.1.1 Molecular Dynamics: Overview ........................................................ 27
  3.2 Simulation Model ......................................................................................... 28
  3.3 Common Neighbor Analysis ........................................................................ 35
  3.4 Grains Identification Method ....................................................................... 37

CHAPTER 4. SIMULATION RESULTS ..................................................... 39
  4.1 Test of the Grains Identification Method .................................................. 39
  4.2 Simulation Results of Grain Boundary Migration .................................... 41
    4.2.1 The System at 1150K .......................................................................... 42
    4.2.2 The System at 1250K .......................................................................... 46
    4.2.3 The System at 1350K .......................................................................... 47
  4.3 Temperature Effect on Grain Boundary Mobility .................................... 49
ABSTRACT

We present a new methodology for measuring the grain boundary mobility for curved boundaries using molecular-dynamics simulation of grain growth in a small, specifically tailored Pd nanocrystalline structure. In the model system, the boundaries move under the forces provided by their curvature and in the presence of the triple junctions. As a consequence of grain boundary migration the boundary area per unit volume is reduced and the mean grain size of grains increases with time. Our investigation shows that at elevated temperatures the activation energy for grain growth in this specifically tailored microstructure is very close to that of grain boundary diffusion. These findings suggest that the migration mechanism of curved grain boundaries might be mediated by short distance diffusion of atoms in the grain boundaries.
CHAPTER 1
INTRODUCTION

1.1. Overview

Grain boundaries are two dimensional lattice defects in polycrystalline materials. They are basically regions separating two parts of the same crystal structure but with different crystalline orientations. The knowledge of their characteristics and properties are of great importance since many properties of polycrystalline materials are determined or affected by the presence of grain boundaries. In particular the, number of grain boundaries per unit volume determine the average grain size which can have a large impact on the material response to plastic deformation. In relation with this, it is worth mentioning one of the most celebrated relations between a material’s microstructure and its physical response, namely, the Hall-Petch relation which states that the yield strength, $\sigma_y$, of a material scales as:

$$\sigma_y = \sigma_0 + \frac{k}{\sqrt{d}},$$  \hspace{1cm} (1.1)

where $d$ is the average grain size and $\sigma_0$ and $k$ are material constants.

The migration of grain boundaries is central to microstructural evolution in a variety of polycrystalline materials as their motion controls the evolution kinetics during materials processing, thus determining microstructural parameters such as grain size and texture. For example, one can say that grain boundary migration is the most important atomic-scale mechanism which occurs during the recovery and recrystallization of deformed materials.

There are two important properties determining the ability of a grain boundary to migrate. These are the grain boundary energy and grain boundary mobility. Grain
boundary energy is given by the excess energy of the atoms located in the defective regions of the grain boundaries and can be determined directly from experiments using the groove angle method or from molecular dynamics simulation by evaluating directly the excess energy of atoms located in grain boundaries.

Grain boundary mobility is an intrinsic property of the grain boundary characterizing grain boundary response to a driving force, that is to say grain boundary mobility is a proportionality constant that relates the driving force to the velocity of migration of grain boundaries. Regardless of the detailed nature of the driving force, $P$, acting on the grain boundaries, more often their migration resembles a continuum viscous movement with a velocity, $v$, given by an equation of the form:

$$v = mP$$  \hspace{1cm} (1.2)  

where $m$ is the grain boundary mobility. Moreover when the grain boundary curvature is the only driving force, $P$ can be written as

$$P = \gamma / R$$  \hspace{1cm} (1.3)

where $R$ is the curvature radius and $\gamma$ is the grain boundary energy.

The grain boundary mobility, $m$, is usually assumed to vary with temperature according to

$$m = m_0 \exp \left(-\frac{E_{GB}}{k_BT} \right)$$  \hspace{1cm} (1.4)

where $m_0$ is a constant, $T$ is the absolute temperature, $k_B$ is the Boltzmann’s constant and $E_{GB}$ is the activation energy for boundary migration. This is well-known Arrhenius relation.
In general, both grain boundary energy and grain boundary mobility depend on the structure and characteristics of grain boundary, which in general depend on both the misorientation across the grain boundary and on the inclination of the boundary plane. Various functional forms for the misorientation dependence of boundaries energies and mobilities have been proposed in literature. Notable is the Read-Shockley formula giving the grain boundary energy for low angle grain boundaries. This was derived analytically starting from the known boundary dislocation structure by summing up the elastic strain energy of the dislocation array comprising the grain boundary. Read-Shockley formula is verified well by the experimental measurements and predicts that the low angle grain boundaries have low energy while the high angle grain boundaries have in general high energy. Although there is no definite functional form established for the mobility dependence on the misorientation it is well known that small-angle boundaries have very low mobilities relative to high-angle boundaries.

While there are well established methods for determining grain boundary energies in both experimental and simulation studies determining grain boundary mobility proved to a more difficult task. The main reason is because one has to simultaneously determine both the driving force and velocity of grain boundary migration. Currently most of our understanding of grain boundary motion is obtained mainly from experiments and simulations on bicrystals. Moreover, given that it is easier to control the driving force and to quantify the motion of a planar boundary, most of these studies focus on planar grain boundaries. This is why in this thesis by focusing on specifically tailored simple nanocrystalline structure we expand the knowledge and determine the mobility and the activation energy for the migration of a curved grain boundary.
1.2. Objectives

The objectives of the present study are to establish and validate a new methodology for determining the mobility and the activation energy for curved grain boundaries. The studies are carried on a nanocrystalline Pd microstructure. The evolution of the microstructure at three different temperatures well below the melting temperature (T= 1150K, 1250K and 1350K) is investigated and the activation energy is determined.
CHAPTER 2
BACKGROUND AND LITERATURE REVIEW

2.1 General Review of Grain Boundaries

Most crystalline solids are composed of a collection of many small crystals or grains; such materials are termed polycrystalline. There are various stages in the solidification of a polycrystalline specimen. Initially, small crystals or nuclei form at various positions. These have random crystallographic orientations. The small grains grow by the constant addition from the surrounding liquid of atoms to the structure of each. As the solidification process approaches completion, the extremities of adjacent grains impinge on one another. Therefore, the crystallographic orientation varies from grain to grain. Also, there exists some atomic mismatch within the region where two grains meet; this area, called a grain boundary.

Generally speaking, a grain boundary is a defective region that separates two small grains or crystals having different crystallographic orientations in polycrystalline materials. Grain boundaries are represented schematically from an atomic perspective in Figure 2.1. Within the boundary region, which is typically just several atom distances wide, there is some atomic mismatch in a transition from the crystalline orientation of one grain to that of an adjacent one.

Various degrees of crystallographic misalignment between adjacent grains are possible. According this, when this misorientation is slight, on the order of a few degrees, then the grain boundary is called small (low) angle grain boundary. When misorientation is greater than 10-15 degree, the boundary is known as a random high-angle grain boundary.
Figure 2.1 Representation of several grains of varying misorientation [1].

Besides these two classes of grain boundaries, one can introduce another special class containing the type of grain boundary, called coincident-site-lattice (CSL). The CSL boundaries are boundaries with misorientations that lie within a given deviation of a special misorientation. These types of boundaries are labeled using the symbol $\Sigma$ followed by integer number which describes the fraction of CSL sites on the boundary plane that belong to both crystals forming the GB. In other words $\Sigma$ represents the reciprocal of the ratio of CSL sites to lattice sites. For instance, a $\Sigma 3$ boundary denotes that every third lattice position in the boundary plane is in coincidence (i.e. belongs to both lattice); moreover $\Sigma 1$ would be the twin boundary. It is important to notice that although in general the misorientation of a typical CSL boundary is not at all small due to the limited ordering in such boundaries they are characterized by low boundary energies.

Regardless of grain boundary type, there are two important properties characterizing a grain boundary; these are the grain boundary mobility and grain boundary energy. In
next two subsections, the basic concepts about these two properties of boundaries will be introduced.

2.1.1 Grain Boundary Energy

The nature of any given boundary depends on the misorientation of the two adjoining grains determining the boundary and on the orientation of the boundary plane relative to them. Similar to most properties characterizing the grain boundaries the energy of a grain boundary depends on the boundary misorientation. Basically as the degree of the disorder in the grain boundary increases with the increase of the boundary misorientation so does the boundary energy.

Low-angle grain boundaries, which are characterized by discrete dislocation structures, have low energies and their transport properties (e.g. grain boundary chemical and thermal diffusion, grain boundary migration and sliding) are slow. In within this boundary representation the energy of a low-angle grain boundary is simply the total energy of the dislocations within unit area of boundary. This energy depends on the dislocation density and therefore on the spacing, D, of the dislocations which, for the simple arrays represented in Figure 2.2, is given by

$$D = \frac{b}{\sin(\theta)} \approx \frac{b}{\theta} \quad (2.1)$$

where $b$ is the Burgers vector of the dislocations and $\theta$ is the angular misorientation across the grain boundary. At very small values of $\theta$ the dislocation spacing is very large and the grain boundary energy $\gamma$ is approximately proportional to the density of dislocations in the boundary (1/D), and to $\theta$ as well. The grain boundary energy $\gamma$ is given by the Read-Shockley formula [2]:

$$\gamma = \gamma_0 \theta (A - \ln \theta) \quad (2.2)$$
where \( \gamma_0 = \frac{Gb}{4\pi(1-\nu)} \) and \( A = 1 + \ln(b/2\pi r_0) \) are material parameters, \( r_0 \) is the radius of the dislocation core (usually between \( b \) to \( 5b \)), \( G \) is the elastic shear modulus and \( \nu \) is the Poisson ratio.

One should be aware that the Read-Shockley formula (Eq. 2.2) applies only to small misorientation values \( \theta \), typically \( \theta < 15^\circ \). This is because by increasing the misorientations (i.e. \( \theta \) larger than \( 15^\circ \)) the dislocation structure becomes more and more diffuse due to dislocation core overlap and model on which the theory was developed does no longer apply. One should also notice that it is often convenient to write the Read-Shockley formula in the normalized form:

**Figure 2.2** Schematic representation of a low-angle tilt grain boundary [1].
\[ \gamma = \gamma_m \frac{\theta}{\theta_m} \left( 1 - \ln \frac{\theta}{\theta_m} \right) \]  

where \( \gamma_m \) is the energy of the corresponding high-angle grain boundary and \( \theta_m \sim 15^\circ \) is the saturation misorientation angle.

High angle grain boundaries do not reveal discrete dislocation structure and therefore have high grain boundary energy and their transport properties are fast. This is because that a high-angle grain boundary contains large areas of poor fit, therefore it has a relatively open structure, and the atoms within the high grain boundary regions are highly distorted.

2.1.2 Grain Boundary Mobility

As mentioned in Chapter 1, grain boundary mobility is an intrinsic property of the grain boundary characterizing grain boundary response to a driving force, that is to say grain boundary mobility is a proportionality constant that relates the driving force to the velocity of migration of grain boundaries. Grain boundary mobility is of great meaning only if the actual grain boundary migration occurs and it is determined by the actual mechanism by the grain boundary migrates. In the following sections 2.2 and 2.3, we will give brief reviews reflecting the current understanding both from the theoretical and experimental point of view of the mechanisms of grain boundary migration.

2.2 Theoretical Investigations of Grain Boundary Migration

Grain Boundaries were discovered in the mid-eighteenth century. The most interesting issue of grain boundary is its ability to move under various driving forces. During recrystallization and grain growth, the key process of microstructural evolution is grain boundaries motion. Despite a lot of efforts and a large number of papers dedicated
to the issues of grain boundary migration, the physical mechanisms and the fundamentals of this process are still not well understood.

### 2.2.1 Fundamentals

As mentioned previously, grain boundary is a defective region that separates two regions the same phase and crystal structure but different orientations. The displacement of a grain boundary is entirely equivalent to the growth of one crystallite at the expense of the shrinking neighbor. A non-zero atomic flux across the boundary will make one grain to shrink (the emitting grain) and the other grain to grow (receiving grain). One can envision two cases related to this mechanism [3]. They are illustrated in Figure 2.3. In the first case (see Figure 2.3 left), the opposite faces of a bicrystalline specimen would move with regard to an external reference frame, but the grain boundary would remain stationary. In the second case (see Figure 2.3 right), the grain boundary would move without the external frame changing.

**Figure 2.3** Diffusion across a grain boundary (left) and grain boundary motion (right) will displace a boundary with regard to an interior sample reference. Boundary motion will also displace the boundary with regard to an external reference [3].

Therefore, diffusion across a grain boundary does not necessarily correspond to grain boundary motion with a displacement of crystallite surfaces. As illustrated in Figure 2.4
the grain boundary motion occurs as a result of the generation of lattice sites at the surface of the growing grain and conversely a destruction of lattice sites at the surface of the shrinking grain. Grain boundary motion comprises the non-zero net exchange of lattice sites across the boundary (Figure 2.4).

There is no real theory of grain boundary migration thus far even if there are extensive treatments in literature. In fact most of the theoretical attempts to describe grain boundary motion are based on simple rate theory of atoms crossing the grain boundary with net energy gain. [3] According to this theory, if the grain boundary is narrow, i.e. can be crossed by a single atomic jump, and each transferred atom displaces the boundary by the diameter of an atom, b, the grain boundary velocity reads [4]

\[ v = b(\Gamma_+ - \Gamma_-) \, , \]  

(2.4)

where \( \Gamma_+ \) and \( \Gamma_- \) are the jump frequencies in the respective directions. If there is no Gibbs free energy differential between the adjacent crystals, then the net flux is zero. If

![Figure 2.4](image)

**Figure 2.4** Grain boundary motion deletes and generates lattice sites on the surface of the shrinking and growing grain, respectively [3].

Gibbs free energy per unit volume of the two crystals is different the there will be a net driving force acting on the grain boundary and is given by:
\[
P = -\frac{dG}{dV}. \tag{2.5}
\]

Therefore each atom of volume \( \Omega \approx b^3 \) will gain the free energy \( Pb^3 \) when becomes attached to the growing grain but has to loose this free energy when moving in the opposite direction. The corresponding free energy variation across the boundary is schematically shown in Figure 2.5. Correspondingly one can write the expression for the velocity of the grain boundary migration:

\[
v = b \left( \nu_+ \exp\left(\frac{G_m^+}{k_BT}\right) - \nu_- \exp\left(\frac{G_m^-}{k_BT}\right) \right) \tag{2.6}
\]

If the attack frequency \( \nu_+ = \nu_- = \nu \approx \nu_D \) (Debye-frequency) and the migration free energy \( G_m \) is the same in both jump direction, then

\[
v = b \nu_D \exp\left(-\frac{G_m}{k_BT}\right) \left(1 - \exp\left(-\frac{Pb^3}{k_BT}\right)\right) \tag{2.7}
\]

**Figure 2.5** The free energy of a moving atom changes by the driving force \( Pb^3 \) when it crosses the boundary. \( G_m \) is the free energy barrier for bulk diffusion [3].
For all practical cases, including recrystallization in cold worked metals, \( P b^3 \ll kT \) at temperatures where boundaries are observed to move \( (T \geq 0.3T_m) \) and, therefore,

\[
\exp\left\{-\frac{P b^3}{k_b T}\right\} \approx 1 - \frac{P b^3}{k_b T}
\]

which yields

\[
v = \frac{b^4 v_B}{k_b T} \exp\left(-\frac{G_m}{k_b T}\right) \cdot P \equiv m \cdot P
\]

where \( m \) is referred to as grain boundary mobility, which is a proportionality factor relating velocity of grain boundary migration and migration driving force.

### 2.2.2 Driving Forces for Grain Boundary Migration

The driving force for grain boundary migration \( P \) has the unit of energy per unit volume, which is conceptually equivalent to a pressure, force acting per unit area on a grain boundary. This is simply because the unit of energy is equivalent to the product of force and distance.

There are various sources of driving force (see Table 2.1). Generally, if the boundary displacement leads to a decrease of the total free energy of the system, then a driving force for grain boundary migration occurs.

In principle, a gradient of any intensive thermodynamic variable offers a source of driving force: a gradient of temperature, pressure, density of defects, density of energy (for example an energy of elastic deformation), contents of impurity, a magnetic field strength etc. Out of these many driving forces we will concentrate and elaborate more those most commonly employed in experiments such as: excess dislocation density (stored in plastic deformation), boundary curvature and magnetic fields (for materials with a sufficiently anisotropic interaction with an applied field) [5].
2.2.2.1 Dislocations and External Shear Stress

When dislocations have an excess density in one of the adjoining grains there is a powerful source for a driving force that would cause the grain boundary to swipe the

Table 2.1 The driving forces for grain boundary migration [3]

<table>
<thead>
<tr>
<th>Source</th>
<th>Equation</th>
<th>Approximate value of parameters</th>
<th>Estimated driving force in MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stored deformation energy</td>
<td>( P = \frac{1}{2} \rho \mu b^2 )</td>
<td>( \rho = ) dislocation density ( 10^{15}/m^2 )</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \frac{\mu b^2}{2} = ) dislocation energy ( 10^{-8}/m )</td>
<td></td>
</tr>
<tr>
<td>Grain boundary energy</td>
<td>( P = \frac{2\sigma_b}{R} )</td>
<td>( \sigma_b = ) grain boundary energy ( 0.5/J/m^2 )</td>
<td>10×2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R = ) grain boundary radius of curvature ( 10^{-4} ) m</td>
<td></td>
</tr>
<tr>
<td>Surface energy</td>
<td>( P = \frac{2\Delta \sigma^d}{d} )</td>
<td>( d = ) sample thickness ( 10^{-3} ) m</td>
<td>2×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta \sigma^d = ) surface energy difference of two neighboring grains ( 0.1 J/m^2 )</td>
<td></td>
</tr>
<tr>
<td>Chemical driving force</td>
<td>( P = R(T_1 - T_0) \ln \frac{c_0}{c} )</td>
<td>( c_0 = ) concentration max. solubility at ( T_0 )</td>
<td>6×10²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( T_1 (&lt; T_0) ) annealing temperature ( (5% Ag ) in ( Cu ) at ( 300^\circ C )</td>
<td></td>
</tr>
<tr>
<td>Magnetic field</td>
<td>( P = \frac{\mu_0 H^2 \Delta \chi}{2} )</td>
<td>( \Delta \chi = ) difference of magnetic susceptibilities ( -1.8×10^{-7} ) (250°C)</td>
<td>3.5×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Theta ) angle between c-axis and field direction ( \Theta_1 = 0^\circ; \Theta_2 = 90^\circ )</td>
<td></td>
</tr>
<tr>
<td>Elastic energy</td>
<td>( P = \frac{\tau^2}{2} \left( \frac{1}{E_1} - \frac{1}{E_2} \right) )</td>
<td>( \tau = ) elastic stress ( 10 ) MPa</td>
<td>2.5×10⁻⁴</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_1, E_2 = ) elastic moduli of neighboring grains ( 10^5 ) MPa</td>
<td></td>
</tr>
<tr>
<td>Temperature gradient</td>
<td>( P = \frac{\Delta S \cdot 2\lambda \text{grad} T}{\Omega_b} )</td>
<td>( \Delta S = ) entropy difference between grain boundary and crystal (approx. equivalent to melting entropy) ( 8×10^3 ) J/K·mol</td>
<td>4×10⁻⁵</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{grad} T = ) temperature gradient ( 10^4 ) K/m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 2\lambda = ) grain boundary thickness ( 5×10^{-10} ) m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Omega_b = ) Molar volume ( 10 ) cm³/mol</td>
<td>4×10⁻⁵</td>
</tr>
</tbody>
</table>
“defective” grain. There are several advantages of this type of driving force: the ease of fabrication, excellent reproducibility, and variation of the magnitude of driving force within a wide range up to a very large force. These advantages as well as their relevance for recrystallization processes explain the widespread use of this kind of driving force in investigations targeting grain boundary migration. There a few drawbacks though among these we might list: instability of the driving force during annealing owing to recovery, local variation of dislocation density etc.

Similarly, to the mechanism by which an external shear stress exerts a force on a single dislocation in a crystal, a force will be exerted on an ensemble of such dislocations when a shear stress is exerted on a bicrystal. It is therefore expected that by applying a shear stress on a low angle grain boundaries (dislocation boundary) it would set the boundary in motion. This was confirmed by Washbrun, Parker and coworkers [6,7] by investigating the displacement of low angle grain boundary in Zn. However, it is commonly agreed that a high angle grain boundary is not affected by an external shear stress since a high angle grain boundary comprising a continuous perturbation of the perfect crystal where dislocations lose identity completely relaxes the stress field in the grain boundary. For example, the motion of low and high angle symmetrical $<112>$ and $<111>$ tilt boundaries under an applied shear stress was observed in various investigations [8].

2.2.2.2 Capillarity Pressure

In general in the absence of other driving forces during the grain growth the motion a given grain boundary is controlled by its curvature, which in turn, is determined by the shape and the size of the grain. Capillary pressure is a measure of the curvature of the
interface separating two phases or two grains. Curvature is a geometric quantity having
the units of reciprocal length. When the shape of all grains is considered to be uniform,
the grain boundary curvature can be described by just one parameter – the mean grain
size. The grain shape can appear isotropic or highly anisotropic depending on whether its
motion is driven by curvature or an external field, respectively, but the mobility itself is
independent of driving force [9].

According to the general understanding the driving force for grain boundary motion
is exerted by the pressure difference on both sides of the boundary. Usually, the pressure
difference originate in the difference of capillary forces on both sides of a curved
boundary and was given by the Equation (1.3). In general for a given boundary, \( \gamma \), the
grain boundary energy, is a function of grain boundary structure and misorientation.
Experimental procedures to study grain boundary migration by using the free energy of
the grain boundary itself as a driving force offers a number of advantages, namely the
possibility to control and to change the driving force, a good reproductibility, and a good
stability at a given temperature. As seen from Table 2.1, the magnitude of the capillary
driving force is of the order of \( 10^{-5}-10^{-3} \) MPa.

2.2.2.3 High Magnetic Field

The anisotropy of any physical property, e.g., the elastic constants or the magnetic
susceptibility, can be utilized as a source of driving force for a grain boundary migration.
The origin of the driving force for grain boundary migration in a magnetically anisotropic
material was considered by Mullins [10].

If the volume density of the magnetic free energy, \( w \), in a crystal induced by a
uniform magnetic field is independent of crystal shape and size and the susceptibility
\( \chi \ll 1 \) then the magnetic driving force acting on the boundary of two crystals that have different susceptibilities is give by

\[
P = g_{m1} - g_{m2} = \frac{\mu_0 H^2}{2} (\chi_1 - \chi_2)
\]

(2.10)

Where \( \chi_1 \) and \( \chi_2 \) are the susceptibilities of crystal 1 and 2, respectively, parallel to the magnetic field \( H \).

The measurement of boundary motion under a constant magnetic driving force provides us a unique opportunity to determine the absolute value of grain boundary mobility. In contrast, experiments using other driving forces, like small angle boundaries or dislocations, need a very accurate estimate of the sub grain boundary or dislocation energy; in many cases, these grain boundary energy or dislocation energy is uncertain. Experiments with curved grain boundaries allow us to determine grain boundary mobility to an accuracy of the surface tension \( \gamma_s \) of the grain boundary [11, 12]; the grain boundary also is not planar. The other significant advantage of a magnetic driving force is that it is possible to vary it by changing the position of the sample with regard to the magnetic filed. However, the main advantage of the magnetic driving force is that it allows us to measure the migration of planar grain boundaries [13, 14]. But there are also some disadvantages to measure grain boundary mobility by using magnetic driving force. The major disadvantage is the restriction of this method to materials with a large magnetic anisotropy.

2.2.2.4 Elastic Strain Filed

In the presence of an externally applied stress on a bicrystal due to the elastic anisotropy of the material the elastic strain energy density in the two crystals will be
different and it will depend on the relative direction of the applies stress and crystal
directions, the grain boundary misorientation and the characteristic elastic constants. If
one considers a tilt grain boundary of misorientation $\theta$ in a material with cubic symmetry
subjected to a compressive elastic straining perpendicular to the boundary plane and
acting along the principal directions of one of the single crystal comprising the bicrystal
system the driving force will given by

$$ P = F_x - F_z = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})^2 C_a \sin^2(2\theta)}{C_{11}[4C_{11}(C_{11} - C_{12} + C_a) - (C_{11} + C_{12})C_a(1 - \cos(4\theta))] } \varepsilon^2 $$

(2.11)

where $C_a = 2C_{44} - C_{11} + C_{12}$ is a measure of anisotropy in the system ($C_a = 0$ for an
isotropic system) and $\varepsilon$ is the externally applied elastic strain. Experimentally available
elastic anisotropy driving forces range between $10^{-5}$ to $10^{-3}$ MPa.

### 2.3 Models for Grain Boundary Migration

Despite the recent developments in the investigation of grain properties there grain
boundary migration is still poorly understood mainly due to the difficulties to
experimentally determine grain boundary mobility. In fact many previous measurements
of grain boundary mobility were obscured by artifacts and gave rise to misleading
conclusions and confusion; especially in connection with the dependence of grain
boundary mobility on external parameters [15,16]. The major obstacles for proper
experimental conduct of grain boundary mobility investigations are [17]:

a. controlling the driving force for grain boundary migration
b. the necessity to continuously monitor the shape and displacement of a moving
   grain boundary
c. the accuracy and reproducibility of grain boundary crystallography and
d. composition and purity of the material.
Despite of these intrinsic difficulties in measuring grain boundary mobilities there have been a lot theoretical studies over the last three decades aimed at the fundamental understanding of boundary migration mechanism itself. In the following, we will give a short presentation of some of the most relevant models of grain boundary migration.

**2.3.1 Single-process models**

The single process model is based on reaction rate theory. In this theory, grain boundary migration is controlled by single atom movements. This model was proposed by Turnbull in 1951.

As shown in Figure (2.6a), a boundary has a thickness $\delta$, moving to the left due to a free energy difference of $\Delta G$. An atom must acquire activation energy of $\Delta G^a$ to break away from its parent grain, as shown in Figure (2.6b). If the frequency of atomic vibration is $\nu$, then the number of times per second that the atom acquires this energy is $\nu \exp(-\Delta G^a / kT)$. If there are $n$ atoms per unit area of boundary which are suitable sites for a jump, then the number of jumps per second from a grain is $n \nu \exp(-\Delta G^a / kT)$.

However, they will not all be in favorable positions to jump, and therefore a grain boundary structure dependent factor $A_J$ is introduced. It means the fraction of atoms that are able to jump. Since not all atoms can find a suitable site for attachment to the other grain, then an accommodation factor $A_A$ is introduced. It means the fraction of successful attachments. Then based on these two factors, we can derive the effective flux from grain 1 to grain 2.

The effective flux of atoms from grain 1 to grain 2 will thus be

$$A_J A_A n \nu \exp\left(-\frac{\Delta G^a}{kT}\right)$$  \hspace{1cm} (2.12)
In the same manner, there will be a flux of atoms from grain 1 to grain 2, given by

\[
A_J A_n n v \exp\left(-\frac{\Delta G^a + \Delta G}{kT}\right)
\]  

(2.13)

There will be a net flux from grain 1 to grain 2 of

\[
J = A_J A_n n v \exp\left(-\frac{\Delta G^a}{kT}\right) \cdot \left[1 - \exp\left(-\frac{\Delta G}{kT}\right)\right]
\]  

(2.14)

If the boundary velocity is \(v\), and the interatomic spacing is \(b\), then we can relate grain boundary velocity to the interatomic spacing:

Figure 2.6 Grain boundary migration by means of atom jumps. (a) The mechanism of migration. (b) The free energy of an atom during a jump across the boundary [3].
\[
v = J_n^b = A_j A \nu \exp(-\frac{\Delta G^a}{kT}) \cdot \frac{\Delta G}{kT} \cdot [1 - \exp(-\frac{\Delta G}{kT})]
\] (2.15)

As the free energy changes during recrystallization are small, we may assume that \(\Delta G << kT\) and expand \(\exp(-\frac{\Delta G}{kT})\) giving

\[
v = A_j A \nu \exp(-\frac{\Delta G^a}{kT}) \cdot \frac{\Delta G}{kT}
\] (2.16)

As the driving pressure is given by \(P = \Delta G\) then

\[
v = A_j A \nu \exp(-\frac{\Delta G^a}{kT}) \cdot \frac{P}{kT}
\] (2.17)

And substituting \(\Delta G = \Delta H - T \Delta S\) then

\[
v = A_j A \nu \exp(-\frac{\Delta H^a}{kT}) \cdot \exp(\frac{\Delta S}{kT}) \cdot \frac{P}{kT}
\] (2.18)

The grain boundary mobility then can be given by

\[
M = \frac{A_j A \nu}{kT} \cdot \exp(-\frac{\Delta H^a}{kT}) \cdot \exp(\frac{\Delta S}{kT})
\] (2.19)

This model is very general and not specific enough to allow prediction of the parameters such as the activation energy.

However, there are some problems with this model. For example, the activated process is identified with grain boundary diffusion for the atoms move across the boundary rather that within it and the two processes are not necessarily identical. In addition, a better defined basis for the parameters \(A_j\) and \(A_A\) needs to be developed. Whether atoms migrate with the boundary region is also a question we should consider.

In the following 2 subsections, step model and boundary defect model will be discussed to attempt to relate the mobility to the movements of defects in grain boundaries.
2.3.2 Step Model

Professor Gleiter and his collaborators proposed a detailed atomistic model in which the effects of boundary structure are incorporated. In this model, boundary migration occurred by the movement of steps or kinks in the boundary, as shown in Figure 2.7. The existence of such steps was proved by Professor Gleiter’s group through transmission electron microscopy. By removal or addition of atoms from the steps, the steps move. And the atoms are assumed to diffuse for short distances within the grain boundary. According to this model they calculated the boundary velocity to be

\[ \nu = b \nu' \Psi \exp\left(-\frac{\Delta G^a}{kT}\right) \cdot \frac{P}{kT} \]  

(2.20)

where factor \( \Psi \) is a function containing details of the step configuration in a boundary of thickness \( \delta \), and \( \Psi \) is given by

\[ \Psi = \frac{c}{\delta} \left(1 + \frac{b}{\delta} \left(\frac{1}{f_1} - \frac{1}{f_2}\right)\right) \]  

(2.21)

where \( c \) is a constant and \( f_1 \) and \( f_2 \) are functions of the step density on the crystals either side of the boundary.

Figure 2.7 The ledge mechanism of boundary migration. An atom is detached from a kink in the ledge, migrates along the ledge and into the boundary [3].
2.3.3 Boundary Defect Model

There is a very close relationship between boundary steps and boundary dislocations, and in general, boundary dislocations have steps in their cores (see King and Smith 1980). The height of these steps depends on the Burgers vector of the dislocation, the boundary plane and the crystallography of the boundary. When such dislocations move, then the steps move and boundary migration inevitably occurs. The Figure 2.8 shows a 1/10 \text{<310>} dislocation in a boundary close to \Sigma = 5 in an fcc material.

![Figure 2.8 Atomic arrangement of a \Sigma = 5 tilt boundary in an fcc lattice which contains dislocations with Burgers vectors (a) parallel to the boundary or (b) inclined to the boundary [3].](image)

2.4 Measurement of Grain Boundary Mobility

There are two important methods used for measuring grain boundary mobility: the polycrystal and the bicrystal method. Each of these two methods has advantages and
disadvantages. In the next subsections, we will give a brief description of these two methods.

2.4.1 Bicrystal Methods

In a variety of bicrystal geometries, the driving force used for the grain boundary migration is the capillary. By bicrystal methods, reliable and reproducible physical data on grain boundary mobility can be obtained. A basic advantage of all techniques, which utilize the capillary driving force, is that the driving force is practically constant over a wide temperature range because the surface tension of a grain boundary depends only slightly on temperature. In Figure 2.9, various bicrystal arrangements designed to measure the grain boundary mobility are illustrated.

![Figure 2.9](image_url) Various boundary geometries in bicrystalline specimens for the study of grain boundary migration: (a) wedge technique; (b) reversed-capillary technique; (c) constant driving force technique (quarter-loop technique); (d) constant driving force technique (half-loop technique) [3].

In table 2.2 their main characteristics are listed for these boundary geometries.
Table 2.2 Characteristics of four bicrystal methods used in experiments for determining grain boundary mobility.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Driving Force</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>“wedge” bicrystal</td>
<td>Simple relation between driving force and the macroscopic grain dimension</td>
<td>In the beginning, the driving force is very small</td>
<td>$P = \frac{\sigma_b}{a}$ where $\sigma_b$ is the grain boundary surface energy, $a$ is radius of curvature</td>
<td>Study the mobility of pure tilt boundaries</td>
</tr>
<tr>
<td>reversed-capillary</td>
<td>1. manufacture and prepare specimens easily</td>
<td>The lack of steady-state motion of grain boundary</td>
<td>$P = \frac{\sigma_r f(\alpha)}{a}$ where $f(\alpha)$ is amplification factor</td>
<td>Investigate grain boundary migration in crystals</td>
</tr>
<tr>
<td>half-loop</td>
<td>steady-state motion of grain boundary</td>
<td>It may cause drag effects by the free surface</td>
<td>$P_{h.l.} = 2\sigma_b/a$</td>
<td>For true steady-state migration using capillarity driving forces</td>
</tr>
<tr>
<td>quarter-loop</td>
<td>steady-state motion of grain boundary</td>
<td>It may cause drag effects by the free surface</td>
<td>$P_{q.l.} = \sigma_b/a$</td>
<td>For true steady-state migration using capillarity driving forces</td>
</tr>
</tbody>
</table>

2.4.2 Polycrystal Methods

The ability of grain boundaries to move forms the basis for such important technological processes as recrystallization and grain growth. Thus, it seems natural to try to extract data on grain boundary motion, i.e. the grain boundary mobility, directly from the temporal evolution of grain size during recrystallization or grain growth in polycrystals. Indeed, this has been the case until recently. A large amount of data was collected over recent decades. However, although this approach might be very useful for some specific investigations it is not very efficient to solve the physical problem
underlying grain boundary migration. This is mainly because the method itself just “averages” the mobility over many differently migrating grain boundaries.

However, if the relationship between grain boundary mobility and its crystallography, the effect of temperature, pressure, and impurity content on the motion of specific grain boundaries, the mechanism of grain boundary migration and other fundamental aspects of grain boundary migration is given, polycrystal method is a good method to measure grain boundary mobility based on mean grain size data of polycrystals.
CHAPTER 3
THE MODEL AND SIMULATION METHODOLOGY

3.1 Molecular Dynamics Simulation of Grain Boundary Migration

3.1.1 Molecular Dynamics: Overview

Molecular dynamics simulation is a technique for computing the equilibrium and transport properties of a classical many-body system. The constraint is that the nuclear motion of the constituent particles obeys the laws of classical mechanics, and most notably Newton’s law:

\[ F_i = m_i a_i , \]

for each atom \( i \) in a system constituted by \( N \) atoms. Here, \( m_i \) is the atom mass, \( a_i = \frac{d^2 r_i}{dt^2} \) its acceleration, and \( F_i \) the force acting upon it, due to the interactions with other atoms. Therefore, molecular dynamics is a deterministic technique: given an initial set of positions and velocities, the subsequent time evolution is in principle completely determined.

Nowadays, MD simulation plays an essential role in scientific research. There are quite a few applications of molecular dynamics in different research areas. Generally, molecular dynamics can be applied in studies of defects, fracture, surfaces, biomolecules, and electronic properties and dynamics in materials science.

Admittedly, MD is a very powerful technique although it some limitations as well. The three most important limitations are: the use of classical forces (realism of the interatomic forces), the simulation time and the system size. One could ask how can we use Newton’s law to move atoms? It is known that the systems at the atomistic level obey quantum laws rather than classical laws, and that Schrödinger’s equation is the one to be
followed. Moreover, quantum effects become important in any system when the temperature is sufficiently low. Moreover, a question is frequently asked: how realistic is a molecular dynamics simulation?

In molecular dynamics, atoms interact with each other and they move under the action of these forces. As the atoms move, their relative positions change and the forces will change as well. The forces are usually obtained as the gradient of a potential energy function, depending on the positions of the particles. The realism of the simulation therefore depends on the ability of the potential chosen to reproduce the behavior of the material under the external conditions at which the simulation is run. Nowadays typical MD simulations can be performed on systems containing thousands or even millions of atoms, and for simulations times ranging from a few picoseconds to hundreds of nanoseconds. A simulation is reasonable when the simulation time is much longer than the relaxation time of the quantities we are interested in measuring. A limited system size can also constitute a problem. In this case, one has to compare the size of the MD cell with the correlation lengths of the spatial correlation functions of interest.

The structure flow chart of the MD program is shown in Figure 3.1.

3.2 Simulation Model

Next we present a novel methodology of measuring the grain boundary mobility and the activation energy of a curved boundary using a combined atomistic and mesoscopic simulation methodology on specifically tailored small microstructure.

To achieve a continuous grain growth and to minimize the number of different grain boundaries present we focused our study on the model system presented in Figure 3.2. In within the periodic boundary condition representation the simulation model
consists of two four-sided square grains and two-eight sided octagons. This octagon-square configuration, when replicated in $x$- and $y$-directions, represents a polycrystal with a bimodal grain-size distribution.

Figure 3.1 Flowchart of a typical molecular dynamics program.
By choosing the same orientation for the crystalline lattice of grains one and four, based on the system symmetry there are potentially only three different grain boundaries in this system. These are labeled $\gamma_{12}$, $\gamma_{13}$ and $\gamma_{23}$ in Figure 3.2. Moreover the value of the dihedral angle, $\beta$, has the same value for all four angles of the grain 1 (or grain 4) and is given by the Herring relation:

$$\beta = \arccos \left( \frac{\gamma_{23}^2 - \gamma_{12}^2 - \gamma_{13}^2}{2\gamma_{12}\gamma_{13}} \right)$$

Figure 3.2 The polycrystal simulation model consisting of two four-sided and two eight-sided grains.

One can simplify further the simulation model by choosing the orientations of grains 2 and 3 with respect to that of the central grain such that the misorientations, and therefore both grain boundary energy and mobility, have the same values for all four grain boundaries of the central grain. This seems to be a convenient choice since having the same grain boundary energy for all grain boundaries of the central grain will also
ensure that there would be no net cumulative torque acting on this grain and therefore no grain rotation, which, otherwise, is known to be a common phenomenon in nanocrystalline metals during grain growth. Such a highly symmetric configuration can be achieved, for example, by considering a <001> textured columnar microstructure and by appropriate choice of the crystalline in plane orientations of the four grains. If the orientations with respect to x-axis are: \( \theta_1 = \theta_4 = 22.5^\circ \), \( \theta_2 = 0^\circ \) and \( \theta_3 = 45^\circ \) there will be only two different grain boundaries in the system, i.e \( \gamma_{12} = \gamma_{13} = \gamma \). Accordingly, following the derivation of von Neumann-Mullins (vNM), one can write the relation for the rate of area change of the central four-sided grain:

\[
\frac{dA_4}{dt} = m\gamma \left[ 2\pi - 4(\pi - \beta) \right]
\]

(3.3)

which can be derived by considering a general value for the dihedral angle \( \beta \) as given by Equation (3.2) in which \( \gamma_{12} = \gamma_{13} = \gamma \) and \( \gamma \neq \gamma_{23} \). Obviously one can verify that if all grain boundaries are assumed identical, therefore \( \beta = 2\pi/3 \), Equation (3.3) leads to the same result as predicted by the classical von Neumann-Mullins relation,

\[
\frac{dA_n}{dt} = \frac{\pi m}{3} (n-6),
\]

(3.4)

which, for \( n=4 \), gives: \( \frac{dA_4}{dt} = -2\pi m/3 \). If a less symmetric grain orientations configuration is chosen then it becomes more difficult to write an analytical expression, similar to that given in Equation (3.3), for the rate of area change. It is therefore reasonable to extract this information using a numerical detailed description of grain boundaries migration in the framework of a mesoscopic simulation model.

For the given geometry and a particular choice of grains orientations the rate of area change of the four-sided grain can be estimated from atomistic molecular dynamics simulations. One can use further these results to extract the numerical factor coupling the rate of the area change to the reduced mobility \( M = m\gamma \). Finally by extracting explicitly the
value of grain boundary energy from the molecular dynamics simulations the absolute value of the grain boundary mobility is obtained.

To simulate grain growth at atomic level, molecular dynamics simulations were used where the only predefined input quantity is the interactive potential between individual atoms which, following Newtonian dynamics, defines their motion. Embedded-atoms-method (EAM) many body potential fitted to reproduce closely the elastic and thermodynamic properties of a perfect Pd crystal was applied. A textured or columnar microstructure model, representing the octagonal-square grains configuration discussed in the previous subsection (see Figure 3.3) was ideal for this study. Periodic boundary conditions in all three dimensions to mimic bulk conditions were used. While providing a fully three-dimensional treatment of the underlying physics, this model makes possible to simulate relatively large grains, because only a few lattice planes needed to be considered in the periodically repeated texture direction. The texture \( z \)-axis is along [001] crystallographic orientation. This made the model structurally similar to the molecular dynamics model used to study successfully grain growth and dynamic grain growth in a typical polycrystalline microstructure. This particular orientation also ensured that all grain boundaries between the grains in the system would be \(<001>\) tilt grain boundaries. This is very convenient because the energies of \(<001>\) tilt grain boundaries do not exhibit cusps for certain special misorientations.

In our model, the larger octagonal grains were misoriented on \( 45^0 \) with respect to each other, forming two \( 45^0 <001> \) symmetric tilt grain boundaries between them. The smaller square grains were misoriented at \( \pm 22.5^0 \) with respect to the two neighboring octagonal grains forming four \( 22.5^0 <001> \) asymmetric tilt grain boundaries. The energy
variation of a representative set of <001> tilt grain boundaries with misorientation angles in the range from 0 to 90° in a columnar molecular dynamics model of a typical polycrystalline microstructure represented by the same interatomic potential was reported by Haslam et al. (2001) (see Figure 3.4) [18]. The energy curve was found to reproduce well the empirical extension of the Read-Shockley equation for high angles:

\[ \gamma(\theta) = \sin(2\theta) \left[ \frac{E_c}{b} - \frac{E_s}{b} \ln(\sin(2\theta)) \right]. \]  

(3.5)

Here \(E_c\) and \(E_s\) are the dislocation-core and strain-field energies and \(b\) is the Burgers vector; the factor 2 multiplying \(\theta\) comes from the 90° rotation symmetry of the <001> axis. The values of the parameters \(E_c/b\) and \(E_s/b\), obtained by a least-square fit to the simulation data [18], were 1.01 J/m² and 0.70 J/m², respectively. According to this data,
the 22.5° and 45° <001> tilt grain boundaries in our octagon-square model are well in the region of high-angle grain boundaries where the energy reaches a plateau around 0.9-1.0 J/m². In that high-energy range it was found that grain boundaries show highly disordered uniform atomic structure and at elevated temperatures exhibit rather fast, liquid-like self diffusion.

The dimensions of the octagonal and square grains were defined by the length of their sides, initially set equal to $a = 20$ nm. The thickness of the system in the texture direction was set equal to 10(002) planes, resulting in a total thickness of 5 lattice parameters $a_0$, ($a_0 = 0.389$ nm at 0K ) i.e., about 3 times the cut-off radius, $R_c=1.35a_0$, of the interatomic potential used. Within these dimensions, the square grains contain initially around 64,000 atoms each and the octagonal grains contain around 245,000 atoms each and the simulation system contains a total of 618,000 atoms.

![Figure 3.4](image)

**Figure 3.4** Variation of the grain-boundary energy as a function of misorientation for <100> tilt boundaries in palladium [18].
The simulations were performed at zero pressure - constant temperature conditions using a combined Parrinello-Rahman, Nose-Hoover constant pressure – constant temperature technique. The grain growth in this model was studied at three elevated temperatures of 1150K, 1250K, 1350K and 1300K, while the melting point for this potential had been estimated at around 1500K.

To quantify the grain growth process a special procedure for automatic grain identification was developed and it will be presented in a separate section. The procedure used common-neighbor-analysis (CNA) technique to identify atoms in a crystalline state (fcc, for a perfect lattice, or hcp, in the case of stacking faults or twin boundaries). The atoms that have not been identified in fcc or hcp state are marked as disordered atoms and are assigned to grain boundaries. Using this grain-identification procedure the process of grain growth was monitored during the simulation by identifying the grains and counting their mass periodically in the course of the simulation.

3.3 Common Neighbor Analysis

In large molecular dynamics simulations, a common problem is to identify regions where something of interest is happening, that is identify the regions in which a different type of crystalline ordering develops during the simulation. For example, imagine a simulation of molten copper. As during the simulation the system cools slowly, one would like to find the first seed(s) of crystallization, as that will give a measure of the transition temperature. Such an identification process can be done using the common neighbor analysis method (CNA) [19].

CNA is a graph-analysis algorithm that can be used to label atoms so that they can be more readily identified as they begin to form crystals of various sorts. Unfortunately, it is
also very computationally expensive, so a parallel implementation is very useful. The steps for performing CNA on a discrete set of atomic data are as follows:

A. Compute the nearest neighbor graph of the atomic data. For a given radius $R_c$, two atoms $i$ and $j$ are considered to be neighbors if the distance between $i$ and $j$ is less than $R_c$. This computation yields a graph with vertex set $I=\{i\}$ and edge set $E = \{e_{ij} | i \text{ and } j \text{ are neighbors}\}$

B. For each edge $e_{ij}$ in $E$, compute the neighborhood $N_e$ by finding all vertices $k$ such that there is an edge from $i$ to $k$ in $E$ and an edge from $k$ to $j$ in $E$.

C. For the list of atoms in $N_e$ compute the number of edges between atoms in $N_e$ and the length of the longest path in $N_e$.

D. Label each edge by the triple (number of vertices in $N_e$, number of edges amongst vertices in $N_e$, length of longest path in $N_e$)

E. For each vertex (atom), label it by the signature of all of the edges.

F. Compute the nearest neighbor graph of the atomic data. For a given radius $R_c$, two atoms $i$ and $j$ are considered to be neighbors if the distance between $i$ and $j$ is less than $R_c$. This computation yields a graph with vertex set $I=\{i\}$ and edge set $E = \{e_{ij} | i \text{ and } j \text{ are neighbors}\}$

G. For each edge $e_{ij}$ in $E$, compute the neighborhood $N_e$ by finding all vertices $k$ such that there is an edge from $i$ to $k$ in $E$ and an edge from $k$ to $j$ in $E$.

H. For the list of atoms in $N_e$ compute the number of edges between atoms in $N_e$ and the length of the longest path in $N_e$.

I. Label each edge by the triple (number of vertices in $N_e$, number of edges amongst vertices in $N_e$, length of longest path in $N_e$)
J. For each vertex (atom), label it by the signature of all of the edges.

### 3.4 Grains Identification Method

In order to measure the rate of shrinkage of the central grain in our simulation system, we must be able to identify at every moment to which grain each atom belongs to. We address this issue by following the grain identification procedure developed by Zhang et al. [20]. This procedure allows us to determine the local orientation of the neighborhood of each atom with respect to an external frame of reference.

The following symmetry parameter for atom $i$ is employed:

$$ f_i = \frac{1}{n} \sum_{j \neq i} (3 - 4 \sin^2 \theta_j \sin^2 \theta_j) $$

where the sum is over the $n$ atoms within a distance of 1.2 $r_{nn}$ of atom $i$, where $r_{nn}$ is the spacing between nearest neighbors in the crystal at the temperature of interest. If we project the vector connecting atom $j$ with atom $j$ on to the X-Y plane, $\theta_j$ is the angle between this vector and the unit vector in the X-direction. A unique value of $f$ exists for each crystal orientation (modulo the rotational symmetry). Therefore, if the symmetry factor for atoms $i$, $f_i$, is closer to that of grain 1 than to that of grain 2, it is assigned to grain 1.

In our simulation system, there are two identical four-sided grains having the same crystalline orientation ($\theta_1 = \theta_4 = 22.5^\circ$; see Figure 3.3), and 2 eight-sided grains with different orientations ($\theta_2 = 0^\circ$ and $\theta_3 = 45^\circ$). Therefore, the symmetry factors for these three distinct orientations are: $f_1 = f_4 = 0.1666$ for the two four-sided grains (grains 1 and 2); $f_2 = 0.0$ for grain 2 and $f_3 = 0.3333$ for grain 3. Moreover, we should also mention that
all the atoms that have symmetry factors different from any of the three values mentioned above are assigned to grain boundaries (i.e. they are labeled grain boundary atoms).
CHAPTER 4

SIMULATION RESULTS

4.1 Test of the Grains Identification Method

In order to be able to quantify the time evolution of the simulation system one needs to be able to monitor the change in time of the grains sizes. We address this issue by implementing the grain identification procedure outlined in the previous section in a fortran code. Next we present a few snapshots documenting the accuracy of our grain identification procedure. We use for visualization the graphic software VMD (visual molecular dynamics) software that is available free of charge on the web (see: http://www.ks.uiuc.edu/Research/vmd/). Figures 4.1, 4.2, 4.3 and 4.4, show clearly using a color code how the atoms comprising the simulation system are sorted out based on the grains or the grain boundaries they belong to. We should mention (see Figure 4.1) that

Figure 4.1 The atoms comprising to the two four-sided grains (grain 1 and 2) as identified by our grain identification algorithm.
based on the symmetry factor alone as defined in equation (3.6) some of the atoms that clearly belong to grain boundaries might be assigned to certain grains. By combining the grain identification method with the common neighbor analysis (CNA) we were able the eliminate this ambiguity and eliminate from the already selected set of atoms belonging to a grain those that are located in a non-crystalline fcc environment; i.e. that atoms located in the grain boundaries or around some crystalline defects. In fact as can be seen from Figure 4.1 the central four-sided grain contains some sort of crystalline defects as those atoms were not selected by the grain identification procedure. Indeed as documented in figures 4.2, 4.3, and 4.4 the grain identification combined with the CNA procedure constitutes an efficient method for monitoring the polycrystal microstructure in our molecular dynamics simulation.

Figure 4.2 The atoms comprising the grains 1, 4 and 2 as selected by our grain identification procedure
4.2. Simulation Results of Grain Boundary Migration

In order to evaluate the activation energy for grain boundary migration we have performed the molecular dynamics simulations at three different temperatures. To speed up the simulations we have selected the following simulation temperatures \( T = 1150\text{K}, 1250\text{K}, \text{and} 1350\text{K} \) which are all relatively close to the melting point of Pd.

In the following 3 subsections, the system at these three temperatures will be introduced individually. In each subsection, 6 of over one hundred snapshots will be illustrated to give a visual description of microstructure evolution during grain boundary migration.

You also can make up a movie of all the snapshots by Microsoft Movie Maker software or other Movie Maker software.

**Figure 4.3** The atoms comprising all four grains of the simulation system as selected by our grain identification procedure
4.2.1 The System at 1150K

Figure 4.5 shows the initial structure of the simulation system (just shortly after 12 ps simulation time). The microstructure is clearly highlighted by the grain boundary atoms that are represented in blue.

At 1150 K the molecular dynamics simulation was carried on for 4.2 ns. Indeed as expected the evolution the four sided grains shrink while the eight sided ones grow. Figures 4.6 give a set of snapshots of the evolving system.

As shown previously (see Equation (3.3)) one can relate the area change of the four-sided grains to the product of grain boundary energy $\gamma$, and mobility, $m$, characterizing the four boundaries delimiting the four-sided grains. Moreover by
knowing that all of these four boundaries have the same misorientation \( \theta = 22.5^\circ \) by using the previously reported grain boundary energy misorientation relationship in Pd (see Equation 3.5 and Figure 3.4) one can extract the value of \( \gamma = 0.856 \text{ J/m}^2 \). Moreover we can also relate the rate of area change, \( dA_4/dt \), of the four-sided grains to the rate of change of the their number of atoms, \( dN_4/dt \). That is, one can write:

\[
\frac{dN_4}{dt} = \frac{d}{dt} \left( \frac{h_z A_4}{\Omega} \right) = \frac{h_z}{\Omega} \frac{dA_4}{dt},
\]

where \( h_z \) is the thickness of the slab along \( z \)-direction and \( \Omega \) is the atomic volume. Knowing the values of all the grain boundary energies allows to also determine the value of the dihedral angle, \( \beta = 107^\circ \), which when introduced in Equation (3.3) yields:

\[
\frac{dA_4}{dt} = m \gamma \left[ 2\pi - 4(\pi - \beta) \right] = -Cm \gamma
\]

\( (4.2) \)

**Figure 4.5** A snapshot the initial square-octagon system after 12ps. The atoms represented in blue are located in the grain boundary region.
Figure 4.6 Six snapshots of the evolving system at 1150K
with the value of the dimensionless constant $C = 1.25$.

Combining relation (4.1) and (4.2) yields an expression for the grain boundary mobility:

$$m = -\frac{\Omega}{C\gamma h_z} \frac{dN_4}{dt}.$$  \hfill (4.3)

Figure 4.7 gives the time evolution of the number of atoms per grain. Obviously the slope of change of the number of atom in a four sided grain can be related directly to the mobility of the grain boundary via relation (4.3). From this simulation data we extract $dN_4/dt = 7227$ atoms/ns which in turn yields a grain boundary mobility $m = 1.75 \times 10^{-7}$ $m^4/Js$.

![Figure 4.7](image)

**Figure 4.7** Time variation of the total number of atoms belonging to the grains comprising the simulation microstructure at 1150K.
4.2.2 The System at 1250K

Figures 4.8 show the time evolution of the simulation system at 1250K.

Figure 4.8 Six snapshots of the evolving system at 1250K

Time evolution of the number atoms in each grain is represented in Figure 4.9.
Figure 4.9 shows the time evolution of the number of atoms belonging to the four grains at 1250K. One can clearly see that the volume of the four-sided grains decreases in time. Moreover, at this temperature the rate of grain size change, expressed in number of atoms lost per unit time, is $\frac{dN_4}{dt} = 12634$ atoms/ns. The corresponding grain boundary mobility is $m = 3.05 \times 10^{-7}$ m$^4$/Js.

4.2.3 The System at 1350K

Figures 4.10 show the time evolution of the simulation system at 1350K. Figure 4.11 shows the time evolution of the number of atoms belonging to the four grains at 1250K. One can clearly see that the volume of the four-sided grains decreases in time. Moreover, at this temperature the rate of grain size change, expressed in number of atoms lost per unit time, is $\frac{dN_4}{dt} = 12634$ atoms/ns. The corresponding grain boundary mobility is $m = 3.05 \times 10^{-7}$ m$^4$/Js.
time. Moreover, at this temperature the rate of grain size change, expressed in number of atoms lost per unit time, is $\frac{dN}{dt} = 21054$ atoms/ns. The corresponding grain boundary mobility is $m = 5.09 \times 10^{-7}$ m$^4$/Js.

**Figure 4.10** Six snapshots of the evolving system at 1350K
Temperature Effect on Grain Boundary Mobility

One can infer the temperature dependence of the grain boundary mobility by analyzing the results of the simulations at various temperatures. These are summarized in Figure 4.12 which, for reference and comparison, shows the time evolution of the number of atoms in the two four-sided grains at temperatures $T=1150\text{K}$, $1250\text{K}$ and $1350\text{K}$ and in Table 4.1 which gives the corresponding values of the calculated grain boundary mobilities.

Our simulation results are clearly in line with the theoretical prediction outlined in Chapter 1 (see Equation 1.3) according to which one would expect a strong temperature

---

**Figure 4.11** Time variation of the total number of atoms belonging to the grains comprising the simulation microstructure at 1350K.
dependence of the grain boundary mobility consistent with an Arrhenius relation

\[ m = m_0 \exp(-E_{GB} / k_B T) \]

in which \( E_{GB} \) is the activation energy for boundary migration.

**Figure 4.12** Time variation of the total number of atoms in the two four-sided grains at three different temperatures

**Table 4.1** Grain boundary mobilities of the <100> tilt boundary at three different temperatures.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( m \times 10^{-7} \text{ m}^4/\text{Js} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>1.75</td>
</tr>
<tr>
<td>1250</td>
<td>3.05</td>
</tr>
<tr>
<td>1350</td>
<td>5.09</td>
</tr>
</tbody>
</table>
Indeed from the ln(m) vs. 1/T plot (see Figure 4.13) we were able to extract the activation energy for the migration of a $<110>$ tilt grain boundary in a specifically tailored Pd microstructure. The activation energy obtained is $E_{\text{GB}} = 0.60$ eV.

Figure 4.13 The Arrhenius plot of the temperature dependence of the grain boundary mobility.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Our work shows that by using a specifically tailored columnar nanocrystalline microstructure one can determine via molecular dynamics the mobility of a <100> tilt grain boundary. In summary the study suggests the following:

a) the grain boundary mobility can be obtained from a molecular dynamics study by following in time the rate of area shrinkage of a four-sided grain in a square-octagon simulation system.

b) by carrying on the simulations at different temperatures one can use this simulation model to extract the activation energy for grain boundary migration. For the <100> tilt grain boundary in palladium we obtained the activation energy obtained in our studies is $E_{GB}=0.60\text{eV}$. This is very close to the activation energy for grain boundary migration in Pd (~0.58eV).

c) our molecular dynamics simulations show the validity of von Neumann relation, according to which grains that have less than six sides will shrink, and those which have more than six sides will grow.

An important future study would be to develop atomistic models that would allow the study of the mobility of the triple junctions in a polycrystalline structures.
REFERENCES


4. J.E. Burke and D. Turnbull, Progress in Metal Physics, 3 (1952) 220


VITA

Shengyu Wang was born in Jinzhou, Liaoning, China, on 25th May, 1977. She got her primary education at her home town Beining. After finishing her high school studies, she took the most rigorous competitive college entrance examinations in 1994. After qualifying in this examination she got admission to the Department of Materials Physics, University of Science and Technology Beijing. She received her Bachelor of Engineering degree in Materials Physics from this University in 1998. She came to the United States for her higher studies in August, 2003, and joined the graduate program in Mechanical Engineering at Louisiana State University (LSU), Baton Rouge, Louisiana, in Fall 2003. She is a candidate for the degree of Master of Science in Mechanical Engineering to be awarded during the commencement of May, 2006. Currently, she is pursuing her doctoral degree in Department of Materials Science and Engineering at Carnegie Mellon University, Pittsburgh, Pennsylvania.