CONTENTS

LIST OF FIGURES
LIST OF TABLES
1. INTRODUCTION 10
1.1 Dislocation nucleation as stress mediated thermally activated transition 10
1.2 Homogeneous Dislocation Nucleation
1.3 Research objectives and construction of this thesis
1.3.1 Homogeneous dislocation: Comparison between Si, Cu, and Mo 16
1.3.2 Homogeneous dislocation nucleation: Comparison with Peierls-Nabarro (PN)
model results
1.3.3 Link between homogeneous and heterogeneous dislocation nucleation 18
1.3.4 The shuffle-glide controversy in silicon
1.4 Arrangement of this document
References
2. METHOD
2.1 Introduction
2.2 Classical molecular dynamics
2.2.1 Periodic boundary conditions
2.2.2 Book keeping and its acceleration technique
2.2.3 Equations of motion
2.2.4 Non-dimensional units
2.3 The Nudged Elastic Band (NEB) Method
2.3.1 Climbing image Nudged Elastic Band Method
2.3.2 Free End Nudged Elastic Band Method 38
2.3.3 Preparation of intermediate images
2.4 Conjugate gradient relaxation
2.5 About empirical inter-atomic potentials
2.6 About stress application
2.7 About visualization
2.8 Summary
References

3. MODELS AND RESULTS 4	18
3.1 Introduction	18
3.2 Shuffle-set homogeneous dislocation nucleation in Si 4	19
3.2.1 Model	19
3.2.2 Results: Activation energy and saddle point configurations	19
3.2.3 Results: Maximum inelastic displacement	53
3.3 Glide-set homogeneous dislocation nucleation in Si	54
3.3.1 Model	54
3.3.2 Results: Activation energies and saddle-point configurations	54
3.3.3 Results: Maximum inelastic displacement	58
3.4 Dislocation nucleation in Cu	59
3.4.1 Model	59
3.4.2 Results: Activation energies and saddle-point configurations	59
3.4.3 Results: Maximum inelastic displacement	54
3.5 Homogeneous dislocation nucleation in Mo	55
3.5.1 Model	55
3.5.2 Results: Activation energies and saddle-point configurations	55
3.5.3 Results: Maximum inelastic displacement7	71
3.6 Summary	12
References	73
4. COMPARISON BETWEEN Si, Cu and Mo 7	15
4.1 Introduction	15
4.2 Activation energy	/6
4.3 Mechanics of the saddle-point configurations	78
4.4 Activation volume	32
4.5 Link between homogeneous and heterogeneous dislocation nucleation	37
4.5.1 Comparison with heterogeneous system 1: Dislocation nucleation from the	
corner of a Cu nanopillar	37
4.5.2 Comparison with heterogeneous system 2: Dislocation nucleation from a	
sharp corner in Si)2
4.5.3 Homogeneous versus heterogeneous dislocation nucleation: Discussion 9) 5
4.6 Ideal strength	98
4.7 Conclusions) 9
References)1

5. COMPARISON WITH PN BASED RESULTS	104	
5.1 Introduction	104	
5.2 Information not handled by PN based models	105	
5.2.1 Actual direction of slip	105	
5.2.2 Extra slip-plane displacements	106	
5.2.3 True dislocation core shapes	107	
5.3 Information handled by PN based models	108	
5.3.1 Activation energy	108	
5.3.2 Inelastic displacements	110	
5.4 Conclusions	112	
References	113	
6. THE SHUFFLE-GLIDE CONTROVERSY IN Si	115	
6.1 Introduction	115	
6.2 Minimum energy paths: Nucleation and mobility		
6.3 Activation energy curves	117	
6.4 Mechanics of the saddle-point configurations	118	
6.5 Activation volumes	120	
6.6 In-plane direction of atomic slip	122	
6.7 Comparison with heterogeneous system: Shuffle-glide controversy for dislocation	n	
nucleation from a sharp corner		
6.8 Conclusions	124	
References	126	
7. CONCLUSIONS AND FUTURE DIRECTIONS	128	
7.1 Conclusions	129	
7.2 Future directions	131	
7.2.1 Other crystal structures	131	
7.2.2 Comparison with other heterogeneous systems	132	
7.2.3 Adaptive hyperdynamics applied to homogeneous dislocation nucleation.	133	
References	135	
Academic activities related to this thesis	136	
Academic activities not related to this thesis	137	
Acknowledgments	138	

LIST OF FIGURES

Figure 1-1 Time-scale (strain-rate) problem in MD simulation. MD, like DFT, cannot approach the experimental region of interest.

Figure 1-2 Schematic illustration of stress mediated thermally activated transitions.

Figure 1-3 Three representative materials that form the subject of this study, namely, comparison of homogeneous dislocation nucleation across materials of different crystal structures: Body-centered cubic Mo (left), face-centered cubic Cu (middle) and Diamond-cubic Si (right).

Figure 1-4 Glide-set and shuffle-set dislocations in Si.

Figure 2-1 Periodic boundary conditions. Surface effects are removed by using image cells containing the identical information as the original unit cell.

Figure 2-2 Efficient book-keeping techniques (left) and 2D outline of the domain subdivision algorithm for book-keeping (right).

Figure 2-3 The Nudged elastic band method. The energy difference between the initial configuration and the saddle-point configuration (corresponding to the highest point on the minimum energy path) is the activation energy input required to affect the transition.

Figure 2-4 Unit cell under shear strain. Under shear stress application, the direction of application of the periodic boundary conditions becomes complex. That is averted with the aid of the transformation matrix.

Figure 3-1 Simulation model for homogeneous dislocation nucleation of the shuffle-set in Si. The slip plane and the direction of the Burgers vector are shown.

Figure 3-2 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of <110>{111} resolved shear stress values for homogeneous dislocation loop nucleation of the shuffle-set in Si.

Figure 3-3 Shear stress dependence of activation energy for nucleation of the shuffle-set dislocation in Si. The slip system is $<110>\{111\}$ for perfect dislocations

Figure 3-4 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the perfect Burgers vector for shuffle-set homogeneous dislocation nucleation in Si.

Figure 3-5 Simulation model for homogeneous dislocation nucleation of the glide-set in Si. The slip plane and the direction of the Burgers vector are shown.

Figure 3-6 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of <112>{111} resolved shear stress values for homogeneous dislocation loop nucleation of the glide-set in Si.

Figure 3-7 Shear stress dependence of activation energy for nucleation of the glide-set dislocation in Si. The slip system is $<112>\{111\}$ for partial dislocations.

Figure 3-8 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the partial Burgers vector for glide-set homogeneous dislocation nucleation in Si.

Figure 3-9 Simulation model for homogeneous dislocation nucleation in Cu. The slip plane and the direction of the Burgers vector are shown.

Figure 3-10 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous partial dislocation loop nucleation in Cu.

Figure 3-11 Shear stress dependence of activation energy for homogeneous dislocation nucleation in Cu. The slip system is $<112>\{111\}$ for partial dislocations.

Figure 3-12 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the partial Burgers vector for homogeneous dislocation nucleation in Cu.

Figure 3-13 Simulation model for homogeneous dislocation nucleation in Mo. The slip plane and the direction of the Burgers vector are shown.

Figure 3-14 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<111>\{110\}$ shear stress values for homogeneous dislocation loop nucleation in Mo.

Figure 3-15 Shear stress dependence of activation energy for homogeneous dislocation nucleation in Mo. The slip system is $<111>\{110\}$ for perfect dislocations.

Figure 3-16 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the perfect Burgers vector for homogeneous dislocation nucleation in Mo.

Figure 4-1 Dependence of activation energy on (a) Resolved shear stress, and (b) Resolved shear stress normalized by respective critical stresses, for homogeneous dislocation nucleation in Cu, Si and Mo.

Figure 4-2 Saddle-point configurations corresponding to a series of resolved shear stress values for homogeneous dislocation nucleation in Si.

Figure 4-3 Saddle-point configurations corresponding to a series of resolved shear stress values for homogeneous dislocation nucleation in Cu.

Figure 4-4 Saddle-point configurations corresponding to a series of resolved shear stress values for homogeneous dislocation nucleation in Mo.

Figure 4-5 The difference of Peierls barriers: Low Peierls barrier (right) in Cu and Mo results in elliptical dislocation cores, while high Peierls barrier (left) in Si results in hexagonal shape of the dislocation cores.

Figure 4-6 Comparison of the shear stress dependence of the maximum inelastic displacement for homogeneous dislocation nucleation in Si, Cu, and Mo. The displacements have been normalized by the Burgers vectors for the respective materials.

Figure 4-7 Diffused dislocation core (red curve) and dislocation core assumed in the classical dislocation theory (black rectangle).

Figure 4-8 Directions of the in-plane atomic displacements for homogeneous dislocation nucleation in Si (left), Cu (middle), and Mo (right). The directions of the respective Burgers vectors are also indicated (black arrows).

Figure 4-9 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation in Cu. The structural definition and the thermodynamic definition are in good agreement.

Figure 4-10 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation in Si. The structural definition gives quite low values as compared to the thermodynamic definition.

Figure 4-11 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation in Mo. The discrepancy between the structural definition and the thermodynamic definition increases with decreasing stress.

Figure 4-12 Extra slip-plane displacements of atoms in Si (left), Cu (left) and Mo (right), and Si (right) for homogeneous dislocation nucleation. Only atoms with displacement in the Burgers vector direction exceeding 0.15Å are shown.

Figure 4-13 Dislocation nucleation from the corner of a Cu nanopillar under compression (Fig. 3(a) in Ref. [19]).

Figure 4-14 Activation energy for homogeneous dislocation nucleation and dislocation nucleation from the corner of a nanopillar under compression in Cu: (a) Resolved shear stress dependence, (b) Normalized resolved shear stress dependence.

Figure 4-15 Saddle point configurations for (a) dislocation nucleation from the corner of a nanopillar under compression and (b) homogeneous dislocation nucleation in Cu.

Figure 4-16 Activation volumes for heterogeneous and homogeneous dislocation nucleation in Cu.

Figure 4-17 Dislocation nucleation from a sharp corner in Si (Fig. 1 in Ref. [20]).

Figure 4-18 Activation energy for homogeneous dislocation nucleation and dislocation nucleation from a sharp corner in Si: (a) Resolved shear stress dependence, (b) Normalized resolved shear stress dependence.

Figure 4-19 Saddle point configurations for (a) dislocation nucleation from the corner of a nanopillar under compression and (b) homogeneous dislocation nucleation in Si.

Figure 4-20 Activation volumes for heterogeneous and homogeneous dislocation nucleation in Si.

Figure 5-1 Directions of the in-plane atomic displacements for homogeneous dislocation nucleation in Si (left), Cu (middle), and Mo (right). The directions of the respective Burgers vectors are also indicated (red arrows). (Reproduced from Chapter 4.)

Figure 5-2 Extra slip-plane displacements of atoms in Si (left), Cu (middle) and Mo (right). Only atoms with displacements > 0.15Å are shown. (Reproduced from Chapter 4.)

Figure 5-3 Dislocation loop from PN results (Fig. 3 from Ref. [5]).

Figure 5-4 Shapes of the dislocation cores: Si (left), Cu (middle), and Mo (right). The directions of the respective Burgers vectors are also indicated.

Figure 5-5 Stress dependence of activation energy reported by PN model (Fig. 4 from Ref. [5]).

Figure 5-6 Atomistic results for stress dependence of activation energy for homogeneous dislocation nucleation in Si, Cu and Mo.

Figure 5-7 Stress dependence of inelastic displacement reported by PN based study (Fig. 2(a) from Ref. [5]).

Figure 5-8 Atomistic results for stress dependence of the maximum inelastic displacement for homogeneous dislocation nucleation in Cu and Si.

Figure 6-1 Typical curve of the configuration energy for a series of images along the minimum energy path for homogeneous dislocation loop nucleation of the shuffle-set (part of Figure 3-2 reproduced).

Figure 6-2 Typical curve of the configuration energy for a series of images along the minimum energy path for homogeneous dislocation loop nucleation of the glide-set (part of Figure 3-6 reproduced).

Figure 6-3 Shear-stress dependence of the activation energy for glide-set and shuffle-set homogeneous dislocation nucleation in perfect crystal Si.

Figure 6-4 Slip vector representation of saddle-point configurations for (a) shuffle-set, and (b) glide-set homogeneous dislocation nucleation (b_S =3.84Å, and b_G =2.22Å) in Si. The directions of the respective Burgers vectors are shown.

Figure 6-5 Shear-stress dependence of the maximum slip vector for glide-set and shuffle-set homogeneous dislocation nucleation (normalized by their respective Burgers vectors) in Si.

Figure 6-6 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation of the shuffle-set and the glide-set. The structural definition gives quite low values as compared to the thermodynamic definition for the shuffle-set whereas the discrepancy is not that significant in case of the glide-set.

Figure 6-7 Extra slip-plane displacements of atoms. Only atoms with displacements greater than 0.15Å are shown. Glide-set (left) and shuffle-set (right).

Figure 6-8 Directions of the in-plane atomic displacements for homogeneous dislocation nucleation of the shuffle-set (left) and glide-set (right). The directions of the respective Burgers vectors are also indicated (black arrows).

Figure 6-9 Dislocation nucleation from a sharp corner in Si (Fig. 1 in Ref. [17]).

Figure 6-10 Shuffle-glide transition for dislocation nucleation from a sharp corner in Si (Fig. 2 in Ref. [17]).

LIST OF TABLES

- Table 1-1
 Glide-set dislocation and shuffle-set dislocation
- Table 2-1
 Non-dimensional parameters for atomistic calculations
- **Table 4-1**Data relevant to dislocations in Cu, Si and Mo
- **Table 4-2** Physical properties of Mo, Si and Cu relevant to dislocations
- **Table 4-3**Comparison of activation volumes
- **Table 4-4**Ideal strengths of Si, Cu and Mo
- **Table 5-1**Activation energy comparison for 60% of critical stress
- Table 5-2
 Comparison of maximum inelastic displacement for 60% of critical stress

1. INTRODUCTION

All solids have an elastic limit beyond which their behavior changes in different ways depending on the material they are made of. Brittle materials fracture—either suddenly or progressively—while ductile materials undergo plastic deformation to differing degrees. This elastic limit is governed by dislocation nucleation inside the crystal. Nucleation, along with mobility of dislocations, therefore plays an important role in the critical mechanical properties of strength and deformation of solid materials.

Because dislocations are by definition atomistic in nature [1-3], they can be best understood through atomistic studies. The fundamental theoretical work on dislocations, however, was for the most part done before researchers had access to atomic scale information from microscopy or atomistic simulations. In this sense it was out of the direct purview of material scientists for a long time. With the amazing progress in numerical computational resources in recent years however, a number of atomistic calculations have begun to elucidate the phenomenon of dislocation nucleation.

1.1 Dislocation nucleation as a stress-mediated thermally-activated transition

Atomistic simulation techniques have been extensively employed in the past in order to study the deformation of materials [4–17]. Molecular dynamics (MD), which can be

used to probe the time-dependent evolution of an atomistic system driven by an applied stress or strain state [18], has been the major atomistic technique used. However, the need to keep track of all the atoms all the time severely limits the time horizon of MD simulations. Stable and accurate numerical integration of the MD equations of motion requires a very small time-step. In MD simulation of solids, in order to keep track of the atomic vibrations the integration step is usually of the order of one femtosecond (10^{-15} s). For this reason the time horizon of MD simulations of solids rarely exceeds one nanosecond (10^{-9} s). This constraint constitutes a severe limitation to the total time that can be feasibly simulated by MD using currently available computational resources. On the other hand, dislocation behaviors of interest typically occur on time scales of milliseconds (10^{-3} s) or longer. Such behaviors therefore remain out of reach of direct MD simulations. Therefore, the deformation studies are limited to extremely high strain rates—on the order of 1×10^8 s⁻¹ at the lowest [10,19].

As a result of these high strain rates forced on MD simulations, the stress driving the formation and propagation of defects typically meets or exceeds the athermal stress at which the processes are expected to occur spontaneously. The same limitation holds for density functional theory (DFT) calculations [20,21] carried out for ideal strength, in that they inevitably give information about strain-rate region that is far removed from the experimental strain range. The gap between typical experimental strain rates and strain rates available to MD and DFT is shown in Figure 1-1. The stress dependence of activation energy for the two transitions shown in Figure 1-1 follow different curves, which is a matter concerning activation volume (described in section 1.3.1). While MD or DFT calculations can give information about athermal stress, they are silent when it comes to information about activation energies required for stresses in the experimental stress regime. Secondly, due to extremely high strain-rates near the athermal threshold, there is a high probability of many complex phenomena occurring simultaneously so it is very difficult to isolate the transition of interest. To find out what is happening in the experimental stress regime is a matter of great interest and utility to engineers and materials scientists.

Dislocation nucleation is a typical stress-mediated, thermally activated transition. Consider a system at equilibrium under applied shear stress, τ , which sits at a

local minimum in the potential energy landscape. The situation at $\tau = 0$ is shown schematically in Figure 1-2 (a). The system requires overcoming the energetic barrier in order for it to transform to another configuration, which is energetically unfavorable, being an unstable configuration as compared to the original configuration. For the system to overcome this barrier, it requires input of activation energy in the form of thermal fluctuations.

When a shear stress is imposed on the system, the potential energy landscape shifts (Figure 1-2 (b)) and the energetic barrier becomes lower and lower as the shear stress increases. Finally, at the athermal stress, $\tau = \tau_{ath}$ in (Figure 1-2 (c)), the activation barrier for the transition disappears altogether. When that happens, the initial configuration becomes unstable and any small perturbation of the system will cause immediate transition.



Figure 1-1 Time-scale (strain-rate) problem in MD simulation: MD, like DFT, cannot approach the experimental region of interest.

If the transition in question is dislocation nucleation, the perfect crystalline lattice becomes mechanically unstable and a dislocation forms spontaneously at this critical stress. For any stress below τ_{ath} , the activation energy Q can be defined as the difference between the energy of the local initial equilibrium configuration and the maximum energy for the transition that must be overcome to complete the transition, which occurs at the energy peak in the 3N dimensional space, called the saddle point configuration. In general a range of stresses lower that the athermal stress exists for which the transition is feasible but requires the application of some thermal energy input to overcome the activation barrier. Increase of temperature therefore has a lowering effect on the strength of a material because thermal fluctuations allow dislocation nucleation to happen at lower and lower stresses as the temperature goes up.



Figure 1-2 Schematic illustration of stress mediated thermally activated transitions.

The effect of temperature on dislocation nucleation can be studied theoretically at three different levels [22]: the continuum based analysis based on the Volterra model of dislocation line [1,23], the Peierls concept of a periodic stress–displacement relation across the slip plane [24–28], and direct atomistic simulation [29]. Although the first two approaches provide a rough basis for understanding the nucleation stress as a function of geometrical and material parameters, dislocation nucleation being an atomistic and highly non-linear phenomenon warrants the atomistic analysis for quantitative predictions.

The need for atomistic analysis of dislocation nucleation along with the inability of MD to approach the experimental strain-rates involved in the process have prompted researchers to look elsewhere for atomistic treatment of the phenomenon. Treating dislocation nucleation as a stress-mediated, thermally activated process [30], a number of works based on the framework of reaction pathway sampling have been reported in recent years: work on dislocation nucleation from a sharp corner in Si [31,32], from a surface step in Ni [33], from a crack tip [34] in Cu, and from the corner of a nanowire [35] in Cu, and homogeneous dislocation nucleation [36] in Cu, to name a few. All these works report the minimum energy path (MEP) for the transition in question; the highest point on this MEP, called the saddle point; and the activation energy—which is the difference in energy between the saddle point and the original configuration—required for the transition to occur.

All these works, with the exception of the last one [36], while atomistic in nature, deal only with heterogeneous systems. The problem with heterogeneous systems is that because the results are subject to influence by the complex effects originating from heterogeneities such as stress fields, surfaces, and other defects, the phenomenon of dislocation nucleation cannot be studied at a fundamental level. Also, the activation energies reported in such studies are presented as a function of nominal stresses, whereas the actual stresses at the dislocation core are much higher because of the presence of heterogeneities. The motivation behind establishing a coherent methodology for predicting the favorability conditions for dislocation nucleation is that once it is achieved, the nucleated dislocation can be handed over to continuum based approaches such as Dislocation Dynamics (DD), which specialize in dealing with the mobility of dislocations, for application in the field of semiconductor and MEMS design.

The activation energies reported as a result of application of reaction pathway sampling methods are connected to the macroscopic behavior of the material through the transition state theory (TST) expression [37]:

$$R = v_{MEP} \exp\left[\frac{-Q(\sigma, T)}{k_{B}T}\right]$$
(1.1)

where *R* is the temperature (*T*) and stress (σ) dependent success rate of the transition, v_{MEP} is the trial frequency along the MEP for the transition, and k_B is the Boltzmann constant. Once the activation energy for a transition can be determined, that information can be used to find out macroscopic information of nucleation rate.

1.2 Homogeneous Dislocation Nucleation

While there are an infinite number of scenarios for heterogeneous dislocation nucleation in crystalline materials, homogeneous dislocation nucleation is the simplest scenario of dislocation nucleation, and is of great academic interest to the materials scientists and engineers in terms of the insight it can provide into the phenomenon of dislocation nucleation at the most fundamental level. The transition of dislocation nucleation cannot be studied at a fundamental level while focusing on inhomogeneous systems because the results are subject to influence by complex effects originating from heterogeneities such as stress fields, surfaces, interfaces, and other defects, which distort the physical picture. Also, the activation energies reported in such studies are presented as functions of nominal stresses, whereas the actual stresses at the dislocation core are much higher than those reported because of the presence of heterogeneities. In this study, we focus on a homogeneous crystal and this allows us to examine the problem at a fundamental level, where complex surface and stress concentration effects are not allowed to distort the physical picture.

Homogeneous dislocation nucleation in a bulk perfect crystal has been observed in experiments of atomic model systems of bulb raft [38] and colloidal crystal [39–41]. Homogeneous dislocation nucleation has also assumed great importance in view of the recent focus on nanoindentation as a means [42–44] of ascertaining the onset of plasticity in crystals. Also, recently there has been experimental evidence [45] of homogeneous dislocation nucleation in MEMS devices. This is significant, considering the implications [46,47] for MEMS devices. Unlike macro-sized specimens, where dislocations invariably nucleate from the surface because of the inherent surface roughness; in nano-sized specimen (as found in nanoindentation and MEMS devices), the smooth surfaces result in higher probabilities of homogeneous dislocations nucleating from the interior regions of the material.

Finally, homogeneous dislocation nucleation is significant because of its close relationship with the ideal strength of materials. The ideal strength is an important parameter for understanding deformation mechanisms of materials. This ideal strength is closely related to the stress required for spontaneous homogeneous dislocation nucleation, i.e., the critical resolved shear stress for dislocation nucleation in a perfect, faultless crystal [48,49].

1.3 Research objectives and construction of this thesis

The objective of this research is to study homogeneous dislocation nucleation in solids in the framework of reaction pathway sampling, with a view to observe the influence of crystal structure on this important transition. This study aims to improve understanding of four major areas of interest to the material scientists and engineers. These areas of interest are as follows:

1.3.1 Homogeneous dislocation: Comparison between Si, Cu, and Mo

The first objective of this research is to compare three representative materials, one each for diamond crystal, face-centered cubic and body-centered cubic materials. Si, Cu, and Mo respectively have been chosen for that purpose (Figure 1-3).

Although many works in the framework of reaction pathway analysis on FCC and DC materials have been reported in the past [27–34], they all deal with heterogeneous systems. In BCC materials, no such past work exists. In this research homogeneous dislocation nucleation in Cu [36] is reproduced and compared with original results of homogeneous dislocation nucleation in Mo and Si. Attention is mainly focused on the activation energy, activation volume, and the mechanics of the saddle point configurations for dislocation nucleation in the three materials. Special focus is placed on activation volume because it is inversely proportional to the strain rate sensitivity for a macroscopic sample, and hence it can be measured experimentally [50]. This is of great significance because activation volume is very closely related to activation energy, which cannot be determined experimentally and therefore activation volume is crucial for linking atomistic simulations to experiments.

Furthermore, the importance of activation volume lies in another practical concern. Although with atomistic calculations one can compute the activation energy for a thermally activated transition, there is a practical limit to the number of calculations being carried out. Since one can only perform a finite number of calculations, it is very important to have a physically sound functional form for activation energy in order to interpolate the data. The activation volume is defined as the stress derivative of the activation energy (refer to chapter 4). Activation volume is a very important quantity to compute [29], because once the activation energy and activation volume at a reference load $\sigma=\sigma_0$ is known, activation energy and therefore nucleation rates at loads not too far from σ_0 can be predicted [30] by employing the Taylor expansion. Therefore one set of calculations can yield activation parameters for points that are not separated too far from the reference point, resulting in enormous

reduction of calculation costs. On an intuitive level, the higher the activation volume, the more "collective" a transition is, that is, more volume of material is involved in the transition. Estimates of activation volume for different processes are $0.02b^3$ to $0.1b^3$ for activated vacancy hops [30], $3b^3$ to $10b^3$ for thermally activated dislocation emission [50], and $1000b^3$ for thermally activated forest dislocation cutting [30], where *b* is the Burgers vector.



Figure 1-3 Three representative materials that form the subject of this study, namely, comparison of homogeneous dislocation nucleation across materials of different crystal structures: Body-centered cubic Mo (left), face-centered cubic Cu (middle) and diamond-cubic Si (right).

One aim of this research is to highlight the differences in the homogeneous dislocation phenomena in the three materials, caused by the different lattice structures and bonding types of the individual materials.

1.3.2 Homogeneous dislocation nucleation: Comparison with Peierls-Nabarro (PN) model results

Treating dislocation behavior as a continuum phenomenon makes it possible to consider dislocations on length and time scales well beyond the reach of atomistic simulations. The Peierls-Nabarro (PN) model [24–28] is a hybrid continuum-atomistic approach that seeks to retain the analytical nature of the continuum theory for the long-range elastic fields but also endeavors to captures the essential non-linear effects in the atomic core. Out of all methodologies that are not fully atomistic in nature, the PN model is closest

to the atomistic models. Viewing the host crystal as an elastic continuum, the linear elasticity theory of dislocations offers a variety of useful analytical and numerical solutions that are no longer subject to constraints of time or length scale. Although quite accurate far away from the dislocation center, where the lattice distortions remain small; continuum theory breaks down near the dislocation center, where lattice discreteness and non-linearity of atomic interactions become important.

Atomistic results obtained in this research are compared with predictions made by PN based models [28] for homogeneous dislocation nucleation, with an aim to highlight the limitations of the PN model in terms of information acquired.

1.3.3 Link between homogeneous and heterogeneous dislocation nucleation

It is of significant interest to find out the link between the generally, but not always, ideal case of homogeneous dislocation nucleation with the more common cases of heterogeneous dislocation nucleation, which come in a very large number of varieties—dislocation nucleation from voids, surfaces, interfaces, corners, notches, cracks, etc.

Two scenarios [32,51] of heterogeneous dislocation nucleation in two different materials are compared with their homogeneous dislocation nucleation counterparts. Due to its importance, particular attention is focused on the activation volume for the different cases of dislocation nucleation. The aim is to improve the understanding about the phenomenon of dislocation nucleation by aiming to build a bridge between homogeneous and heterogeneous dislocation nucleation. Finally, the ideal strength of the perfect crystal followed by the quantitative effects of heterogeneities in terms of lowering of the strength of the material from the reference ideal strength value are discussed.

1.3.4 The shuffle-glide controversy in silicon

Two types [9] of dislocations can exist in the diamond cubic crystal structure of Si. If the atoms belonging to wider (111) planes slip, the dislocation is called shuffle-set dislocation (SD); if atoms on the narrower (111) planes slip, the dislocation is called glide-set dislocation (GD) (Figure 1-4). In general the glide-set dislocation exists as partial dislocation, and the direction and magnitude of its Burgers vector is different from that of the shuffle-set, as shown in Table 1-1 (*a* is the lattice constant for Si). The relevance of this debate to this research is that this whole shuffle-glide debate is a peculiar result of the influence of crystal structure, because the diamond cubic structure is made up of one FCC lattice placed at $(1/4\mathbf{i} + 1/4\mathbf{j} + 1/4\mathbf{k})a$ with respect to another FCC lattice. Like FCC, the most dense plane (and hence the slip-plane) in Si is the (111) plane, but with two choices for the (111) plane, the wide (111) plane and the narrow (111) plane.



Figure 1-4 Glide-set and shuffle-set dislocations in Si [52].

A large number of studies have been performed over the years on dislocation mobility in silicon. The presence of stacking faults is possible only in the case of the GD and the widely accepted traditional understanding, based on experimental [53–55] as well as theoretical [56,57] studies, has been that above the ductile-brittle transition, the mobility of the GD is higher than that of the SD at high temperature and under low stress. Duesbery's model [56] clearly presents this picture. In contrast, a series of recent experiments [58–61] have suggested that SD nucleates and moves at and below room temperature under high values of hydrostatic pressure and shear stress. Pizzagalli and Beauchamp [62], contradicting Duesbery's work, have recently reported that SD are more mobile than GD over the complete stress range, reviving the shuffle-glide dislocation controversy.

	Burgers vector	Туре
Glide-set dislocation	1/6[1 1-2] <i>a</i>	Partial
Shuffle-set dislocation	1/2[0 1-1] <i>a</i>	Perfect

Table 1-1 Glide-set dislocation and shuffle-set dislocation

In recent years, numerous studies have employed atomistic calculations to investigate the nucleation of dislocations in silicon. Godet *et al.* [63], using molecular dynamics, have recently demonstrated the existence of two plastic regimes in dislocation nucleation from a surface step in Si, with SD being nucleated at low temperature and under high stress, and GD being nucleated at high temperature and under low stress. On the other hand, the shear-stress dependences of the activation energy for nucleation of SD and GD from a sharp corner in the framework of the reaction pathway sampling method have also recently been reported [32], again confirming the existence of the two plastic regimes. All these atomistic studies have dealt with heterogeneous systems.

In this research, the shuffle-glide controversy is examined at a fundamental level, free from complex surface and stress concentration effects that distort the physical picture. The aim is to gain new insight on the shuffle-glide controversy in Si in terms of activation parameters (activation energy, activation volume) and mechanics of the dislocation core configurations. The homogeneous results are also compared with the shuffle-glide results for heterogeneous dislocation nucleation from a sharp corner [32].

1.4 Arrangement of this document

This document consists of seven chapters, including this, the introductory first chapter. In Chapter 2, the simulation techniques used throughout this research are presented in some detail. The details of artificial loop insertion, the methodology of applying the resolved shear stress on the slip-plane, and the visualization techniques used throughout this document to present the atomistic saddle-point configurations are also described. Readers familiar with the details of atomistic simulation techniques such as MD and NEB may skip this chapter without any loss of continuity.

Chapter 3 contains the details of simulation models constructed for all the situations considered in this research—homogeneous dislocation nucleation in Cu and

Mo; and that of the glide-set and shuffle-set in Si. All primary simulation results are also presented in this chapter. While no analysis of those results follows here, all these results are used extensively for analysis and discussion in the later chapters as and when required. It is believed that this segregation of primary results from secondary results, discussion and conclusions makes for better coherence of this document.

Chapter 4 starts with the comparison of homogeneous dislocation nucleation in three representative materials: diamond-cubic Si, face-centered cubic Cu and body-centered cubic Mo. The comparison is presented in the form of activation energies, mechanics of the saddle-point configurations and activation volumes. The aim is to understand the influence of the different crystal structures on the dislocation nucleation transition. Also in chapter 4 is presented a comparison between the results for homogeneous dislocation nucleation and results previously published for two typical situations of heterogeneous dislocation nucleation in an attempt to find the link between homogeneous and heterogeneous dislocation nucleation. Finally, the influence of heterogeneities in the reduction of strength from the maximum strength (ideal strength) is also touched upon. While only two heterogeneous cases by no means cover the whole range of heterogeneous systems, the discussion presented is considered as the first step toward building the bridge between homogeneous and heterogeneous dislocation nucleation.

Comparison of atomistic results with PN based models for homogeneous dislocation nucleation is the subject of Chapter 5. The limitations of PN models are highlighted along with the information that can only be made available by fully atomistic approaches.

Chapter 6 deals with the shuffle-glide controversy in Si in terms of the activation energy, activation volume and mechanics of saddle point configurations. The role of mobility is also touched upon, along with comparison with traditional and recent results regarding the shuffle-glide debate. Comparison is also made with heterogeneous results for dislocation nucleation from a sharp corner, as a continuation of the effort to find out the link between homogeneous and heterogeneous dislocation nucleation.

Chapter 7 concludes this document with a summary of the conclusions drawn from this research, followed by the utility of this work in terms of future direction of research that can be based on it. The contents of this document are summed up as follows:

Chapter 1	Background and aims of research	
Chapter 2	Methods employed	
Chapter 3	Simulation models and primary results	
Chapter 4	Comparison between Si, Cu and Mo	
	Comparison with heterogeneous systems	
Chapter 5	Comparison with PN based models	
Chapter 6	The shuffle-glide controversy in Si	
	Comparison with corresponding heterogeneous system	
Chapter 7	Conclusions and future directions	

References

- [1] J. P. Hirth and J. Lothe, *Theory of Dislocations*, Wiley, 1982.
- [2] Z. C. Xia, and J. W. Hutchinson, Crack tip fields in strain gradient plasticity, *Journal of the Mechanics and Physics of Solids*, Vol. 44 (10), pp. 1621–1648, 1996.
- [3] J. C. H. Spence, Y. M. Huang and O. Sankey, Lattice trapping and surface reconstruction for silicon cleavage on (111). Ab-initio quantum molecular dynamics calculations, *Acta Metallurgica et Materialia*, Vol. 41 (10), pp. 2815–2824, 1993.
- [4] V. Yamakov, D. Wolf, M. Salazar, S. R. Phillpot and H. Gleiter, Length-scale effects in the nucleation of extended dislocations in nanocrystalline Al by molecular-dynamics simulation, *Acta Materialia*, Vol. 49 (14), pp. 2713–2722, 2001.
- [5] H. Van Swygenhoven, P. M. Derlet, and A. G. Froseth, Stacking fault energies and slip in nanocrystalline metals, *Nature Materials*, Vol. 3 (6), pp. 399–403, 2004.
- [6] V. Bulatov, M. Nastar, J. Justo and S. Yip, Atomistic modeling of crystal-defect mobility and interactions, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, Vol. 121 (1-4): pp. 251–256, 1997.
- [7] T. Rasmussen, T. Vegge, T. Leffers, O. B. Pedersen and K. W. Jacobsen, Simulation of structure and annihilation of screw dislocation dipoles, *Philosophical Magazine A*, Vol. 80 (5), pp. 1273–1290, 2000.
- [8] E.C.C.M. Silva, J. Li, D. Liao, S. Subramanian, T. Zhu and S. Yip, Atomic scale chemo-mechanics of silica: Nano-rod deformation and water reaction, *Journal of Computer-Aided Materials Design*, Vol. 13 (1-3), pp. 135–159, 2006.
- [9] C. Z. Wang, J. Li, K. M. Ho and S. Yip, Undissociated screw dislocation in Si: Glide or shuffle set? *Applied Physics Letters*, Vol. 89 (5), p. 051910, 2006.
- [10] V. Yamakov, D. Wolf, S. R. Phillpot, A. K. Mukherjee and H. Gleiter, Dislocation processes in the deformation of nanocrystalline aluminium by molecular-dynamics simulation, *Nature Materials*, Vol. 1 (1), pp. 45–49, 2002.
- [11] B. Decelis, A.S. Argon, and S. Yip, Molecular dynamics simulation of crack tip processes in alpha-iron and copper, *Journal of Applied Physics*, Vol. 54 (9), pp. 4864–4878, 1983.
- [12] A. C. Lund, T. G. Nieh, and C. A. Schuh, Tension/compression strength

asymmetry in a simulated nanocrystalline metal, *Physical Review B*, Vol. 69 (1), p. 012101, 2004.

- [13] R. D. Boyer, J. Li, S. Ogata and S. Yip, Analysis of shear deformations in Al and Cu: empirical potentials versus density functional theory, *Modelling and Simulation in Materials Science and Engineering*, Vol. 12 (5), pp. 1017–1029, 2004.
- [14] D. Farkas and W. A. Curtin, Plastic deformation mechanisms in nanocrystalline columnar grain structures, *Materials Science and Engineering: A*, Vol. 412 (1–2), pp. 316–322, 2005.
- [15] K. S. Cheung and S. Yip, A Molecular-dynamics simulation of crack-tip extension: the brittle-to-ductile transition, *Modelling and Simulation in Materials Science and Engineering*, Vol. 2 (4), pp. 865–892, 1994.
- [16] J. Chang, W. Cai, V. V. Bulatov and S. Yip, Dislocation motion in BCC metals by molecular dynamics, *Materials Science and Engineering A*, Vol. 309–310, pp. 160–163, 2001.
- [17] A. C. Lund and C. A. Schuh, Molecular simulation of amorphization by mechanical alloying, *Acta Materialia*, Vol. 52 (8), pp. 2123–2132, 2004.
- [18] M. P. Allen, and D. J. Tildesley, *Computer simulation of liquids*, Oxford science publications, Clarendon Press, New York, 1989.
- [19] J. Schiotz, F. D. Di Tolla and K.W. Jacobsen, *Softening of nanocrystalline metals at very small grain sizes*, *Nature*, Vol. 391 (6667), pp. 561–563, 1998.
- [20] D. Roundy, C. R. Crenn, M. L. Cohen, J. W. Morris, Ideal shear strengths of fcc Aluminum and Copper, *Physical Review Letters*, Vol. 82 (13), pp. 2713–2716, 1999.
- [21] S. Ogata, J. Li, S. Yip, Ideal pure shear strength of Aluminum and Copper, *Science*, Vol. 298 (5594), pp. 807–811, 2002.
- [22] T. Zhu and J. Li, Ultra-strength materials, *Progress in Materials Science*, Vol. 55 (7), pp. 710–757, 2010.
- [23] A.H. Cottrell, *Dislocations and plastic flow in crystals*, Oxford University press, UK, 1956.
- [24] J.R. Rice and G.E. Beltz, The activation energy for dislocation nucleation at a crack, *Journal of the Mechanics and Physics of Solids*, Vol. 42 (2), pp. 333–360, 1994.
- [25] G. Xu, A.S. Argon and M. Ortiz, Nucleation of dislocations from crack tips under

mixed modes of loading: implications for brittle against ductile behaviour of crystals, *Philosophical Magazine A*, Vol. 72 (2), pp. 415–451, 1995.

- [26] W. Yang, J. C. Tang, Y. S. Ing and C. C. Ma, Transient dislocation emission from a crack tip, *Journal of the Mechanics and Physics of Solids*, Vol. 49 (10), pp. 2431–2453, 2001.
- [27] Y. Xiang, H. Wei, P. Ming and W. E, A generalized Peierls-Nabarro model for curved dislocations and core structures of dislocation loops in Al and Cu, *Acta Materialia*, Vol. 56 (7), pp. 1447–1460, 2008.
- [28] G. Xu and A. S. Argon, Homogeneous nucleation of dislocation loops under stress in perfect crystals, *Philosophical Magazine Letters*, Vol. 80 (9), pp.605–611, 2000.
- [29] T. Zhu, J. Li, A. Samanta, H. G. Kim and S. Suresh, Interfacial plasticity governs strain rate sensitivity and ductility in nanostructured metals, Proceedings of the National Academy of Sciences of the United States of America, Vol. 104 (9), pp. 3031–3036, 2007.
- [30] J. Li, The mechanics and physics of defect nucleation, *MRS Bulletin*, Vol. 32, pp. 151–159, 2007.
- [31] S. Izumi and S. Yip, Dislocation nucleation from a sharp corner in silicon, *Journal of Applied Physics*, Vol. 104 (3), p. 033513, 2008.
- [32] K. Shima, S. Izumi and S. Sakai, Reaction pathway analysis for dislocation nucleation from a sharp corner in silicon: Glide set versus shuffle-set, *Journal of Applied Physics*, Vol. 108 (6), p. 063504, 2010.
- [33] S. Hara, S. Izumi, and S. Sakai, Reaction pathway analysis for dislocation nucleation from a Ni surface step, *Journal of Applied Physics*, Vol. 106 (9), p. 093507, 2009.
- [34] T. Zhu, J. Li, and S. Yip, Atomistic study of dislocation loop emission from a crack tip, *Physical Review Letters*, Vol. 93 (2), p. 025503, 2004.
- [35] T. Zhu, J. Li, A. Samanta, A. Leach, and K. Gall, Temperature and strain-rate dependence of surface dislocation nucleation, *Physical Review Letters*, Vol. 100 (2), p. 025502, 2008.
- [36] R. D. Boyer, Stress-mediated reaction pathways for dislocation nucleation in Cu, Ph.D. Thesis, *MIT*, 2007.
- [37] H. Eyring, The activated complex in chemical reactions, *Journal of Chemical Physics*, Vol. 3, pp. 107–115, 1935.

- [38] A. Gouldstone, K. J. Van Vliet and S. Suresh, Nanoindentation: simulation of defect nucleation in a crystal, *Nature*, Vol.411 (6838), p. 656, 2001.
- [39] P. Schall, I. Cohen, D. A. Weitz and F. Spaepen, Visualization of dislocation dynamics in colloidal crystals, *Science*, Vol. 305 (5692), pp. 1944–1948, 2004.
- [40] P. Schall, I. Cohen, D. A. Weitz and F. Spaepen, Visualizing dislocation nucleation by indenting colloidal crystals, *Nature*, Vol. 440, pp. 319–323, 2006.
- [41] S. Suresh, Crystal deformation: Colloid model for atoms, *Nature Materials*, Vol. 5 (4), pp. 253–254, 2006.
- [42] J. Li, K. J. V. Vliet, T. Zhu, S. Yip and S. Suresh, Atomistic mechanisms governing elastic limit and incipient plasticity in crystals, *Nature*, Vol. 418 (6895), pp. 307–310, 2002.
- [43] A. Gouldstone, N. Chollacoop, M. Dao, J. Li, A. M. Minor, Y. L. Shen, Indentation across size scales and disciplines: Recent developments in experimentation and modeling, *Acta Materialia*, Vol. 55 (12), pp. 4015–4039, 2007.
- [44] J. K. Mason, A. C. Lund and C. A. Schuh, Determining the activation energy and volume for the onset of plasticity during nanoindentation, *Physical Review B*, Vol. 73 (5), p. 054102, 2006.
- [45] Taeko Ando, Takafumi Takumi and Kazuo Sato, Fracture toughness of single-crystal silicon thin film—temperature effect in low-temperature environment, *Japan Society of Mechanical Engineers 2nd Micro-nanoengineering* proceedings, MNM-3A-1 (in Japanese), 2010.
- [46] R. E. Miller, L. E. Shilkrot and W. A. Curtin, A coupled atomistic and discrete dislocation plasticity simulation of nanoindentation into single crystal thin films, *Acta Materialia*, Vol. 52 (2), pp. 271–284, 2004.
- [47] D. Saraev and R. E. Miller, Atomic-scale simulations of nanoindentation-induced plasticity in copper crystals with nanometer-sized nickel coatings, *Acta Materialia*, Vol. 54 (1), pp. 33–45, 2006.
- [48] Y. Umeno and M. Cerny, Effect of normal stress on the ideal shear strength in covalent crystals, *Physical Review B*, Vol. 77 (10), p. 100101(R), 2008.
- [49] H. Bei, Y. F. Gao, S. Shim, E. P. George and G. M. Pharr, Strength differences arising from homogeneous versus heterogeneous dislocation nucleation, *Physical Review B*, Vol. 77 (6), p. 060103(R), 2008.

- [50] R. J. Asaro and S. Suresh, Mechanistic models for the activation volume and rate sensitivity in metals with nanocrystalline grains and nano-scale twins, *Acta Materialia*, Vol. 53 (12), pp. 3369–3382, 2005.
- [51] S. Hara and J. Li, Adaptive strain-boost hyperdynamics simulations of stress-driven atomic processes, *Physical Review B*, Vol. 82 (18), p. 184114, 2010.
- [52] W. Cai, V. V. Bulatov, J. Chang, J. Li, and S. Yip, Dislocation core effects on mobility, *Dislocations in Solids*, Chapter 64, Vol. 12, pp. 1–80, 2004.
- [53] K. Wessel and H. Alexander, On the mobility of partial dislocations in silicon, *Philosophical Magazine*, Vol. 35 (6), pp. 1523–1536, 1977.
- [54] A. Gomez, D. J. H. Cockayne, P. B. Hirsch, and V. Vitek, Dissociations of near-screw dislocations in germanium and silicon, *Philosophical Magazine*, Vol. 31 (1), pp. 105–113, 1975.
- [55] M. Sato, K. Hiraga, and K. Sumino, HVEM structure images of extended 60° and screw dislocations in silicon, *Japanese Journal of Applied Physics*, Vol. 19, L155–L158, 1980.
- [56] Q. Ren, B. Joos, and M. S. Duesbery, Test of the Peierls-Nabarro model for dislocations in silicon, *Physical Review B*, Vol. 52 (18), pp. 13223–13228, 1995, (Erratum: Test of the Peierls-Nabarro model for dislocations in silicon, *Physical Review B*, Vol. 53 (17), p. 11883, 1996.
- [57] M. S. Duesbery and B. Joos, Dislocation motion in silicon: the shuffle-glide controversy, *Philosophical Magazine Letters*, Vol. 74 (4), pp. 253–258, 1996.
- [58] T. Suzuki, T. Yasutomi, T.T. Okuoka, and I. Yonenaga, Plastic deformation of GaAs at low temperatures, *Philosophical Magazine A*, Vol. 79 (11), pp. 2637–2654, 1999.
- [59] J. Rabier and J. L. Demenet, Low temperature high stress deformation of semiconductors: the silicon case, *physica status solidi* (b), Vol. 222 (1), pp. 63–74, 2000.
- [60] J. Rabier, J. L. Demenet, On the nucleation of shuffle dislocations in Si, *physica status solidi (a)*, Vol. 202 (5), pp. 944–948, 2005.
- [61] J. Rabier, High-stress plasticity and the core structures of dislocations in silicon, *physica status solidi* (*a*), Vol. 204 (7), pp. 2248–2255, 2007.
- [62] L. Pizzagalli and P. Beauchamp, Dislocation motion in silicon: the shuffle-glide controversy revisited, *Philosophical Magazine Letters*, Vol. 88 (6), pp. 421–427, 2008.

[63] J. Godet, P. Hirel, S. Brochard, and L. Pizzagalli, Evidence of two plastic regimes controlled by dislocation nucleation in silicon nanostructures, *Journal of Applied Physics*, Vol. 105 (2), p. 026104, 2009.

2. METHOD

2.1 Introduction

This chapter presents brief descriptions of the simulation tools employed in this research. An overview of the Nudged Elastic Band (NEB) algorithm and extended schemes, which form the backbone of this research as the reaction pathway sampling technique employed, is presented. Furthermore, established methods used in this research, such as classical molecular dynamics and relaxation techniques, are summarized because of their application in preparing the crucially important input images for the NEB algorithm. Finally, details of input image preparation, stress application, and visualization techniques employed for presentation of results are described.

2.2 Classical molecular dynamics

Molecular dynamics (MD) is an established technique and extensive literature pertaining to its basis and implementation is available [1–3]. MD keeps track of the position and velocity of individual atoms by calculating the force applied on each atom. This force calculation is made by using empirical potentials based on inter-atomic

interactions. The laws of classical mechanics are applied to each atom and the resulting differential equations are solved numerically. For *N* number of atoms, specification of initial conditions for position and velocity locates the system in the 6*N*-dimensional topological space, and the time evolution of each atom can be followed deterministically. Thus it is possible to define the instantaneous values for dynamic quantities of the system after each subsequent time interval. By assuming the Ergodic hypothesis [4], whereby the long-term time average of instantaneous values of a measured quantity along a trajectory equals the phase space average of that quantity, values of macroscopic physical quantities can be determined.

In MD simulations, the motion of the individual atoms is traced by repeating steps 2 through 5 after defining the initial conditions, as explained in the following algorithm:

- 1. Define initial conditions (initial positions, initial velocities)
- 2. Based on the boundary conditions, figure out the atomic clusters to be used for efficiently calculating inter-atomic forces (Book-keeping method).
- Compute inter-atomic forces based on the atomic positions and empirical inter-atomic potentials.
- 4. Calculate the atomic positions and velocities for the moment after time interval Δt based on the Verlet algorithm.
- 5. Calculate relevant physical quantities
- 6. Go back to 2.

2.2.1 Periodic boundary conditions

The number of atoms contained in one cubic centimeter of a solid material is of the order of the Avogadro's number ($N_A = 6.022 \times 10^{23}$). In comparison, a typical simulation on a desktop workstation can handle only 10^3 to 10^6 atoms. Even in the billion-atom simulations on massively parallel computers [5], the total number of atoms is still very small compared to the Avogadro's number. Therefore, unless one is specifically interested in isolated nano-sized atomic clusters, the actual simulation volume is only a very small portion of the material of interest. The behavior of atoms in the simulation

volume is affected by a large number of surrounding atoms that cannot be explicitly included in the simulation. The influence of these surrounding atoms is therefore included implicitly and approximately, through periodic boundary conditions (PCB), utilization of which is crucial for a successful atomistic simulation.

The idea of PCB is to embed the simulation volume or simulation cell into an infinite, periodic array of replicas or images. This is illustrated in Figure 2-1 for a two-dimensional simulation. The atoms in the replica are assumed to behave in the same way as the atoms in the original or primary simulation cell [6]. Because the primary and image cells are identical, the boundary of the primary cell can be shifted arbitrarily, and such a shift has no effect on the dynamics of any atom, thus the translational invariance of space is fully preserved [7], causing no artificial surface effects as long as the size of the simulation cell is reasonably large. Atoms that escape the primary cell enter with the same velocity into the primary cell from the image cell of the opposite side. Moreover, forces are computed for atoms in the primary cell by including the contribution from atoms of the image cells in addition to that from atoms of the primary cell. This makes the simulation domain infinite, and it becomes possible to represent bulk characteristics by using a very small computational domain. However, the dimensions of each length of the unit cell must be made at least half of the cut-off radius of the inter-atomic potential being used.



Figure 2-1 Periodic boundary conditions. Surface effects are removed by using image cells containing the identical information as the original unit cell.

2.2.2 Book keeping and its acceleration technique

If one is not interested in long-range inter-atomic interactions such as the Coulomb force, it is possible to generally approximate the force between atoms separated by more than a few Ångströms by zero. If the range of inter-atomic interactions is expressed as a cut-off radius r_c , then by preparing neighbor lists of all atoms located inside the sphere with a radius r_c , it is possible to save computational cost by only considering the interactions between atoms that are present in the neighbor list of a certain atom.

In addition, by setting another domain for neighbor lists with a radius R_c , which is slightly bigger than r_c , it is possible to dispense with the need to figure out the latest neighbor lists after each simulation step, which improves the efficiency of computation further. These methods are referred to as book-keeping, and are shown schematically in Figure 2-2 (left).



Unit MD cell

Figure 2-2 Efficient book-keeping techniques (left) and 2D outline of the domain subdivision algorithm for book-keeping (right).

Radius R_c , and the frequency of updating book-keeping information in terms of number of simulation steps N_{up} is determined as follows:

The average particle velocity v_{ave}^{T} is computed from the kinetic energy of the particles resulting from the system temperature T_{K} . The maximum particle velocity is about three times their average velocity ($v_{max}^{T} \rightleftharpoons 3v_{ave}^{T}$)[8]. The product of this velocity

and the computation time (simulation steps multiplied by step interval $N_{uv}\Delta t$) yields the maximum displacement of a particle inside the time interval involved. This comes out to be $\Delta r_c = v_{max}^T N_{up} \Delta t$. Therefore, for N_{up} , as long as $R_c = r_c + \Delta r_c$, particles from outside cannot enter within the cut-off domain with radius rc.

By exploitation of the above book-keeping method, the computation time required at each information update becomes proportional to $O(N^2)$. Despite the fact that it is not necessary to do an update at every step, the algorithm can still not be called a very efficient one if applied to big systems. In this research we have employed the domain subdivision algorithm, which reduces the simulation time for each update to O(N).

The outline of the domain subdivision algorithm is shown in Fig. 2-2 (right). The simulation cell is divided into small sub-cells of side lengths longer than R_c . All the atoms are assigned to one of these sub-cells. During calculation of inter-atomic forces for atoms assigned to a certain sub-cell, the interacting atoms come from either the same sub-cell or from immediate neighbor sub-cells. For a two dimensional system, the number of immediate neighbor sub-cells is only 9; for a three dimensional system, 27. This reduction in the domain of updating causes a large-scale shrinking of required computation time.

2.2.3 Equations of motion

In molecular dynamics, distinct equations of motion are used according to the ensemble that is set up. The most fundamental ensemble is the Micro-canonical (NVE) ensemble, which specifies the number of atoms (N), volume (V), and energy (E) as constant. For NVE, the equations to solve are Newton's equations of motion (Eq. 2.1).

$$\overrightarrow{F_i} = m_i \frac{d^2 \overrightarrow{r_i}}{dt^2}$$
(2.1)

In this research in addition to NVE, the Canonical (NVT) ensemble, which specifies the temperature to be constant, is also used.

Temperature control

From the point of view of statistical thermodynamics, the temperature (T) of the system can be expressed in terms of fluctuation of velocity v of the particles (Eq. 2.2).

$$\frac{3}{2}Nk_{B}T = \sum_{a} \frac{1}{2}m_{a}v_{a}^{2}$$
(2.2)

Nose's method [9] and velocity-scaling method are well-known ways of temperature control. In this research the latter, which is simpler of the two approaches, has been employed. In the velocity-scaling method, the temperature of the system is brought near the desired temperature by adjusting its kinetic energy by forcibly scaling the velocity v_a of each atom in the system. If the temperature measured from atomic velocities at time *t* is *T*, the desired temperature is T_c , the velocity adjustment is applied as (Eq. 2.3):

$$v_a' = \sqrt{\frac{T_c}{T}} v_a \tag{2.3}$$

Numerical integration of equations of motion

Once the ensemble is specified, the next step is to solve the equations of motion by using some suitable numerical integration technique. In this research, the integration of molecular dynamics equations is performed by using the Velocity Verlet method [10]. Total system-energy conservation without error was confirmed after setting the time-step Δt about 0.01 of the vibration cycle of the materials simulated.

2.2.4 Non-dimensional units

Computation results were rendered generality by non-dimensioning all physical quantities into Å–eV system. The non-dimensional units used in this research are as follows:

Distance
$$x^* = \frac{x}{d} \left(r^* = \frac{r}{d}\right)$$
 (2.4)

Mass
$$m^* = \frac{m}{m_{mat}}$$
 (2.5)

Time
$$t^* = \frac{t}{d\sqrt{\frac{m}{eV}}}$$
(2.6)

Velocity
$$v^* = \frac{v}{d\sqrt{\frac{eV}{m}}}$$
 (2.7)

Force
$$F^* = \frac{F}{\frac{eV}{d}}$$
 (2.8)

Acceleration
$$a^* = \frac{a}{\frac{eV}{md}}$$
 (2.9)

Temperature
$$T^* = \frac{T}{\frac{eV}{k_B}}$$
 (2.10)

Pressure (stress)
$$\sigma^* = \frac{\sigma}{\frac{eV}{d^3}}$$
 (2.11)
Potential $\Phi^* = \frac{\Phi}{eV}$ (2.12)

Table 2-1 Non-dimensional parameters for atomistic calculations

Parameter	Description	Value
m_{Si}	Mass of Si atom	4.6643445×10 ⁻²⁶ (kg)
m_{Cu}	Mass of Cu atom	1.0552068×10 ⁻²⁵ (kg)
m_{Mo}	Mass of Mo atom	1.5931222×10 ⁻²⁵ (kg)
k _B	Boltzmann constant	1.38062×10 ⁻²³ (J/K ⁻¹)
eV	1 Electron Volt	1.60219×10 ⁻¹⁹ (J)
D	Non-dimensional parameter for	1.00×10 ⁻¹⁰ (m)
	atomic diameter	

2.3 The Nudged Elastic Band (NEB) Method

Nudged Elastic-Band (NEB) method [11–13] is a transition pathway sampling algorithm that takes two distinct stable atomistic configurations on the reaction path, sets one as the initial configuration and the other as the final configuration, and searches the minimum energy path (MEP) that joins the two points in the configuration space. The highest-energy point on the MEP (called the saddle point) represents the activation energy involved in the transition (Figure 2-3).



Reaction coordinate

Figure 2-3 The Nudged elastic band method. The energy difference between the initial configuration and the saddle-point configuration (highest point on the minimum energy path) is the activation energy input required to affect the transition.

In general, a number of intermediate images are prepared between the initial and final configuration by linear interpolation. The neighboring images are joined with imaginary springs. The force on each intermediate image is expressed by Eq. 2.13. By using the resultant of the spring force parallel to the path and the potential force perpendicular to the path, the force on each image is minimized to search the MEP. The component of the potential force perpendicular to the path is calculated using Eq. 2.14. In cases where a number of distinct reaction paths between the initial and final configurations are probable, or where the linearly interpolated images are feared to be far from reaction path, convergence to the required MEP can be achieved at low
computation cost by preparing in advance intermediate images between the initial and final configurations.

The calculations of potential energy in NEB method involve the same inter-atomic potentials and periodic boundary conditions as employed in the molecular dynamics computations.

$$\vec{F}_{i} = -\nabla V \left(\vec{R}_{i} \right)_{\perp} + \left(\vec{F}_{i}^{s} \cdot \vec{\tau}_{i} \right) \vec{\tau}_{i}$$
(2.13)

$$-\nabla V\left(\overrightarrow{R_{i}}\right)_{\perp} = -\nabla V\left(\overrightarrow{R_{i}}\right) + \left(\nabla V\left(\overrightarrow{R_{i}}\right) \cdot \overrightarrow{\tau_{i}}\right)\overrightarrow{\tau_{i}}$$
(2.14)

where

$\overrightarrow{F_i}$:	Force acting on image # <i>i</i>
$\overrightarrow{R_i}$:	Position vector of atoms of image # <i>i</i>
$\overrightarrow{F_i^s}$:	Spring force acting on image #i
V :	Potential energy
$\overrightarrow{\tau_i}$:	Vector tangent to the path of image $#i$

To help achieve convergence to the MEP, improved tangent method has been used throughout [11]. This modification has been found to be very useful when the force parallel to the replicas is large as compared to the force perpendicular to it, resulting in undesirable kinks in the elastic band, especially when the number of images is large.

2.3.1 Climbing image Nudged Elastic Band Method

It is possible to obtain images before and after the saddle-point by applying Eq. 2.13 to all images. However, it is not possible to obtain the converged image at the saddle-point, and therefore impossible to calculate the activation energy precisely. The Climbing image NEB (CI-NEB) [12] addresses that limitation. As shown in Eq. 2.15, for the

maximum energy image on the reaction pathway, the saddle-point image is located by combining the component normal to the potential force and the negative of the one parallel to the reaction pathway.

$$\vec{F}_{i} = -\nabla V \left(\vec{R}_{i} \right)_{\perp} + \left(\nabla V \left(\vec{R}_{i} \right) \cdot \vec{\tau}_{i} \right) \vec{\tau}_{i}$$
(2.15)

2.3.2 Free End Nudged Elastic Band Method

If the energy difference between the initial and the final configurations is significantly greater than the saddle-point energy, the density of images near the saddle-point becomes low, resulting in loss of accuracy in the calculation of activation energy.

If the saddle-point lies in close proximity to the initial image on the reaction pathway, the final image is not important in terms of calculation of the activation energy. In the free end NEB (FE-NEB) [13], the calculation is commenced by treating an intermediate point on the reaction pathway joining the saddle-point and the final image as the new final configuration. Thus it becomes possible to increase the density of images near the saddle-point without increasing the computational cost.

As shown by Eq. 2.16, without fixing the final image, by applying only spring force normal to the potential force it becomes possible to converge to the MEP without the need to change the energy of the final image.

$$\overrightarrow{F_{N}} = \overrightarrow{F_{N}^{s}} - \frac{\left(\overrightarrow{F_{N}^{s}} \cdot \nabla V\left(\overrightarrow{R_{N}}\right)\right) \nabla V\left(\overrightarrow{R_{N}}\right)}{\left|\nabla V\left(\overrightarrow{R_{N}}\right)^{2}\right|}$$
(2.16)

In this work, the CI-NEB and the FE-NEB techniques have been employed in combination. FE-NEB makes it possible to use lower number of replicas than would be necessary in the ordinary NEB algorithm. This results in considerable saving of time and resources. CI-NEB helps in converging to the saddle-point configuration and prevents the conflict between competing configurations near the saddle point, which can be detrimental to successful convergence to the MEP.

A typical cycle of NEB convergence to the MEP consists of a preliminary fixed-end run, followed by extensive free-end calculations. Once close to the converged solution, the climbing-image algorithm is switched on.

2.3.3 Preparation of intermediate images

Intermediate images are prepared in ways depending on the problem to be handled and the material in question. For materials with relatively high mobility (Cu and Mo), linear interpolation between the initial and final image suffices as a good start, resulting in the solution converging to the minimum energy path (MEP).

For the shuffle-set dislocation in Si, which has a relatively low mobility, MD unloads provide reasonable intermediate images to be used as input for the NEB algorithm. For glide-set dislocation and its extremely low mobility, even the MD unloads are not satisfactory in terms of providing intermediate images fit for convergence to the minimum energy path. For the glide-set dislocation, the dislocation interpolation [14] method is used, which consists of making a series of artificial loops as intermediate images to be used as input for the NEB algorithm.

2.4 Conjugate gradient relaxation

Conjugate gradient relaxation [15] is a very useful technique to search the stable structure when dealing with an atomistic structure in a static manner, as opposed to the dynamic manner in which MD approaches the problem. The working of the conjugate gradient method is explained as follows.

To avoid having to deal with second order partial derivatives of complex many-body potentials as used in MD, a method that does not involve the calculation of the Hessian is employed. In the conjugate gradient relaxation, the direction of the steepest descent of the potential energy and the one used in the search immediately before are used to determine the next search direction. Once the search direction is determined, linear search is carried out and the displacements that minimize the potential energy are calculated and the position of atoms is kept on updated. In concrete terms, the following takes place: 1. The initial search direction is determined based on the steepest descent direction.

$$d_1 = -\nabla \Phi(x) \tag{2.17}$$

2. From the last search, β_k is determined so as to minimize $\Phi(x_k + \beta_k d_k)$. β_k is determined by the bifurcation method in a way that it satisfies the Armijo criterion. That is, for a constant *v* that does not depend on the number of steps for the conjugate gradient relaxation, *k*, such that it satisfies 0 < v < 1:

$$\Phi(x_k + \beta d_k) < \Phi(x_k) + \nu \beta \nabla \Phi(x_k)^T d_k$$
(2.18)

The greatest β that satisfies the above equation is selected as β_k according to the Armijo condition. As long as Armijo's condition is not met for the specified *v*, 1/2 is kept on multiplied to β .

3. The atomic positions are updated.

$$x_{k+1} = x_k + \beta_k d_k \tag{2.19}$$

4. The search direction is updated.

$$d_{k+1} = -\nabla \Phi(x_{k+1}) + \gamma_k d_k$$
 (2.20)

5. For k=k+1, the calculation is repeated by returning to step 2.

In this research, for determining the stability of the atomistic structure, v is taken to be 0.001, and the initial value for β is set as 0.00125. For calculations demanding the stability of all atomic distances, v is set to be 0.0001, and the initial value of β is assigned as 0.000125.

2.5 About empirical inter-atomic potentials

In atomistic calculations, the inter-atomic potentials are expressed as functions of position of all particles. The inter-atomic force is then determined by differentiating the potential Φ (Eq. 2.21).

$$F_{\alpha} = -\frac{\partial \Phi}{\partial r_{\alpha}} \tag{2.21}$$

The physical properties and reproducibility of structure is dependent on the accuracy of the empirical potential employed. Consequently a number of potentials have been developed over the years for a diverse range of applications. The shape of the potential function generally depends on the bonding characteristics of the material concerned. For example, for inorganic compounds pair-potentials of the Lennard-Jones type or Morse type [16] are widely used. On the other hand, for covalent bonded materials, 3-body potentials (Tersoff type [17], Keating type [18]) are employed. For metals, electron density functions embedded potentials of the EAM type have shown considerable success over the years [19]. For Cu and Mo, the Mishin potential [20] and the GEAM potential [21] have been used respectively in this research.

Because of the need to consider the strong directionality of covalent bonds in Si, it is difficult to use pair potentials. Therefore many implementations of the more complicated multi-body potentials have been proposed, the major ones being the Stillinger-Weber (SW) potential [22], Tersoff potential [17], EDIP potential [23]. In this research the SW potential has been employed because of its suitability [24] to the phenomenon of dislocations in Si.

2.6 About stress application

For the nucleation of dislocations, it is necessary for stress to be applied on the slip plane in the Burgers vector direction. A variety of methods for stress application have traditionally been applied in atomistic simulations such as MD, such as distorting the unit cell, or fixing atoms in a certain range [25–27]. In this work we apply stress by deforming the unit cell.

For an arbitrary stress in the direction of the Burgers vector, elastic constants are used to determine strain corresponding to that stress.

$$\sigma = C \times \varepsilon \tag{2.22}$$

where σ is the stress tensor, *C* is the elastic constant matrix, and ε is the strain tensor. Based on the strain calculated, the unit cell of the periodic boundary conditions is deformed and thereby shear stress is applied to the slip plane.

When shear stress is applied to the slip plane, the direction of the application of the periodic boundary conditions in the atomic coordinate system becomes difficult to determine. For example, as shown in Figure 2-4, for an atomic displacement in the y direction, it sometimes becomes necessary to apply the periodic boundary condition in the x direction as well, making the application of PCB complicated.



Figure 2-4 Unit cell under shear strain. Under shear stress application, the direction of application of the periodic boundary conditions sometimes becomes complex and problematic. That is averted with the aid of the transformation matrix.

To avoid this complication, a transformation matrix is used. By multiplying this transformation matrix with the parallel hexahedron unit cell, the length of the unit cell is transformed into a cube of length 1, and the atomistic calculations are executed thereafter. The transformation matrix M is given by

$$M = H^{-1}, \quad H = \begin{bmatrix} \mathbf{x} \\ \mathbf{y} \\ \mathbf{z} \end{bmatrix}$$
(2.23)

Where \mathbf{x} , \mathbf{y} , and \mathbf{z} are non-parallel vectors with distinct 3 axes.

2.7 About visualization

In this research, we deal with diamond-cubic Si, face-centered cubic Cu, and body-centered cubic Mo. The last two centro-symmetric materials and the defects (dislocations) therein can be visualized in the form of Central Symmetric Parameter [28]. That is because the central symmetric parameter is a measure of how much a crystal has departed from its symmetry as a result of slip of atoms. However, defects in the highly unsymmetrically covalent-bonded Si cannot be viewed in this way. In this document we present visual results in terms of the Slip Vector Representation [29] for the most part, with an occasional use of centro-symmetry parameter [28] when comparing different configurations of Cu.

Slip-vector is an expression of how much an atom has moved relative to its immediate neighbors. It is defined as follows:

$$s^{\alpha} = -\frac{1}{n_s} \sum_{\beta \neq \alpha}^n \left(x^{\alpha\beta} - X^{\alpha\beta} \right)$$
(2.24)

where n_s is the number of slipped atoms, n is the number of nearest neighbors, $x^{\alpha\beta}$ and $X^{\alpha\beta}$ are the vectors representing the relative position of atoms α and β at the current and reference positions respectively. The reference configuration is the arrangement of atomic positions associated with zero mechanical strain. Although for slip occurring at two adjacent atomic layers the direction of slip vector has a problem in terms of the sense, it is a useful indicator of atomic displacements.

Equation 2.34 results in the Burgers vector for the slip of adjacent atomic planes, where the atom lies on one of those planes. The slip vector yields a large

magnitude for any inhomogeneous deformation near an atom and provides quantitative information about the deformation.

2.8 Summary

Simulation and presentation tools employed in this research have been briefly described in this chapter.

The major simulation tool employed is the NEB algorithm. However, proper working of NEB depends to a large extent on careful preparation of the initial input images; and classical techniques such as MD and CG relaxation have been extensively employed to prepare those. These simulation techniques have been described in some detail.

Concrete methods for the preparation of input images, the application of stress on the slip plane, and the visualization techniques employed in the presentation of results have also been described briefly.

References

- [1] W. G. Hoover, *Molecular Dynamics—Lecture Notes in Physics*, Vol.258, Springer-Verlag, 1986.
- [2] D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, 2nd edition, Cambridge University Press, 2004.
- [3] J. M. Haile, *Molecular Dynamics Simulation—Elementary Methods*, John Wiley and Sons, 1992.
- [4] C. R. de Oliveira and T. Werlang, Ergodic hypothesis in classical statistical mechanics, *Revista Brasileira de Ensino de Fisica*, Vol. 29 (2), pp. 189–201, 2007.
- [5] F. F. Abraham, R. Walkup, H. Gao, M. Duchaineau, T. D. De la Rubia and M. Seager, Simulating materials failure by using up to one billion atoms and the world's fastest computer: Work-hardening, *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 99 (9), pp. 5783–5787, 2002.
- [6] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, Oxford, 1989.
- [7] E. Orowan, Plasticity of Crystals, Zeitschrift fur Physik, Vol. 89 (9–10), pp. 605–659, 1934.
- [8] W. G. Hoover, *Computational Statistical Mechanics*, Elsevier Science, B. V., 1991.
- [9] S. Nose, A unified formation of the constant temperature molecular dynamics methods, *Journal of Chemical Physics*, Vol. 81, pp. 511–519, 1984.
- [10] L. Verlet, Computer "experiments" on classical fluids, I. Thermodynamical properties of Lennard-Jones molecules, *Physical Review*, Vol. 159 (1), pp. 98–103, 1967.
- [11] G. Henkelman and H. Jonsson, Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points, *Journal of Chemical Physics*, Vol. 113 (22), pp. 9978–9985, 2000.
- [12] G. Henkelman, B. P. Uberuaga, and H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *Journal of Chemical Physics*, Vol. 113 (22), pp. 9901–9904, 2000.
- [13] T. Zhu, J. Li, A. Samanta, H. G. Kim, and S. Suresh, Interfacial plasticity governs strain rate sensitivity and ductility in nanostructured metals, *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 104 (9), pp.

3031-3036, 2007.

- [14] K. Shima, S. Izumi and S. Sakai, Reaction pathway analysis for dislocation nucleation from a sharp corner in silicon: glide set versus shuffle-set, *Journal of Applied Physics*, Vol. 108 (6), p. 063504, 2010.
- [15] M. R. Hestenes and E. Stiefel, Methods of Conjugate Gradients for Solving Linear Systems, *Journal of Research of the National Bureau of Standards*, Vol. 49 (6), pp. 409–436, 1952.
- [16] P. M. Morse, Diatomic molecules according to wave mechanics. II. Vibrational levels, *Physical Review*, Vol. 34 (1), pp. 57-64, 1929.
- [17] J. Tersoff, Empirical interatomic potential for silicon with improved elastic properties, *Physical Review B*, Vol. 38 (14), pp. 9902–9905, 1988.
- [18] P. N Keating, Effect of invariance requirements on the elastic strain energy of crystals with application to the diamond structure, *Physical Review*, Vol. 145 (2), pp. 637–645, 1966.
- [19] M. S. Daw and M. I. Baskes, Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals, *Physical Review B*, Vol. 29 (12), pp. 6443–6453, 1984.
- [20] Y. Mishin, M J. Mehl, D. A. Papaconstantopoulus, A. F. Voter, and J. D. Kress, Structural stability and lattice defects in copper: Ab initio, tight-bonding, and embedded-atom calculations, *Physical Review B*, Vol. 63 (12), p. 224106, 2001.
- [21] X. W. Zhou, H. N. G. Wadley, R. A. Johnson, D. J. Larson, N. Tabat, A. Cerezo, A. K. Petford-Long, G. D. W. Smith, P. H. Clifton, R. L. Martens and T. F. Kelly, Atomic scale structure of sputtered metal multilayers, *Acta Materialia*, Vol. 49 (19), pp. 4005–4015, 2001.
- [22] F. H. Stillinger and T. A. Weber, Computer simulation of local order in condensed phases of silicon, *Physical Review B*, Vol. 31 (8), pp. 5262–5271, 1985.
- [23] M. Z. Bazant, E. Kaxiras, and J. F. Justo, Environment-dependent interatomic potential for bulk silicon, *Physical Review B*, Vol. 56 (14), pp. 8542–8552, 1997.
- [24] J. Godet, L. Pizzagalli, S. Brochard and P. Beauchamp, Theoretical study of dislocation nucleation from simple surface defects in semiconductors, *Physical Review B*, Vol. 70 (5), p. 054109, 2004.
- [25] H. C. Andersen, Molecular dynamics simulations at constant pressure and/or temperature, *Journal of Chemical Physics*, Vol. 72 (4), pp. 2384–2393, 1980.
- [26] M. Parrinello and A. Rahman, Polymorphic transitions in single crystals: A new

molecular dynamics mehod, Journal of Applied Physics, Vol. 52 (12), pp. 7182–7190, 1981.

- [27] M. Parrinello and A. Rahman, Strain fluctuations and elastic constants, *Journal of Chemical Physics*, Vol. 76 (5), pp. 2662–2666, 1982.
- [28] C. L. Kelchner, S. J. Plimpton, and J. C. Hamilton, Dislocation nucleation and defect structure during surface indentation, *Physical Review B*, Vol. 58 (17), pp.11085–11088, 1998.
- [29] J. A. Zimmerman, C. L. Kelchner, P. A. Klein, J. C. Hamilton, and S. M. Foiles, Surface step effects on nanoindentation, *Physical Review Letters*, Vol. 87 (16), p. 165507, 2001.

3. MODELS AND RESULTS

3.1 Introduction

This chapter contains information about simulation models and simulation results of reaction pathway sampling for homogeneous nucleation of dislocations of the shuffle-set and glide-set in Si, and homogeneous dislocation nucleation in Cu and Mo.

All results listed in this chapter are primary results, presented without analysis and conclusions. These results are used as and when required in the next three chapters where homogeneous dislocation nucleation is examined from different perspectives. The analyses and conclusions from the relevant perspectives can be found there.

In order to efficiently obtain activation barriers and saddle-point configurations under various stress levels, various techniques of the nudged elastic band (NEB) method, such as the improved tangent method [1], climbing image method [2], and free-end method [3] have been employed. The calculation is considered to have converged when the potential force on each replica vertical to the path becomes less than 0.005eV/Å. The approach has been similar to that of Zhu [4] and Boyer [5].

3.2 Shuffle-set homogeneous dislocation nucleation in Si

3.2.1 Model

The basic simulation cell, shown in Figure 3-1, which simulates a perfect crystal, consists of 302,400 atoms and is $23.0 \times 11.5 \times 22.8 \text{ nm}^3$. Periodic boundary conditions are imposed in all directions. Shear stresses are applied on the (111) plane in the $[01\overline{1}]$ direction by deforming the simulation cell so as to maximize the resolved shear stress on the slip plane. The interatomic potential employed is the SW potential [6].



Figure 3-1 Simulation model for homogeneous dislocation nucleation of the shuffle-set in Si. The slip plane and the direction of the Burgers vector are shown.

The initial NEB replicas for the shuffle-set are comprised of snapshots obtained from molecular dynamics shrinking of an artificially introduced perfect dislocation loop. The replicas are used after CG relaxation [7] to remove the effects of atomic vibrations. The number of images for the NEB algorithm is 12.

3.2.2 Results: Activation energy and saddle point configurations

The configuration energy for a series of images along the minimum energy path (of length unity), and saddle-point atomistic configurations for homogeneous dislocation loop nucleation of the shuffle-set in Si under a series of $<110>{111}$ resolved shear stress values are plotted in Figure 3–2. The solid squares are the energies for atomistic configurations along the reaction pathway calculated by the NEB method, and the curve is a spline interpolation taken from the gradient of the energy landscape at the atomistic configurations. This interpolation, as applied to the NEB algorithm was proposed by Henkelman et al. [1], and it aims to satisfy the energy values and first order derivative

between two points by a third order derived function; the curve is therefore not continuous. The reaction coordinate has been normalized by the final coordinate value. The saddle-point atomistic configurations are shown in the form of slip vector representation [8].



(b) 5.5 GPa

Figure 3-2 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<110>\{111\}$ resolved shear stress values for homogeneous dislocation loop nucleation of the shuffle-set in Si.





0.8

1

0.6

0

-2

0

0.2

0.4

Reaction coordinate

Figure 3-2 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of <110>{111} resolved shear stress values for homogeneous dislocation loop nucleation of the shuffle-set in Si.





Figure 3-2 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<110>\{111\}$ resolved shear stress values for homogeneous dislocation loop nucleation of the shuffle-set in Si.

The shear stress dependence of activation energy for nucleation of the shuffle-set dislocation loop in Si is shown in Figure 3-3.



Figure 3-3 Shear stress dependence of activation energy for nucleation of the shuffle-set dislocation in Si. The slip system is $<110>\{111\}$ for perfect dislocations.

3.2.3 Results: Maximum inelastic displacement

Figure 3-4 shows the stress dependence of the maximum inelastic shear displacement of the dislocation embryo as defined by the length of the slip vector [8] normalized by the perfect Burgers vector for shuffle-set dislocation.



Figure 3-4 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the perfect Burgers vector for shuffle-set homogeneous dislocation nucleation in Si.

3.3 Glide-set homogeneous dislocation nucleation in Si

3.3.1 Model

The basic simulation cell, shown in Figure 3-5, which simulates a perfect crystal, consists of 302,400 atoms and is $23.0 \times 11.5 \times 22.8 \text{ nm}^3$. Periodic boundary conditions are imposed in all directions. Shear stresses are applied on the (111) plane in the $[11\overline{2}]$ direction. The interatomic potential employed is the SW potential [6].



Figure 3-5 Simulation model for homogeneous dislocation nucleation of the glide-set in Si. The slip plane and the direction of the Burgers vector are shown.

Owing to the very low mobility (high activation energy) [9,10] of dislocations of the glide-set, glide-set partial dislocation loops of successive sizes were inserted artificially by displacing atoms based on the dislocation-interpolation method [11] followed by CG relaxation [7]. The initial input NEB images are 21, with images which corresponding to negative potential energies (for big dislocation radii) disposed off. The minimum number of NEB images till final convergence is 13.

3.3.2 Results: Activation energies and saddle-point configurations

The configuration energy for a series of images along the minimum energy path (of length unity), and saddle-point atomistic configurations for homogeneous dislocation loop nucleation of the glide-set in Si under a series of $<112>\{111\}$ resolved shear stress values are plotted in Figure 3–6. The solid squares are the energies for atomistic

configurations along the reaction pathway calculated by the NEB method, and the line is a spline interpolation [1] taken from the gradient of the energy landscape at the atomistic configurations. The reaction coordinate has been normalized by the final coordinate value. The saddle-point atomistic configurations are shown in the form of slip vector representation [8].



(b) 5.5 GPa

Figure 3-6 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of <112>{111} resolved shear stress values for homogeneous dislocation loop nucleation of the glide-set in Si.



(d) 6.5 GPa

Figure 3-6 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous dislocation loop nucleation of the glide-set in Si.



(e)	7	GPa
$\langle \mathbf{v} \rangle$		01 4

Figure 3-6 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous dislocation loop nucleation of the glide-set in Si.

The shear stress dependence of activation energy for nucleation of the glide-set dislocation in Si is shown in Figure 3-7.



Figure 3-7 Shear stress dependence of activation energy for nucleation of the glide-set dislocation in Si. The slip system is $<112>\{111\}$ for partial dislocations.

3.3.3 Results: Maximum inelastic displacement

Figure 3-8 shows the stress dependence of the maximum inelastic shear displacement of the dislocation embryo as defined by the length of the slip vector [8] normalized by the partial Burgers vector for glide-set dislocation.



Figure 3-8 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the partial Burgers vector for glide-set homogeneous dislocation nucleation in Si.

3.4 Dislocation nucleation in Cu

3.4.1 Model

For Cu, the basic simulation cell (shown in Figure 3-9) comprises 151,200 atoms and simulates a $15.3 \times 7.7 \times 15.2$ nm³ perfect crystal. The interatomic potential employed is the Mishin potential [12]. Shear stresses are applied on the (111) plane in the $[11\overline{2}]$ direction, which coincides with the partial Burgers vector for Cu, as it is energetically more favorable for the perfect dislocation to dissociate into two Shockley partial dislocations in face-centered cubic Cu [13,14]. Shear stress is applied by deforming the simulation cell so as to maximize the resolved shear stress on the respective slip planes. Periodic boundary conditions are imposed in all directions to remove all surfaces.



Figure 3-9 Simulation model for homogeneous dislocation nucleation in Cu. The slip plane and the direction of the Burgers vector are shown.

The initial NEB replicas are comprised of linear interpolations between the initial atomic configuration and the final atomic configuration that has an artificially introduced partial dislocation loop introduced into it by displacing atoms according to the displacement field based on the dislocation theory, followed by CG relaxation [7]. The number of NEB replicas used is 12.

3.4.2 Results: Activation energies and saddle-point configurations

The configuration energy for a series of images along the minimum energy path (of length unity), and saddle-point configurations for homogeneous dislocation loop nucleation in Cu under a series of $<112>\{111\}$ resolved shear stress values are plotted

in Figure 3–10. The solid squares are energies for atomistic configurations along the reaction pathway calculated by the NEB method, and the line is a spline interpolation [1] taken from the gradient of the energy landscape at the atomistic configurations. The reaction coordinate has been normalized by the final coordinate value. The saddle-point atomistic configurations are shown in the form of slip vector representation [8].



(b) 2.5 GPa

Figure 3-10 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous partial dislocation loop nucleation in Cu.





Figure 3-10 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous partial dislocation loop nucleation in Cu.





Figure 3-10 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous partial dislocation loop nucleation in Cu.



(g) 4.75 GPa

Figure 3-10 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<112>\{111\}$ resolved shear stress values for homogeneous partial dislocation loop nucleation in Cu.

The shear stress dependence of activation energy for homogeneous dislocation nucleation in Cu is shown in Figure 3-11.



Figure 3-11 Shear stress dependence of activation energy for homogeneous dislocation nucleation in Cu. The slip system is $<112>\{111\}$ for partial dislocations.

3.4.3 Results: Maximum inelastic displacement

Figure 3-12 shows the stress dependence of the maximum inelastic shear displacement of the dislocation embryo as defined by the length of the slip vector [8] normalized by the partial Burgers vector for Cu.



Figure 3-12 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the partial Burgers vector for homogeneous dislocation nucleation in Cu.

3.5 Homogeneous dislocation nucleation in Mo

3.5.1 Model

For Mo, the basic simulation cell (Figure 3-13) comprises 77,600 atoms and simulates a $12.3 \times 12.3 \times 8.0$ nm³ perfect crystal. The interatomic potential employed is the GEAM potential [15]. Shear stresses are applied on the (1-1 0) plane in the [111] direction, which coincides with the Burgers vector for Mo. Shear stress is applied by deforming the simulation cell so as to maximize the resolved shear stress on the respective slip planes. Periodic boundary conditions are imposed in all directions to remove all surfaces.



Figure 3-13 Simulation model for homogeneous dislocation nucleation in Mo. The slip plane and the direction of the Burgers vector are shown.

The initial NEB replicas are comprised of linear interpolations between the initial atomic configuration and the final atomic configuration that has an artificially introduced perfect dislocation loop introduced into it by displacing atoms according to the displacement field based on the dislocation theory, followed by CG relaxation [7]. The number of NEB replicas used is 9.

3.5.2 Results: Activation energies and saddle-point configurations

The configuration energy for a series of images along the minimum energy path (of length unity), and saddle-point configurations for homogeneous dislocation loop nucleation in Mo under a series of $<111>\{110\}$ resolved shear stress values is plotted in Figure 3–14. The solid squares are the energies for atomistic configurations along the

reaction pathway calculated by the NEB method, and the line is a spline interpolation [1] taken from the gradient of the energy landscape at the atomistic configurations. The reaction coordinate has been normalized by the final coordinate value. The saddle-point atomistic configurations are shown in the form of slip vector representation [8].



(b) 13.5 GPa

Figure 3-14 Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of <111>{110} resolved shear stress values for homogeneous dislocation loop nucleation in Mo.





Figure 3-14 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<111>\{110\}$ resolved shear stress values for homogeneous dislocation loop nucleation in Mo.





Figure 3-14 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<111>\{110\}$ resolved shear stress values for homogeneous dislocation loop nucleation in Mo.





Figure 3-14 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<111>\{110\}$ resolved shear stress values for homogeneous dislocation loop nucleation in Mo.



(j) 17.5 GPa

Figure 3-14 (continued) Configuration energy for a series of images along the minimum energy path (left), and slip vector representation of the saddle-point atomic configuration (right) under a series of $<111>\{110\}$ resolved shear stress values for homogeneous dislocation loop nucleation in Mo.

The shear stress dependence of activation energy for homogeneous dislocation nucleation in Mo is shown in Figure 3-15.



Figure 3-15 Shear stress dependence of activation energy for homogeneous dislocation nucleation in Mo. The slip system is $<111>\{110\}$ for perfect dislocations.

3.5.3 Results: Maximum inelastic displacement

Figure 3-16 shows the stress dependence of the maximum inelastic shear displacement of the dislocation embryo as defined by the length of the slip vector [8] normalized by the perfect Burgers vector for Mo.



Figure 3-16 Stress dependence of the maximum inelastic displacement of the dislocation core as defined by the length of the slip vector normalized by the perfect Burgers vector for homogeneous dislocation nucleation in Mo.

71

3.6 Summary

In this chapter, details of simulation models used, and primary results obtained from reaction pathway analysis performed for homogeneous dislocation nucleation in Si, Cu, and Mo have been presented. These results are used in the following chapters where they are analyzed and conclusions are presented based on those analyses.
References

- [1] G. Henkelman and H. Jonsson, Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points, Journal of Chemical Physics, Vol. 113 (22), pp. 9978–9985, 2000.
- G. Henkelman, B. P. Uberuaga, and H. Jonsson, A climbing image nudged elastic [2] band method for finding saddle points and minimum energy paths, Journal of Chemical Physics, Vol. 113 (22), pp. 9901–9904, 2000.
- T. Zhu, J. Li, A. Samanta, H. G. Kim, and S. Suresh, Interfacial plasticity governs [3] strain rate sensitivity and ductility in nanostructured metals, Proceedings of the National Academy of Sciences of the United States of America, Vol. 104 (9), pp. 3031-3036, 2007.
- [4] T. Zhu, J. Li, A. Samanta, A. Leach, and K. Gall, Temperature and strain-rate dependence of surface dislocation nucleation, Physical Review Letters, Vol. 100 (2), p. 025502, 2008.
- [5] R. D. Boyer, Ph.D. Thesis, Stress-mediated reaction pathways for dislocation nucleation in copper, MIT, 2007.
- F. H. Stillinger and T. A. Weber, Computer simulation of local order in condensed [6] phases of silicon, *Physical Review B*, Vol. 31 (8), pp. 5262–5271, 1985.
- M. R. Hestenes and E. Stiefel, Methods of Conjugate Gradients for Solving Linear [7] Systems, Journal of Research of the National Bureau of Standards, Vol. 49 (6), pp. 409-436, 1952.
- J. A. Zimmerman, C. L. Kelchner, P. A. Klein, J. C. Hamilton, and S. M. Foiles, [8] Surface step effects on nanoindentation, Physical Review Letters, Vol. 87 (16), p. 165507, 2001.
- [9] V. V. Bulatov, S. Yip and A. S. Argon, Atomic modes of dislocation mobility in silicon, Philosophical Magazine A, Vol. 72 (2), pp. 453–496, 1995.
- [10] V. V. Bulatov, J. F. Justo, W. Cai, S. Yip, A. S. Argon, T. Lenosky, M. de Koning, and T. Diaz de la Rubia, Parameter-free modeling of dislocation motion: the case of silicon, Philosophical Magazine A, Vol. 81 (5), pp. 1257–1281, 2001.
- [11] K. Shima, S. Izumi and S. Sakai, Reaction pathway analysis for dislocation nucleation from a sharp corner in silicon: glide set versus shuffle-set, Journal of Applied Physics, Vol. 108 (6), p. 063504, 2010.
- [12] Y. Mishin, M J. Mehl, D. A. Papaconstantopoulus, A. F. Voter, and J. D. Kress, Structural stability and lattice defects in copper: Ab initio, tight-bonding, and embedded-atom calculations, Physical Review B, Vol. 63 (12), p. 224106, 2001.

- [13] D. Hull and D. J. Bacon, *Introduction to Dislocations*, fourth ed., Butterworth-Heinemann, 2001.
- [14] J. P. Hirth and J. Lothe, *Theory of Dislocations*, Wiley, 1982.
- [15] X. W. Zhou, H. N. G. Wadley, R. A. Johnson, D. J. Larson, N. Tabat, A. Cerezo, A. K. Petford-Long, G. D. W. Smith, P. H. Clifton, R. L. Martens and T. F. Kelly, Atomic scale structure of sputtered metal multilayers, *Acta Materialia*, Vol. 49 (19), pp. 4005–4015, 2001.

4. COMPARISON BETWEEN Si, Cu and Mo

4.1 Introduction

In this chapter, homogeneous dislocation nucleation is examined in three different materials. Si, Cu and Mo are taken as representative of diamond cubic, face-centered cubic and body-centered cubic crystals respectively, with an aim to highlight the differences between them in terms of homogeneous dislocation nucleation. The Nudged Elastic Band (NEB) method and extended schemes are employed for the reaction pathway sampling of these materials (detailed results have been given in Chapter 3). The work on homogeneous dislocation nucleation in Si and Mo is original, whereas the results for Cu are a reproduction of Boyer's results [1] for Cu in order to bring them up to the point where they can be compared with original results for Si and Mo. The three materials are compared in terms of the mechanics of their saddle-point configurations and the respective stress dependences of their activation energies and activation volumes. Focusing on the homogeneous system enables the comparison of the three materials from the viewpoint of dislocation nucleation at the most fundamental level possible, free from the complex effects of heterogeneities.

Homogeneous dislocation nucleation is also compared with two cases of heterogeneous dislocation nucleation with an aim to understand the phenomenon of

dislocation nucleation by linking the two forms of nucleation. Finally, ideal strength determined for the homogeneous case is discussed, followed by the reduction of strength caused by the presence of heterogeneities.

Data relevant to dislocations in the three materials under consideration is tabulated in Table 4-1 below.

	Burgars	Slip		Lattice
	Durgers	nlane	Туре	constant
	vector	plane		<i>a</i> [Å]
Cu	1/6[1 1-2] <i>a</i>	(111)	Partial	3.61
Si	1/2[0 1-1] <i>a</i>	(111)	Perfect	5.43
Мо	1/2[1 1 1] <i>a</i>	(1-10)	Perfect	3.15

Table 4-1 Data relevant to dislocations in Cu, Si and Mo

4.2 Activation energy

The shear-stress dependence of activation energy for homogeneous dislocation nucleation in Cu, Si and Mo is presented in Figure 4-1. From Figure 4-1 (a) it is obvious that the stress ranges corresponding to activation energies less than 5eV (realistically feasible energy range) for the three materials are widely separated. Mo is by far the most stress intensive material in terms of homogeneous dislocation nucleation, followed by Si and Cu in the same order. The stronger BCC bonds of Mo make it more resistant to dislocation nucleation. In fact the high stress values (in excess of 13 GPa) for activation energies less than 5 eV make homogeneous dislocation nucleation in Mo a practically unrealistic transition. Covalent bonded Si also shows considerable resistance, albeit less than that displayed by Mo, to dislocation nucleation. Weaker FCC bonds of Cu make it least resistant to homogeneous dislocation nucleation.

Unlike the case of Cu and Mo, where activation energies are determinate for all stress values, saddle-point configurations for dislocation nucleation corresponding to activation energy values less than 1.5eV could not be determined for Si. The dominance of competing mechanisms such as twinning in this high-stress range may be the cause of the absence of an athermal stress, where the transition is expected to occur spontaneously without any input of thermal activation, for homogeneous dislocation

nucleation in Si. Figure 4-1 (b) presents the comparison between the dependence of activation energy on normalized shear-stress for homogeneous dislocation nucleation in the three materials. The stress values are normalized by the critical shear stress values for the relevant slip systems of Cu, Si and Mo respectively. Our result for Cu is in reasonable agreement with Boyer's result [1], which is also shown.



(b)

Figure 4-1 Dependence of activation energy on (a) Resolved shear stress, and (b) Resolved shear stress normalized by respective critical stresses, for homogeneous dislocation nucleation in Cu, Si and Mo.

Various relevant material properties of Mo, Si and Cu are shown in Table 4-2. The ideal strength values are taken from Density functional theory (DFT) calculations [2]. The unstable stacking fault energies for Mo, Si [3], and Cu [4] are obtained by using the GEAM, SW, and Mishin potentials respectively. The high stress ranges involved in homogeneous dislocation nucleation in Mo and Si, and the comparatively lower stress ranges involved in the corresponding process in Cu qualitatively fit in with the respective values of ideal strengths for the three materials.

The unstable stacking fault energy (γ_{us}) is considered to be closely related to dislocation nucleation [5]. The stacking fault energy converted into absolute energy units by multiplying it with the square of the Burgers vector ($\gamma_{us}b^2$) can also be considered as an indicator for the resistance to dislocation nucleation in a material. Although these quantities do provide rough estimates, they cannot provide quantitative information about activation energies under given stress conditions. Therefore, there really is no replacement of fully atomistic analysis for studying thermally activated transitions such as dislocation nucleation.

Material	Unstable SF	Shear	Burgers	$\gamma_{\rm us} \cdot \boldsymbol{b}^2$	Ideal Strength
	Energy	Modulus	Vector	[eV]	[2]
	$\gamma_{us} [J/m^2]$	G [GPa]	b [Å]		τ_{ideal} [GPa]
Mo	1.437	134	2.73	0.67	14.82
Si	0.830	64	3.84	0.76	9.62
Cu	0.160	41	1.47	0.02	2.16

Table 4-2 Physical properties of Mo, Si and Cu relevant to dislocations

4.3 Mechanics of the saddle-point configurations

Figures 4-2, 4-3 and 4-4 show saddle-point configurations, presented in the form of slip-vector representation [6], corresponding to a series of resolved shear stress values for Si, Cu and Mo. For Mo and Cu, the dislocation cores are elliptical in shape. For Cu, this agrees with both atomistic [1] work as well as works performed in the PN framework [7,8]. The elliptical shape of the dislocation core in Mo and Cu is a result of the anisotropy of the Peierls barrier, which is lower for edge components than screw

components of the dislocation loop [9-12]. The smooth and gradual bends for Cu and Mo are attributable to their lower Peierls barrier, which means that the dislocation loop can afford to take a shape which makes its overall length as short as possible [13]. In Si, on the other hand, the dislocation cores corresponding to all stress values are hexagonal in shape. The hexagonal shape is a result of the higher Peierls barrier for Si, which causes the dislocation segments to lie along energy troughs such that short and sharp kinks are formed. Due to the higher Peierls barrier, the dislocation segments prefer to lie along the energy troughs as much as possible, which results in the hexagonal shape of the core [13]. This also fits in with the observation in recent low-temperature experiments [14] and simulation work [4] where dislocation loops in Si display hexagonal shapes whose edges are parallel to <110> Peierls valleys on the {111} slip plane.



Figure 4-2 Saddle-point configurations corresponding to a series of resolved shear stress values for homogeneous dislocation nucleation in Si.



Figure 4-3 Saddle-point configurations corresponding to a series of resolved shear stress values for homogeneous dislocation nucleation in Cu.



Figure 4-4 Saddle-point configurations corresponding to a series of resolved shear stress values for homogeneous dislocation nucleation in Mo.

The difference between the Peierls barrier of Si on the one hand and Cu and Mo on the other is shown in the form a schematic drawing in Figure 4-5. In the former, due to the higher Peierls barrier, the dislocation segments prefer to lie along the energy troughs as much as possible, which results in the hexagonal shape of the core. In the latter, the dislocation can afford to take a shape which makes its overall length as short as possible.



Figure 4-5 The difference in Peierls barriers: Low Peierls barrier (right) in Cu and Mo results in elliptical dislocation cores, while high Peierls barrier (left) in Si results in hexagonal shape of the dislocation cores.

Despite the differences in the length and direction of their respective Burgers vectors, the slip vector distributions for Cu and Si, as shown in Figures 4-2 and 4-3, are similar in the following respect: At low stresses the maximum slip vectors, which approach the respective Burgers vectors, are observed for atoms at or near the center of the loop, and they decrease gradually with increasing distance of the atoms from the center. Mo (Figure 4-4) is different from both Cu and Si in that the maximum displacement reaches a very small percentage of the Burgers vector (even for comparatively low stresses). As the stress increases, for all materials the range of the slip vectors of atoms in the dislocation core becomes smaller and smaller until the

maximum slip vectors are reduced to very small fractions of the respective Burgers vectors for the three materials.



Figure 4-6 Comparison of the shear stress dependence of the maximum inelastic displacement for homogeneous dislocation nucleation in Si, Cu, and Mo. The displacements have been normalized by the Burgers vectors for the respective materials.

Figure 4-6 presents the shear-stress dependence of the maximum inelastic displacement as expressed by the slip vector normalized by the partial Burgers vector for Cu and perfect Burgers vectors for Mo and Si. While for Cu and Mo the maximum slip vector decreases monotonically with the increase in applied stress, for Si the maximum slip vector flattens out after decreasing steadily. This flattening might be related to the fact that homogeneous dislocation nucleation in Si does not exhibit an athermal stress.



Figure 4-7 Diffused dislocation core (red curve) and dislocation core assumed in the classical dislocation theory (black rectangle).

The fact that the dislocation cores for all materials show a diffused nature (Figures 4-2, 4-3, 4-4 and 4-6), that is, maximum slip reaches a fraction of the Burgers vector (shown schematically in Figure 4-7) means that dislocation nucleation can't be treated correctly by using the classical dislocation theory.

Fig 4-8 shows directions of the in-plane atomic displacements for homogeneous dislocation nucleation in Si, Cu, and Mo. The directions of the respective Burgers vectors are also indicated. For Si and Cu, the in-plane atomic displacements are in the direction of their perfect and partial Burgers vectors respectively.



Figure 4-8 Directions of the in-plane atomic displacements for homogeneous dislocation nucleation in Si (left), Cu (middle), and Mo (right). The directions of the respective Burgers vectors are also indicated (black arrows).

In the case of Mo however, the direction of motion of central atoms is inclined with respect to the Burgers vector direction. Atomic displacements are in the $\langle 421 \rangle$ directions and make an angle of 29° with the Burgers vector on the slip plane. Perfect dislocations in Mo are understood not to dissociate into partial ones because it is understood that due to the high unstable stacking fault energy, stacking faults don't exist in Mo. The inclined displacement of atoms is therefore surprising. The minimum energy path for Mo indicates that the central atoms moving in directions inclined to the Burgers vector decreases the energy requirements for the transition to occur, as compared to the scenario where the atoms move parallel to the Burgers vector direction.

4.4 Activation volume

Activation volume is a measure of the extent of atomic movement involved in a thermally activated process. On an intuitive level, the higher the activation volume, the more "collective" a transition is, that is, more volume of material is involved in the transition [15]. Also, the higher the activation volume, the less sensitive the transition is to thermal activations.

In practice, the activation volume has traditionally been considered to have a number of different definitions [16,17]. The thermodynamics based conceptual measure of activation volume for a thermally activated process is given as the stress derivative of the activation energy [18]. This thermodynamics-based conceptual measure of the activation volume of a thermally activated transition is expressed mathematically as:

$$\Omega = -\frac{\partial Q(\tau)}{\partial \tau} \tag{4.1}$$

where $Q(\tau)$ is the stress-dependant activation energy and τ is the shear stress. Therefore, the higher the gradient of the energy curve for a transition, the higher is its activation volume.

From the continuum point of view, there are descriptions such as those developed by Cottrell and Kocks [16], where the activation volume is typically defined structurally as the area swept out by the dislocation loop at the saddle point multiplied by the Burgers vector of the dislocation. While this structural definition of activation volume holds for continuum descriptions, it has a problem when dealing with atomistic studies where very few atoms, if any, are displaced by amounts equal to the length of the Burgers vector. In the current work fully atomistic methods have been employed to study homogeneous dislocation nucleation, and it is aimed to provide a better understanding of the stress dependant behaviour of the activation volume. The structural definition of activation core as well as the actual inelastic displacements moved by the respective atoms. This is the most rigorous description of the activation volume because it considers the discrete contribution from each individual atom in the dislocation core that lies on the slip plane. This structural description is given by:

$$\Omega' = \iint u(x, y) dx dy \tag{4.2}$$

where u(x,y) is the in-plane inelastic displacement across the slip plane.

The markedly steeper curve for Si and Mo, as is clear from Figure 4-1(b), in the thermally activated region indicates that homogeneous nucleation in Si as well as Mo is accompanied by a significantly higher activation volume than the corresponding transition in Cu. Therefore, the dislocation nucleation process in Cu is much more sensitive to thermal activations than the corresponding processes for Si and Mo. The lower gradient of the energy curve for Cu confirms the higher temperature sensitivity for homogeneous dislocation nucleation in Cu than in corresponding transitions in Si and Mo. Therefore, although homogeneous dislocation nucleation is theoretically possible with the aid of thermal activations in both Cu as well as Si (contrary to the traditional understanding), the likelihood of that happening with the help of thermal activations in Cu is much more realistic and feasible than in Si, although it cannot be ruled out in Si either. The stresses required for homogeneous dislocation nucleation and Mo are so great that it can be safely said that homogeneous dislocation nucleation cannot happen in Mo even with the help of thermal activations.



Figure 4-9 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation in Cu. The structural definition and the thermodynamic definition are in good agreement.

Activation energy curve for a thermally activated transition is required in advance in order to determine the thermodynamic interpretation of activation volume for a certain stress level. On the other hand, the advantage of the structural activation volume is that it can, in theory, be calculated for any one arbitrary point through simulation or experiment. Figures 4-9, 4-10 and 4-11 compare the two definitions of the activation volume—the thermodynamic definition (Eq. 4.1) and the structural definition (Eq. 4.2)—for homogeneous dislocation in Cu, Si and Mo respectively. It can be seen that for the case of Cu, the two are in reasonable agreement (Figure 4-9).



Figure 4-10 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation in Si. The structural definition gives quite low values as compared to the thermodynamic definition.



Figure 4-11 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation in Mo. The discrepancy between the structural definition and the thermodynamic definition increases with decreasing stress.

For Si, on the other hand, the structural values are a very small percentage of the thermodynamic values throughout the range of the values shown (Figure 4-10). Mo shows good agreement near the athermal threshold but as the stress becomes lower, the discrepancy becomes larger and larger (Figure 4-11).

The discrepancies between the two definitions depending upon the material and the stress range in question can be explained by observing the atomic displacements in the layers above and below the slip-plane. Figure 4-12 shows representative atomic displacements in the direction of the respective Burgers vectors exceeding 0.15Å for the three materials. The saddle point configurations shown in Figure 4-12 correspond to comparatively low stress regime for the three materials.



Figure 4-12 Extra slip-plane displacements of atoms in Si (left), Cu (middle), and Mo (right) for homogeneous dislocation nucleation. Only atoms with displacement in the Burgers vector direction exceeding 0.15Å are shown.

Inspection of saddle point configurations shows that for Cu, the dislocation nucleation process is essentially a two-plane process in which the two planes slide past each other with little effect on atoms on other planes. This is irrespective of the stress applied to the crystal. This would explain why the two definitions of activation volume are in agreement in the case of Cu.

Si shows the opposite of this behavior in that many layers of atoms are affected, irrespective of the applied stress values. Mo is an interesting case in that for high stress values the core approaches the two-plane core similar to Cu; but as the stress is decreased and the transition goes into the thermal activation regime, atoms in many more layers are displaced considerably. It appears that for Si and Mo (in the low stress regime) it is energetically favorable for the atomic displacements to happen in this collective, cup-like manner as opposed to the strictly two-plane, disc-like mechanism in Cu. The extra slip-plane displacements seem to be more pronounced for Si than Mo. It could be the effect of the directionality because Si is more directional than Mo, which in turn is more directional than Cu. The difference between perfect Burgers vector for Si and Mo on the one hand, and partial Burgers vector for Cu on the other, might also be the reason behind this behavior. This would explain the greater discrepancy between the two definitions of activation volume for Si as compared to Mo. This extra slip-plane displacement is another consideration that cannot be taken into account by methodologies other than fully atomistic techniques, such as the PN methodology. The structural definition of activation volume, therefore, can underestimate the activation volume depending on the material and stress range in question. It gives reasonably accurate results for Cu whereas it underestimates the activation volume for Si for the whole stress range, and Mo for low stresses.

4.5 Link between homogeneous and heterogeneous dislocation nucleation

In this section the relationship between dislocation nucleation in homogeneous and heterogeneous systems is examined. Results for homogeneous dislocation nucleation in Cu and Si reported in this research are compared with heterogeneous results reported in literature.

Out of the very wide variety of heterogeneous systems, dislocation nucleation from the corner of a Cu nanopillar [19] and dislocation nucleation from a sharp corner in Si [20,21] are selected for this comparison.

4.5.1 Comparison with heterogeneous system 1: Dislocation nucleation from the corner of a Cu nanopillar

Results for homogeneous dislocation in Cu are compared with heterogeneous dislocation nucleation from the corner of a Cu nanopillar under compressive stress [19]. This comparison is relevant because the same potential (Mishin potential) [22] has been used in both studies. The sharp-corner model [19] is shown in Figure 4-13. There are surfaces normal to the x [100] and y [010] directions, whereas in the z direction [001] periodic boundary condition is imposed.



Figure 4-13 Dislocation nucleation from the corner of a Cu nanopillar under compression (Fig. 3(a) in Ref. [19]).

Activation energy

The comparison of activation energy curves for homogeneous and heterogeneous nucleation in Cu is presented in Figure 4-14. The compressive stresses for Cu nanopillar have been converted to resolved shear stresses by using the Schmid factor.

Activation energies under stresses of 70% of the respective athermal (critical) stresses for the heterogeneous case and the homogeneous case are 0.05 eV and 1.2 eV respectively. This translates into a 95% reduction of the activation energy for the heterogeneous system as compared to the homogeneous case. The athermal stresses for the heterogeneous system and the homogeneous system are 4.85 and 2.12 GPa respectively.



Figure 4-14 Activation energy for homogeneous dislocation nucleation and dislocation nucleation from the corner of a nanopillar under compression in Cu. (a) Resolved shear stress dependence, (b) Normalized resolved shear stress dependence.

(b)

0.4

Normalized resolved shear stress

0.6

0.8

1

Saddle point configurations

0

0

0.2

The comparison of saddle point atomistic configurations for homogeneous and heterogeneous nucleation in Cu under stresses of 70% of their respective athermal

stresses is presented in Figure 4-15. Atomistic configurations are shown in the form of centro-symmetry representation [23], with only atoms without centro-symmetry being displayed. The size of the dislocation core for the heterogeneous system is much smaller than that for the homogenous case. In terms of the number of atoms in the dislocation core at the saddle point, it is 9 against 52 for heterogeneous and homogeneous nucleation respectively.



Figure 4-15 Saddle point configurations for (a) dislocation nucleation from the corner of a nanopillar under compression and (b) homogeneous dislocation nucleation in Cu.

The size of the dislocation core for heterogeneous dislocation nucleation is smaller because of geometric as well as structural reasons. The loop radius itself is smaller because of the physics of the phenomenon. In addition to this, as opposed to the full elliptical loop for homogeneous dislocation nucleation, there is quarter of a loop in case of nucleation from the corner, because of geometrical reasons.

Another important consideration is the fact that the stress figures quoted for the heterogeneous case are the nominal stress values, whereas the actual stress values near the heterogeneity (corner in this instance) are markedly higher because of the inevitable stress concentration. The high true stresses would result in smaller radii of the dislocation core and hence lower activation energies.

Activation volume curves

The comparison of activation volumes for homogeneous and heterogeneous dislocation nucleation from the corner of a nanopillar in Cu is presented in Figure 4-16. The compressive stress values for carbon nanopillar are converted to resolved shear stresses by using the Schmid factor. The comparison of activation volumes is presented as a function of the normalized resolved shear stress, with stress values normalized by the athermal (critical) stress values for the respective cases.



Figure 4-16 Activation volumes for heterogeneous and homogeneous dislocation nucleation in Cu.

Activation volumes for stresses of 70% of the respective athermal (critical) stresses for the heterogeneous case and the homogeneous case are $7b^3$ and $18b^3$ respectively. This translates into a 61% reduction of the activation volume for the heterogeneous system as compared to the homogeneous case. The reduction of activation volume is on account of the markedly smaller dislocation core for the heterogeneous case.

4.5.2 Comparison with heterogeneous system 2: Dislocation nucleation from a sharp corner in Si

Results for homogeneous dislocation in Si are compared with heterogeneous dislocation nucleation from a sharp corner in Si [20,21]. This comparison is relevant because the same potential (SW potential) [24] has been used in both studies. The sharp-corner model [20] is shown in Figure 4-17. Periodic boundary conditions have been imposed in all directions.



Figure 4-17 Dislocation nucleation from a sharp corner in Si (Fig. 1 in Ref. [20]).

Activation energy

The comparison of activation energy curves for homogeneous and heterogeneous nucleation in Si is presented in Figure 4-18. Activation energies for stresses of 70% of the respective athermal (critical) stresses for the heterogeneous case and the homogeneous case are 5.6 eV and 10.1 eV respectively. This translates into a 41.2% reduction of the activation energy for the heterogeneous system as compared to the homogeneous case. The athermal stresses for the heterogeneous system and the homogeneous system are 5.85 and 8.25 GPa respectively.

Saddle point configurations

The comparison of saddle point atomistic configurations for homogeneous and heterogeneous nucleation in Si under stresses of 70% of their respective athermal stresses is presented in Figure 4-19. Atomistic configurations are shown in the form of

the slip vector representation [6]. The size of the dislocation core for the heterogeneous system is smaller than that for the homogenous case.



(b)

Figure 4-18 Activation energy for homogeneous dislocation nucleation and dislocation nucleation from a sharp corner in Si: (a) Resolved shear stress dependence, and (b) Normalized resolved shear stress dependence.



Figure 4-19 Saddle point configurations for (a) dislocation nucleation from a sharp corner, and (b) homogeneous dislocation nucleation in Si.

The size of the dislocation core for heterogeneous dislocation nucleation is smaller because of geometric as well as structural reasons. The loop radius itself is smaller because of the physics of the phenomenon. Also, as opposed to the full elliptical loop for homogeneous dislocation nucleation, there is half of a loop in case of nucleation from the sharp corner, because of geometrical reasons.

Another important consideration is the fact that the stress figures quoted for the heterogeneous case are the nominal stress values, whereas the actual stress values near the heterogeneity (corner in this instance) are markedly higher because of the inevitable stress concentration. The high true stresses would result in smaller radii of the dislocation core and hence lower activation energies. While the size of the dislocation core is greater for the homogeneous case, the maximum slip vector is greater for heterogeneous dislocation. This would be because of the greater true stress near the sharp corner.

Activation volume curves

The comparison of activation volumes for homogeneous and heterogeneous dislocation nucleation from a sharp corner in Si is presented in Figure 4-20. The comparison of activation volumes is presented as a function of the normalized resolved shear stress, with stress values normalized by the critical stress values for the respective cases.



Figure 4-20 Activation volumes for heterogeneous and homogeneous dislocation nucleation in Si.

Activation volumes for stresses of 70% of the respective athermal (critical) stresses for the heterogeneous case and the homogeneous case are $14.9b^3$ and $20.5b^3$ respectively. This translates into a 27.3% reduction of the activation volume for the heterogeneous system as compared to the homogeneous case. The reduction of activation volume is on account of the markedly smaller dislocation core for the heterogeneous case.

4.5.3 Homogeneous versus heterogeneous dislocation nucleation: Discussion

The total energy of a dislocation is given by

$$E_{\text{total}} = E_{\text{self}} + E_{\text{stress}} + E_{\text{ledge}}$$
(6.3)

 E_{self} is the strain energy that is caused by the distortion of the crystal lattice. E_{stress} is the energy caused by the application of the external stress. E_{ledge} corresponds to the energy required for creating a new surface. This amount of energy is required to nucleate a dislocation loop. E_{ledge} does not exist in the case of homogeneous dislocation nucleation, and can cause complex effects in the heterogeneous case.

 E_{ledge} can be negative or positive depending on whether the surface area increases or decreases. In general, in case of an already present step, surface area is reduced in the process of nucleation of a dislocation loop; whereas if no such step is there to begin with, surface area increases in the process of dislocation loop nucleation [25]. In the first case taken in this comparison between homogeneous and heterogeneous dislocation nucleation (dislocation nucleation from the corner of a Cu nanopillar) the surface area increases, whereas in the second case (nucleation from a sharp corner in Si), the surface area is reduced. Therefore the correlation between the activation energy and activation volume is not straightforward in the case of heterogeneous dislocation nucleation. That is because in the former case, part of energy is used for creating a new surface, whereas in the latter case, the reduction of surface area frees up energy that can be utilized for the creation of the dislocation loop, decreasing the requirement of activation energy input from the outside. The creation/reduction of surface areas therefore makes the heterogeneous cases complex, and comparison with many heterogeneous systems is needed in order to quantify the contribution of E_{ledge} .

Another important consideration is the fact that the stress figures quoted for the heterogeneous case are the nominal stress values, whereas the actual stress values near the heterogeneity (corner in this instance) are markedly higher because of the inevitable stress concentration. The high true stresses would result in smaller radii of the dislocation core and hence lower activation energies.

The size of the dislocation core for heterogeneous dislocation nucleation is smaller from geometric as well as structural reasons. The loop radius itself is smaller because of the physics of the phenomenon. In addition to this, as opposed to the full elliptical loop for homogeneous dislocation nucleation, there is half or a quarter of a loop in case of heterogeneous nucleation depending on the geometry. This difference has been reported to be decisive in terms of strength difference between homogeneous and heterogeneous cases based on experimental studies [26].

Table 4-3 summarizes the activation volumes for the different systems under consideration at 70% and 80% of the respective critical stress conditions. The lower activation volumes for heterogeneous system have been confirmed in this comparison, and they prove to be decisive in that they result in heterogeneous dislocation nucleation

typically being more favorable than the homogeneous ones. However, the activation volumes are of the same order of magnitude, as is clear from Table 4-3.

The stress requirements for heterogeneous dislocation nucleation, which are already low as a result of their lower activation volumes, are rendered even lower because of the presence of the singularity of the heterogeneity. At and near that singularity, even low nominal stresses are magnified into very high true stresses and therefore heterogeneous nucleation becomes much more energetically favorable as compared with homogeneous dislocation nucleation. In the same way, the specific kind of heterogeneity would also cause a difference in activation energy requirements. For example, for a Cu nanowire [27] under identical stress conditions, energy requirements for nucleation from a side surface and from a corner have been reported to be 0.64 eV and 0.1 eV (six times lower) respectively. The type of heterogeneity therefore has a strong influence on the activation energy requirements.

System	Activation volume [b ³] 70% of critical stress	Activation volume [b ³] 80% of critical stress	Reference	Dislocation loop shape
Si homogeneous	20.5	12	This work	Hexagonal
Si sharp corner	14.9	9.5	Shima et al. [20,21]	Half- hexagonal
Cu homogeneous	18	12	This work	Elliptical
Cu nanopillar	7	5	Hara et al. [19]	Quarter- elliptical

Table 4-3 Comparison of activation volumes

The two cases considered here—dislocation nucleation from the corner of a Cu nanopillar under compression, and from a sharp corner in Si—are only two cases out of a very large variety of cases of heterogeneous dislocation nucleation. Similar comparisons of the homogeneous case with dislocation nucleation from other configurations (crack, surface step, corner, etc) promises to be insightful in terms of the quantitative correlation between heterogeneity and the lowering of the activation energy and activation volume. Also, the complex surface effects need to be studied with an aim to quantify their effect.

4.6 Ideal strength

Since the elastic limit of a perfect crystal is referred to as the theoretical or the ideal strength [26], the ideal strength of Si, Cu and Mo are the athermal (critical) stresses for homogeneous dislocation nucleation calculated in this research. The ideal strength can be considered as the stress for which a material without a preexisting defect ceases to remain elastic. Strictly speaking, the elastic limit, taken as the instance of first emergence of a dislocation defect, may not necessarily have a direct correspondence with the ideal strength, because other mechanisms (such as twinning) may govern the ideal strength, alone or in combination with dislocation nucleation.

However, the critical stress for dislocation nucleation can be considered as a measure of ideal strength if dislocation nucleation can be taken as the unalloyed governing mechanism for material failure (plasticity). Under that assumption, the ideal strength (critical stress for the homogeneous system) is discussed as follows:

For Cu and Mo, activation energies for homogeneous dislocation nucleation are determinate for points very close to the critical stress, and therefore the critical stress can be referred to as the athermal stress without a major error. For Si, on the other hand, energies lower than 1.5 eV are not determinate, indicating the absence of any athermal stress for homogeneous dislocation nucleation in Si. That is, other competing mechanisms such as twinning might be dominant in that region.

However, like Cu and Mo, the critical stress was taken for discussion of the ideal strength for Si too. The critical stress is defined as the maximum possible shear on the relevant slip plane in the direction of the perfect or partial Burgers vector depending on the material in question. The relevance of these critical stresses to homogeneous dislocation nucleation calculations is that they fit in smoothly with the activation energy curves.

Table 4-4 compares the ideal strengths from this study with those published in literature. The atomistic results for Cu and Si are based on the same potentials (Mishin [22] and SW [24] respectively) as have been used in this research.

Motorial	DFT [2]	Atomistic	This study
Material	[GPa]	[GPa]	[GPa]
Si	9.62	9.6 [28]	8.25
Cu	2.16	2.91 [29]	4.85
Мо	14.82	-	17.9

Table 4-4 Ideal strengths of Si, Cu and Mo

The ideal strength values reported in literature for Si and Cu are different by 16.3% and 40% than those calculated in this research. The stress values reported can be greatly dependent on the manner in which stresses on planes other than the slip plane are handled. In this research, stresses perpendicular to the slip plane have been ignored and their effect has not been determined. In this respect, the comparison between the ideal stress values presented above is not completely fair.

The decrease of strength from the ideal or theoretical strength to the real strength of systems with heterogeneities is examined next. The strengths of Cu and Si fall to 2.12 GPa and 5.85 GPa respectively (see sections 4.5.1 and 4.5.2) because of the presence of heterogeneities. This translates to a reduction of strength (from the ideal strength) of 56.2% for Cu and 29% for Si respectively. The specific type of heterogeneity would be expected to play a significant role in the amount of reduction of strength. A comparison with other heterogeneous systems should be able to deepen understanding on this issue.

4.7 Conclusions

Reaction pathway analyses for homogeneous dislocation nucleation in FCC Cu, BCC Mo and covalently bonded DC Si were carried out and the three materials were compared in terms of their energy curves and the mechanics of their saddle-point configurations. The choice of perfect crystals enabled the comparison of dislocation nucleation in the three materials at the most fundamental level, free of any complexities arising from heterogeneities.

Homogeneous dislocation nucleation is possible with the aid of thermal activations in both Cu and Si, although, admittedly, the likelihood of that happening is much more realistic and feasible in Cu than in Si. Homogeneous dislocation nucleation in Mo, on the other hand, can be ruled out because of unrealistically high activation energy requirements for realistic levels of stress. The high stress requirements for Mo (in excess of 13 GPa for activation energy values less than 5 eV) would be on account of the stiffer BCC bonds of Mo. This stiffness is also apparent in the lower saddle-point atomistic displacements in Mo than the other two materials. The values of athermal (critical) stresses are in reasonable agreement with ideal strengths of the three materials.

Another effect of crystal structure makes itself apparent is the extra slip-plane displacements of saddle-point configurations of the three materials. The mechanics of dislocations cores show that unlike Cu, in which dislocation nucleation is essentially a two-plane phenomenon; Mo and Si show considerable atomic displacements in many planes above and below the slip plane. The structural definition of activation volume therefore underestimates the activation volume for Mo and Si. Furthermore, although perfect dislocations in Mo (unlike Cu) are not known to dissociate into partial dislocations, the direction of atomic displacements is at an angle with respect to the perfect Burgers vector. The reason for this is unknown but it is reasonable to interpret that it results in lowering of the activation energy.

Although they provide a rough estimation of resistance to dislocation nucleation in a material, parameters such as γ us and γ us b^2 don't provide quantitative information provided by fully atomistic techniques. Also, for all materials the presence of a diffused core region makes the nucleation inaccessible to classical dislocation theory. Atomistic analysis is therefore indispensable in order to accurately explain the phenomenon of dislocation nucleation.

References

- [1] R. D. Boyer, *Stress-mediated reaction pathways for dislocation nucleation in Cu*, Ph.D. Thesis, MIT, 2007.
- [2] S. Ogata, J. Li, N. Hirosaka, Y. Shibutani and S. Yip, Ideal shear strain of metals and ceramics, *Physical Review B*, Vol. 70 (10), p. 104104, 2004.
- [3] J. Godet, L. Pizzagalli, S. Brochard, and P. Beauchamp, Comparison between classical potentials and ab initio methods for silicon under large shear, *Journal of Physics: Condensed Matter*, Vol. 15 (41), pp. 6943–6953, 2003.
- [4] S. Izumi and S. Yip, Dislocation nucleation from a sharp corner in silicon, *Journal of Applied Physics*, Vol. 104 (3), p. 033513, 2008.
- [5] J. R. Rice, Dislocation nucleation from a crack tip: An analysis based on the Peierls concept, *Journal of Mechanics and Physics of Solids*, Vol. 40 (2), pp. 239–271, 1992.
- [6] J. A. Zimmerman, C. L. Kelchner, P. A. Klein, J. C. Hamilton, and S. M. Foiles, Surface step effects on nanoindentation, *Physical Review Letters*, Vol. 87 (16), p. 165507, 2001.
- [7] Y. Xiang, H. Wei, P. Ming, W. E, A generalized Peierls-Nabarro model for curved dislocations and core structures of dislocation loops in Al and Cu, *Acta Materialia*, Vol. 56 (7), pp. 1447–1460, 2008.
- [8] G. Xu, A. S. Argon, Homogeneous nucleation of dislocation loops under stress in perfect crystals, *Philosophical Magazine Letters*, Vol. 80 (9), pp. 605–611, 2000.
- [9] G. Schoeck and M. Krystian, The peierls energy and kink energy in fcc metals, *Philosophical Magazine*, Vol. 85 (9), pp. 949–966, 2005.
- [10] C. H. Henager and R. G. Hoagland, Dislocation and stacking fault core fields in fcc metals, *Philosophical Magazine*, Vol. 85 (36), pp. 4477–4508, 2005.
- [11] W. Xu and J. A. Moriarty, Accurate atomistic simulations of the Peierls barrier and kink-pair formation energy for (111) screw dislocations in bcc Mo, *Computational Materials Science*, Vol. 9 (3–4), pp. 348–356, 1998.
- [12] D. Hull and D. J. Bacon, *Introduction to Dislocations*, fourth ed., Butterworth-Heinemann, pp. 198–200, 2001.
- [13] R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, third ed., John Wiley & Sons, p. 56, 1989.

- [14] J. Rabier and J. L. Demenet, On a change in deformation mechanism in silicon at very high stress - New evidences, *Scripta Materialia*, Vol. 45 (11), pp. 1259–1265, 2001.
- [15] J. Li, The mechanics and physics of defect nucleation, MRS Bulletin, Vol. 32, pp. 151–159, 2007.
- [16] A. H. Cottrell, *Dislocations and plastic flow in crystals*, 1956, Oxford University Press, UK.
- [17] L. Zuo, A.H.W. Ngan, and G..P. Zheng, Size dependence of incipient dislocation plasticity in Ni₃AI, *Physical Review Letters*, Vol. 94 (9), p. 095501, 2005.
- [18] U. F. Kocks, A.S. Argon and M.F. Ashby, Thermodynamics and kinetics of slip, 1st ed., *Progress in materials science*, Vol. 19, Pergamon Press, New York, 1975.
- [19] S. Hara and J. Li, Adaptive strain-boost hyperdynamics simulations of stress-driven atomic processes, *Physical Review B*, Vol. 82 (18), p. 184114, 2010.
- [20] K. Shima, S. Izumi and S. Sakai, Reaction pathway analysis for dislocation nucleation from a sharp corner in silicon: Glide set versus shuffle-set, *Journal of Applied Physics*, Vol. 108 (6), p. 063504, 2010.
- [21] K. Shima, *Behaviour analysis of dislocation nucleation of the glide-set in Si*, Master's thesis (in Japanese), University of Tokyo, 2010.
- [22] Y. Mishin, M J. Mehl, D. A. Papaconstantopoulus, A. F. Voter, and J. D. Kress, Structural stability and lattice defects in copper: Ab initio, tight-bonding, and embedded-atom calculations, *Physical Review B*, Vol. 63 (12), p. 224106, 2001.
- [23] C. L. Kelchner, S. J. Plimpton, and J. C. Hamilton, Dislocation nucleation and defect structure during surface indentation, *Physical Review B*, Vol. 58 (17), pp.11085–11088, 1998.
- [24] F. H. Stillinger and T. A. Weber, Computer simulation of local order in condensed phases of silicon, *Physical Review B*, Vol. 31 (8), pp. 5262–5271, 1985.
- [25] S. Hara, S. Izumi, and S. Sakai, Reaction pathway analysis for dislocation nucleation from a Ni surface step, *Journal of Applied Physics*, Vol. 106 (9), p. 093507, 2009.
- [26] H. Bei, Y. F. Gao, S. Shim, E. P. George and G. M. Pharr, Strength differences arising from homogeneous versus heterogeneous dislocation nucleation, *Physical Review B*, Vol. 77 (6), p. 060103(R), 2008.

- [27] T. Zhu, J. Li, A. Samanta, A. Leach, and K. Gall, Temperature and strain-rate dependence of surface dislocation nucleation, *Physical Review Letters*, Vol. 100 (2), p. 025502, 2008.
- [28] J. Godet, L. Pizzagalli, S. Brochard and P. Beauchamp, Comparison between classical potentials and ab initio methods for silicon under large shear, *Journal of Physics: Condensed Matter*, Vol. 15 (41), pp. 6943–6953, 2003.
- [29] R. D. Boyer, J. Li, S. Ogata and S. Yip, Analysis of shear deformation in Al and Cu: empirical potentials versus density functional theory, *Modelling and Simulation in Materials Science and Engineering*, Vol. 12 (5), pp. 1017–1029, 2004.

5. COMPARISON WITH PN BASED RESULTS

5.1 Introduction

In this chapter the results and insight gained as a result of atomistic simulation of homogeneous dislocation nucleation in this research is compared with Peierls-Nabarro (PN) model based results for homogeneous dislocation nucleation. PN models [1–5] have been very informative because they removed Volterra [6,7] model's singularity at the core of the dislocation. Another major advantage of PN based models is that they don't suffer from the limitation of time-scale, therefore macro scale properties of materials can be hoped to be extracted out of them. However, not being fully atomistic in nature, they can't consider the discrete nature of atoms at the core of the dislocation, and dislocation nucleation—being an atomistic phenomenon—cannot be accurately seen in that framework.

This chapter aims to quantitatively determine the extent to which the above limitations affect the predictions made by PN based models. By comparison with

atomistic results achieved in this research, limitations of PN models in terms of their predictive capability are highlighted.

5.2 Information provided by PN based models

Because the PN methodology does not fully incorporate the discrete nature of atoms, it cannot handle the following information:

- 1. Actual direction of slip
- 2. Extra slip-plane displacements
- 3. True dislocation core shapes

5.2.1 Actual direction of slip

Fully atomistic simulations yield the direction of the in-plane displacement of individual atoms. While these directions are generally thought to be in the direction of the partial or perfect Burgers vector applicable to the material in question, this is not always the case. It was seen in Chapter 4 that in the case of Mo, the in-plane direction of atoms close to the centre of the dislocation core were displaced at an angle to the direction of the Burgers vector.

Figure 5-1, which is reproduced from Chapter 4, shows the inclined direction of atomic displacements for Mo with respect to the Burgers vector direction, while displacements for Cu and Si are along the direction of their respective Burgers vectors. This information is not available from PN based simulations, and because this inclined movement appears to lower the activation energy requirements, this might seriously affect the activation energy predictions made by PN models. Fully atomistic methods are therefore necessary to make this information available.



Figure 5-1 Directions of the in-plane atomic displacements for homogeneous dislocation nucleation in Si (left), Cu (middle), and Mo (right). The directions of the respective Burgers vectors are also indicated (red arrows). (Reproduced from Ch. 4.)

5.2.2 Extra slip-plane displacements

PN based methodologies are also unable to take into consideration the presence or absence of extra slip-plane displacements that, as seen in Chapter 4, can be significant depending upon the material and stress range in question. Figure 5-2, which is reproduced from Chapter 4, shows the extra slip-plane displacements for saddle-points in Si, Cu and Mo. Dislocation nucleation in Cu is essentially a two-plane phenomenon, while that in Si and Mo is accompanied by significant extra slip-plane displacements. It would appear that the directionality of bonds in Mo and Si result in a cup-like displacement of atoms more energetically favourable than a disc like slip, similar to that displayed by Cu.



Figure 5-2 Extra slip-plane displacements of atoms in Si (left), Cu (middle), and Mo (right). Only atoms with displacements > 0.15Å are shown. (Reproduced from Chapter 4.)

The inability of PN models to differentiate between the disc-like (Cu) and cup-like (Si, Mo) displacement contours can also have severe effects on the accuracy of activation energy predictions made based on it. Depending on the material, the directionality of bonds might result in the cup-like displacement to be less energy intensive than the disc-like displacement contour. This information can only be made available through atomistic calculations, and the inability of the PN model to provide this information would count as limitation of the PN models.

However, the above information acquired from atomistic results, if utilized for calibration of PN models can lead to improved accuracy of the latter. This area has promise for further research.

5.2.3 True dislocation core shapes

Figure 5-3 shows a typical dislocation loop as reported by a PN model [5]. It does not differentiate between individual materials; the shape is in the form of an ellipse irrespective of the material in question. Atomistic studies, on the other hand, can deal with the discrete nature of atoms at the core and therefore differentiate between the different crystal structures and bonding types, and therefore are able to provide information not accessible to the PN methodology.



Figure 5-3 Dislocation loop from PN results (Fig. 3 from Ref. [5]).

In reality, due to the influence of the specific crystal structure, the shapes of the dislocation cores are peculiar to the material, as shown by atomistic calculations carried out in this research (Figure 5-4).



Figure 5-4 Shapes of the dislocation cores: Si (left), Cu (middle), and Mo (right). The directions of the respective Burgers vectors are also indicated.

However, this limitation is a result of an approximation that forms the basis of PN methodologies, and this in itself doesn't count against the significance or usefulness of the PN methodology.

5.3 Information provided by PN based models

The information described in the last section notwithstanding, the following important information is made available by the PN models:

- 1. Activation energy
- 2. Inelastic displacements

The above are considered one by one in the following sections:

5.3.1 Activation energy

Figure 5-5 shows the stress dependence of activation energy reported by the PN model for homogeneous dislocation nucleation. Fig 5-6 presents the corresponding atomistic results for Cu and Si.



Figure 5-5 Stress dependence of activation energy reported by PN model (Fig. 4 from Ref. [5]).


Figure 5-6 Atomistic results for stress dependence of activation energy for homogeneous dislocation nucleation in Si, Cu and Mo.

The first quantitative comparison between the atomistic and PN results is between the activation energies for 60% of the critical stress reported by the atomistic and the PN based approach [5]. PN results for homogeneous dislocation nucleation in Mo are not available, therefore only results for Si and Cu are compared. As shown in Table 5-1, it is obvious that the PN method is overestimating the energy requirements for dislocation nucleation for both Cu as well as Si.

Material	P-N [eV]	Atomistic [eV]	Overestimation factor
Cu	10	2	5
Si	36	18	2

Table 5-1 Activation energy comparison for 60% of critical stress

5.3.2 Inelastic displacements

Figure 5-7 shows the stress dependence of activation energy reported by the PN model for homogeneous dislocation nucleation. Figure 5-8 presents the corresponding atomistic results for Cu and Si.



Figure 5-7 Stress dependence of inelastic displacement reported by PN based study (Fig. 2 (a) from Ref. [5]).



Figure 5-8 Atomistic results for stress dependence of the maximum inelastic displacement for homogeneous dislocation nucleation in Cu and Si.

The next quantitative comparison is between the maximum inelastic displacements for 60% of the critical stress for atomistic results achieved in this research and the PN results reported [5] for homogeneous dislocation nucleation. PN results for homogeneous dislocation nucleation in Mo are not available so only results pertaining to Si and Cu are compared. From Table 5-2 it is obvious that the PN method overestimates the energy requirements for dislocation nucleation for both Cu as well as Si.

Material	P-N	Atomistic	Overestimation
	[b]	[b]	%
Cu	1	0.65	35
Si	1	0.85	15

Table 5-2 Comparison of maximum inelastic displacement for 60% of critical stress

PN studies of homogeneous systems [4,5] conclude that homogeneous dislocation nucleation is not feasible because of the unrealistically high activation energy requirement. They overestimate the activation energy requirements although the recent estimates for energy requirement are much smaller than the original estimate by Rice [1]. However they are still too high as compared to atomistic predictions presented in this research, which show that for both Cu and Si homogeneous dislocation nucleation is feasible, although more so for Cu than Si. Xu et al. [5], for example, overestimate the activation energy for homogeneous nucleation in Cu by a factor of 5 and in Si by a factor of 2 as compared with atomistic results. However, homogeneous nucleation is more likely to occur in Cu than in Si because of the markedly higher energy requirements for Si, which is a consequence of its higher Peierls barrier as compared to Cu. PN models therefore, are in a sense similar to rough estimates such as the unstable stacking fault energy (γ_{us}) , which is considered to be closely related to dislocation nucleation [8]. Stacking fault energy is greater for Si by a factor of 5 (0.83 J/m^2 for Si [9] as compared to 0.16 J/m^2 for Cu [10], obtained by using the SW [11] and the Mishin [12] potentials respectively), and therefore predicts a marked higher resistance to dislocation nucleation for Si than that for Cu. But it does not provide quantitative results in terms of concrete energy requirements. Similarly the PN model, although it does provide quantitative results, overestimates the activation energy requirements, therefore, at the present time its results can only be used as qualitative indicators, similar to the unstable stacking fault energy and its other variants such as the product of the stacking fault energy and the square of the Burgers vector.

The discrepancy of atomistic results and those predicted by PN based models prove that at present there is no realistic substitute for atomistic calculations as a predicting methodology applicable to the problem of dislocation nucleation.

5.4 Conclusions

PN based models cannot capture the extra slip-plane atomistic displacements, and the direction of in-plane displacements at the saddle-point. They also overestimate the magnitude of atomic displacements and the activation energies as compared to atomistic predictions.

Contrary to the traditional understanding obtained from studies in the PN framework, homogeneous dislocation nucleation is possible with the aid of thermal activations in both Cu and Si, although, admittedly, the likelihood of that happening is much more realistic and feasible in Cu than in Si.

Therefore, despite the inherent advantages of PN based methods, and the fact that later improvements have resulted in improvement in their results; PN models in their present form still overestimate energy requirements for dislocation nucleation, and hence fully atomistic methods are indispensable for accurate description of this phenomenon.

References

- [1] J.R. Rice and G.E. Beltz, The activation energy for dislocation nucleation at a crack, *Journal of the Mechanics and Physics of Solids*, Vol. 42 (2), pp. 333–360, 1994.
- [2] G. Xu, A.S. Argon and M. Ortiz, Nucleation of dislocations from crack tips under mixed modes of loading: implications for brittle against ductile behaviour of crystals, *Philosophical Magazine A*, Vol. 72 (2), pp. 415–451, 1995.
- [3] W. Yang, J. C. Tang, Y. S. Ing and C. C. Ma, Transient dislocation emission from a crack tip, *Journal of the Mechanics and Physics of Solids*, Vol. 49 (10), pp. 2431–2453, 2001.
- [4] Y. Xiang, H. Wei, P. Ming and W. E, A generalized Peierls-Nabarro model for curved dislocations and core structures of dislocation loops in Al and Cu, *Acta Materialia*, Vol. 56 (7), pp. 1447–1460, 2008.
- [5] G. Xu and A. S. Argon, Homogeneous nucleation of dislocation loops under stress in perfect crystals, *Philosophical Magazine Letters*, Vol. 80 (9), pp.605–611, 2000.
- [6] J. P. Hirth and J. Lothe, *Theory of Dislocations*, Wiley, 1982.
- [7] A.H. Cottrell, *Dislocations and plastic flow in crystals*, Oxford University Press, UK, 1956.
- [8] J. R. Rice, Dislocation nucleation from a crack tip: An analysis based on the Peierls concept, *Journal of the Mechanics and Physics of Solids*, Vol. 40 (2), pp. 239–271, 1992.
- [9] J. Godet, L. Pizzagalli, S. Brochard, and P. Beauchamp, Comparison between classical potentials and ab initio methods for silicon under large shear, *Journal of Physics: Condensed Matter*, Vol. 15 (41), pp. 6943–6953, 2003.
- [10] S. Izumi and S. Yip, Dislocation nucleation from a sharp corner in silicon, *Journal of Applied Physics*, Vol. 104 (3), p. 033513, 2008.
- [11] F. H. Stillinger and T. A. Weber, Computer simulation of local order in condensed phases of silicon, *Physical Review B*, Vol. 31 (8), pp. 5262–5271, 1985.
- [12] Y. Mishin, M J. Mehl, D. A. Papaconstantopoulus, A. F. Voter, and J. D. Kress, Structural stability and lattice defects in copper: Ab initio, tight-bonding, and embedded-atom calculations, *Physical Review B*, Vol. 63 (12), p. 224106, 2001.

[13] J. A. Zimmerman, C. L. Kelchner, P. A. Klein, J. C. Hamilton and S. M. Foiles, Surface step effects on nanoindentation, Physical Review Letters, Vol. 87 (16), p. 165507, 2001.

6. THE SHUFFLE-GLIDE CONTROVERSY IN Si

6.1 Introduction

In this chapter, the shuffle-glide controversy in Si is examined at a fundamental level, i.e., for homogeneous dislocation nucleation, where complex surface and stress concentration effects are not allowed to distort the physical picture. Analysis of results of reaction pathway sampling (presented in chapter 3) is carried out in the following sections, leading to conclusions aimed at increasing understanding regarding the recently rekindled shuffle-glide controversy in Si. Finally, the shuffle-glide transition for homogeneous dislocation nucleation is also compared with corresponding results for the heterogeneous case.

6.2 Minimum energy paths: Nucleation and mobility

Figures 6-1 and 6-2 show typical energy curves for the minimum energy paths taken by the atomistic configurations for nucleation of the shuffle-set dislocation (SD) and the glide-set dislocation (GD) respectively in Si. While the curve for SD is smooth, there are undulations in the curve for GD. This is because of the very high mobility of the GD as compared with the SD [1,2].



Figure 6-1 Typical configuration energy curve of a series of images along the minimum energy path for homogeneous dislocation loop nucleation of the shuffle-set (part of Figure 3-2 reproduced).



Figure 6-2 Typical configuration energy curve of a series of images along the minimum energy path for homogeneous dislocation loop nucleation of the glide-set (part of Figure 3-6 reproduced).

Another difference between the two curves is the respective fractions of the reaction coordinate length accounted for by nucleation and mobility. For the SD, nucleation accounts for the bulk of the reaction coordinate length, but once the critical point (corresponding to the saddle-point) is crossed, the loop increases in size quickly

with a corresponding decrease in activation energy of the system. In the GD on the other hand, nucleation accounts for only a minor part of the reaction coordinate length. However, even after the critical point is crossed in GD nucleation, the energy does not come down quickly; the curve goes on undulating for some while before finally coming down. Thus the mobility part accounts for the major part of the reaction coordinate length. It is therefore obvious that while nucleation is the critical phenomenon in the SD, mobility is the more critical part as far as the GD is concerned.

6.3 Activation energy curves

Figure 6-3 compares the shear-stress dependence of the activation energy for nucleation of SD and GD.





Although the two curves do cross over, the location of the cross over point suggests that unless the applied stress is extremely high (greater than 6.5GPa), GD would be favored to nucleate. However, the high energy requirement in the lower stress regime would also necessitate input of large thermal energy (high temperature) for the GD nucleation to happen. This result agrees with the results of recent atomistic studies [3,4] for heterogeneous systems, which in turn agree with past experimental results [5,6].

However, these results for dislocation nucleation, which indicate a higher

activation energy requirement for SD than for GD in all but the very high stress region, differ from the results for dislocation *mobility* reported by Pizzagalli *et al.* [7] which suggest lower activation energy for SD as compared to GD for all values of stress. On the other hand, the results of this study are similar to those reported for dislocation mobility by Duesbery et al. [8] which were declared as inconclusive by Pizzagalli *et al.* on grounds that they did not take into consideration the atomistic effects occurring during the migration of a kink.

The kink migration energy for SD is at least one order of magnitude lower [9] than that for GD. On the other hand the kink formation energy is known to be lower for GD (0.4 to 0.7eV) [10] than for SD (0.90 to 1.36eV for SD) [9]. The atomistic results of this study confirm that nucleation is a completely distinct phenomenon from mobility; and while mobility is lower for GD for all stress values, favorability of nucleation depends on the stress value in question because of the presence of the cross-over point. The cross-over point of 6.5 GPa corresponds with an activation energy of 5 eV.

6.4 Mechanics of the saddle-point configurations

Figure 6-4 compares the saddle-point configurations for GD and SD nucleation corresponding to a series of resolved shear stress values. The comparison is presented in the form of slip-vector representation [11]. As is evident from Figure 6-4, in both sets the dislocation elongates along different Peierls valleys and at all times shows a hexagonal shape. It is well known that dislocation loops in Si display a hexagonal shape whose edges are parallel to <110> Peierls valleys on the {111} slip plane. This is a result of the high Peierls barrier for Si, and also fits in with observation in recent low temperature experiments [12] and simulation work [13]. Also from Figure 6-4, it can be seen that the area of the SD core is bigger than that of the GD core for the complete range of stress values.

Figure 6-5 shows the shear-stress dependence of the maximum inelastic shear displacement of the dislocation embryo as defined by the length of the slip vector normalized by the partial and perfect Burgers vectors, respectively, for GD and SD. From Figures 6-4 and 6-5 it is clear that the rate of decrease of the normalized maximum slip vector with respect to stress for SD is significantly greater than that for GD.



Figure 6-4 Slip vector representation of saddle-point configurations for shuffle-set (above), and glide-set (below) homogeneous dislocation nucleation (b_S =3.84Å, and b_G =2.22Å respectively) in Si. The directions of the respective Burgers vectors are shown.



Figure 6-5 Shear-stress dependence of the maximum slip vector for glide-set and shuffle-set homogeneous dislocation nucleation (normalized by their respective Burgers vectors) in Si.

From Figure 6-4 it is also evident that the distribution of slip in the dislocation core is very different for the two sets. For low stress values the dislocation core for SD exhibits a highly non-uniform distribution of slip, but this situation changes drastically with increasing stress, as the distribution of slip becomes more and more uniform. Glide-set cores, on the other hand, show a uniform slip distribution for low as well as high stress values. Both the slip distribution at the dislocation cores and the maximum slip vector in SD are more sensitively dependent on the shear-stress as compared to GD.

6.5 Activation volumes

An analysis of activation volume of GD and SD nucleation, similar to that performed in Chapter 4 for different materials, was carried out. Thermodynamics-based conceptual measure of the activation volume of a thermally activated transition is given by [14, 15] (Eq. 4.1 reproduced)

$$\Omega = -\frac{\partial Q(\tau)}{\partial \tau} \tag{6.1}$$

where $Q(\tau)$ is the stress-dependent activation energy, and τ is the shear stress. The steeper energy curve in Figure 1 for SD indicates that SD nucleation is accompanied by a higher activation volume than GD nucleation. The greater activation volumes for SD confirm that the activation process for SD is more collective, and that there is less thermal uncertainty involved than for the corresponding process for GD. In other words, in the region where thermal activation is important (the low stress region), GD nucleation is likely to occur. The higher shear-stress dependence of both the distribution of slip at the dislocation core and the maximum slip vector (see section 6.4) in SD explains the higher activation volume for SD as compared to GD.

From the structural point of view, the activation volume is given by [16] (Eq. 4.2 reproduced)

. .

$$\Omega' = \iint u(x, y) dx dy \tag{6.2}$$

where u(x,y) is the in-plane inelastic displacement across the slip plane. Figure 6-6 presents results based on the two definitions of activation volume for SD and GD nucleation.



Figure 6-6 Comparison of the two definitions of activation volume for homogeneous dislocation nucleation of the shuffle-set and the glide-set. The structural definition gives significantly low values as compared to the thermodynamic definition for the shuffle-set, whereas the discrepancy is not that significant in case of the glide-set.

It is clear from Figure 6-6 that the discrepancy between the two definitions—thermodynamic and structural—is greater for the SD than it is for the GD. Figure 6-7 shows representative atomic displacements exceeding 0.15Å for the two sets. Examination of the saddles show that the extra slip-plane displacement for SD is more pronounced than is the case with GD. This would explain why the two definitions of activation volume are in more disagreement in the case of SD than in the case of GD.

The difference between the two definitions would be accounted for by the displacement of atoms above and below the slip plane. The structural definition of activation volume (Eqn. 6.2), therefore, has limitations when applied to covalent bonded Si, although it gives satisfactory results for dislocations in FCC Cu because of planar cores that are confined to the slip plane [14], and this limitation is more pronounced in the case of SD than it is in GD.



Figure 6-7 Extra slip-plane displacements of atoms: only atoms with displacements greater than 0.15Å are displayed: Glide-set (left) and shuffle-set (right).

6.6 In-plane direction of atomic slip

Figure 6-8 shows directions of the in-plane atomic displacements for homogeneous dislocation nucleation of the GD and SD. The directions of the respective Burgers vectors are also indicated.



Figure 6-8 Directions of the in-plane atomic displacements for homogeneous dislocation nucleation of the shuffle-set (left) and glide-set (right). The directions of the respective Burgers vectors are also indicated (black arrows).

Only GD is known to dissociate into partial dislocations, therefore its partial Burgers vector is 57% of the perfect Burgers vector for SD. In the nucleation of both the SD and GD however, the in-plane atomic displacements are in the directions of their perfect and partial Burgers vectors respectively.

6.7 Comparison with heterogeneous system: Shuffle-glide controversy for dislocation nucleation from a sharp corner

In continuation of comparison between the homogeneous and heterogeneous systems (section 4.5.1 to 4.5.3), the results for homogeneous dislocation nucleation are compared with results for dislocation nucleation from a sharp corner [17].

This comparison is relevant because the same potential (SW potential) has been used in both studies. The sharp-corner model [17] is shown in Figure 6-9.



Figure 6-9 Dislocation nucleation from a sharp corner in Si (Fig. 1 in Ref. [17]).



Figure 6-10 Shuffle-glide transition for dislocation nucleation from a sharp corner in Si (Fig. 2 in ref. [17]).

The shuffle-glide cross-over point occurs at 4.7 GPa and corresponds to an activation energy of 2.6 eV. The corresponding cross-over point for homogeneous dislocation nucleation occurs at 6.5 GPa with a corresponding activation energy of 5 eV (section 6.3). The transition stress is lowered by 27% and the transition activation energy is lowered by 48% as a result of the sharp corner.

The reduction of loop radius because of the presence of heterogeneity (section 4.5) means less activation energy requirements for nucleation from a sharp corner. In addition to this, as opposed to the full hexagonal loop for homogeneous dislocation nucleation, there is a half hexagonal loop in case of nucleation from the sharp corner. Also, for an already present corner, the area surface area is known to decrease, causing a surplus of energy available (section 4.5.3). The surface energy component therefore complicates the situation.

Finally, the stress value at which the shuffle-glide transition occurs (4.7 GPa) for the heterogeneous case is the nominal stress; the actual stresses near the corner are markedly higher because of stress concentration effects. Sharp corner is just one form of heterogeneity; comparison of the homogeneous case with dislocation nucleation from other configurations (crack, surface step, corner, etc) promises to be insightful in terms of understanding of the correlation between a heterogeneity and the lowering of the shuffle-glide transition.

6.8 Conclusions

Atomistic reaction pathway sampling for dislocation of the glide-set and the shuffle-set in a homogeneous Si crystal was carried out with the aim of explaining the favorability conditions of the two sets in terms of the activation energy, activation volume and the mechanics of the dislocation core. The choice of a homogeneous crystal makes it possible to examine this problem at a fundamental level.

The presence of a diffused core region (in both sets) makes the nucleation inaccessible to classical dislocation theory. Nucleation accounts for bulk of the reaction pathway in the shuffle-set. The low mobility of the glide-set, on the other hand, results in undulations in the energy curve even after the saddle-point configuration is reached.

Two nucleation regimes are confirmed. In the low stress regime dislocation of the glide-set is likely to nucleate. However, the high energy requirement would necessitate introduction of large thermal activation. As stress increases, the two curves come closer and finally intersect at 6.5 GPa with a corresponding activation energy of 5 eV. In the high stress regime (stresses greater than 6.5 GPa) dislocation of the shuffle-set is likely to nucleate. The shuffle-glide transition for homogeneous dislocation nucleation is compared with the corresponding transition in dislocation nucleation from a sharp corner. The transition stress and activation energy are lowered for the heterogeneous case by 27% and 48% respectively from the ideal homogeneous case. Comparison with other heterogeneous systems promises to improve insight into the relationship between a certain kind of heterogeneity and the lowering of the shuffle-glide transition.

Activation energy for stresses near athermal stress cannot be determined for either set. In fact it can be said that no athermal stress exists for either set. The extrapolation of energy curves gives a lower (imaginary) athermal stress for shuffle set than that for glide set. Other competing mechanisms (such as twinning) are considered to be the reason for absence of any distinct athermal stress.

Shuffle-set nucleation is accompanied by a higher activation volume than glide set. The activation process for dislocation nucleation of the shuffle-set is more 'collective' (accompanying less thermal uncertainty) than nucleation of the glide-set. The differences in the mechanics of the saddle-point dislocation core structures explain the lower activation volume for the glide-set nucleation, which makes it more sensitive to thermal activation. The number of atoms exhibiting extra slip-plane displacements is also higher for the shuffle-set. The structural definition of activation volume therefore underestimates the activation volume since it does not take the extra slip-plane displacements into consideration. This discrepancy between the thermodynamic and structural definitions of activation energy is more pronounced for shuffle-set because of the greater extent of exta slip-plane displacements in the shuffle-set nucleation as compared to the glide-set nucleation.

References

- [1] V. V. Bulatov, S. Yip and A. S. Argon, Atomic modes of dislocation mobility in silicon, *Philosophical Magazine A*, Vol. 72 (2), pp. 453–496, 1995.
- [2] V. V. Bulatov, J. F. Justo, W. Cai, S. Yip, A. S. Argon, T. Lenosky, M. de Koning, and T. Diaz de la Rubia, Parameter-free modeling of dislocation motion: the case of silicon, *Philosophical Magazine A*, Vol. 81 (5), pp. 1257–1281, 2001.
- [3] J. Godet, P. Hirel, S. Brochard, and L. Pizzagalli, Evidence of two plastic regimes controlled by dislocation nucleation in silicon nanostructures, *Journal of Applied Physics*, Vol. 105 (2), p. 026104, 2009.
- [4] K. Shima, S. Izumi and S. Sakai, Reaction pathway analysis for dislocation nucleation from a sharp corner in silicon: Glide set versus shuffle-set, *Journal of Applied Physics*, Vol. 108 (6), p. 063504, 2010.
- [5] A. Gomez, D. J. H. Cockayne, P. B. Hirsch, and V. Vitek, Dissociations of near-screw dislocations in germanium and silicon, *Philosophical Magazine*, Vol. 31 (1), pp. 105–113, 1975.
- [6] M. Sato, K. Hiraga, and K. Sumino, HVEM structure images of extended 60° and screw dislocations in silicon, *Japanese Journal of Applied Physics*, Vol. 19, L155–L158, 1980.
- [7] L. Pizzagalli and P. Beauchamp, Dislocation motion in silicon: the shuffle-glide controversy revisited, *Philosophical Magazine Letters*, Vol. 88 (6), pp. 421–427, 2008.
- [8] M. S. Duesbery and B. Joos, Dislocation motion in silicon: the shuffle-glide controversy, *Philosophical Magazine Letters*, Vol. 74 (4), pp. 253–258, 1996.
- [9] L. Pizzagalli, A. Pedersen, A. Arnaldsson, H. Jonsson and P. Beauchamp, Theoretical study of kinks on screw dislocation in silicon, *Physical Review B*, Vol. 77 (6), p.064106, 2008.
- [10] H. Gottschalk, N. Hiller, S. Sauerland, P. Specht and H. Alexander, Constricted dislocations and their use for TEM measurements of the velocities of edge and 60° dislocations in silicon. A new approach to the problem of kink migration, *physica status solidi* (*a*), Vol. 138 (2), pp. 547–555, 1993.
- [11] J. A. Zimmerman, C. L. Kelchner, P. A. Klein, J. C. Hamilton and S. M. Foiles, Surface step effects on nanoindentation, *Physical Review Letters*, Vol. 87 (16), p. 165507, 2001.

- [12] J. Rabier and J. L. Demenet, On a change in deformation mechanism in silicon at very high stress - New evidences, *Scripta Materialia*, Vol. 45 (11), pp. 1259–1265, 2001.
- [13] S. Izumi and S. Yip, Dislocation nucleation from a sharp corner in silicon, Journal of Applied Physics, Vol. 104 (3), p. 033513, 2008.
- [14] U. F. Kocks, A. S. Argon and M. F. Ashby, Thermodynamics and kinetics of slip, *Progress in Materials Science: Vol. 19*, Pergamon Press, New York, 1975.
- [15] J. Li, The mechanics and physics of defect nucleation, *MRS Bulletin*, Vol. 32, pp. 151–159, 2007.
- [16] R. D. Boyer, *Stress-mediated reaction pathways for dislocation nucleation in copper*, Ph.D. thesis, MIT, 2007.
- [17] K. Shima, S. Izumi and S. Sakai, Reaction pathway analysis for dislocation nucleation from a sharp corner in silicon: Glide set versus shuffle-set, *Journal of Applied Physics*, Vol. 108 (6), p. 063504, 2010.

7. CONCLUSIONS AND FUTURE DIRECTIONS

This thesis presents analyses of homogeneous dislocation nucleation in three common materials—namely Si, Cu and Mo—based on atomistic reaction pathway sampling. The three materials were chosen as representative of the diamond-cubic, face-centered cubic and body-centered cubic crystal structures respectively. Focus on homogeneous system makes it possible to study the phenomenon of dislocation nucleation at a fundamental level, free from complex effects of stress fields, surfaces and interfaces, etc. Utilizing the NEB algorithm and extended schemes enables the analysis of the phenomenon of homogeneous dislocation nucleation under strain rates not accessible to dynamic atomistic schemes such as MD. Analyses of the same thermally-activated stress-mediated transition in three materials with different crystal structures enables consideration of the influence of lattice structure and bonding on this transition, resulting in improved insight about the academically fundamental phenomenon of homogeneous dislocation nucleation. The shuffle-glide controversy in Si, from the point of view of dislocation nucleation, was also examined for the fundamental homogeneous case.

The atomistic insight about homogeneous dislocation nucleation gained via this research has also been compared with the PN model, with the aim of highlighting the

pros and cons of the PN approximation. Next, the atomistic information gained about the homogeneous systems is compared with corresponding information about heterogeneous dislocation nucleation with an aim to provide a link between homogeneous and heterogeneous dislocation nucleation. Finally, discussion of ideal strength followed by the deterioration of strength as a result of heterogeneities is also presented.

The conclusions of this research, as stated in individual chapters, are briefly summarized once again in this chapter (section 7.1). Possible extensions of these results, in terms of future work based on this work, are also presented (section 7.2).

7.1 Conclusions

The first three chapters set the stage for the analysis and discussion. Chapter 1 provides the overall background and aims of this research. The simulation and analysis tools employed in this research have been introduced in Chapter 2. Chapter 3 presents primary results of all reaction pathway calculations without analysis. Chapters 4, 5 and 6 discuss and analyze those results, leading up to conclusions.

Chapter 4 compares DC Si, FCC Cu, and BCC Mo from the point of view of influence of crystal structure on homogeneous dislocation nucleation. It is demonstrated that dislocation nucleation in Mo and Si is much more stress intensive than in Cu. This is because of the stiffer BCC and DC bonds of bonds of Mo and Si respectively. Dislocation nucleation in Mo and Si is a more 'collective' process than in Cu, because of markedly higher activation volumes. Therefore homogeneous dislocation nucleation in Cu is significantly more sensitive to thermal activations than either Mo or Si. Dislocation nucleation is possible in Cu and Si, although it is much more feasible in Cu than Si; whereas it is not feasible in Mo on account of the extremely high stresses involved.

Furthermore, it is shown that the presence of diffused cores in all three materials makes nucleation inaccessible to classical dislocation theory. It is also demonstrated that as opposed to rough qualitative figures provided by simplistic parameters such as γ us and γ us b^2 , atomistic analysis provides quantitative values for activation energies. There is therefore no replacement of atomistic analysis of dislocation nucleation.

One influence of crystal structure and bonding type has been shown to be the presence of atoms exhibiting extra slip-plane displacements to differing extents depending on the material and stress range in question. Minimum energy requirements dictate that Cu displays an essentially two-plane dislocation core whereas Si shows considerable displacement in many planes above and below the slip plane. Mo shows two-plane cores like Cu under high stresses, but under low stresses it shows considerable extra-slip plane displacements. In general, the more directional the bonding, the more the extra slip-plane displacements appear to be energetically favorable. This results in the structural definition underestimating the activation volume depending upon the material and/or stress range.

Chapter 4 next presents the comparison of our results for homogeneous dislocation nucleation with two cases of heterogeneous dislocation nucleation, namely, nucleation from a corner of Cu nanopillar under compression, and from a sharp corner in Si. The activation volumes for homogeneous and heterogeneous dislocation nucleation under equal percentages of the respective critical stresses are of the same order of magnitude, although with those for heterogeneous dislocation lower than those for homogeneous ones. The smaller loop radii and the nucleation of half or quarter-loop as opposed to a full loop (for homogeneous dislocation) account for the lower activation volume and hence the lower activation energy.

Chapter 4 concludes with the discussion of ideal strength and the reduction of strength as a result of the presence of heterogeneities for the two heterogeneous cases studied. The reduction of strength would depend on the kind of heterogeneity; therefore comparison with more heterogeneous cases needs to be made before reduction of strength on account of a particular heterogeneity can be predicted.

Chapter 5 presents the comparison between our atomistic results with results for homogeneous dislocation nucleation based on the PN atomistic-continuum hybrid model. Despite a number of improvements from its original formulation, the PN based model in its present form can't replace the information available from fully atomistic methods. It has an obvious advantage in terms of computational cost but it overestimates the energy requirements for homogeneous dislocation nucleation because of its inability to factor in discrete atomistic details.

Chapter 6 compares dislocation nucleation of the shuffle-set with that of the glide-set in Si. Two nucleation regimes are confirmed for homogeneous dislocation nucleation in Si. The transition occurs at 6.5 GPa; dislocations of the glide-set being likely to nucleate under stresses lower than that, and those of the shuffle-set for stresses greater than that. Also, shuffle-set nucleation is more 'collective' (with less thermal uncertainty) than glide-set nucleation. The extra slip-plane displacements are also more pronounced for the shuffle-set than the glide-set, resulting in higher discrepancy between the structural and thermodynamic definitions of activation volume. The corresponding shuffle-glide transition stress for heterogeneous dislocation nucleation from a sharp corner is 4.7 GPa. The extent of shift of the shuffle-glide transition would also be dependent on the kind of heterogeneity; therefore comparison with more heterogeneous cases needs to be made before it can be predicted.

Nucleation accounts for bulk of the reaction pathway in the shuffle-set. The low mobility of the glide-set on the other hand, results in undulations in the energy curve even after the saddle-point configuration is reached. Contrary to the glide-set, once nucleation of the shuffle-set is realized, the dislocation loop grows in size smoothly with a quick decrease in energy.

7.2 Future directions

7.2.1 Other materials

In this research homogeneous dislocation nucleation in FCC Cu, BCC Mo and DC Si was studied and results compared among the different materials and with PN based results from the point of view of influence of atomic crystal structure. In addition, comparison was made with some heterogeneous situations in order to quantify the influence of heterogeneities.

There are, inevitably, other classes of materials, such as hexagonal close-packed (HCP) materials and ionic bonded materials, which have not been explored in this research. Similar treatment for them, followed by similar comparison with typical heterogeneous cases will be a welcome addition to this comparison across crystal structures and bonding types in terms of dislocation nucleation.

Another approach can be that of focusing on one category of crystal structures, comparing a number of materials belonging to that category. Taking the example of the FCC crystal structure, comparing Cu, Al, Ag, etc, will result in insight into the subtle differences between solids with a common crystal structure, in terms of dislocation nucleation.

7.2.2 Comparison with other heterogeneous systems

The two cases considered here, dislocation nucleation from the corner of a Cu nanopillar and from a sharp corner in Si, are only two cases out of a large variety of cases of heterogeneous dislocation nucleation that exist in engineering applications. Similar comparisons of the homogeneous case with dislocation nucleation from other heterogeneities (crack, surface step, corner, etc) promises to be insightful in terms of the quantitative correlation between heterogeneity and the lowering of the activation energy and activation volume, improving the understanding of dislocation nucleation.

*

On an academic level, it is hoped that the information gained via comparison of the homogeneous case with the more complex heterogeneous situations for a variety of materials combined with the conclusions obtained in this study would lead to an improvement in insight about the dislocation nucleation phenomenon in general. On a practical level, once a reliable method for predicting the favorability conditions for dislocation nucleation is established, the nucleated dislocation can be handed over to continuum mechanics based DD for further analysis of dislocation mobility. This overall methodology then holds promise to be used in the design of semiconductor and MEMS design, where the nucleation of even one dislocation line can potentially jeopardize the correct functioning of the device. The ultimate goal would be to eliminate the trial and error aspect [1] of design currently prevailing in dislocation dynamics based studies.

7.2.3 Adaptive hyperdynamics applied to homogeneous dislocation nucleation

Recently, an accelerated MD technique known as adaptive strain-boost hyperdynamics [2] has very effectively increased the accessible time available to MD calculations by factors as high as 11 orders of magnitude for the best cases. This new algorithm is an improvement in terms of robustness and efficiency on an earlier scheme [3] for accelerating atomic simulations, and has been shown to be useful for simulating transitions such as dislocation nucleation.

NEB gives valuable insight into thermally activated transitions at the experimental strain rates, but its inherent limitation is that it gives a prediction for 0 K. In reality, activation energy depends on temperature, and therefore the effects of dynamics and entropy have to be considered for a more accurate description of transitions such as dislocation nucleation. According to the harmonic approximation [4] of the transition-state theory (TST) [5], the temperature and stress dependent activation energy can be broken down as

$$Q(\sigma, T) = Q_0(\sigma) - TS(\sigma), \qquad (7.1)$$

where $Q_0(\sigma)$ is the stress-dependant activation enthalpy that corresponds to the activation energy at T = 0 K and $S(\sigma)$ is the stress-dependence activation entropy [4].

Using the Eshelby transformation mechanics model [6], activation energy from experiments can be smartly utilized to explore thermally activated stress-driven processes such as dislocation nucleation. That is, the size of these strain-boosting Eshelby inclusions may be matched to the experimentally inferred spectrum of activation volume [7].

In the present research, activation energies and activation volumes for a range of stress values for homogeneous dislocation nucleation in three materials has been determined; this information can be efficiently employed in the application of the adaptive strain-boost algorithm for the simulation of homogeneous dislocation nucleation at two different levels. Activation energies can be utilized to calibrate and compare results for 0 K calculations, and activation volumes can be used as a guide for strain boost.

Therefore, the present work would be a useful starting point for application of the accelerated molecular dynamics technique to the analysis of homogeneous dislocation nucleation. Once that is achieved, it will be possible to include the entropic contribution to the activation energy, which is non-negligible at room temperature, as proved by analysis of dislocation nucleation in a Cu nanopillar under compressive stress [2,8].

References

- [1] M. Kammler, D. Chidambarrao, K. W. Schwarz, C. T. Black and F. M. Ross, Controlled nucleation of dislocations by a spatially localized stress field, *Applied Physics Letters*, Vol. 87 (13), p. 133116, 2005.
- [2] S. Hara and J. Li, Adaptive strain-boost hyperdynamics simulations of stress-driven atomic processes, *Physical Review B*, Vol. 82 (18), p. 184114, 2010.
- [3] R. A. Miron and K. A. Fichthorn, Accelerated molecular dynamics with the bond-boost method, *Journal of Chemical Physics*, Vol. 119 (12), pp. 6210–6216, 2003.
- [4] G. H. Vineyard, Frequency factors and isotope effects in solid state rate processes, *Journal of Physics and Chemistry of Solids*, Vol. 3 (1–2), p. 121–127, 1957.
- [5] H. Eyring, The activated complex in chemical reactions, *Journal of Chemical Physics*, Vol. 3, p. 107–115, 1935.
- [6] J. D. Eshelby, The determination of Elastic Field of an Ellipsoidal Inclusion, and Related Problems, *Proceedings of Royal Society of London*, Series A, Vol. 241 (1226), pp. 376–396, 1957.
- [7] T. Zhu, J. Li, A. Samanta, H.G. Kim and S. Suresh, Interfacial plasticity governs strain rate sensitivity and ductility in nanostructured metals, *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 104 (9), pp. 3031–3036, 2007.
- [8] T. Zhu, J. Li, A. Samanta, A. Leach, and K. Gall, Temperature and strain-rate dependence of surface dislocation nucleation, *Physical Review Letters*, Vol. 100 (2), p. 025502, 2008.

Academic activities related to this thesis

Publications

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, Homogeneous Dislocation Nucleation: Comparison between Copper, Molybdenum and Silicon, submitted.

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, Reaction Pathway Analysis of Homogeneous Dislocation Nucleation in Silicon, submitted.

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, Reaction Pathway Analysis of Homogeneous Dislocation Nucleation in a Perfect Molybdenum crystal, Materials Research Society Proceedings, submitted.

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, Transition Pathway Analysis of Homogeneous Dislocation Nucleation in a Perfect Silicon Crystal, Mechanical Behavior at Small Scales–Experiments and Modeling, Mater. Res. Soc. Symp. Proc. Volume 1224, 1224-FF05-14, 2010.

International conferences

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, "Reaction Pathway Analysis of Homogeneous Dislocation Nucleation in a Perfect Molybdenum Crystal", 2010 Materials Research Society (MRS) Fall Meeting, Boston, U.S.A., 2010 (poster presentation).

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, "Transition Pathway Analysis of Homogeneous Dislocation Nucleation in a Perfect Silicon Crystal", 2009 Materials Research Society (MRS) Fall Meeting, Boston, U.S.A., 2009 (poster presentation).

Domestic conferences

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, "Influence of Crystal Structure on Activation Energy in Homogeneous Dislocation Nucleation", Japan Society of Mechanical Engineering (JSME), 23rd Computational Mechanics Conference, Kitami, Japan, 2010.

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, "Shuffle-set and Glide-set Homogeneous Dislocation Nucleation in Silicon", Japan Society of Materials Science (JSMS), 15th Molecular Dynamics Symposium, Hokkaido, Japan, 2010 (poster presentation).

H. A. Saeed, S. Izumi, S. Hara and S. Sakai, "Reaction Pathway Analysis of Homogeneous Dislocation Nucleation in Diamond-Cubic Silicon Crystal", Japan Society of Mechanical Engineering (JSME), 22nd Computational Mechanics Conference, Kanazawa, Japan, 2009.

Academic activities not related to this thesis

Publications and conferences

H. A. Saeed, S. Izumi, S. Sakai, S. Haruyama, M. Nagawa, H. Noda, "Development of new metallic gasket and its optimum design for leakage performance", Journal of Solid Mechanics and Materials Engineering, Special Issue on M & M 2007, Vol.2, No.1, pp.105-114, 2008.

H. A. Saeed, S. Izumi, S. Sakai, S. Haruyama, M. Nagawa, H. Noda, "Robust design methodology for sealing performance of gaskets", International Conference on Computational & Experimental Engineering and Sciences, Honolulu, USA, 2008.

H. A. Saeed, S. Izumi, S. Sakai, S. Haruyama, M. Nagawa, H. Noda, "Optimum design for the leakage performance of new metallic gasket", Third Asia-Pacific Congress on Computational Mechanics in conjunction with Eleventh International Conference on Enhancement and Promotion of Computational Methods in Engineering and Sciences, Kyoto, Japan, 2007.

H. A. Saeed, S. Izumi, S. Sakai, S. Haruyama, M. Nagawa, H. Noda, "Optimum design for the leakage performance of new metallic gasket", Japan Society of Mechanical Engineering (JSME) Mechanics of Materials (M&M) Conference, Tokyo, Japan, 2007.

Awards

- 2009 GMSI PBL Award for Outstanding GMSI Research Assistant, 2010.
- GMSI PBL Award for Outstanding Project Execution, 2009.
- University of Tokyo, Faculty of Engineering Dean Award, 2008.
- JSME-Miura Award, 2008.

Acknowledgments

I would like to thank Professor Sakai and Associate Professor Izumi for their sustained support, which was much more than just academic. They are directly responsible for the excellent computational facilities and the overall atmosphere at the lab, which went a long way in making this work possible. Their personal help and guidance—pertaining to research matters and more—was invaluable.

Input from Dr. Hara has also been crucial, and I owe a big debt of gratitude to him. He was always available for discussions despite his very busy schedule; words cannot express my gratitude to him.

Although he is not part of this Lab any more, but for two years the presence of Koichi Shima in the Lab was a source of delight for all concerned, not least for me. It was a privilege to have worked with him side by side on similar problems and to have had an opportunity to discuss each others' work. I wish him a very successful career at his new work place. Discussions with Yu Sun have always been helpful and fun and I thank her for that. I also owe a big thank-you to Dr. Tanaka for all those philosophical debates. It's always gratifying to be able to hear Kansai-ben in Tokyo.

Finally, I thank all the B4 and masters students of Sakai-Izumi Lab for making the lab such a lively and exciting place. Your energetic presence was always appreciated.

I wish everybody a highly successful professional career and, more importantly, a very happy life.

February, 2011 Hasan Aftab Saeed