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ATOMISTIC SIMULATIONS TO STUDY MAGNETIC, MECHANICAL, AND THERMAL PROPERTIES OF MATERIALS USING DENSITY FUNCTIONAL THEORY AND SEMI-EMPIRICAL METHODS

By

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ATOMISTIC SIMULATIONS TO STUDY MAGNETIC, MECHANICAL, AND THERMAL PROPERTIES OF MATERIALS USING DENSITY FUNCTIONAL THEORY AND SEMI-EMPIRICAL METHODS

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Candidate for Degree of Doctorate of Philosophy

We performed atomistic modeling to study magnetic, mechanical, and thermal properties of materials. We executed molecular statics and dynamics simulations for this study, using density functional theory (DFT) and semi-empirical methods, such as embedded atom method (EAM) and modified embedded atom method (MEAM) potentials. In our first study, we showed that when Al atoms are substituted in barium hexaferrite, the total magnetization monotonically decreases due to the fact that Al atoms preferentially occupy the majorly contributing magnetic sites. The second study was to explore the diffusion mechanism of Ba atoms in hematite in order to study new techniques to build spherical nano-magnetic-particles. In the third study, we showed tungsten carbide growth is inhibited in the presence of vanadium carbide. In the fourth study, we showed how the mechanical and thermal properties of iron changes with vanadium doping with a newly developed MEAM interatomic potential. The physical properties of calcium were calculated
in the next study, by the development of a MEAM potential which can be used for multi-scale modeling. In the sixth study, the melting temperature of nanoparticles was analyzed and shown to decrease with a decrease of its size, confirming that the bulk properties of the material significantly change in its nano counterpart. Finally a portion of this research was dedicated for the simulation of sintering mechanisms of tungsten nanoparticles at different temperatures and pressures. While the first three studies were based on DFT, the last four studies focused on understanding physical phenomena using EAM/MEAM potentials.

Key words: DFT, EAM, MEAM, sintering, nanoscience, potential development, diffusion, tungsten, iron-vanadium, tungsten-carbide, vanadium-carbide, magnetic materials
DEDICATION

To my Guru Dadu-Dida, who made me believe in God.

To my beloved wife, who made me believe in myself.

To my MAA, who made me.
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First I would like to thank my adviser Dr. Seong-Gon Kim for directing this work. His explaining skills and resourcefulness, familiarity with VASP and ab initio simulations in general, productive thinking and deep understanding of the area of research, plus his availability for discussions were extremely helpful to me. The discussions we had always gave me a new insight and understanding. His advice and guidance transformed a curious and unfocused student to a professional researcher with a goal on mind. Without his help, guidance, understanding, and support, this work would have never graduated to successful published research.

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who brought me up. I also appreciate JayantaDa and Boudi for their support. I wish my father was alive to enjoy my success.

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LIST OF SYMBOLS, ABBREVIATIONS, AND NOMENCLATURE

A Wavefunction

$\rho$ Charge density

$n$ Electron density

Volume element

$k_B$ Boltmann constant

$J$ Exchange interaction energy

$e^{\exp(-\varepsilon/T)}$ Boltzmann factor

$H = U + pV$ Enthalpy

$\sigma$ Entropy

$G = U - T\sigma + pV$ Gibbs free energy

$F = U - T\sigma$ Helmholtz free energy

$T$ Temperature

$C_{ij}$ Elastic constants

$C_{\text{max}}, C_{\text{min}}$ Screening parameters

$B_0$ Bulk modulus

$E_c$ Cohesive energy

$E_f^{\text{vac}}$ Vacancy formation energy

$E_{sf}$ Stacking fault energy

$E_{\text{surf}}$ Surface ornamentation energy

$F_i(\rho)$ Embedding energy function

$H_f$ Heat of formation
$Z_{0}$ First nearest neighbor coordination of the reference system

$a_{0}$ Equilibrium lattice parameter

$\alpha$ Coefficient of thermal expansion

$\epsilon_{ij}$ Strain component

**VASP** Vienna *ab initio* Simulation Package

**LAMMPS** Large-scale Atomic/Molecular Massively Parallel Simulator

**MPI** Message Passing Interface

**GMR** Giant Magneto Resistance

**EAM/FS** Finnis Sinclair method of Embedded Atom Method

**AEAM** Analytical Embedded Atom Method

**CNA** Common Neighbor Analysis

**DFT** Density Functional Theory

**EAM** Embedded Atom Method

**FEA** Finite Element Analysis

**MEAM** Modified Embedded Atom Method

**k-mesh** regular mesh in the space of $k$ vectors

**bcc** body centered cubic

**cub** simple cubic

**fcc** face centered cubic

**hcp** hexagonal close packed

**dia** diamond cubic
CHAPTER 1

INTRODUCTION

1.1 Introduction

Over the last few decades, computational science has extended the range of its studies extensively. The phenomena that can be investigated within the framework of physics are versatile. Computer experiments offer one way to gain knowledge of such, which are extremely difficult to perform for realistic systems. While our familiarity with many types of materials makes this fact unimpressive, it is indeed extraordinary when we consider the origin. The origin of all the properties of materials is nothing more than the interaction between electrons in the outer shells of atoms, the so called valence electrons. To get deeper insight of those interactions, one needs to do electronic structure calculations in order to understand variations of resistivity or the brittleness or the fracture of materials or thermal reactions, such as melting temperatures.

In modern electronic structure calculations, the goal is to solve the Schrödinger equation, $\hat{H} = E$, for the N-electron system of interest. Here $\hat{H}$ is the Hamiltonian operator for the 3N dimensional wavefunction and $E$ is the total energy of the system. Solution of this equation is almost impossible with the \textit{ab initio} method for a system containing more than 10 electrons. In density functional theory (DFT), instead of deal-
ing with a 3N dimensional wavefunctions one expresses the total energy as a functional of the electron density. The key idea is to replace a difficult problem of interacting electrons in an external potential with a simpler problem of noninteracting electrons in an effective potential with equivalent electron density. With the rapid advent of reliable functionals (especially the benefits of the generalized gradient approximation over the local spin density approximation), the theory has become the most popular method in electronic structure calculations of materials and has made a notable impact in condensed matter physics, chemistry, and material science. Despite the accuracy and modern functionals, DFT requires much computational memory and/or time.

While present DFT can handle only a few hundred atoms, many realistic simulations need a few millions of atoms to be simulated. One alternative is to use empirical or semi-empirical inter-atomic potentials that can be incorporated efficiently. One popular semi-empirical potential based on the embedded atom method (EAM) was modified to include the angular dependencies to generate the modified embedded atom method (MEAM) potential. These potentials can easily handle a few millions atoms in a convenient time. MEAM was the first semi-empirical atomic potential using a single formalism for fcc\(^1\), bcc\(^2\), hcp\(^3\), diamond-structured material and even gaseous elements, in good agreement with experiments or first principle calculations. EAM and MEAM have been applied to

\(^1\text{face centered cubic crystal}\\^2\text{body centered cubic crystal}\\^3\text{hexagonal closed packed crystal}
observe realistic shear behavior, tensile debonding, surface formation, and several defect formation energies for single element or alloy systems.

1.2 Application

The structure of crystals can be understood to some extent by taking a close look to the properties of the atoms of which they are composed. The valence electrons interact strongly with similar electrons in neighboring atoms. The rest of the electrons are tightly bound to the nuclei; their wavefunctions do not extend far from the nuclei and are very little affected when surrounded by neighbors. A basic nature of binding forces can be understood by the number of valence electrons. Atoms with no valence electrons (such as He, Ne, Ar, Kr, etc.) have no mediator to interact with neighbors and hence they interact very weakly with other atoms: resulting in an instable solid with a very low melting point. They tend to accommodate as many neighboring atoms as possible, such as fcc or hcp structures (12 neighbors). When we have one valence electron for an atom, the force increases and structure stabilizes in the bcc structure (8 neighbors, next of 12 neighbors). Other elemental structures could be understood in view of the shape of the valence electron orbital, such as s, p, d etc.

1.2.1 Defects

Defects are important properties of crystals and hence the materials are controlled by defects, as much as by the nature of the host-crystal, which acts as a solvent or matrix for the imperfections. In reality, growth of a pure material is very expensive and it is very
likely that the material will have many kinds of defects such as vacancy defect, line defect, surface defect etc. The conductivity, color, luminescence are of few examples where there are direct relations to the defect properties of matter. Atomic diffusion may be accelerated enormously by impurities or imperfections. Mechanical and plastic properties are usually controlled by imperfections. In my PhD study, I have calculated extensively several point defects, such as monovacancy, substitutional and interstitial defects in different positions, such as octahedral or tetrahedral, for material. Line defects, such as dislocations, grain-boundaries and stacking faults, were also observed by molecular dynamic simulations. Several surface defects were monitored by calculation of several surface formation energies and also surface adsorption energies for similar or dissimilar elements.

1.2.2 Nanoscience

Nanoscience is a new way of thinking about building up complex materials and devices by exquisite control of the functionality of matter and its assembly at the nanometer-length scale. On this scale, new properties (electrical, mechanical, optical, chemical, and biological) that are fundamentally different from bulk or molecular properties can emerge. Nanoscience is about creating new nanostructures, uncovering and understanding their novel properties, and ultimately about learning how to organize these new nanostructures into larger and more complex functional structures and devices. The material properties change significantly in their nanoscale physical regime compared to the bulk properties. Simulations at the atomistic level often bring up new science in the nanoscale regime:
melting of tungsten nanoparticles, sintering of tungsten nanoparticles, diffusion of barium atom in hematite, etc. all reflect new areas in the field of nanoscience.

1.2.3 Potentials

Accurate inter-atomic potentials are the basic need for atomistic simulations to compute the total energy of the system. First-principles calculations can provide the most reliable inter-atomic potentials. However, realistic simulations often require a number of atoms that render these methods impractical: they either require too much computer memory or take too long to be completed in a reasonable amount of time. One alternative is to use empirical or semi-empirical interaction potentials that can be evaluated efficiently. Construction of these potentials has an immense impact on this research community. MEAM includes the angular binding of neighboring atoms, and therefore essentially MEAM can better represent material properties in terms of cracks, deformations, etc. I developed a iron-vanadium MEAM inter-atomic potential to show how the pure iron material properties will change with vanadium substitution. I have also developed a MEAM calcium potential which can represent the bulk, defects, and surface properties of calcium.

1.2.4 Sintering

Sintering, a method for making objects from powder by heating the material below its melting point (solid state sintering) until the particles adhere to each other, is the most common method to manufacture today’s material. Tungsten, along with its alloys and
compounds, occupies a unique position in materials science. The material properties that make tungsten attractive to the metals industry are high density, hardness, high melting temperature, elastic modulus and conductivity in conjunction with low thermal expansion. The combination of these unique properties explains the diverse applications of tungsten. The Hall-Petch effect (the hardness increases in proportional to the inverse square-root of grain size) suggests that significant opportunities exists if powders could be consolidated to full densities with minimal coarsening. I have simulated the sintering process of tungsten nanoparticle, in different external scenarios, such as temperature, pressure and size of the particles. I have also been studied how the grain boundary influences the whole process of coalescence and sintering. Here I would like to mention that atomistic scale sintering studies are only possible with a semi-empirical potential, because of the fact that DFT cannot handle too many atoms. For example a 10 nm (bcc) nanoparticle has about 33,000 atoms which are beyond the scope of DFT capabilities. Hence the need for good semi-empirical inter-atomic potentials to understand such kinds of atomistic mechanisms is prudent.

1.2.5 Magnetic materials

We first define the terms used to describe the various types of magnetic behavior. A system is called paramagnetic if it has no inherent magnetization, but when subject to an external field, it develops magnetization which is aligned with the field: a similar situation is when microscopic magnetic moments tend to be oriented in the same direction as the external magnetic field. A system is called diamagnetic if it has no inherent magnetization,
but when subject to an external field it develops magnetization that is opposite to the
direction of the magnetic field: a similar situation is when microscopic magnetic moments
tend to shield the external magnetic moment. If the microscopic magnetic moments tend to
be oriented in the same direction even in the absence of external magnetic field, the system
is called ferromagnetic. A variation could be where microscopic magnetic moments tend
to have parallel orientation, but they are not necessarily equal at neighboring sites; thus
is named ferrimagnetic. If the magnetic moments at neighboring sites tend to point in
opposite directions, the system is referred to as antiferromagnetic.

There is a dominating role played by antiferromagnetic superexchange coupling in
barium ferrite (BaM) that has been established as a permanent magnetic material among
the various M-type hexaferrites MFe₁₂O₁₉ (M= Sr, Ba, Pb). Due to the high saturation
of magnetization, good chemical stability and large magneto-crystalline anisotropy, this
material has been investigated intensively. The magnetic Fe³⁺ ions are arranged in five
different kinds of interstitial sites. The ensemble of ferric ions in the 12k, 2a and 2b sites
are anti-parallel to those of the other two sublattices, the ferric ions in 4f₁ and 4f₂ sites.
Aluminium-substituted M-type hexagonal ferrite has a very large coercivity. However, it
has been found experimentally that the saturation magnetization decreases monotonically
with an increase of Al substitution. The site preference for substituted Al atoms plays the
key role in this effect. It is shown here why Al substitution decreases the total magnetic
moment. It has also been shown why Al atoms preferentially occupy the 2a and 12k sites
by calculating the substitutional defect energies and available site volumes. I used DFT to
understand the electronic reasoning of why Al substitution did not help in increasing the
total magnetization of BaM, and gained knowledge of what elements can be substituted to get higher magnetic moment.

1.2.6 Diffusion

Diffusion of foreign material into the bulk of another material is important to study to realize the design of novel materials. Especially the surface diffusion process can generally be thought of in terms of particles jumping between adjacent adsorption sites on a surface. Just as in bulk diffusion, this motion is typically a thermally promoted process with rates increasing with increasing temperature. Where there are many experimental mechanisms, such as STM, to elucidate the mechanism and rate, computationally we can also track down the adatom (atom is in consideration) to see how it moves over the surface as well as within the bulk. There are different mechanisms, such as hopping, exchange, vacancy-assisted, tunneling, etc. Computationally we also have few modern techniques to find diffusion paths using the Nudged Elastic Band (NEB) or the CLIMB methods. I studied barium atom diffusion in hematite to explore how magnetic nanoparticles could be manufactured. I also studied the self diffusion mechanisms of Fe-V binary systems using NVT ensembles and Einstein-Smoluchowski equation\(^4\) with several percentage of V diffusion.

---

\(^4\)According to Fick’s second law of diffusion \(j(r, t) = -D \nabla n(r, t)\) and definition of current density \(j(r, t) = n(r, t)v(r, t)\), we derive the equation of continuity \(\nabla \cdot j(r, t) + \frac{\delta n(r, t)}{\delta t} = 0\), and combined to get the diffusion equation \(\nabla^2 n(r, t) - \frac{1}{D} \frac{\delta n(r, t)}{\delta t} = 0\). We solved this equation to get the Einstein-Smoluchowski equation \(<r^2> = 6Dt\) and combining Langevin’s result we get the mobility of the system from Einstein relationship \(D = \frac{Bk_B T}{m}\).
2.1 Introduction

With advances in available computing power, density functional theory (DFT) has become an excellent tool for investigating the properties of atoms, molecules, gases, and solid state matter. Since the underlying task of most DFT calculations is to find the ground state density of electrons in a crystal, the DFT method is limited to the systems of a few hundreds of atoms in the simulation cell. The application of periodic boundary conditions allows us to investigate the properties of bulk-like materials. This chapter introduces the basic assumptions and methods used in the DFT calculations. The key idea in DFT is to solve the Schrödinger equation in an environment such that instead of solving the wavefunctions, we are solving for the electron density $n$. The theory reduces the intractable complexity of electron many-body interactions to an effective single electron equation determined by the exchange-correlation functional which depends on the electron-density only [60].

2.1.1 Born-Openheimer Approximation

The ground state wave function $\psi(R_1\ldots R_M; r_1\ldots r_N)$ for a stationary state of a system with M nuclei at positions $R_1\ldots R_M$ and N electrons at positions $r_1\ldots r_N$ can
be obtained from the time-independent Schrödinger equation: \( \hat{H} (R_1,...,R_M; r_1,...,r_N) = E (R_1,...,R_M; r_1,...,r_N) \) with the Hamiltonian operator \( \hat{H} \) equal to

\[
\hat{H} = -\sum_{i=1}^{M} \left( \frac{\hbar^2}{2m_{Z_i}} \nabla_{R_i}^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \nabla_{r_i}^2 \right) + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{M} \sum_{j>i}^{M} \frac{Z_i Z_j e^2}{|R_i - R_j|} \\
- \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{Z_j e^2}{|r_i - R_j|} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{|r_i - r_j|} 
\]  

(2.1)

where \( m_e \) is the electron mass, \( Z_i \) is the atomic number of the \( i^{th} \) nucleus, \( m_{Z_i} \) is the mass of the \( i^{th} \) nucleus, \( \hbar \) is the reduced Planck’s constant and \( \epsilon_0 \) is the permittivity of vacuum. The first two terms represent the kinetic energies of nuclei and electrons; the remaining terms provide potential energies of nucleus-nucleus, nucleus-electron, and electron-electron Coulomb pair interactions, respectively. Since the nuclei are much heavier and move much slower than electrons, we can assume they are stationary and fix their positions \( R_i,...,R_M \). The first term in the Equation (2.1), representing the kinetic energy of nuclei, will be set to zero. The third term in the Equation (2.1) will be a constant determined by the \( R_1,...,R_M \), resulting in a constant contribution to the total energy \( V_{II} \). The electron wave functions will be considered separately, with the nuclei positions as fixed parameters. The Hamiltonian for the electronic system will simplify to

\[
\hat{H}_e = -\sum_{i=1}^{N} \left( \frac{\hbar^2}{2m_e} \nabla_{r_i}^2 \right) + V_{II} - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{Z_j e^2}{|r_i - R_j|} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{|r_i - r_j|} 
\]  

(2.2)

resulting in the electronic time-independent Schrödinger equation

\[
\hat{H}_e (r_1,...,r_N) = E_e (r_1,...,r_N) 
\]  

(2.3)
The electronic wave function in Equation (2.3) will be a function of only electronic positions $r_1\ldots r_N$, while the positions of nuclei $R_1\ldots R_N$ will be constant parameters. Solving Equation (2.3) is the central task of most problems involving electronic structure theory.

### 2.1.2 Hohenberg-Kohn Theorem

Two classic theorems of Hohenberg and Kohn state that any property of a many-particle system can be described as a functional (function of a function) of the spatial particle density distribution in the system. The first theorem states that for a system of particles in an external potential $V_{\text{ext}}(r)$, the ground state particle density $n(r)$ uniquely (except for a constant) determines the external potential. An important corollary of this theorem is that any property of the system can be described in terms of the particle density $n(r)$. The second theorem states that a functional for energy in terms of density $E[n(r)]$ that is valid for any external potential $V_{\text{ext}}(r)$ can be defined. The minimum of the functional corresponds to the ground state energy and the corresponding density is the ground state density of the system. The corollary of this theorem is that the functional $E[n(r)]$ alone is sufficient to determine the ground state energy and the particle density of the system.

### 2.1.3 Density Functional Theory

A density functional approximates the Kohn-Sham approach \(^1\) [87], utilizing the solution for the system of independent particles, and providing the exact solution for the interacting system of particles if the exchange-correlation energy is represented exactly.

\(^1\)to replace the difficult interacting many-body system obeying an Hamiltonian equation with a different auxiliary system which can be solved more easily.
The most important factors determining the level of theory of a quantum-mechanical simulation are the choice of an exchange-correlation functional, the choice of basis set for the expansion of Kohn-Sham orbitals, charge and spin densities and potentials, and the algorithm to solve the Kohn-Sham equations for calculating the energies, forces, and stresses. The challenge of techniques using the Kohn-Sham approach is to find a good approximation of the exchange-correlation energy functional. Many approximations to the exchange-correlation functional that would produce the exact same ground state as the solution of many-body Schrödinger equation have been proposed. Two available density functional approximations are the local density approximation (LDA) and the generalized gradient approximation (GGA).

2.1.3.1 Local Density Approximation

The local density approximation (LDA) [or the more general local spin density approximation (LSDA) including spin effects] assumes that the exchange-correlation energy is only determined by the local electron density as

\[ E_{xc}[n(r)] = \int n(r)\epsilon_{xc}[n(r)] \, dr. \]  \hspace{1cm} (2.4)

The \( \epsilon_{xc}[n(r)] \) is an energy per electron that only depends on the density \( n(r) \) close to the point \( r \). Since the exchange-correlation functional \( \text{Exc}[n(r)] \) is universal, it could be the same as the one for a homogeneous electron gas. If this is true, the exchange part has an analytical form. The correlation part was calculated by Ceperley and Alder using Monte-Carlo methods [30].
2.1.3.2 Generalized Gradient Approximation

In contrast to the LDA equation, the generalized gradient approximation (GGA) includes the gradient of the electron density when evaluating the exchange-correlation energy, and is given by

\[ E_{xc}[n(r), \nabla n(r)] = \int (n(r)\varepsilon_{xc}[n(r), \nabla n(r)]) \, dr. \]  \hspace{1cm} (2.5)

The parametrization of GGA includes those of Perdew-Wang (PW91) and Perdew-Burke-Ernzerhof (PBE). They are two different functionals to represent the gradient of electron densities, we use PBE in our calculations.

2.1.3.3 Pseudo-potential

The electrons close to an atomic core are much less affected by surrounding atoms than are the valence electrons. Assuming the core electrons and core are fixed, a pseudo-potential approach replaces the combined effects of the core electrons and Coulomb potential from the atomic core by a single pseudo-potential that acts only on the valence electrons. The resulting pseudo-wave functions of the valence electrons are then smoother and the number of plane waves required to represent them is lower, resulting in faster convergence of the total energy with respect to the plane wave energy cutoff. For \( r \) less than the cutoff radius \( r_c \), the full wave function and pseudo-wave function match each other. The norm conservation condition ensures that pseudo-wave functions and all electron wave functions generate the same charge densities. Ultrasoft pseudo-potentials introduced later do not impose the norm conservation constrain, providing the benefit of softer wave
functions and smaller cutoff radii than the norm conserving pseudo-potentials. A certain drawback of pseudo-potentials is due to the nonlinearity of the exchange-correlation functional in DFT, elaborate nonlinear core corrections are required for an accurate description of valence-core interaction in all systems where the overlap between core and valence electron densities is not negligible. The projector-augmented wave (PAW) approach developed by Blöchl reconstructs the full all-electron density and avoids the necessity of nonlinear core-corrections. In the present work, I used PAW-GGA.

2.1.3.4 Basis Set

In practice, the Kohn-Sham equations are solved iteratively, using an expansion of the orbitals in as appropriately chosen set of basis functions. The plane-wave (PW) basis-set adopted in VASP offers two main advantages: (a) control of basis set convergence; and (b) the calculation of the forces acting on the atoms and of the stresses on the unit cell using the Hellmann-Feynman theorem [44]. The last advantage opens the way to quantum ab-initio molecular dynamic simulations to understand the time evolution of a system.

2.2 Introduction

Molecular dynamics (MD) simulations are a useful numerical tool for the investigation of mechanical properties of materials. In most cases, MD simulations calculate the trajectory of each atom, taking into account interactions with surrounding atoms by means of an inter-atomic potential. The MD simulations can be used to model systems containing millions of atoms for the time interval of several picoseconds. In this work, we
addressed a challenge of constructing inter-atomic potentials by fitting the results of DFT calculations. The new potential was then used to investigate the nanoscale mechanisms of materials. For our MD simulations, we used the LAMMPS code provided by Sandia National Laboratories. Parallel computing capabilities of the code are implemented using MPI libraries. The simulation domain (simulation box) is spatially divided between processors. To integrate the Newton’s equations of motion, the LAMMPS package implements the velocity Verlet algorithm. Given the initial position \( x(t) \) and initial velocity \( \dot{x}(t) \), the velocity Verlet algorithm first estimates the velocity of an atom at the time \( t + h/2 \)

\[
\dot{x}(t + h/2) = \dot{x}(t) + (h/2)\ddot{x}(t) \tag{2.6}
\]

with the acceleration \( \ddot{x}(t) \) computed from force

\[
\ddot{x}(t) = \frac{F(t)}{m}. \tag{2.7}
\]

Then the coordinate \( x \) at the time \( t + h \) is updated using the velocity \( \dot{x}(t + h/2) \) from Equation (2.6)

\[
x(t + h) = x(t) + h\dot{x}(t + h/2). \tag{2.8}
\]

Given the new atomic positions \( x(t + h) \), the forces \( F(t + h) \) are recalculated. The velocities at the time \( t + h \) are then estimated as

\[
\dot{x}(t + h) = \dot{x}(t + h/2) + (h/2)\ddot{x}(t + h) \tag{2.9}
\]
The integration is repeated every time step of \( h \) units. The time step \( h \) needs to be small enough to account for the largest vibrational frequency of the system. Common time steps are of the order of 1 fs.

### 2.2.1 Statistical Ensembles

For the simulations at constant temperature, canonical (NVT) ensembles are commonly used. NVT designates that the number of particles \( N \), volume \( V \) and temperature \( T \). The statistical averages of samples obtained from canonical ensembles reproduce the averages of real-world systems. In order to keep the temperature constant in an NVT ensemble, a temperature regulator is incorporated into the integration algorithm. In our MD simulations, we used the Nosé-Hoover thermostat. If it is desired to model a system with a constant number of particles at constant pressure and temperature, the isothermal-isobaric (NPT) ensemble is used. In case of microcanonical ensembles (NVE), the number of particles, volume, and energy remain constant.

### 2.2.2 Boundary Conditions

Computational requirements of MD simulations are linearly proportional to the number of atoms and to the number of time steps in the simulations. To model the properties of a bulk material with a periodic structure, a technique of introducing periodic boundary conditions is applied. The basic periodic unit cell of a simulation, usually in the shape of parallelepiped, is thus repeated in the direction of the selected base cell vector(s), in distances that are integer multiples of the unit cell vector(s) length.
2.2.3 Inter-atomic Potentials

2.2.3.1 EAM

The potential energy of an atom in EAM is

\[ E_i = F(n_i) + \frac{1}{2} \sum_{j \neq i} V(r_{ij}) \]  

(2.10)

where \( j \) points to a neighbor atom located at the position \( r_{ij} \) with the origin at \( i \). \( V(r_{ij}) \) is a standard pair interaction term between \( i \) and \( j \), and \( F \) is the embedding function of atom \( i \). \( n_i \) is the total atomic density at the site of atom \( i \).

\[ n_i = \sum_{j \neq i} \rho(r_{ij}). \]  

(2.11)

The first term in 2.10 represents the sum of pair potential contributions from surrounding atoms. For Lennard-Jones type of MD potential, this pair potential term is the only component of the potential energy.

The second term of 2.10, specific for EAM, represents the energy needed to embed an atom into the background atomic density created by a host environment. The background atomic density is computed as the sum of contributions from surrounding atoms.

2.2.3.2 MEAM

The total energy \( E \) of a system of atoms in MEAM is approximated as the sum of the atomic energies

\[ E = \sum_i E_i \]  

(2.12)
The energy of atom $i$ consists of the embedding energy and the sum of the pair potential terms,

$$E_i = F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{i \neq j} \Phi_{ij}(r_{ij})$$  \hspace{1cm} (2.13)

$F$ is the embedding function, $\bar{\rho}_i$ is the background atomic density at the site of atom $i$, and $\Phi_{ij}(r_{ij})$ is the pair potential between atoms $i$ and $j$ separated by distance $r_{ij}$. The embedding energy $F_i(\bar{\rho})$ represents the energy cost to insert atom $i$ at a site where the background atomic density is $\bar{\rho}_i$. The embedding energy is given in the form

$$F_i(\bar{\rho}_i) = A_i E_i^0 \bar{\rho}_i \ln(\bar{\rho}_i)$$  \hspace{1cm} (2.14)

where the sublimation energy $E_i^0$ and parameter $A_i$ depend on the element type of atom $i$. The background electron density $\rho_i$ is given by

$$\bar{\rho}_i = \frac{\rho_i^{(0)}}{\rho_i^0} G(\Gamma_i)$$  \hspace{1cm} (2.15)

where

$$\Gamma_i = \sum_{k=1}^{3} \rho_i^{(k)} \left( \frac{\rho_i^{(0)}}{\rho_i^0} \right)^2$$  \hspace{1cm} (2.16)

and

$$G(\Gamma) = \sqrt{1 + \Gamma}.$$  \hspace{1cm} (2.17)

The zeroth and higher order densities, $\rho_i^{(0)}$, $\rho_i^{(1)}$, $\rho_i^{(2)}$, and $\rho_i^{(3)}$ are given in equations below.

The composition-dependent electron density scaling $\rho_i^0$ is given by

$$\rho_i^0 = \rho_{i0} Z_{i0} (\Gamma_i^{ref})$$  \hspace{1cm} (2.18)
where \( \rho_{i0} \) is an element-dependent scaling, \( Z_{i0} \) is the nearest-neighbor coordination of the reference system, and \( \Gamma_{i}^{ref} \) is given by

\[
\Gamma_{i}^{ref} = \frac{1}{Z_{i0}^2} \sum_{k=1}^{3} \rho_{i}^{(k)} S_{i}^{(k)}
\]  
(2.19)

where \( s_{i}^{(k)} \) is the shape factor that depends on the reference structure for an atom \( i \). Shape factors for various structures are specified in the work of Baskes. The partial atomic densities are given by

\[
\rho_{i}^{(0)} = \sum_{j \neq i} \rho_{j}^{(0)} (r_{ij}) S_{ij}
\]  
(2.20)

\[
\left( \rho_{i}^{(1)} \right)^2 = \sum_{\alpha} \left[ \sum_{j \neq i} \rho_{j}^{(1)} \frac{r_{ij} \alpha}{r_{ij}} S_{ij} \right]^2
\]  
(2.21)

\[
\left( \rho_{i}^{(2)} \right)^2 = \sum_{\alpha, \beta} \left[ \sum_{j \neq i} \rho_{j}^{(2)} \frac{r_{ij} \alpha r_{ij} \beta}{r_{ij}^3} S_{ij} \right]^2 - \frac{1}{3} \left[ \sum_{j \neq i} \rho_{j}^{(2)} (r_{ij}) S_{ij} \right]^2
\]  
(2.22)

\[
\left( \rho_{i}^{(3)} \right)^2 = \sum_{\alpha, \beta, \gamma} \left[ \sum_{j \neq i} \rho_{j}^{(3)} \frac{r_{ij} \alpha r_{ij} \beta r_{ij} \gamma}{r_{ij}^3} S_{ij} \right]^2 - \frac{3}{5} \sum_{\alpha} \left[ \sum_{j \neq i} \rho_{j}^{(3)} \frac{r_{ij} \alpha}{r_{ij}} S_{ij} \right]^2
\]  
(2.23)

where \( r_{ij}^{\alpha} \) is the \( \alpha \) component of the displacement vector from atom \( i \) to atom \( j \). \( S_{ij} \) is the screening function between atoms \( i \) and \( j \) and is defined in equations below. The atomic densities are computed as

\[
\rho_{i}^{a(k)} (r_{ij}) = \rho_{i0} \exp \left[ \left( \beta_{i}^{(k)} \frac{r_{ij}}{r_{i0}^{(k)}} - 1 \right) \right]
\]  
(2.24)

where \( r_{i0}^{(k)} \) is the nearest-neighbor distance in the single-element reference structure and \( \beta_{i}^{(k)} \) is an element-dependent parameter. Finally, the average weighting factors are given by
\[ t_{ij}^{(k)} = \frac{1}{\rho_i^{(0)}} \sum_{j \neq i} t_{0,ij} a_j^{(0)} S_{ij} \] (2.25)

where \( t_{0,ij}^{(k)} \) is an element-dependent parameter.

The pair potential is given by

\[ \Phi_{ij}(r_{ij}) = \Phi_{ij}(r_{ij}) S_{ij} \] (2.26)

\[ \Phi_{ij}(r_{ij}) = \frac{1}{Z_{ij}} [2E_{ij}^u(r_{ij}) - F_i(\hat{\rho}_j(r_{ij})) - F_j(\hat{\rho}_j(r_{ij}))] \] (2.27)

\[ E_{ij}^u(r_{ij}) = -E_{ij}(1 + a_{ij}^*(r_{ij})) exp(-a_{ij}^*(r_{ij})) \] (2.28)

\[ a_{ij}^* = \alpha_{ij} \left( \frac{r_{ij}}{r_{ij}^0} - 1 \right) \] (2.29)

where \( E_{ij}, \alpha_{ij} \) and \( r_{ij}^0 \) are element-dependent parameters and \( Z_{ij} \) depends upon the structure of the reference system. The background densities \( \hat{\rho}_i(r_{ij}) \) are the densities for the reference structure computed with inter-atomic spacing \( r_{ij} \).

The screening function \( S_{ij} \) is designed so that \( S_{ij} = 1 \) if atoms \( i \) and \( j \) are un-screened and within the cutoff radius \( r_c \), and \( S_{ij} = 0 \) if they are completely screened outside the cutoff radius \( r_c \). \( S_{ij} \) varies smoothly between 0 and 1 for partial screening.

The total screening function is the product of a radial cutoff function and three body terms involving all other atoms in the system:
\[ S_{ij} = S_{ij} f_c \left( \frac{r_c - r_{ij}}{\Delta r} \right) \]  

(2.30)

\[ \tilde{S}_{ij} = \prod_{k \neq i,j} S_{ikj} \]  

(2.31)

\[ \tilde{S}_{ikj} = f_c \left( \frac{C'_{ikj} - C'_{\text{min},ikj}}{C'_{\text{max},ikj} - C'_{\text{min},ikj}} \right) \]  

(2.32)

\[ C_{ikj} = 1 + 2 \frac{r_{ij}^2 r_{ik}^2 + r_{ij}^2 r_{jk}^2 - r_{ij}^4}{r_{ij}^4 - (r_{ik}^2 - r_{jk}^2)^2} \]  

(2.33)

\[ f_c(x) = \begin{cases} 
1 & x \geq 1 \\
[1 - (1 - x)^4]^2 & 0 \leq x \leq 1 \\
0 & x \leq 0 
\end{cases} \]  

(2.34)

Note that \( C'_{\text{min}} \) and \( C'_{\text{max}} \) can be defined separately for each \( i - j - k \) triplet, based on their element types. The parameter \( \Delta r \) which controls the distance over the radial cutoff, is smoothed from 1 to 0 near \( r = r_c \).
CHAPTER 3

MAGNETIC PROPERTIES OF BARIUM HEXAFERRITE

3.1 Introduction

Due to high saturation of magnetization, good chemical stability, high coercivity and large magneto-crystalline anisotropy, barium hexaferrite (BaFe$_{12}$O$_{19}$) has been established as one of the most useful permanent magnetic materials among the various M-type hexaferrites MFe$_{12}$O$_{19}$ (M = Sr, Ba, or Pb) [28, 125, 174]. Recently the material has drawn even more attention for its usefulness in high density magnetic recording media, microwave devices and electromagnetic wave absorber [34, 170].

The crystal structure of an M-type hexaferrite material (space group $P6_3/mmc$) is based on the hexagonal lattice as shown in Fig. 3.1. The magnetic Fe$^{3+}$ ions are arranged in five different types of interstitial sites: three octahedral sites (12$k$, 4$f_2$, and 2$a$), one tetrahedral site (4$f_1$) and one trigonal bipyramid or hexahedral site (2$b$), as listed in Table 3.1. The total magnetization is from the contribution of all Fe atoms in these sites. The structure of hexaferrite is symbolically described as $RSR^*S^*$ where $R$ denotes a three-layer block containing two O$_4$ and one BaO$_3$ with the composition Ba$^{2+}$Fe$_6^{3+}$O$_{11}^{2-}$ and $S$ denotes a two-layer block containing two O$_4$ with the composition Fe$_6^{3+}$O$_8^{2-}$ [145]. The asterisk signifies the rotation of the corresponding block by 180° about the $c$-axis.
Figure 3.1 The Structure of M-type barium hexaferrite.

Red, magenta, ash, blue and yellow colored spheres represent iron atoms in $2a$, $4f_1$, $12k$, $4f_2$, and $2b$ sites respectively, small green spheres are oxygen atoms, and larger cyan spheres are barium atoms.
Table 3.1 The coordinates of atoms and their symmetries in barium hexaferrite.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Wyckoff site</th>
<th>Symmetry</th>
<th>Atom coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>$2d$</td>
<td>6m2</td>
<td>1/3, 2/3, 3/4</td>
</tr>
<tr>
<td>Fe(1)</td>
<td>$2a$</td>
<td>3m</td>
<td>0, 0, 0</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>$2b$</td>
<td>6m</td>
<td>0, 0, 1/4</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>$4f_1$</td>
<td>3m</td>
<td>1/3, 2/3, 0.02718</td>
</tr>
<tr>
<td>Fe(4)</td>
<td>$4f_2$</td>
<td>3m</td>
<td>1/3, 2/3, 0.19091</td>
</tr>
<tr>
<td>Fe(5)</td>
<td>$12k$</td>
<td>m</td>
<td>0.16886, 0.33772, 0.89083</td>
</tr>
<tr>
<td>O(1)</td>
<td>$4e$</td>
<td>3m</td>
<td>0, 0, 0.1514</td>
</tr>
<tr>
<td>O(2)</td>
<td>$4f$</td>
<td>3m</td>
<td>0, 0, 0.9446</td>
</tr>
<tr>
<td>O(3)</td>
<td>$6h$</td>
<td>mm</td>
<td>0.1819, 0.3639, 1/4</td>
</tr>
<tr>
<td>O(4)</td>
<td>$12k$</td>
<td>m</td>
<td>0.1564, 0.3127, 0.05252</td>
</tr>
<tr>
<td>O(5)</td>
<td>$12k$</td>
<td>m</td>
<td>0.5039, 0.0078, 0.15092</td>
</tr>
</tbody>
</table>
The knowledge of magnetic interactions of iron ions of barium hexaferrite (BaM) on different sites is necessary to help in predicting several properties of substituted hexaferrite. Néel (1948) and Anderson (1950) proposed a superexchange interactions through oxygen ions [7, 88, 128]. Later Gorter [56] proposed the exchange scheme of the compound, considering the magnetization values of BaM with Anderson’s indirect exchange theory. From Gorter’s configuration of the magnetization of five sites, the ensemble of ferric ions in the $12k$, $2a$ and $2b$ sites are anti-parallel to those of the other two sites that have the ferric ions in $4f_1$ and $4f_2$ sites[29]. Electronic structure of the stoichiometric strontium hexaferrite (SrM) was calculated by Fang et. al. [42] using the local spin density approximation in density functional theory. Recently Novák et. al. [134] have calculated the exchange interaction of BaM by employing the differences of the total energy of different collinear spin configurations assuming that the electronic structure of all the configurations corresponds to an insulator.

It is important to study the coercivity, anisotropy, and saturation magnetization in order to understand the magnetic behavior. A few groups have investigated the modification of the magnetic properties of BaM by substituting Fe$^{3+}$ with Mn$^{3+}$ [83], Cr$^{3+}$ [82], and Al$^{3+}$ [182]. Interestingly Al-substituted BaM is known to have a very large coercivity. However, it has been found experimentally that the saturation magnetization decreases monotonically with an increase of Al substitution. The site preference for substituted Al atoms is a key factor in understanding these effects. A few reports [28, 176] have concluded that substituted Al atoms occupy $2a$, $12k$, and $4f_1$ sites, while others [29, 145] have reported that $2a$, $12k$, $4f_1$, and $4f_2$ are the sites occupied by Al atoms. However,
these experimental studies are not conclusive enough to distinguish the nearly equal hyperfine parameters for $2a$ and $4f_1$ [6]. Studies also have revealed that for up to a certain level of Al substitution into BaM, Al atoms go to $2a$, $4f_1$, $12k$, and $4f_2$ sites and for higher levels of substitution, the Al atoms go to the $12k$ site only [6]. Moreover, coercivity increases up to a certain level ($x = 2$) of substitution for Al-substituted BaM, further substitution decreases the coercivity. Although theoretical studies have been done on the exchange integrals [134] and electronic structure [42] of BaM and SrM, respectively, no significant study to unambiguously determine the site preferences of other elements, such as Al, has been done.

The objective of the present research is to resolve the ambiguity in site preference for Al-substituted BaM by comparing the ground state energies of various possible configurations using first-principles calculations. We find that Al$^{3+}$ ions preferentially occupy the $2a$ and $12k$ sites, and not the $4f_1$ and $4f_2$ sites which were reported earlier as occupied by Al atoms. Our result also shows that the total magnetic moment decreases monotonically with an increase of Al substitution, that is in good agreement with experiments.

3.2 Method

All simulations we carried out using a supercell of 64 atoms. Energy calculations and geometry optimizations of various structures we performed using Blöchl’s all-electron projector augmented wave method [21] as implemented by Kresse and Joubert [93]. For the treatment of electron exchange and correlation, we use the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof scheme [74]. For the standard
interpolation for the correlation part of the exchange correlation functional, the Vosko, Wilk and Nusair formula [181] is used. This usually enhances the magnetic moments and the magnetic energies of the system. The plane-wave cut off energy was set to 400 eV in all calculations. All geometry relaxations were done with tetrahedron method with Blöchl’s correction using the conjugate gradient algorithm. Geometry relaxations are performed until the energy difference between two successive ionic optimizations is less than 0.001 eV. The Brillouin zone is sampled with a density equivalent to 50 kpoints using Monkhorst-Pack scheme [121].

3.3 Results and Discussions

The unit cell of the hexagonal lattice comprises 11 un-equivalent sites: Ba (multiplicity 2), five Fe sites (multiplicity 2, 2, 4, 4, 12), and the five oxygen sites (multiplicity 4, 4, 6, 12, 12). Table 3.1 shows coordinates of all the atoms with their Wyckoff sites and symmetries. The total number of sites in the unit cell is 64.

We have calculated the energy of ferrite for different spin configurations. The calculated results of relaxed energy differences from Gorter’s [56] spin orientation and total magnetic moments are shown in Table 3.2. Table 3.2 also validates our method of calculation by reproducing the magnetic moment of the ground state reasonably (nominal magnetic moment is 40 $\mu_B$ [134]). The structure with octahedral Fe at 4$f_2$ with antiparallel spins has a lower energy than that with tetrahedral Fe at 4$f_1$ site. This behavior

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1In mathematics, the conjugate gradient method is an algorithm for the numerical solution of particular systems of linear equations, namely those whose matrix is symmetric and positive-definite. The conjugate gradient method is an iterative method, so it can be applied to sparse systems that are too large to be handled by direct methods. Such systems often arise when numerically solving partial differential equations.
has also been reported previously for strontium hexaferrite[42], which is isomorph to the magnetoplumbite BaFe\(_{12}\)O\(_{19}\) [135]. It can also be seen that the 12\(k\) sites cost the most energy (5 eV) to excite their spin to “down” compared to other sites.

Table 3.2 Energies with magnetizations for different spin-system of BaM\(^1\).

<table>
<thead>
<tr>
<th>(4f_1)</th>
<th>(4f_2)</th>
<th>(2a)</th>
<th>12(k)</th>
<th>2(b)</th>
<th>(\Delta E) (eV)</th>
<th>(\mu) ((\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>–</td>
<td>–</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>0.00</td>
<td>39.82</td>
</tr>
<tr>
<td>+</td>
<td>–</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>4.25</td>
<td>66.61</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>4.99</td>
<td>-45.92</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>0.84</td>
<td>19.94</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>+</td>
<td>+</td>
<td>1.21</td>
<td>19.59</td>
</tr>
<tr>
<td>–</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>2.86</td>
<td>52.70</td>
</tr>
</tbody>
</table>

\(^{1}\) (+) signs represent the spin up (down) Fe atoms at different sites

To substitute Al atoms in BaFe\(_{12-x}\)Al\(_{x}\)O\(_{19}\) from \(x = 1\) to \(x = 3\) in steps of 0.5, we used the unit cell which contains double formula units. From experimental observations, either by wet chemical process [29], microwave adsorption [145] or by the sol gel method [28], it is very likely that Al atoms will occupy the Fe sites only. This might be the result of similarity of outer electronic configuration of Fe\(^{3+}\) and Al\(^{3+}\). Hence we have only performed Al substitutions at Fe sites.
For \( x = 1 \), two Al atoms are substituted into different sites, and the corresponding energies relative to the ground state are shown in Table 3.3. The total number of possibilities of how two Al atoms can be arranged in five sites is a sum of two different possibilities. The first one is of how to put two Ba atoms in five different sites \( (5C_2) \) and the second one is how two Ba atoms occupy same site \( (5C_1) \). The energies after relaxation of these 15 \( (5C_2 + 5C_1) \) configurations are compared in Table 3.3. It can be seen that the 2\( a \) site is the most favorable site for the \( x = 1 \) case. In Table 3.3, the numbers in the columns represent the number of Al atoms in that corresponding site. We have also tried to see if any spin configurations other than Gorter’s configuration is favored while Al atoms are substituted. We have found that other spin configurations (altering the spin configuration from Gorter’s structure), where Al is substituted at different sites, are not favored. We also found in the substitutional process that the system may have different relaxed energies depending on the distance between two substituted Al atoms. For example, while calculating the relaxed energies when two Al atoms are substituted at the 12\( k \) site, both of the Al atoms may occupy the same basal plane or be in different planes. We have explored the possibilities of broken symmetries and found that 2\( a \) is the most favorable site.

It is worthwhile to mention here that when two Al atoms are shared in the 2\( a \) and 12\( k \) sites (second row in Table 3.3), the total energy compared to the ground state is small (0.03 eV). Therefore, a finite probability exists for Al atoms to occupy 12\( k \) site along with the 2\( a \) site at room temperature. Therefore, we conclude that the ground state spin orientation where the Al atoms occupy only the 2\( a \) site or share 2\( a \) and 12\( k \) sites are the favored structures.
Table 3.3  Site preferences and relative energies for Al atoms for x=1.0\textsuperscript{1}.

<table>
<thead>
<tr>
<th>$4f_1$</th>
<th>$4f_2$</th>
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<th>$12k$</th>
<th>$2b$</th>
<th>$\Delta E$ (eV)</th>
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</tbody>
</table>

\textsuperscript{1}Energies are relative to the first row of the table.
For \( x=1.5 \), three Al atoms are substituted into different sites, and the corresponding energies relative to the ground state are shown in Table 3.4. The total number of combinations of how to put three Ba atoms in five different sites is the sum of three different possibilities. The first one is of putting three Ba atoms in five different sites \((5C_3)\). The second one is the possibilities of two Ba atoms occupying one site \((5C_1)\) and the remaining atom occupies any of the remaining four sites \((4C_1)\). Therefore the second possibility is a product of \(5C_1\) and \(4C_1\). The third one is of how three Ba atoms occupy the same sites: \(3C_1\), because there are only three different sites which can accommodate three Ba atoms. All 33 \((5C_3 + 5C_1 \cdot 4C_1 + 3C_1)\) combinations are shown in Table 3.4. In Table 3.4, the numbers in the columns represent the number of Al atoms in that particular site. We have observed that once \(2a\) site is filled, the \(12k\) site is the most preferential site for Al atoms to occupy for the \(x=1.5\) case. Similar to the \(x=1\) case, we also have found here that Al-substituted BaM structures with spin configurations other than the Gorter’s configuration are not favorable. Various possibilities of broken symmetries have been tested and found that once the \(2a\) site is filled, the \(12k\) is the next favorable site. We can see in Table 3.4 that when three Al atoms share the \(2a\) and \(12k\) sites, the relative energy compared to the ground state energy is small (second row in Table 3.4). Hence at room temperature, Al atoms can share \(2a\) and \(12k\) sites.

We have found that for \(x=1\) and 1.5, Gorter’s spin configuration is favored. Therefore for further Al substitution calculations \(x=2, 2.5\) or 3, we have assumed that Gorter’s spin configuration is the most favored. For further substitution of Al atoms \((x = 2, 2.5, 3)\) it has been found that two Al atoms go to the \(2a\) site and the rest of the
Table 3.4  Site preferences and relative energies for Al atoms for x=1.5.

<table>
<thead>
<tr>
<th>$4f_1$</th>
<th>$4f_2$</th>
<th>$2a$</th>
<th>$12k$</th>
<th>$2b$</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>0</td>
<td>2</td>
<td>1.44</td>
</tr>
</tbody>
</table>
atoms preferentially occupy the 12k site. In Table 3.5, we have showed the ground states for the various Al substitutional configurations along with their magnetic moments. For the case of maximum substitution $x = 4$, we have calculated only the magnetic moment, considering Al atoms to only occupy the 2a and 12k sites in the ground state spin configuration.

Table 3.5 Site preferences and magnetic moments of Al substituted BaM.

<table>
<thead>
<tr>
<th>$x$</th>
<th>4$f_1$</th>
<th>4$f_2$</th>
<th>2a</th>
<th>12k</th>
<th>2b</th>
<th>$\mu(\mu_B)$</th>
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<td>39.82</td>
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<td>0</td>
<td>0</td>
<td>29.00</td>
</tr>
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<td>1.5</td>
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<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>24.57</td>
</tr>
<tr>
<td>2.0</td>
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<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>19.52</td>
</tr>
<tr>
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<td>0</td>
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<td>3</td>
<td>0</td>
<td>14.41</td>
</tr>
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<td>0</td>
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<td>4</td>
<td>0</td>
<td>9.59</td>
</tr>
<tr>
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<td>0</td>
<td>2</td>
<td>6</td>
<td>0</td>
<td>-0.33</td>
</tr>
</tbody>
</table>

In Fig. 3.2, we have shown the behavior of the magnetic moments with increase of Al substitution. The decrease of the magnetic moment in increasing order of Al substitution is similar to what has previously been reported, monotonically decreasing order [176]. This is due to the fact that the Al atoms occupy the 2a and 12k sites, which are major contributors to the total magnetic moment of the system. Substitution of Al atoms
Figure 3.2   Magnetic moment of BaM decreases with Al substitution.

of zero magnetic moment decreases the contribution of the magnetic moment from those sites and hence decrease in the total magnetic moment are expected.

To understand the Al site preference further, we have calculated the substituted point defect energy for \( x = 0.5 \). One Al atom is substituted for a designated \( \text{Fe}^{3+} \) site, and then the whole system is relaxed. The relaxed energy is compared with the same system without any substitution and the substitutional defect energy has been calculated using the formula

\[
E_{\text{sub}} = E_{\text{tot}} - E_{\text{BaM}} + \epsilon_{\text{Al}} - \epsilon_{\text{Fe}}
\]  

(3.1)

where \( E_{\text{tot}} \) is the total energy of a system of BaM with one Al atom that has replaced one Fe atom, \( E_{\text{BaM}} \) is the total energy of the original system without a defect, \( \epsilon_{\text{Fe}} \)
and $\epsilon_{Al}$ are the total energies per atom for Fe and Al in their ideal bulk structure. The substitutional point defect energies for different sites are shown in Table 3.6. From Table 3.6 it is seen that the minimum energy required for an Al atom is to substitute a $2a$ site occupying $Fe$ atom. $12k$ is the next possible site of Fe atoms to be substituted by Al atoms. Hence for a diluted limit, the substituted Al atoms preferentially occupy the $2a$ site. Also the $2b$ site is the most improbable to be substituted by Al atoms.

To further elucidate the substitution process, the available site volumes ($V_{av}$) have been calculated as those of spheres with radii equivalent to the nearest neighbor distances. It has been found that the $2a$ site has an available volume of $4.44 \, \text{Å}^3$, while the others have less. For example, the $12k$ site has a $V_{av}$ of $3.82 \, \text{Å}^3$, which is the next largest available volume among the rest. The $2b$, $4f_2$, and $4f_1$ sites have available volumes of $3.26$, $2.66$, and $3.59 \, \text{Å}^3$, respectively. Moreover, the ionic radius of $0.50 \, \text{Å}$ for the $\text{Al}^{3+}$ ions is less than that of $0.64 \, \text{Å}$ for $\text{Fe}^{3+}$ ions [145]. Table 3.6 shows the available volumes for corresponding sites.

Larger available site volume surely plays an important role in site preference. However exchange interaction energies ($J$) may also have their contribution towards the site preference. Novák and Rusz [134] have calculated the exchange integrals of BaM for intersites and intrasites interactions in their GGA+U calculation. They have assumed that the exchange interaction is short range, which is generally accepted. For $U = 4$, their calculations [134] show that the intersite exchange interaction costs $9 \, \text{meV}$ for the $2a$ site and $18 \, \text{meV}$ for the $12k$ site. Moreover the $2a$ sites are far apart from each other with negligible intrasite interaction between them. Whereas the intrasite interaction is $3 \, \text{meV}$ for each
Table 3.6  Comparison of site preferences of Al in BaM.

<table>
<thead>
<tr>
<th>Site</th>
<th>$E_f^{\text{sub}}$ (eV)</th>
<th>$V_{av}$ ($\text{Å}^3$)</th>
<th>$J$ (meV) [134]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1.22</td>
<td>4.445</td>
<td>9</td>
</tr>
<tr>
<td>12k</td>
<td>1.55</td>
<td>3.823</td>
<td>24</td>
</tr>
<tr>
<td>4f_2</td>
<td>2.08</td>
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<td>20</td>
</tr>
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</tr>
<tr>
<td>2b</td>
<td>2.30</td>
<td>3.591</td>
<td>11.25</td>
</tr>
</tbody>
</table>

pair of 12k sites. In the BaM unit cell, periodically there are three 12k sites that form a triangle on the basal planes. Hence compared to the occupancy of 2a site that costs 9 meV, the cost of occupancy in 12k sites is high 24 meV ($18 + 3\times2$). For 2b, 4f_1 and 4f_2 sites, these exchange interaction energies are 11.25 meV, 17.25 meV, and 20 meV, respectively. Interaction energies corresponding to the sites are shown in Table 3.6. We conclude that the exchange interaction energies are very small in comparison to the substitutional defect energies and may be neglected in order to find the intriguing source of the site preference.

3.4 Conclusions

We have shown that for Al substitution in BaM material, Al atoms preferentially go to the 2a site. Once the 2a site is filled up, further substitutional Al atoms occupy the 12k site. We have also supported the experimental fact that since spin zero Al atoms substitute the Fe atoms which are major contributors towards the total magnetic moment.
of the system, the magnetic moment monotonically decreases in increasing order of Al substitution. Finally we have found a possible explanation for the site preference of $2a$ and $12k$ sites over the others by calculating the substitutional defect energies, available site volumes, and exchange interaction energies.
4.1 Introduction

Hardness and strength are the two most important properties for materials for mechanical machining tools, such as ceramics, high speed steel, etc. But the hardness in high speed steel is less and the strength of ceramics is not very high. Instead of these intrinsic disadvantages of metals and ceramics, generally metals possess high strength and ceramics have high hardness. To develop novel materials with both the advantages, many kinds of metal-ceramic composites have been fabricated intensively, largely by the powder metallurgical method. WC-Co is one of those cermets, which have much attention because their hardness, strength and wear resistance are well balanced at a high level. The mechanical properties of WC-Co compounds are known to be dependent on the grain size of the carbides. Materials with smaller grain size have high mechanical properties [59]. Since WC-Co consists of WC grains with a Co-rich phase in between [80, 180] in order to improve the mechanical properties of WC-Co compounds, we need to obtain the microstructure with smaller carbide grain size [159, 48]. Among the various transition metal carbides as additives to control the grain growth of WC, VC is the most effective dopant to retard the grain growth of WC [185]. It is known that a few % of VC addi-
tion is sufficient to inhibit the grain growth efficiently, but the inhibition mechanism is not clear so far [24, 152]. In this study, we investigated the inhibition mechanism from a quantum mechanical view, using density functional theory. Adsorption and desorption are two mechanisms of sintering. The objective of the present work is to explore the structure and the effect on the adsorption/desorption process of a monolayer of VC on top of a WC (0001) surface. The structure of WC is hexagonal in base, and the (0001) surface could be either a W or C terminated surface. It is reported that the WC (0001) surface is either purely W terminated or W terminated with 30% of available hcp hollow sites occupied by additional carbon atoms [8]. In this study, we consider W terminated (0001) WC for a simpler approach to provide a fundamental mechanism of inhibited grain growth of WC in the presence of VC.

4.2 Method

The adsorption energy of a single adatom $E_{ads}$ at height $z$ is given by

$$E_{ads}(z) = E_{tot}(z) - E_{tot}(\infty)$$

(4.1)

where $E_{tot}(z)$ is the total energy of the structure with the adatom adsorbed at height $z$ on the surface and $E_{tot}(\infty)$ is the total energy of the same surface with the adatom at an infinite distance. All ab initio total-energy calculations and geometry optimizations we performed within density functional theory (DFT) using the Blöchls all-electron projector augmented wave (PAW) [21] method as implemented by Kresse et. al. [93]. For the treatment of electron exchange and correlation, we use the generalized gradient approximation (GGA) of Perdew et al [74]. The Kohn-Sham equations are solved using a preconditioned
band-by-band conjugate-gradient (CG) minimization [92]. The plane-wave cutoff energy is set to 400 eV in all calculations. Ionic relaxations are performed until the root-mean-square (rms) force is less than 0.001 eV/Å. The Brillouin zone is sampled with a density equivalent to 54 k-points in the (1X1) surface Brillouin zone using the Monkhorst-Pack scheme [121]. A Fermi-level smearing of 0.2 eV was applied using the Methfessel-Paxton method [118]. We used a standard supercell technique in modeling the WC (0001) surface with (3X2) surface unit cell by a slab consisting of three W and two C substrate layers, separated by 15.0 Å of vacuum. Atoms in the bottom layers (one W and one C substrate layers) are fixed at their bulk positions, while all other atoms are allowed to relax.

4.3 Results and Discussions

Tungsten carbide is related to the hcp lattice with space group $P_6_3m_2$. From the full relaxation of lattice parameters, we found that $a = 2.905$ Å and $c = 2.836$ Å, which are very close to reported value of hexagonal WC ($a = 2.906$ Å, $c = 2.837$ Å) [58]. We also have found that the lattice parameter of VC in a NaCl structure is 4.159 Å which is very close to the reported value of 4.16 Å [99]. To prepare the foundation to study the adsorption of W and C atoms on top of the WC (0001) surface with a VC monolayer, we construct three different models for vanadium carbide (VC) monolayer on top of the WC substrate. Fig. 1 shows the three different models we considered.

We compare these three different models of VC on top of WC (0001) surface to determine the minimum energy configuration. Model 1 (Fig. 1a) was constructed in such a way that all the V and C atoms lay on the same plane. The V and C atoms are alternatively
Figure 4.1 Models of VC monolayer on top of the WC (0001) surface.

In Model I (top left) vanadium and carbon atoms are in a plane with alternate arrangement of V and C, where in Model II (top right) V atoms are terminating the surface and in Model III (below) C atoms are terminating the surface.
Table 4.1  Comparison of total energies of three models of VC.

<table>
<thead>
<tr>
<th>Model 1 (eV)</th>
<th>Model II (eV)</th>
<th>Model III (eV)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>99.12</td>
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</tbody>
</table>

arranged, such that it has the same structure as a (001) plane of VC in a NaCl structure. In models 2 and 3, we placed V and C atoms in separate planes as in (111) planes of VC in a NaCl structure. In model 2 (Fig. 1b), V atoms form the terminating surface while C atoms form the terminating surface for model 3 (Fig. 1c). Out of the three different models, model 1 is energetically the most favorable configuration. Table 1 shows the comparison of the three different models. Our study of adsorption process continued with model 1 of the VC layer on WC (0001) surface.

Table 4.2  W and C adsorption energies with heights from surface of WC (0001) surface.

<table>
<thead>
<tr>
<th>Adatom</th>
<th>Configuration</th>
<th>$E_{ads}$ (eV)</th>
<th>Z (Å)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
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<td>W</td>
<td>Without VC</td>
<td>-8.46</td>
<td>1.93</td>
<td>-1.732</td>
</tr>
<tr>
<td></td>
<td>With VC</td>
<td>-10.19</td>
<td>4.18</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Without VC</td>
<td>-7.73</td>
<td>1.23</td>
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<tr>
<td></td>
<td>With VC</td>
<td>-8.93</td>
<td>3.5</td>
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</table>
Figure 4.2  W adsorption energies from the surface.

The adsorption energy $E_{ads}(z)$ of a tungsten adatom on a clean tungsten-carbide (WC) (0001) (open circles) surface and on a vanadium-carbon (VC) monolayer on a WC (0001) surface (filled circles) as a function of the height from the surface. The position of the VC monolayer is shown by a dashed line.
Fig. 4.2 shows the adsorption energy of a W adatom on two different surfaces of W terminated WC, a clean WC (0001) and a VC monolayer on top of the WC (0001), as a function of the height. The position of the VC monolayer is depicted by a dotted line. In order to get the lowest energy points for both of the cases, only two bottom layers are fixed and all other atom positions are fully relaxed. Other points in Fig 4.2 are generated by additionally fixing the height of the W adatom. It is manifested from Table 4.1 and Fig. 4.2 that a W atom needs more energy to be adsorbed on the WC surface covered with a VC monolayer, compared to a clean WC surface. The depth of the adsorption well is a measure of the strength of binding to the surface, where minimum on the horizontal axis corresponds to the equilibrium distance for the adsorbed W atom on the WC (0001) surface with or without a VC monolayer. Compared to the direct adsorption to the WC (0001) surface in the absence of a VC monolayer, adsorption through a VC monolayer is much more hindered because the adsorption energy of W atom through VC monolayer is significantly higher (1.73 eV). The W and C adsorption energies and the corresponding heights for these configurations are listed in Table 4.2.

Fig. 4.3 is the energy-height diagram similar to Fig. 4.2 for a C adatom. Fig. 4.3 shows the C adatom adsorption on two different surfaces of W terminated WC, a clean WC (0001) and a VC monolayer on top of the WC (0001). Using a similar procedure as described for W adatom adsorption, we found that the C atom needs more energy to be adsorbed onto a WC surface covered with a VC monolayer, compared to a clean WC surface. Therefore, C atom adsorption through a VC monolayer is much less likely because the adsorption energy of C atom through VC monolayer is significantly higher (1.21 eV).
Figure 4.3  C adsorption energies from the surface.

The adsorption energy $E_{ads}(z)$ of a carbon adatom on a clean tungsten-carbide (WC) (0001) (open circles) surface and on a vanadium-carbon (VC) monolayer on a WC (0001) surface (filled circles) as a function of the height from the surface. The position of the VC monolayer is shown by a dashed line.
than the direct adsorption to the clean WC (0001) surface. We also found that the C adatom interacts strongly with the VC monolayer on top of the WC surface due to C-C interaction. A further detailed investigation will be required to elucidate the chemistry of C adatom interaction with the VC layer of atoms. Our result is consistent with the experimental observation that the addition of a small amount of VC inhibits the WC growth in sintering. It is also evident from the Fig. 4.2 and 4.3 that the W and C adatom needs much energy to overcome the barrier height generated by the VC monolayer, and it is barely possible for them to cross the barrier and adsorbed on the WC surface. The larger adsorption energy of W or C atom on a VC monolayer-covered WC strongly suggests that VC retards the grain growth of WC.

4.4 Conclusions

We presented a first principles DFT investigation of the structure and energetic landscape of a W and C adatoms on a WC (0001) surface with and without a VC monolayer. We found that the W and C adsorption energies increase significantly in the presence of VC. In conclusion observing the adsorption mechanism, it is evident that a VC monolayer retards the process of the grain growth of a WC system.
CHAPTER 5
DIFFUSION OF BA ATOMS IN HEMATITE

5.1 Introduction

Among the iron oxides, corundum-type $\alpha$ Fe$_2$O$_3$ (hematite) is the most common on earth. At ambient conditions, it crystallizes in the rhombohedral corundum structure (space group $R\bar{3}c$). Below the Néel temperature or magnetic ordering temperature $^1 T_N = 955$ K [162], $\alpha$ Fe$_2$O$_3$ is an antiferromagnetic (AF) insulator showing weak ferromagnetism above the Morin temperature $^2 T_m = 260$ K due to a slight canting of the two sublattice magnetization [148]. Below $T_m$, the direction of the magnetic moments is parallel to the [111] axis of the hexagonal unit cell [12]. The localization of the iron 3d electrons due to the strong on-site Coulomb repulsion results in a large splitting of the d bands and a gap of 2 eV [120]. As the upper edge of the valence band is dominated by oxygen p states, hematite is generally considered to be a charge-transfer $^3$ rather than a Mott-Hubbard insulator (predicted to be conductors but insulators due to electron-

$^1$the temperature at which an antiferromagnetic material becomes paramagnetic, that is, the thermal energy becomes large enough to destroy the macroscopic magnetic ordering within the material.

$^2$where the antiferromagnetic ordering is reorganized from being aligned perpendicular to the c-axis to be aligned parallel to the c-axis below $T_m$.

$^3$charge transfer insulators are a class of materials that are predicted to be conductors following conventional band theory, but which are in fact insulators due to a charge transfer process; electrons in charge transfer insulators move between atoms within the unit cell.
electron interactions which are not considered in the formulation of conventional band
theory; when the repulsive Coulomb potential \( U \) is large enough to create an energy gap or
transfer integral for all neighbors) \([123]\). There has been a considerable amount of experi-
mental work on hematite regarding its structural \([4, 38, 148]\), magnetic \([89]\) and electronic
properties \([51, 149]\) in bulk as well as in nanoparticles.

On the other hand, barium ferrite (BaM) has been established as a permanent mag-
netic material among the various M-type hexaferrites \( \text{MFe}_{12}\text{O}_{19} \) (M= Sr, Ba, Pb). Due to
the high saturation of magnetization, good chemical stability and large magneto-crystalline
anisotropy, this material has been investigated intensively \([28]\). It has been a long experi-
mental effort to make spherical BaM nanoparticles for magnetic recording media, in order
to make possible a media which is magnetically isotropic, well dispersed, low in noise,
and free of magnetically inferior broken particles \([54, 166, 68]\).

To understand the Ba diffusion mechanism in hematite, it is necessary to model
accurately manufacturing processes such as thermal annealing. Barium ferrite particulate
media are capable of supporting recording densities above 160 Kfci (Kilo Flux Change
per Inch). The advantages offered by BaM, notably low noise, high coercivity (Hc), and
smaller particle size than recently developed metal particles with size of 0.08 nm can
readily exploit the more sensitive GMR heads \([68]\).

Atomic diffusion is a process whereby the random thermally-activated movement
of atoms in a solid results in the net transport of atoms. For example, helium atoms inside
a balloon can diffuse through the wall of the balloon and escape, resulting in the balloon
slowly defating. In the crystal solid state, diffusion within the crystal lattice occurs by
either interstitial or substitutional mechanisms and is referred to as lattice diffusion. Since
the prevalence of point vacancies increases in accordance with the Arrhenius equation
\[
A \exp \left( -\frac{E}{kT} \right)
\]
the rate of crystal solid state diffusion increases with temperature. The
objective of the present research is to find the diffusion barrier of a Ba atom to diffuse
inside hematite, such that the corresponding temperature \((E = k_BT)\) shall guide to set up
experiments to develop spherical barium hexaferrite nanoparticles.

5.2 Method

All the simulations were carried out using a supercell of 60 atoms containing 24
iron atoms and 36 oxygen atoms. All atomic positions were relaxed using total energies
and forces calculated with the generalized gradient approximation to spin-polarized den-
sity functional theory (DFT), as implemented in VASP [91, 92]. Energy calculations and
geometry optimizations of various structures were performed using Blöchl’s all-electron
projector augmented wave method [21] as implemented by Kresse and Joubert [93]. For
the treatment of electron exchange and and correlation, we use the generalized gradient ap-
proximation (GGA) using the Perdew-Burke-Ernzerhof scheme [74]. The plane-wave cut
off energy is set to 400 eV in all calculations. The spin interpolation of Vosko [181] was
used. All the geometry relaxations were done with the tetrahedron method with Blöchl
correction using the conjugate gradient algorithm. Geometry relaxations were performed
until the energy difference between two successive ionic optimizations is less than 0.001
eV. The Brillouin zone is sampled using the Monkhorst-Pack scheme [121]. The number
\(n_k\) of the \(k\) points in the irreducible part of the Brillouin zone was 64.
5.3 Results

All calculations were carried out under rhombohedral symmetry constrains. The complete hexagonal unit cell of hematite is shown in Figure 5.1, that has been duplicated to be used in our calculation. All iron atoms have an equivalent octahedral environment. The octahedra built by oxygen atoms and centered by iron atoms are slightly rotated against each other. We note that there are two types of pairs of Fe atoms. They are characterized by short Fe-Fe distance (type A) and by a large Fe-Fe distance (type B) along the hexagonal axis. There are two internal degrees of freedom, commonly named $z_{Fe}$ and $x_{O}$, by which the positions of the atoms inside the primitive cell can be described (see Table 5.1).
Table 5.1 Atom positions with internal coordinates of $\alpha$ Fe$_2$O$_3$ hematite [155].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff symbol</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>(c)</td>
<td>$z$</td>
<td>$z$</td>
<td>$z$</td>
</tr>
<tr>
<td></td>
<td>1/2-$z$</td>
<td>1/2-$z$</td>
<td>1/2-$z$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2+$z$</td>
<td>1/2+$z$</td>
<td>1/2+$z$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-$z$</td>
<td>1-$z$</td>
<td>1-$z$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>(e)</td>
<td>$x$</td>
<td>1-$x$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1-$x$</td>
<td>0</td>
<td>$x$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>$x$</td>
<td>1-$x$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2-$x$</td>
<td>1/2+$x$</td>
<td>1/2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2+$x$</td>
<td>1/2</td>
<td>1/2-$x$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1/2-$x$</td>
<td>1/2+$x$</td>
<td></td>
</tr>
</tbody>
</table>

$z = 0.1054 (0.1053)$

$x = 0.3086 (0.3059)$
We have relaxed the positions of the atoms in terms of the parameters, as well as the c/a ratio of the supercell, by using the conjugate gradient method until the force on each atom was below 1 meV/Å. We found that the values of the two internal degrees of freedom agree well with the experimental values [155]. It has been also shown in Table 5.2 that the relaxed hexagonal lattice parameters and Fe-Fe distances are in good agreement with the experimental values [96].

Table 5.2 Experimental [96] and simulation results of hematite coordinates (in Å).

<table>
<thead>
<tr>
<th></th>
<th>c</th>
<th>a</th>
<th>c/a</th>
<th>Fe-Fe (A)</th>
<th>Fe-Fe (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.730</td>
<td>5.029</td>
<td>2.730</td>
<td>2.883</td>
<td>3.982</td>
</tr>
<tr>
<td>2</td>
<td>13.803</td>
<td>5.003</td>
<td>2.758</td>
<td>2.930</td>
<td>4.00</td>
</tr>
</tbody>
</table>

We also found that the adsorption energy of one Ba atom on hematite (0001) surface is less for a bridge site (3.39 eV) rather than for a three fold site (5.32 eV) for iron terminating surface, while the adsorption energy for a bridge site (5.66 eV) is slightly less than of the three-fold site (5.70 eV) for the oxygen terminating (0001) surface of hematite. To get these adsorption energies, we fixed the bottom layer of hematite unit cell and relaxed the whole structure.

4Positions of atoms $\mathbf{x} = \alpha \mathbf{a} + \beta \mathbf{b} + \gamma \mathbf{c}$ inside the primitive unit cell of $\alpha$-Fe$_2$O$_3$ with respect to the basis vector $\mathbf{a}, \mathbf{b}, \mathbf{c}$ of the primitive cell in terms of the two internal degrees of freedom $\varepsilon_{Fe}$ and $\varepsilon_{O}$. Numbers (in Å) in the parentheses represent the experimental values [155].
Diffusion kinetics can be thought of in terms of adatoms residing at adsorption sites on a lattice, moving between adjacent (nearest-neighbor) adsorption sites by a jumping process. The jump rate is characterized by an attempt frequency and a thermodynamic factor which dictates the probability of an attempt resulting in a successful jump. The attempt frequency $\nu$ is typically taken to be simply the vibrational frequency of the adatom, while the thermodynamic factor is an exponential term containing the Boltzmann factor times the temperature and $E_{\text{diff}}$, the potential energy barrier for diffusion. Equation 5.1 describes the relationship:

$$\Gamma = \nu e^{-E_{\text{diff}}/k_B T}$$  \hspace{1cm} (5.1)

where $\nu$ and $E_{\text{diff}}$ are as described above, $\Gamma$ is the jump or hopping rate, $T$ is temperature (in Kelvin), and $k_B$ is the Boltzmann constant. Importantly, Equation 5.1 tells us how strongly the jump rate varies with temperature. The manner in which diffusion takes place is dependent on the relationship between $E_{\text{diff}}$ and $k_BT$ as is given in the thermodynamic factor: when $E_{\text{diff}} < k_BT$ the thermodynamic factor approaches unity and $E_{\text{diff}}$ ceases to be a meaningful barrier to diffusion. This case, known as mobile diffusion, is relatively uncommon and has only been observed in a few systems.

The diffusion mechanism we are interested in this study is how one Ba atom can diffuse in the hematite system. Since all the Fe atoms are crystallographically symmetric/identical, we are interested in the process where initially one Ba atom is substituted for one Fe atom inside the hematite structure and then the Ba atom diffuses to the nearest Fe site. The diffusion energy barrier will be very small if we consider the mechanism as a vacancy assisted diffusion. However in order to generate nano-sized particles of barium
Figure 5.2  Diffusion path of Ba atom in hematite.

Diffusion path and energy for one Ba (gold sphere) atom to diffuse in hematite (Red spheres are Fe and green spheres are oxygen). Corresponding relaxed energies are also shown in this picture.
hexaferrite from hematite, it is not only undesirable that we have several vacancy defect in the hematite, but also in order to get BaM from hematite we may need a huge number of vacancy defects that are impossible to have in a realistic system. One of the possible diffusion mechanisms we identified is cluster diffusion. That involves motion of atomic clusters ranging in size from dimers to islands containing hundreds of atoms. Motion of the cluster may occur via the displacement of individual atoms, sections of the cluster, or the entire cluster moving at once. All of these processes involve a change in the clusters center of mass. Of particular interest concerted mechanisms are those that involve movement of either sections of the cluster or the entire cluster all at once.

Here we consider the motion of both Ba and Fe atoms simultaneously in such a way that they swap their positions. In order to get the energies of the intermediate structures, we did the following: we fixed the atom positions of the two corner atoms of the unit cell, such that the structure does not rotate and to avoid any undesirable movements of the atoms. Then we chose two Fe sites halfway in the unit cell. We substituted each one of those two Fe atom by Ba atoms and relaxed the structure to get the two extreme points of the diffusion path. In order to get the intermediate structures, we substituted only one Fe atom with a Ba atom. Now we move the Fe and Ba atoms slowly to swap their positions. At each step we relaxed the structure, keeping the two corner atoms position fixed. We found that the diffusion barrier in this method is 3.27 eV. This energy barrier predicts the upper bound of the plateau of the diffusion path. However, our collaborators at University of Alabama found that the process of generating nano barium hexaferrite particles from BaCO$_3$ and hematite happens at 1000° C [75]. From the Arrhenius theorem, we found that
\[ \Gamma = 10^{13} e^{-\frac{E_{diff}}{k_B T}} \]  

(5.2)

\( \Gamma \) turns out to be 1.3 when \( T = 1000^\circ C \), \( E_{diff} = 3.27 \) eV, and \( \nu \), the phonon frequency is taken to be \( 10^{13} \) Hz.

Figure 5.2 shows the concerted diffusion barrier for Ba and Fe atoms. The schematic diagram in Figure 5.3 shows how the two atoms swap their places. For more clarity, we put the Fe and Ba atoms in along with the surrounding O atoms. The diffusion path starts from left and ends at right. All the configurations in the diffusion path were built manually in this scheme. The hopping rate found through this method is comparatively less in order to get sufficient swapping of Ba and Fe atoms and hence less probable diffusion of Ba in hematite. However this value is the lower bound of the hopping rate, since the diffusion barrier from the method predicts the upper bound of the barrier.

We now employ a method where the diffusion path and the barrier could be determined from the simulation, namely the Nudged Elastic Band (NEB) method [168]. The nudged elastic band (NEB) is a method for finding saddle points and minimum energy paths between known reactants and products. The method works by optimizing a number
of intermediate images along the reaction path. Each image finds the lowest energy possible while maintaining equal spacing to neighboring images. This constrained optimization is done by adding spring forces along the band between images and by projecting out the component of the force due to the potential perpendicular to the band.

We found from our simulations that the NEB method predicts a diffusion barrier of 2.9 eV. In other words, the jumping/hopping rate becomes high (33). The high hopping rate predicts that the diffusion of Ba atom inside hematite is possible by a concerted diffusion mechanism with a diffusion barrier of \( \approx 3.0 \text{ eV} \). This diffusion barrier corresponds to a temperature of \( \approx 1000^\circ \text{C} \) and supports the experimental work at the University of Alabama [75].

5.4 Conclusions

We found the concerted diffusion energy barrier for Ba and Fe atom inside the hematite to understand how Ba atoms could diffuse in hematite to form barium hexaferrite nanoparticles. The diffusion path were determined by both a manual search and by implementing the Nudged Elastic Band (NEB) method. We found the NEB method produces a lower value of the diffusion barrier than the manual search diffusion path. Our result supports the fact that at high temperature (\( 1000^\circ \text{C} \)) it will be possible for Ba atoms to diffuse inside hematite to form magnetic nanoparticles.
CHAPTER 6
EFFECTS OF VANADIUM IMPURITY IN IRON

6.1 Introduction

Vanadium (V) is an important alloying element of steels and has a significant effect on the mechanical and thermal properties of the resultant material. High-V steels have attracted attention among the candidates for structural materials for use in future fusion reactors [72, 114, 127]. The relatively high thermal conductivity and low thermal expansion coefficient of vanadium-base alloys, which result in lower thermal stresses for a given heat flux compared to most other candidate alloys, should enhance the reactor wall-load and lifetime capability [45, 46, 131, 132, 156, 177]. Since the mechanical strength of vanadium-base alloys is retained at relatively high temperatures, higher operating temperatures are projected for these alloys than for austenitic or ferritic steels. Vanadium-based alloys do not readily become radioactive, they exhibit good strength at elevated temperatures, are compatible with liquid helium and exhibit high thermal stress factor [26, 66, 67, 126, 130, 156, 193]. To obtain the desired mechanical and thermal properties, it is important to understand the governing mechanism of defects and the effects of individual alloying elements on steel. These effects are atomic scale phenomenon and are difficult to examine experimentally. But can be estimated relatively easily by
atomistic scale simulations. Atomistic simulations can be a useful tool to analyze and predict fundamental physical quantities that can also be used as input data for multi scale simulations. An accurate calculation involving ab initio method usually deals with a few hundreds of atoms which are insufficient for many realistic simulations. On the other hand, semi-empirical inter-atomic potentials can deal with millions of atoms. In such simulations using semi-empirical potentials, the reliability of the potential is significant. A dependable semi-empirical inter-atomic potential should produce thermal and mechanical properties of the materials accurately.

Mendelev et al [117] studied the effect of Fe in V and fitted an inter-atomic potential for the V-Fe system to understand the system configurations under neutron radiation using the EAM/FS formalism. They intensively studied the diffusion mechanism of V for dilute limit of Fe; however thorough treatments of their potential by calculating the coefficients of thermal expansion, specific heat or melting were absent. Also the variation of the lattice parameter of Fe with different amounts of V substitution has a large disagreement with experiment. The most important factor for molecular dynamics is the inter-atomic potential, which determines the forces on the atoms. There are many forms of empirical many-body potentials of which the most general is the embedded atom method (EAM) [33]. EAM has been modified to MEAM to include angular dependencies. Out of several models of inter-atomic potentials, MEAM is highly applicable since it can describe atomic potentials of a wide range of elements (fcc, bcc, hcp, diamond and even gaseous elements) using a common formalism, while achieving good agreement with experimental or ab initio calculations. The objective of this work was to present a new MEAM potential
suitable for a Fe-V binary system. The procedure for the determination of the potential parameters will be briefly described. It will be shown that the potential can successfully reproduce several fundamental properties for the Fe-V binary system. The potential was used to estimate the effect of V on Fe on several mechanical and thermal properties. The estimated results are in good agreement with DFT or experimental values.

6.2 Method

All the *ab initio* calculations were performed within the density-functional theory (DFT) as implemented in the (VASP) [91, 92]. Energy calculations and geometry optimizations of various structures were performed using Blöchl’s all-electron projector augmented wave (PAW) method [21] as implemented by Kresse and Joubert [93]. For the treatment of electron exchange and correlation, we use the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof scheme [74]. The plane-wave cutoff energy is set to 350 eV in all calculations. Geometry relaxations are performed until the energy difference between two successive ionic optimizations is less than 0.005 eV. The Brillouin zone is sampled using the Monkhorst-Pack scheme [121] and a Fermi-level smearing of 0.2 eV was applied using the Methfessel-Paxton method [118].

The total energy $E$ of a system of atoms in the MEAM [143, 144] is approximated as the sum of the atomic energies

$$ E = \sum_i E_i $$

(6.1)

The energy of atom $i$ consists of the embedding energy and the pair potential terms,

$$ E_i = F_i(\rho_i) + \frac{1}{2} \sum_{i\neq j} \Phi_{ij}(r_{ij}) $$

(6.2)
where \( F \) is the embedding function, \( \bar{\rho}_i \) is the background atom density at the site of atom \( i \), and \( \Phi_{ij}(r_{ij}) \) is the pair potential between atoms \( i \) and \( j \) separated by distance \( r_{ij} \). The embedding energy \( F_i(\bar{\rho}) \) represents the energy cost to insert atom \( i \) at a site where the background atom density is \( \bar{\rho}_i \). The embedding energy is given in the form

\[
F_i(\bar{\rho}) = A_i E_i^0 \bar{\rho}_i \ln(\bar{\rho}_i) \tag{6.3}
\]

where the sublimation energy \( E_i^0 \) and parameter \( A_i \) depend on the element type of atom \( i \) and the background atom density \( \rho_i \).

### 6.3 Potential Construction Procedure

A traditional procedure for constructing a potential involves a two step iterative process. First, a single crystal designed as the reference structure is chosen and MEAM parameters are fitted to construct MEAM potential that reproduces a handful of critical materials properties of the element in the reference structure. Second, the potential is tested for its accuracy and transferability by applying it to systems under circumstances not used during its construction phase. To develop our potential, we used two systems to include their formation energies, different lattice parameters, vacancy formation energy, and point defect energies (substitutional and interstitial) for different structures. If the validation is not satisfactory, one needs to go back to the first step and adjust the parameters in a way that improves the overall quality of the potential.

To develop the Fe-V MEAM potential, we calculated the substitutional and interstitial defect formation energies and matched them with their DFT counterparts. Additionally, we considered two Fe-V compound structures that are based on bcc structure, one is
FeV and another is $\text{Fe}_{15}\text{V}$. For $\text{Fe}_{15}\text{V}$ structure we replaced one of the Fe atoms in a 2X2X2 bcc supercell with one V atom. We then calculated the lattice parameters and formation energies for those structures. Table 6.1 presents those defect and formation energies along with their lattice parameters for both DFT and MEAM.

Table 6.1 The physical parameters used to fit MEAM potential for FeV binary systems

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>DFT</th>
<th>MEAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substitutional Defect Energy</td>
<td>eV</td>
<td>-0.73</td>
<td>-0.57</td>
</tr>
<tr>
<td>Interstitial Defect Energy (Oct.)</td>
<td>eV</td>
<td>4.4</td>
<td>2.10</td>
</tr>
<tr>
<td>Interstitial Defect Energy (Tetr.)</td>
<td>eV</td>
<td>4.6</td>
<td>5.64</td>
</tr>
<tr>
<td>Lattice parameter for FeV</td>
<td>Å</td>
<td>2.90</td>
<td>2.88</td>
</tr>
<tr>
<td>Heat of Formation Energy for FeV</td>
<td>eV</td>
<td>-0.10</td>
<td>-0.15</td>
</tr>
<tr>
<td>Lattice parameter for $\text{Fe}_{15}\text{V}$</td>
<td>Å</td>
<td>5.73</td>
<td>5.77</td>
</tr>
<tr>
<td>Heat of Formation Energy for $\text{Fe}_{15}\text{V}$</td>
<td>eV</td>
<td>-0.05</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Table 6.1 also suggests that our developed MEAM potential can satisfactorily reproduce the formation and defect energies and lattice parameters for the systems. We used zero temperature configurations for the calculations to develop the potential. The MEAM parameters for Fe and V [101] are listed in Table 6.2.

Table 6.3 shows the developed MEAM inter-atomic potential we developed. Note that all other $C_{\text{max/min}}$ are 4.0 and 2.0, respectively.
Table 6.2  Iron and Vanadium MEAM potential parameters.

<table>
<thead>
<tr>
<th>type</th>
<th>$E^0$</th>
<th>$r^0$</th>
<th>A</th>
<th>$\alpha$</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(3)}$</th>
<th>$t^{(0)}$</th>
<th>$t^{(1)}$</th>
<th>$t^{(2)}$</th>
<th>$t^{(3)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>4.29</td>
<td>2.866</td>
<td>0.89</td>
<td>5.073</td>
<td>2.93</td>
<td>1.0</td>
<td>1.0</td>
<td>5.13</td>
<td>4.12</td>
<td>-2.7</td>
</tr>
<tr>
<td>V</td>
<td>5.3</td>
<td>3.04</td>
<td>1.0</td>
<td>4.83</td>
<td>4.11</td>
<td>1.0</td>
<td>1.0</td>
<td>4.20</td>
<td>4.099</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

Table 6.3  The developed MEAM interaction potential for Fe–V systems.

<table>
<thead>
<tr>
<th>lattice</th>
<th>$E_c$</th>
<th>$\alpha$</th>
<th>$r_e$</th>
<th>$r_c$</th>
<th>delr</th>
<th>delta</th>
<th>gsmooth</th>
<th>$C_{\min}(1, 2, 2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>5.0</td>
<td>6.0</td>
<td>2.5</td>
<td>4.5</td>
<td>0.1</td>
<td>0.1</td>
<td>99.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### 6.3.1 Formation Energies

The formation energy of an alloy of two elements is defined as the energy cost to create that alloy. For FeV and Fe$_{15}$V systems, they are defined in the following manner:

1. $E_{\text{form}}^{FeV} = \frac{1}{2}E_{FeV} - \frac{1}{2}E_{Fe} - \frac{1}{2}E_{V}$,

2. $E_{\text{form}}^{Fe_{15}V} = \frac{1}{16}E_{Fe_{15}V} - \frac{15}{16}E_{Fe} - \frac{1}{16}E_{V}$,

where $E_{XX}$ is the total energy of a system of $XX$ atoms.

The present MEAM potential predicts correct signs for these energies with similar order of magnitude compared to DFT.
6.3.2 Defect Energies

6.3.2.1 Interstitial Energy

The formation energy of an interstitial point defect $E_f^{\text{int}}$ is given by

$$E_f^{\text{int}} = E_{\text{tot}}[N + 1] - (E_{\text{tot}}[N] + \varepsilon),$$

(6.4)

where $E_{\text{tot}}[N]$ is the total energy of a system with $N$ Fe atoms, $E_{\text{tot}}[N + 1]$ is the total energy of a system with $N$ Fe atoms plus one V atom inserted at one of the interstitial sites, and $\varepsilon$ is the total energy per V atom in its most stable bcc bulk structure. Interstitial defect formation energies were calculated for V at octahedral and tetrahedral sites within Fe. Atomic position and volume relaxation were performed. The present MEAM potential predicts correct signs for these energies. It is interesting to note here that the tetrahedral interstitial defect formation energy is higher than for the octahedral site, similar to what DFT predicts. However, the octahedral defect formation energy is much less than the DFT prediction. Since the defect formation energies are already much higher and unless at very high temperature, the system merely shows the interstitial defected system, the authors did not put too much effort in matching them accurately. Nevertheless, the authors believe that for any special case where octahedral defect formation energy is very crucial, the MEAM potential parameters can be adjusted to get the desired result. In the later part of this chapter we precisely show that this deviation from DFT does not affect other properties, such as lattice parameter or melting temperature.
6.3.2.2 Substitutional Energy

The formation energy of a substitutional point defect $E_{f_{\text{sub}}}^\text{sub}$ is given by

$$E_{f_{\text{sub}}}^\text{sub} = E_{\text{tot}}[V_{Fe}] - (E_{\text{tot}}[FeFe] - \varepsilon_{Fe} + \varepsilon_{V})$$ (6.5)

where $E_{\text{tot}}[V_{Fe}]$ is the total energy of a system of Fe atoms plus one V atom that replace one Fe atom, $E_{\text{tot}}[FeFe]$ is the total energy of a system of Fe atoms without any substitution, and $\varepsilon_{V/Fe}$ is the total energy per V/Fe atom in their most stable bcc bulk structure. Table 6.1 shows that the substitutional defect formation energy closely matches with the DFT counterpart.

6.4 Results and Discussion

6.4.1 Materials Properties

The energy volume curve for the two structures (FeV and Fe$_{15}$V) have been evaluated with our MEAM potential and using DFT calculations as well. Figure 6.1 and Figure 6.2 represent the energy volume curves for FeV and Fe$_{15}$V structures, respectively. It has been shown that how well the energy values match with their DFT counterparts. It is also worthwhile to mention here that the bulk modulus for the FeV system turns out to be 225 GPa in comparison with the 290 GPa of DFT value and for the Fe$_{15}$V, it is 24 GPa compared to the DFT value of 21 GPa.
Figure 6.1  The energy per atom of FeV system.
Figure 6.2  The energy per atom of $Fe_{15}V$ system.
6.4.2 Structural Properties

To validate the present MEAM potential further, we calculated several additional materials properties of the Fe-V binary system that were not used as objectives during the construction of the potential. Since the objective of the present study is to see the effect of V substitution in Fe, we will concentrate on the effect of several percentages of V substitution in Fe. At the end, we will find that the process leads to a potential that gives reasonable mechanical and finite temperature properties.

6.4.2.1 Lattice Parameter

To calculate the lattice parameters at different V substitution within Fe, we first developed a system containing 4000 atoms of Fe. Then we picked a few Fe atoms randomly and replaced those Fe atoms by V atoms. That is how every time we generated a model having a definite percentage of V substitution. Then each model was equilibrated with an NVT ensemble at 300 K until we get a zero pressure lattice parameter.

Figure 6.3 shows the variation of lattice parameter versus the V substitution percentage. It is clear from the figure that our developed Fe-V MEAM inter-atomic potential has better agreement with experiment [172, 117] in predicting changes of the lattice parameter with V substitution than Mendelev’s [117] potential. Our MEAM potential however underestimates the lattice parameter at 50% of V substitution in Fe. On the other hand the Mendelev’s [117] potential highly overestimate this lattice parameters at 50 % V substituted Fe. Overall our potential has a better agreement with experimental values in predicting the variation of lattice parameter when defects are introduced.
Figure 6.3  Variation of lattice parameter with V substitution.

Red squares are experimental values, green squares are from previous potential, and black circles are from our MEAM potential.
6.4.2.2 Bulk Moduli

Fundamentally the bulk modulus is defined as:

\[ B = - \frac{dP}{d} = \frac{d^2E}{d^2} \]  \hspace{1cm} (6.6)

where \( d \) is the differential change in the volume element, for which the differential pressure change occurring is dP and where pressure is defined as:

\[ P = - \frac{dE}{d} \]  \hspace{1cm} (6.7)
Fig 6.4 shows the variation of bulk modulus with different amounts of V substitution. Calculations were done using an NVT ensemble at 300 K for 10 ps and the statistics were taken from the last half of the simulation with 4 fs MD time steps. The filled square shows the experimental value of bulk modulus for pure Fe.

6.4.2.3 Elastic Constants

Cubic crystals have three independent elastic constants: $C_{11}$, $C_{12}$, and $C_{44}$ [100].

The elastic constants are calculated numerically by applying small strains to the lattice. For small deformations, the relationship between deformation strain and elastic energy in a cubic crystal is quadratic [108]. Although the obvious method of computing $C_{11} - C_{12}$ uses the tetragonal strain [116], we prefer the volume conserving orthorhombic strain,

1. $\Delta E(x) = \Delta E(-x) = V(\dot{C}_{11} - \dot{C}_{12}) x^2 + O[x^4]$, for deformation $e_1 = -e_2 = x; e_3 = x^2/(1 - x^2); e_4 = e_5 = e_6 = 0$,

2. $\Delta E(x) = \Delta E(-x) = V(\dot{C}_{14}) x^2/2 + O[x^4]$, for deformation $e_6 = x; e_3 = x^2/(4 - x^2); e_1 = e_2 = e_4 = e_5 = 0$,

where $\Delta E$ is the elastic energy due to the deformation, and $e$’s are the small strain applied to the lattice. We follow the procedure described by Mehl et al [116] and apply several different strains ranging from $-2.0\%$ to $+2.0\%$. The elastic constants are obtained by fitting the resultant curves to quadratic functions. We found that this method gives much more stable results than using one strain value [108]. In order to get $C_{11}$ and $C_{12}$ individually, we employed the fact that

$$3B = C_{11} + 2C_{12} \quad (6.8)$$

in addition to the previous equations.
Table 6.4  Experimental [23] and MEAM elastic constants for FeV binary systems (in GPa)

<table>
<thead>
<tr>
<th>Elastic Constants</th>
<th>Fe (Expt.)[23]</th>
<th>Fe</th>
<th>FeV</th>
<th>Fe15V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>243</td>
<td>305</td>
<td>403</td>
<td>63</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>138</td>
<td>103</td>
<td>135</td>
<td>5</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>121</td>
<td>68</td>
<td>134</td>
<td>75</td>
</tr>
<tr>
<td>$B$</td>
<td>168</td>
<td>170</td>
<td>225</td>
<td>24</td>
</tr>
<tr>
<td>$Y$</td>
<td>211</td>
<td>206</td>
<td>335</td>
<td>89</td>
</tr>
</tbody>
</table>

where $Y$ is Young’s modulus which is obtained from:

$$Y = \frac{9GB}{G + 3B}$$  \hspace{1cm} (6.9)

where $G$ is given by:

$$G = \frac{1}{2} \left[ \frac{C_{11} - C_{12} + 3C_{44}}{5} + \frac{5}{\frac{4}{C_{11} - C_{12}} + \frac{3}{C_{44}}} \right]$$  \hspace{1cm} (6.10)

6.4.3 Thermal Properties

To validate the potential for molecular dynamics simulations, we calculated several thermal properties of the Fe-V system. It is worthwhile to mention here that all the realistic simulations take place at finite temperature. Therefore the thermal properties produced by any developed potential has to be tested at finite temperature and the developed potential must reproduce thermal properties close enough to understand properly the
atomistic behavior of that material. Here in this section, we calculate four individual thermal properties: specific heat, coefficient of thermal expansion, diffusion mechanism, and melting temperature.

6.4.3.1 Specific Heat

The specific heat is the amount of heat per unit mass required to raise the temperature by one degree. The relationship between heat and temperature change is usually expressed in the form $Q = cm\Delta T$ where $c$ is the specific heat. The relationship does not apply if a phase change is encountered, because the heat added or removed during a phase change does not change the temperature.

To calculate the specific heat, we considered a model of 4000 atoms containing Fe and a specific percentage of V atoms in bcc structure and then we equilibrated that model with an NVT ensemble for 20 ps with a 2 fs MD time step at each temperature with a 100 K temperature step. The energy of the system then calculated from the statistics from the last part of the 10 ps simulation. Figure 6.5 depicts the variation of the energy per atom with respect to temperature for different amounts of V substitution. We then calculated the specific heat from $C_v = \left(\frac{\partial U}{\partial T}\right)_v$. It turns out that our calculated specific heat decreases in increasing order of V substitution. Figure 6.6 shows how the specific heat decreases with V substitution. The filled square in Fig. 6.6 also validates our potential by showing the close agreement of the experimental [23] specific heat of pure Fe.
Figure 6.5  Specific heat for Fe-V binary systems.

The internal energies of Fe crystal in bcc structure with different amount of V substitution, as a function of temperature. The energies are obtained from the ensemble average of the MD simulations containing 4000 atoms.
Figure 6.6 Variation of specific heats of Fe-V binary systems.

Filled square is the experimental [23] value of pure Fe specific heat.
6.4.3.2 Diffusion Mechanism

To study diffusion from the Brownian motion point of view [137], we denote the number density of the Brownian particles in the fluid by the symbol \( n(\vec{r}, t) \) and their current density by \( j(\vec{r}, t) = n(\vec{r}, t)\vec{v}(\vec{r}, t) \), then according to Fick’s law,

\[
j(r, t) = -D \nabla n(r, t)
\]

(6.11)

where \( D \) stands for the diffusion coefficient of the medium. We also have the equation of continuity, viz.

\[
\nabla \cdot j(r, t) + \frac{\partial n(r, t)}{\partial t} = 0
\]

(6.12)

Combining those two equations, we obtain the diffusion equation

\[
\nabla^2 n(r, t) - \frac{1}{D} \frac{\partial n(r, t)}{\partial t} = 0
\]

(6.13)

Of the various possible solutions of this equation, the one relevant to the present problem is

\[
n(r, t) = \frac{N}{(4\pi Dt)^{3/2}} e^{\frac{-r^2}{4Dt}}
\]

(6.14)

which is a spherically symmetric solution and is already normalized:

\[
\int_{0}^{\infty} n(r, t)4\pi r^2 dr = N
\]

(6.15)

Now by virtue of distribution, we obtain

\[
\langle r(t) \rangle = 0; \text{ and } \langle r^2(t) \rangle = \frac{1}{N} \int_{0}^{\infty} n(r, t)4\pi r^4 dr = 6Dt \propto t^1
\]

(6.16)

This equation \( \langle r^2 \rangle = 6Dt \) is known as the Einstein-Smoluchowski equation. On the other hand, Langevin’s theory shows that
\[
\langle r^2 \rangle \cong \frac{6kT\tau}{M} t = (6BkT)t
\]  

(6.17)

where \( \tau \) is the relaxation time and \( \tau = MB \), which is essentially the same as the Einstein-Smoluchowski result. Incidentally, we obtain here a simple, but important Einstein relationship between the coefficient of diffusion \( D \) and the mobility \( B \)

\[
D = BkT
\]  

(6.18)

Figure 6.7 shows the temperature dependence of the self-diffusivity of Fe for different V substitution. To get the diffusivity at each temperature, we simulated five different NVT ensembles at a particular temperature for 20 ps with 2 fs MD step. Then we saved the last snapshot (atom positions) and averaged out the statistics to get \( \langle \Delta r^2 \rangle \). The diffusivity constants qualitatively matches earlier work [117].

Finally with Equation 6.18, we determine the mobility of the system at each temperature. We find in Figure 6.8 that mobility decreases with an increase of V substitution.

### 6.4.3.3 Coefficient of Thermal Expansion (CTE)

When temperature increases so does the length of the molecular bonds. As a result, solids typically expand in response to heating and contract on cooling; this dimensional response to temperature change is expressed by its coefficient of thermal expansion (CTE). The volume and hence the lattice parameter of a solid expands with increase of temperature with the following relation:

\[
a_1 = a_0 \left( 1 + \alpha(T_2 - T_1) + \beta(T_2 - T_1)^2 + ... \right)
\]  

(6.19)
Figure 6.7  Diffusivity of Fe with various amount V substitution.
Figure 6.8 The variation of the mobility of the Fe-V systems.
Figure 6.9 Calculation of CTE for Fe-V system.

Therefore the linear thermal expansion coefficient is the one-dimensional length change with temperature can be defined as

\[ \alpha = \frac{1}{a_0} \left( \frac{\delta a}{\delta T} \right) \]  

(6.20)

where \( a_0 \) is the original lattice parameter, \( a \) the new lattice parameter and \( T \) the temperature.

A molecular dynamics simulation was performed in an NVT ensemble, so at each temperature we performed several simulations for different volumes in order to find the corresponding zero-pressure lattice constants at corresponding temperature for each dif-
Figure 6.10  Variation of CTE for Fe-V systems.

Filled square represents the experimental value [23] of CTE for pure Fe

derent V substituted Fe-V system. In f gure 6.9, we display the variation of the lattice
parameter with temperature for different amounts of V substitution.

We found that $\alpha$ decreases with an increase of the amount of V substitution. Figure 6.10 shows how the CTE changes with the amount of vanadium substitution. The developed MEAM potential is validated by the close agreement of the experimental [23] value of CTE for pure Fe.
6.4.3.4 Melting Temperature

We also found the melting temperature of Fe-V systems for several V substitutions in Fe. We followed a single-phase method as described by Kim and Tománek [85], in which the temperature is increased at a constant rate and the internal energy of the system is monitored. Fig. 6.11 shows a portion of the internal energies of Fe with V substitution as a function of temperature. The plot was obtained from the statistical average of the last half of the 10 ps NVT ensemble simulation with 4 fs MD time-step, containing 4000 Fe-V atoms. The initial velocity vectors were set randomly according to the Maxwell-Boltzmann velocity distribution at $T = 300$ K. The temperature of the system was controlled using a Nosé-Hoover thermostat [69, 133].

It is clearly seen from Fig. 6.11 that the internal energy curve makes an abrupt transition from one linear region to another, marking the melting point. Fig. 6.12 shows the variation of the melting point for several % of V substitution. It is also interesting to note here that the experimental [23] melting temperature of pure Fe is in close proximity with the melting temperature of Fe with 10% of V substitution.

6.4.3.5 Grünseisen Ratio

The Grünseisen parameter defined as

$$\gamma = -\frac{d\ln \Theta(V)}{d\ln V} = V \frac{dP}{dE} \left(1 + \frac{\alpha K_s}{C_P \rho} = \frac{\alpha K_T}{C_V \rho} \right)$$

(6.21)

where $V$ is volume, $P$ is pressure, $E$ is energy, $\alpha$ is thermal expansivity, $K$ is bulk modulus, $S$ is entropy and $\rho$ is density. This parameter is an important thermodynamic
Figure 6.11 Melting response of Fe-V system.
Figure 6.12  Variation of melting response of Fe-V system.

Filled square represents the experimental value [23] of the melting point of pure Fe.
Figure 6.13  Grünsein parameter of Fe-V systems.

Filled square represents the Grünsein parameter for pure Fe.
parameter used to quantify the relationship between thermal and elastic properties, particularly for understanding shock dynamics. Figure 6.13 shows the decrease of the Grüneisen parameter with increasing amount of V substitution. The close proximity of the experimental Grüneisen parameter for pure Fe and for Fe with 10% of V substitution validates our MEAM potential.

### 6.4.4 Discussion

Considering the fact that the atomic volume of V is bigger than the atomic volume of Fe, when we substitute Fe by V within a given cell volume, the ‘free volume’ decreases. Therefore, for an increasing amount of V substitution the coupling between atoms increases. For an increasing amount of V substitution, the bigger V atoms try to accommodate themselves in a way that minimizes the interaction energy, and hence the lattice parameter increases as we increase the V substitution. Since the coupling increases with an increasing amount of V substitution, the elastic constants, including the bulk modulus and Young’s modulus, increase when we go from a pure Fe system to the crystalline FeV system. Similarly, since the coupling increases between the atoms with V substitution, it will require less energy to raise the temperature of the system compared to a pure Fe system. The transfer of the energy within the atoms will be more loss-free than for a pure Fe system where the ‘free space’ is more compared to a V substituted system. This fact leads us to explain the decrease of the specific heat with an increase the amount of V substitution. The self-diffusivity is directly proportional to the ‘free space’ of the system; more ‘free space’ leads to more diffusivity of the system. Since V substitution reduces the
‘free space’, diffusivity and consequently the mobility of the system decreases. Following the same reasoning, V substitution increases the coupling or the bond energy between the atoms; it will thus be necessary to provide more energy to break those bonds for melting and the melting temperature increases with an increase of V substitution.

6.4.5 Conclusions

We have developed an inter-atomic potential for Fe-V binary systems using MEAM. Structural, elastic, and thermal properties were calculated with this developed MEAM potential. It has been shown that those physical properties match with either the DFT counterparts or the values obtained from experimental results. The potential can be used in the metal industries to understand V substitution in Fe to elucidate the atomistic mechanisms for improvement of steel.
CHAPTER 7

STRUCTURAL AND THERMAL PROPERTIES OF CALCIUM

7.1 Introduction

Calcium is essential for living organisms, particularly in cell physiology, where movement of the calcium ion $\text{Ca}^{2+}$ into and out of cytoplasm functions as a signal for many cellular processes. One of the key issues related to the transduction of $\text{Ca}^{2+}$ signals in eukaryotic cells is the binding of the atoms to the regulatory cytoplasmic calmodulin [105]. As a major material used in mineralization of bones and shells, calcium is the most abundant metal by mass in many animals. A considerable number of studies have been published on the nutritious facts of calcium [167], its importance in osteoporosis [64, 107] and even in cancer treatment. Several studies based on density functional theory (DFT) have been done to elucidate the structures of aryl calcium hydride [36], physicochemical understanding of calcium coordination number [111], interaction of sphingomyelin lipid molecule with calcium cation [175], and the binding nature of $\text{Ca}$ with entamoeba histolytica [55].

$\text{Ca}$ belongs to the Group-III A alkaline-earth metals with closed-shell electronic configuration [Ar]$4s^2$, and is a very abundant element that plays an important role in a variety of compounds, mechanisms and processes. This element is of interest since its po-
tential usage in excimer lasers, carbon chemical engineering, ion depositions, etc. Yoon et al [190] investigated Ca as a super-coating metal in functionalization of carbon fullerenes for high-capacity hydrogen storage. Wolverton et al [184] found calcium alanate as another hydrogen storage media, Car-Parrinello MD simulations [11] and electronic structure of Ca clusters have also been studied [119]. However, not enough work has been done to investigate the materialistic properties of calcium, such as stacking fault energies, melting, structure of grain boundaries, dislocation dynamics, etc. These kind of large scale atomistic simulations require accurate atomic interaction potentials to compute the total energy of the system. First-principles calculations certainly can provide the most reliable inter-atomic potentials. However, realistic large scale atomistic simulations often require a number of atoms that renders these methods impractical – they either require too much computer memory or take too long to be completed in a reasonable amount of time. One alternative is to use (semi-)empirical interaction potentials that can be evaluated efficiently, so that the atomistic approaches that use them can, in certain cases, handle systems with more than a million atoms.

Daw and Baskes developed the embedded-atom method (EAM) to obtain reliable and transferable semi-empirical inter-atomic potentials for metals [31, 33]. EAM is able to reproduce physical properties of many metals and impurities, including hydrogen embrittlement in nickel and palladium [32, 33]. To overcome a few shortcoming, Baskes and others developed the modified embedded-atom method (MEAM) by extending the EAM to include angular forces [18, 14]. One of our major objectives is to study the structural and thermal properties of Fe with Ca substitution. After developing calcium potential
followed by a Ca-Fe MEAM inter-atomic potential, it will be shown how the doping of calcium in iron affects the material properties of iron.

The purpose of the present work is twofold: (1) to develop a MEAM potential for Ca based on first-principles calculations using DFT and experimental values, and (2) to validate the Ca potential to demonstrate its reliability and transferability. For construction, we first calculated the equilibrium lattice parameter and cohesive energy for several basic crystal structures, including bcc, fcc and hcp. The results will be compared with those obtained from DFT calculations. Furthermore, several elastic constants, monovacancy energy, and interstitial defect energies were calculated. All the calculated values were found to be in good agreements with DFT or experimental values. Once there is a good agreement in the construction phase, we moved on to the validation part, where we calculated surface formation energies, stacking fault energies, melting temperature, coefficient of thermal expansion and specific heat. We found that all the values are in good agreement with their experimental or DFT counterparts.

Sec 7.2 presents the method of our calculations. In Sec. 7.3, the procedure for determining the MEAM parameters for Ca is presented. In Sec. 7.4, validation of the developed MEAM potential is presented and discussed. Different bulk structures, surfaces, surface defects, and point defects calculations were determined and compared with DFT calculations. Finally, Sec. 8.4, summarizes the results and draws conclusions.
7.2 Method

All the *ab initio* calculations were performed within density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package (VASP) [91, 92]. Energy calculations and geometry optimizations of various structures were performed using Blöchl’s all-electron projector augmented wave (PAW) method [21] as implemented by Kresse and Joubert [93]. For the treatment of electron exchange and correlation, we used the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof scheme [74]. The plane-wave cutoff energy is set to at least 350 eV in all calculations. Geometry relaxations were performed until the energy difference between two successive ionic optimizations is less than 0.005 eV. The Brillouin zone is sampled using the Monkhorst-Pack scheme [121] and a Fermi-level smearing of 0.2 eV was applied using the Methfessel-Paxton method [118].

Molecular dynamics simulation with millions of atoms is a key theoretical tool in understanding microstructural effects in metals at the atomistic level and investigating collective phenomena. The most important factor for molecular dynamics is the interatomic potential, which determines the forces on the atoms. There are many forms of empirical many-body potentials of which we used the Modified Embedded Atom Method (MEAM) [33].

The total energy $E$ of a system of atoms in MEAM [143, 144] is approximated as the sum of the atomic energies

$$E = \sum_i E_i$$

(7.1)
The energy of atom $i$ consists of the embedding energy and the pair potential terms,

$$E_i = F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{i \neq j} \Phi_{ij}(r_{ij})$$  \hspace{1cm} (7.2)

where $F$ is the embedding function, $\bar{\rho}_i$ is the background electron density at the site of atom $i$, and $\Phi_{ij}(r_{ij})$ is the pair potential between atoms $i$ and $j$ separated by distance $r_{ij}$. The embedding energy $F_i(\bar{\rho})$ represents the energy cost to insert atom $i$ at a site where the background electron density is $\bar{\rho}_i$.

### 7.3 Potential Construction Procedure

A traditional procedure for constructing a potential involves a two step iterative process. First, a single crystal is designed as the reference structure. Then the MEAM parameters are fitted to construct an MEAM potential that reproduces a handful of critical material properties of the element in that reference structure. Second, the potential is tested for its accuracy and transferability by applying it to atoms under circumstances not used during its construction phase. To develop our potential, we used various systems, including different crystal structures, elastic constants, vacancy formation energy, and interstitial defect formation energies. If the validation is not satisfactory, one needs to go back to the first step and adjust the parameters in a way that improves the overall quality of the potential.

Whenever possible, the experimental values are chosen as the target values. If the experimental values are not available or known to be unreliable, the computed values from the first-principles method are used.
7.3.1 Cohesive Energies

The cohesive energy of Ca atom is defined as the heat of formation per atom when Ca atoms are assembled into a crystal structure:

\[ E_{coh} = \frac{E_{tot} - NE_{atom}}{N}, \]  

(7.3)

where \( E_{tot} \) is the total energy of the system, \( N \) is the number of Ca atoms in the system, and \( E_{atom} \) is the total energy of an isolated Ca atom. The cohesive energies of Ca atoms in hcp, fcc, and bcc crystal structures for several atomic volumes near the equilibrium atomic volumes were calculated. Fig. 7.1 is an example of the cohesive energy plot of Ca atoms as a function of the lattice constant. The minimum of this curve determines the equilibrium lattice constant \( a_0 \) and cohesive energies \( E_{coh} = E_{fcc} \) in Table 7.1.

7.3.2 Elastic constants

Cubic crystals have three independent elastic constants: \( C_{11}, C_{12}, \) and \( C_{44} \) [100]. The elastic constants are calculated numerically by applying small strains to the lattice. For small deformations, the relationship between deformation strain and elastic energy increase in a cubic crystal is quadratic [108]. Although the obvious method of computing \( C_{11} - C_{12} \) uses the tetragonal strain, we prefer the volume conserving orthorombic strain,

1. \( \Delta E(x) = \Delta E(-x) = V(C_{11} - C_{12})x^4 + O[x^4], \) for deformation \( e_1 = -e_2 = x; \ e_3 = x^2/(1 - x^2); \ e_4 = e_5 = e_6 = 0, \)

2. \( \Delta E(x) = \Delta E(-x) = V(C_{44})x^2/2 + O[x^4], \) for deformation \( e_6 = x; \ e_3 = x^2/(4 - x^2); \ e_1 = e_2 = e_4 = e_5 = 0, \)

where \( \Delta E \) is the elastic energy due to the deformation, and \( es \) are the small strain applied to the lattice. We followed the procedure described by Mehl et al [116] and ap-
plied several different strains ranging from $-2.0\%$ to $+2.0\%$. The elastic constants were
obtained by fitting the resultant curves to quadratic functions. We found that this method
gives much more stable results than using one strain value [108]. In order to get the $C_{11}$
and $C_{12}$ individually, we employed the fact that

$$3B = C_{11} + 2C_{12}$$

in addition to the previous equations.

### 7.3.3 Vacancy Formation Energies

The formation energy of a single vacancy $E_{vac}$ is defined as the energy cost to create a vacancy

$$E_{vac} = E_{tot}[N] - N\varepsilon$$

where $E_{tot}[N]$ is the total energy of a system with $N$ Ca atoms containing a vacancy and $\varepsilon$ is the energy per atom of Ca in its the most stable (fcc) bulk structure.

### 7.3.4 Interstitial Defects

The formation energy of an interstitial point defect $E^{int}_f$ is given by

$$E^{int}_f = E_{tot}[N + 1] - (E_{tot}[N] + \varepsilon),$$

where $E_{tot}[N]$ is the total energy of a system with $N$ Ca atoms, $E_{tot}[N + 1]$ is the total energy of a system with $N$ atoms plus one Ca atom inserted at one of the interstitial sites, and $\varepsilon$ is the total energy per Ca atom in its most stable bulk structure. Interstitial atom formation energies were calculated for Ca at octahedral and tetrahedral sites. Atomic
position and volume relaxation were performed. The results of these calculations are listed in Table 7.1, and we compared with the results from DFT calculations. The present MEAM potential predicts the correct signs for these energies and the magnitudes are in very good agreement with those predicted by DFT.

7.4 Results and Discussion

7.4.1 Materials Properties

The MEAM potential for Ca we developed is given in Table 7.2 where $C_{\text{max}}$ and $C_{\text{min}}$ are kept at their usual values of 2.8 and 2.0, respectively.

The energy volume curve for three basic structures (fcc, bcc and hcp) have been evaluated with our MEAM potential and through DFT calculations as well and we found that fcc is the most stable structure. Figure 7.1 only represents the energy volume curve for the fcc structure, calculated with the present MEAM potential and DFT. It has also been shown that the energy volume curve has a good agreement with the Rose’s universal equation of state\(^1 [150].\)

The present MEAM potential reproduces the experimental lattice constant, cohesive energy, and bulk modulus correctly. We also note that the sequence of the structures is predicted correctly in the order of stability by the present Ca MEAM potential as shown

\[^1\text{Ionic, metallic, covalent and rare-gas solids have qualitatively different forms for total energy versus inter-atomic spacing. It has been discovered, however, that there is a universal form for pressure as a function of volume for all classes of solids in compression.}\]
Table 7.1  Objectives or the target quantities for Ca potential.

<table>
<thead>
<tr>
<th>Objective</th>
<th>Unit</th>
<th>Expt</th>
<th>DFT</th>
<th>MEAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $a_0$</td>
<td>Å</td>
<td>5.58</td>
<td>5.59</td>
<td>5.58</td>
</tr>
<tr>
<td>2 $E_{coh} = E_{fcc}$</td>
<td>eV</td>
<td>1.84</td>
<td>1.83</td>
<td>1.84</td>
</tr>
<tr>
<td>3 $B$</td>
<td>GPa</td>
<td>16.9</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>4 $E_{bcc} - E_{fcc}$</td>
<td>meV</td>
<td>-</td>
<td>09</td>
<td>12</td>
</tr>
<tr>
<td>5 $E_{hcp} - E_{fcc}$</td>
<td>meV</td>
<td>-</td>
<td>04</td>
<td>10</td>
</tr>
<tr>
<td>6 $C_{11}$</td>
<td>GPa</td>
<td>16.0</td>
<td>-</td>
<td>23.28</td>
</tr>
<tr>
<td>7 $C_{12}$</td>
<td>GPa</td>
<td>12.0</td>
<td>-</td>
<td>13.71</td>
</tr>
<tr>
<td>8 $C_{44}$</td>
<td>GPa</td>
<td>8</td>
<td>-</td>
<td>4.36</td>
</tr>
<tr>
<td>9 $E_{vac}$</td>
<td>eV</td>
<td>-</td>
<td>1.02</td>
<td>1.02</td>
</tr>
<tr>
<td>10 $E^{Oct}_{Int}$</td>
<td>eV</td>
<td>-</td>
<td>1.93</td>
<td>2.39</td>
</tr>
<tr>
<td>11 $E^{Tet}_{Int}$</td>
<td>eV</td>
<td>-</td>
<td>2.18</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Table 7.2  The developed Calcium MEAM potential.

<table>
<thead>
<tr>
<th>$E^0$</th>
<th>$r^0$</th>
<th>A</th>
<th>$\alpha$</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$\beta^{(2)}$</th>
<th>$\beta^{(3)}$</th>
<th>$t^{(0)}$</th>
<th>$t^{(1)}$</th>
<th>$t^{(2)}$</th>
<th>$t^{(3)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.84</td>
<td>5.58</td>
<td>1.0</td>
<td>4.7</td>
<td>2.1</td>
<td>0.01</td>
<td>1.0</td>
<td>1.0</td>
<td>12.0</td>
<td>0.3</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7.1  Energy volume curve for Ca.

The energy per atom of Ca crystal in fcc structures as a function of lattice parameter. The Rose’s equation of state is constructed from experimental values of bulk modulus equilibrium volume and cohesive energy. DFT values are also shown for comparison purpose.
The defect formation energies and the elastic constants are also in good agreement with the DFT and experimental values, respectively.

7.4.2 Structural Properties

To validate the present MEAM potential further, we calculated a few additional material properties of Ca that were not used as objectives during the construction of the potential. For most applications, energy differences and defect symmetries of relaxed structures are the most relevant quantities. Consequently, we have two lower indexed surface energies and stacking fault energies. Finally we calculated three different thermal properties of Ca. Ultimately, the process leads to a potential that gives reasonable mechanical and finite temperature properties.

7.4.2.1 Surface Formation Energies

Surface formation energy per unit surface area is defined as

\[ \gamma = \left( \frac{E_{\text{tot}} - N \varepsilon}{A} \right) \]

where \( E_{\text{tot}} \) is the total energy of the system with a surface, \( N \) is the number of atoms in the system, \( \varepsilon \) is the total energy per atom in the bulk, and \( A \) is the surface area.

Table 7.3 lists the surface formation energies used in this study of the (100) surface of fcc crystals. Different surface energies calculated through \textit{ab initio} and MEAM methods are shown in Table 7.3.

---

2The objectives optimized to construct the MEAM potential parameters for Ca. The target values chosen for optimization are given in bold face. \( E_{\text{coh}} \) is the cohesive energy, \( B \) is the bulk modulus, \( E_{\text{bcc}/\text{hcp}} - E_{\text{fcc}} \) is the relative energies of Ca from its fcc structure, \( C_{ij} \) are the elastic constants, \( E_{\text{vac}} \) is the vacancy formation energy, \( E_{\text{int}} \) is the interstitial defect formation energies.
Table 7.3  The relaxed surface energies of three different low index surfaces (in J/m$^2$).

<table>
<thead>
<tr>
<th>Surface</th>
<th>DFT</th>
<th>MEAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.45</td>
<td>0.75</td>
</tr>
<tr>
<td>(110)</td>
<td>0.34</td>
<td>0.70</td>
</tr>
<tr>
<td>(111)</td>
<td>0.46</td>
<td>0.66</td>
</tr>
</tbody>
</table>

The MEAM surface energies are consistently higher than the \textit{ab initio} calculations. Also DFT calculations predict the (110) surface to be the lowest energy surface. However our MEAM potential predicts the (111) surface to be the lowest energy surface. It is not known whether this is associated with the MEAM parameters used here or the cut off radii or that the MEAM potential is too simplified to reproduce all minute differences in surface properties of an actual metal. At this time we have no definite option to precisely match these surface energies, keeping the other results unaffected. Nevertheless, in future this potential could be a good foundation to explore.

7.4.2.2 Stacking Fault Energies

Stacking fault formation energy per unit area is defined by

\[
E_{sf} = \frac{(E_{tot} - N \varepsilon)}{A},
\]

where $E_{tot}$ is the total energy of the structure with a stacking fault, $N$ is the number of atoms in the system, $\varepsilon$ is the total energy per atom in the bulk, and $A$ is the unit cell area that is perpendicular to the stacking fault. For Ca, three stacking fault types are exam-
ined. The sequences of the atomic layers within the unit cell of our simulations are: \( I = ABABABCACACB, \ T = ABABABCBABAB, \) and \( E = ABABABCABABAB. \) We note that the unit cells for \( I \) contain two stacking faults and the quantities obtained from Eq. (7.8) must be divided by two to obtain the correct formation energies.

Table 7.4 Three different stacking fault energies of Calcium in fcc crystal.

<table>
<thead>
<tr>
<th>type</th>
<th>DFT</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I )</td>
<td>4</td>
<td>12.4</td>
</tr>
<tr>
<td>( T )</td>
<td>9</td>
<td>12.6</td>
</tr>
<tr>
<td>( E )</td>
<td>15</td>
<td>13.0</td>
</tr>
</tbody>
</table>

In the Table 7.4, it has been shown that our MEAM potential overestimates the DFT results. However, the order of magnitudes for three different stacking fault energies and their order of the energies are the same for both DFT and MEAM calculations. It may be worthwhile to mention here that in order to simulate dislocation movements within a grain or across a grain-boundary, one needs to change the potential parameters to get a better agreement with DFT values.

7.4.3 Thermal Properties

To validate the potential for molecular dynamics simulations, we calculated several thermal properties of single crystal calcium. It is worthwhile to mention here that all
the realistic simulations take place at finite temperature. Therefore the thermal properties produced by any developed potential has to be tested at finite temperature, and the developed potential must reproduce the thermal properties close enough to understand properly the atomistic behavior of that material. Here in this section we calculate three individual thermal properties: the melting temperature, the specific heat and the coefficient of thermal expansion.

7.4.3.1 Specific Heat

The specific heat is the amount of heat per unit mass required to raise the temperature by one degree. The relationship between heat and temperature change is usually expressed in the form $Q = cm\Delta T$ where $c$ is the specific heat. The relationship does not apply if a phase change is encountered, because the heat added or removed during a phase change does not change the temperature.

To calculate the specific heat, we considered a model of 4000 Ca atoms in fcc structure and then we equilibrated that with an NVT ensemble for 20 ps with a 2 fs MD time step at each temperature with a 100 K temperature step. The energy of the system then was calculated from the statistics from the last part of the 10 ps simulation. Figure 7.2 depicts the variation of the energy per atom with respect to temperature. We then calculate the specific heat from $C_v = \frac{\partial W}{\partial T}$, $v$. It turns out that our calculated specific heat, 25.71 J/mol/K has wonderful agreement with the experimental specific heat 25.38 J/mol/K of single crystal calcium [23].
Figure 7.2  Specific heat of Ca.

The internal energies of Ca crystal in fcc structure as a function of temperature. The energies are obtained from the ensemble average of the MD simulations containing 4000 Ca atoms.
7.4.3.2 Coefficient of Thermal Expansion (CTE)

When temperature increases, so does the length of the molecular bonds. As a result, solids typically expand in response to heating and contract on cooling; this dimensional response to temperature change is expressed by its coefficient of thermal expansion (CTE). The volume and hence the lattice parameter of a solid expands with increase of temperature with the following relation

\[ a_1 = a_0 \left( 1 + \alpha (T_2 - T_1) + \beta (T_2 - T_1)^2 + \ldots \right) \]  

(7.9)

Therefore the linear thermal expansion coefficient is the one-dimensional length change with temperature can be defined as

\[ \alpha = \frac{1}{a_0} \left( \frac{\delta a}{\delta T} \right) \]  

(7.10)

where \( a_0 \) is the original lattice parameter, \( a \) the new lattice parameter and \( T \) is the temperature.

A molecular dynamics simulation is performed in an NVT ensemble, so at each temperature, we do several simulations for different volumes in order to find the corresponding zero-pressure lattice constants at the corresponding temperature. In Figure 7.3 we display the variation of lattice parameter versus the temperature. The simulation data can be fitted to the polynomial function of temperature as:

\[ a(T) = 5.58 + 6.26 \times 10^{-5}T + 2.0 \times 10^{-8}T^2 \]  

(7.11)
Figure 7.3  Temperature dependencies of lattice parameter of Ca.

Performed with NVT ensembles with 4fs MD time step.
We found that $\alpha$ varies linearly with temperature, and the value of CTE at room temperature is $1.12 \times 10^{-5}$ which is closely resemble to the experimental value $2.23 \times 10^{-5}$ [23].

### 7.4.3.3 Melting Temperature

We calculated the melting temperature of pure Ca crystal in fcc structure. We followed a single-phase method as described by Kim and Tománek [85], in which the temperature is increased at a constant rate and the internal energy of the system is monitored. Fig. 7.4 shows a portion of the internal energies of Ca crystal in fcc structure as a function of temperature. The plot was obtained from the statistical average of a 10 ps NVT ensemble simulation, containing 4000 Ca atoms. The initial velocity vectors were set randomly, according to the Maxwell-Boltzmann velocity distribution at $T = 100$ K. The temperature of the system was controlled by using a Nosé-Hoover thermostat [69, 133]. It is clearly seen from Fig. 7.4 that the internal energy curve makes an abrupt transition from one linear region to another, marking the melting point.

We calculated the specific heat by differentiating the internal energy at different temperatures. The discontinuity in specific heat in Fig. 7.5 clearly shows the melting temperature of Ca. Using this method, we obtained 1140 K as the melting temperature of Ca crystal. Our melting temperature for single crystal Calcium is slightly higher than the experimental value of 1120 K [23]. It is known that the calculated melting temperature with the single phase method usually increases the melting temperature due to superheating of the system. In order to calculate the melting temperature precisely, one might need to
Figure 7.4 Melting response of Ca.

The internal energies of Ca crystal in fcc structure as a function of temperature. The energies are obtained from the ensemble average of the MD simulations containing 4000 Ca atoms.
adopt a method employing the dual phase of material with an interface of solid and liquid; alternatively one could calculate the free energies for both solid phase and liquid phase, and then the melting temperature can be designated as the temperature where those two free energy lines crossover.

7.5 Conclusions

We have developed a calcium potential using MEAM. Several physical parameters are calculated using that potential. It has been shown that those physical properties match with either the DFT counterparts or the values obtained from the experimental results. The

Figure 7.5 Temperature dependence of specific heat of Ca crystal.
bulk, elastic, mechanical and thermal properties are calculated with this developed MEAM potential. We hope this potential can be used in the metal industries as well as in medical industries to probe the effect of calcium in osteoporosis or osteoarthritis.
8.1 Introduction

Tungsten, along with its alloys and compounds, occupies a unique position in materials science. The material properties that make tungsten attractive to the metals industry are high density, hardness, melting temperature, elastic modulus, and conductivity in conjunction with low thermal expansion. The combination of these unique properties explains the diverse applications of tungsten ranging from home lighting to thermonuclear fusion first-wall protection [97, 187]. With nanoscale tungsten powders available at a reasonable cost, its usage will increase greatly and a new approach is required to balance the size-dependent advantages against the temperature-dependent limitations. Therefore, it is of great importance to understand the thermal stability of tungsten nanoparticles for their applications at higher temperatures. It has been seen previously that nanoparticles exhibit significant decrease in melting temperatures compared to infinite bulk solids [22]. This is related to the fact that the liquid-vapor interface energy is generally lower than the average solid-vapor interface energy [57]. Based on thermodynamics, a phenomenological relation between the melting temperature and particle size has been obtained: the melting temperature of a nanoparticle decreases in inverse proportion to the particle diam-
eter [22, 57, 140]. It is also known that premelting, the phenomenon where the surface atoms of nanoparticles lose their solid ordering and hence melt prior to complete melting of the whole particle [40, 94, 95, 106, 140], plays an important role in understanding the melting of nanoparticles. On the other hand, the Hall-Petch effect—the hardness increases in proportion to the inverse square-root of grain size [61, 141]—suggests that significant opportunities exist if nanoscale powders could be consolidated to full densities with minimized coarsening. Hence, knowledge of accurate melting temperatures for different particle sizes plays an important role for the advancement of present engineering and technological growth.

Molecular dynamics simulations offer an effective tool to study the melting and coalescence of nanoparticles [169, 86]. These atomistic simulations require accurate atomic interaction potentials to compute the total energy of the system. First-principles calculations can provide the most reliable inter-atomic potentials. However, realistic simulations of the melting of nanoparticles often require a number of atoms that renders these methods impractical: they either require too much computer memory or take too long to be completed in a reasonable amount of time. One alternative is to use empirical or semi-empirical interaction potentials that can be evaluated efficiently. In this study, we use the modified embedded atom method (MEAM) originally proposed by Baskes et al. [14, 18]. MEAM was the first semi-empirical atomic potential using a single formalism for fcc, bcc, hep, diamond-structured materials and even gaseous elements, to yield good agreement with experiments or first-principles calculations [14, 17]. The MEAM is an extension of the
embedded-atom method (EAM) \cite{31, 32, 33} to include angular forces. Cherne \textit{et al} made a careful comparison of MEAM and EAM calculations in a liquid nickel system \cite{27}.

Atomistic simulations of a wide range of elements and alloys have been performed using MEAM potentials. A realistic shear behavior for silicon was first obtained using the MEAM by Baskes \textit{et al} \cite{18}. The MEAM was also applied to various single elements \cite{14} and to silicon-nickel alloys and interfaces \cite{16}. Gall \textit{et al} \cite{47} used MEAM to model the tensile debonding of an aluminum-silicon interface. Lee and Baskes \cite{102} extended MEAM to include second nearest-neighbor interactions. A new analytic modified embedded-atom method (AMEAM) many-body potential was also proposed and applied to several hcp metals, including Mg \cite{70, 71}. For the Mg-Al alloy system, a set of EAM potentials has been developed using the “force matching” method by Liu \textit{et al} \cite{109}. Recently, a new set of MEAM potentials for Mg-Al alloy system was developed by Jelinek \textit{et al} \cite{76}. These new potentials show a significant improvement over previously published potentials, especially for surface formation, stacking faults, and point defect formation energies.

The chapter is organized in the following manner. In Sec. 8.2, the procedure for melting simulation is presented. MD simulation results are presented and discussed in Sec. 8.3. Finally in Sec. 8.4, we summarize our findings.
8.2 Molecular Dynamics Simulation

8.2.1 Atomic Potential

We used the MEAM potential parameters for tungsten (W) proposed by Baskes [14]. The potential parameters that are used for our simulation of W nanoparticles are listed in Table 8.1\(^1\). These parameters are obtained by fitting the room temperature elastic properties using bcc as the reference structure. \(C_{\text{max}}\) and \(C_{\text{min}}\) are chosen to consider only the first nearest-neighbor interactions [15].

Table 8.1 W MEAM potential parameter we used for our simulations.

<table>
<thead>
<tr>
<th>(E^0) [eV]</th>
<th>(r^0) [Å]</th>
<th>(A)</th>
<th>(\alpha)</th>
<th>(\beta^{(0)})</th>
<th>(\beta^{(1)})</th>
<th>(\beta^{(2)})</th>
<th>(\beta^{(3)})</th>
<th>(t^{(0)})</th>
<th>(t^{(1)})</th>
<th>(t^{(2)})</th>
<th>(t^{(3)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.66</td>
<td>2.74</td>
<td>0.98</td>
<td>5.63</td>
<td>3.98</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>3.16</td>
<td>8.25</td>
<td>-2.70</td>
</tr>
</tbody>
</table>

We validated the potential by computing different physical properties of tungsten systems and comparing them with DFT calculations. The results are compared with those of DFT calculations as shown in Table 8.2\(^2\). Energy calculations and geometry optimizations of various structures were performed using Blöchl’s all-electron projector augmented

\(^1\)The MEAM potential parameters for W from Ref. [15]. \(E^0\) is the sublimation energy, \(r^0\) is the equilibrium nearest-neighbor distance, \(A\) is the scaling factor for the embedding energy, \(\alpha\) is the exponential decay factor for the universal energy function, \(\beta^{(0-3)}\) are the exponential decay factors for the atomic densities, \(t^{(0-3)}\) are the weighting factors for the atomic densities, the screening parameters \(C_{\text{max}}\) and \(C_{\text{min}}\) are 2.8 and 2.0 respectively.

\(^2\)Calculated physical properties of W using the present MEAM parameters in comparison with DFT calculations. \(B_0\) is the bulk modulus (GPa); \(C_{11}, C_{12}, C_{44}\) are the elastic constants (GPa); \(E_{(100)}, E_{(110)}, E_{(111)}\) are surface energies of corresponding surfaces (mJ/m\(^2\)); \(\Delta E\)’s are the structural energy differences (eV/atom).
wave (PAW) method [21] as implemented by Kresse and Joubert [93]. For the treatment of
electron exchange and correlation, we used the generalized gradient approximation (GGA)
using the Perdew-Burke-Ernzerhof scheme [74]. We specifically used VASP for our DFT
calculations with cut off energy for plane wave basis set was 350 eV, and $15 \times 15 \times 15$
Kpoints. Almost 2000 atoms were used in WARP, for this MEAM calculations. Because
MEAM consistently underestimates all the calculations in Table 8.2, compared to DFT,
we can only predict a consistent shifting of melting temperature from the actual.

Table 8.2 MEAM and DFT comparison for W calculations relevant to our simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DFT</th>
<th>MEAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$</td>
<td>330</td>
<td>270</td>
</tr>
<tr>
<td>$(C_{11} - C_{12})/2$</td>
<td>190</td>
<td>160</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>280</td>
<td>160</td>
</tr>
<tr>
<td>$E_{(100)}$</td>
<td>7810</td>
<td>5980</td>
</tr>
<tr>
<td>$E_{(110)}$</td>
<td>6390</td>
<td>5660</td>
</tr>
<tr>
<td>$E_{(111)}$</td>
<td>7190</td>
<td>5030</td>
</tr>
<tr>
<td>$\Delta E_{bctofcc}$</td>
<td>0.494</td>
<td>0.325</td>
</tr>
<tr>
<td>$\Delta E_{bctohcp}$</td>
<td>0.397</td>
<td>2.168</td>
</tr>
</tbody>
</table>
8.2.2 Simulation Procedure

We performed a detailed MD simulation of the melting of unsupported spherical bcc W nanoparticles, that are 2–12 nm in diameter (259–56905 atoms). The surface boundary condition was not periodic and has vacuum without any external pressure. Each nanoparticle was constructed by cutting out atoms within a specified radius from the tungsten bulk in bcc structure, since we found bcc is the stable structure, according to MEAM as well as in nature. All the nanoparticles were then annealed at room temperature for ten different time spans (1-3ps). The equations of motion were integrated using time steps $\Delta t = 4 \times 10^{-15}$ s. We began each MD run by randomizing the atomic velocities of the nanoparticle according to the Maxwell-Boltzmann distribution. We increased the temperature of the heat bath in steps of $\Delta T = 100$ K from the initial temperature $T_i = 500$ K to the final temperature up to $T_f = 4000$ K. We let the nanoparticles come to equilibration for 50,000 time steps at each temperature. Statistical (time-averaged) data for the energetics we collected after the system had adjusted to the new temperature, which was typically after 25,000 time steps following a temperature increase. For the particles of diameters less than 8 nm, 20,000 time steps were used to adjust the particles to each new temperature. The isothermal condition was maintained by using a Nosé-Hoover thermostat [69, 133]. Finally we averaged over the results of ten different annealed samples.

8.3 Results and Discussion

The most straightforward method to identify the melting of atomistic structures in MD simulations is to monitor the variation of the internal energy with temperature.
Fig. 8.1 shows the internal energies of the W nanoparticles with different diameters as a function of temperature. It is clearly seen from Fig. 8.1 that each internal energy curve goes from one linear region to another. The overall melting is clearly identified for the bulk material by the abrupt “jump” in the internal energy curve. The height of the jump is a measure of $\Delta H_m$, the amount of heat required for melting, and it decreases as the size of nanoparticle decreases. Although the abrupt jump of internal energy is not quite prominent for nanoparticles, rather they have a slower slope to climb-up, but definitely the first discontinuity in their internal energy curve is a sign of a temperature-assisted first-order phase transition. The approximate melting temperatures calculated based on the present MD simulation of W nanoparticles are listed in Table 8.3. We note that the melting temperature of bulk W from our MD simulation, 3900 K, is slightly higher than the experimentally measured value of 3695 K [39]. The discrepancy in this result is mainly due to the super-heating of the simulated lattice, as it has been observed that the confined lattice without free surface can be significantly superheated [77, 110]. Although it is not the main focus of this study, one can follow the procedure prescribed by Morris et al [124] to establish the co-existence of solid and liquid phases to determine the melting temperature of the bulk W system without super-heating. More importantly, we also note that the melting temperature decreases drastically as the size of the particle decreases. This result suggests that the thermal stability of small nanoparticles must be carefully investigated before they can be used in applications such as nano-devices.

The melting behavior of 2 nm particle seems to be different from those of bigger particles: at the onset of the melting, the internal energy curve dips down before climbing
Figure 8.1  Melting responses for different nanoparticles.

Internal energies of the W nanoparticles with different diameters as a function of temperature. The same data for W bulk are also shown.
up again. A similar behavior has been observed in the melting of small Au nanoparticles of
diameters up to 2.8 nm [169]. The onset of melting provides surface atoms an opportunity
to rearrange themselves to optimize the local morphology and lower their portion of the
internal energy. For extremely small particles, where the surface area to volume ratio is
large, this will cause the total internal energy of the particle to decrease briefly as shown in
Fig. 8.1. However, a further detailed study focusing on small nanoparticles will be required
to elucidate this peculiar behavior. Nevertheless, the surface premelting phenomenon is
not the proper description for the melting of this nanoparticle. But the dip and rise in the
internal energy predicts a dynamical equilibrium where individual atoms passes between
solid-like and liquid-like states [192].

Table 8.3 Melting temperatures of various sizes of W nanoparticles.

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>No. of atoms</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>259</td>
<td>1000</td>
</tr>
<tr>
<td>4.0</td>
<td>2085</td>
<td>1900</td>
</tr>
<tr>
<td>6.0</td>
<td>7119</td>
<td>2200</td>
</tr>
<tr>
<td>8.0</td>
<td>16865</td>
<td>2300</td>
</tr>
<tr>
<td>10.0</td>
<td>33079</td>
<td>2400</td>
</tr>
<tr>
<td>12.0</td>
<td>56905</td>
<td>2500</td>
</tr>
<tr>
<td>Bulk</td>
<td>$\infty$</td>
<td>3900</td>
</tr>
</tbody>
</table>
The variation of the melting temperature with the size of the W nanoparticles is plotted in Fig. 8.2. The melting point depression of W nanoparticles exhibit the same qualitative behavior found in the MD simulation of Au nanoparticles [40, 169]. A similar size dependence of melting point depression has been observed experimentally over a broad range of particle sizes for particles in cluster beams [19, 20, 157, 158] as well as particles on substrates [2, 94, 95, 142].

For spherical particles of diameter \( R \), a melting temperature \( T_m(R) \) can be obtained phenomenologically [25, 57, 140] by equating the Gibbs free energies of solid and liquid spherical clusters, assuming constant pressure conditions:

\[
T_m(R) = T_m^* \left( 1 - \frac{R_1}{R} \right)
\]

(8.1)

where \( T_m^* \) is the melting temperature of the bulk tungsten and \( R_1 \) is a parameter related to physical quantities, such as the solid and liquid densities, the bulk latent heat of melting, and solid-vapor and liquid-vapor interface energies. In obtaining this model, the surface energy anisotropy of the solid is not taken into account, and the possibility of inhomogeneous phases (such as a liquid layer due to premelting) is also neglected. The solid line in Fig. 8.2 corresponds to the simple thermodynamical model of Eq. (8.1), with constant parameters \( T_m^* = 2900 \) K and \( R_1 = 1.5 \) nm. The curve shows clearly that the melting point of W nanoparticles decrease according to \( 1/R \) dependence as predicted in Eq. (8.1). However, the fitted value of \( T_m^* \) is significantly lower than the melting temperature of the bulk tungsten. This result indicates that the characteristics of the curve are likely to change for nanoparticles with larger diameters, and further study with larger nanoparticles will be needed to test the applicability of this model to W nanoparticles.
Figure 8.2  Size dependence of the melting temperatures of W nanoparticles.

Symbols represent the calculated values from the present MD simulation and the solid line is calculated in terms of Eq. (8.1).
Figure 8.3  Melting response through specific heat calculations.

The specific heat of all the nanoparticles from 2–12 nm. The specific heat of the bulk has also been shown here.
Hanszen [62] proposed another model of melting in terms of classical thermodynamics, assuming that a liquid over-layer forms at the surface of the solid cluster and grows towards the solid core, below the melting point [37, 191]. When the liquid layer thickness exceeds a critical thickness, the whole cluster melts homogeneously. In this model, the melting point \( T_m(R) \) of W nanoparticles with diameter \( R \) can be expressed as [94, 95]

\[
T_m(R) = T_m^* \left( 1 - \frac{R_1}{R - t_0} + \frac{R_2}{R} \right),
\]

(8.2)

When the data of Table 8.3 were fitted to Eq. (8.2), we obtained negligibly small values for \( t_0 \) and \( R_2 \), thus returning to the model of Eq. (8.1). Figure 8.3 shows the temperature dependence of the specific heat for all the nanoparticles. From Figure 8.3 one can precisely identify the melting temperatures for 8, 10, and 12 nm radius nanoparticles. However the melting temperature is not clear from the variation of specific heats of the nanoparticles of smaller size, i.e., of 2, 4 and 6 nm radius nanoparticles.

Fig. 8.4 shows the cross sections through the center of two particles of a W nanoparticle with a diameter 10 nm. The displacement vectors, represented by colors, at different times during the MD simulation run at the temperature 2000 K are plotted. Fig. 8.4 shows that at a temperature below the melting point the atoms in the entire nanoparticle vibrate in their places while retaining their bcc crystal structure. As the temperature increases, several surface layers of atoms start to lose their periodicity and form a liquid shell as shown in Fig. 8.4. Once the thickness of the liquid layer reaches a critical thickness, the whole nanoparticle melts. Our MD simulation conf rms the experimental observation that nanoscale materials simultaneously display solid-like and liquid-like characteristics, and under thermodynamic equilibrium, a fraction of the atoms in the outer shell of the particle
Figure 8.4  Displacement vectors at different temperatures and times.

First four pictures at 2000 K, at 28–36 ps, 72–96 ps, 96–136 ps, and 144–200 ps, respectively. Last two figures are at 16–32 ps at 2500 and 3000 K, respectively.
exhibit liquid-like behavior and the remaining fraction in the inner core act as solid [94]. Hence, melting point depression and the presence of disorder in nanoscale W powders will play an important role in various industries, including microelectronic industries for printed circuit board drill bits [53].

We note that our simulations do not show pronounced faceted or step-like structures. We found a similar result when the nanoparticles are heated to the melting temperature and cooled down slowly. Our results are in good agreement with an earlier experiment that found no evidence for a faceted or step-like microstructure in a single tungsten crystal [113].

### 8.4 Conclusions

The thermal stability of unsupported W nanoparticles has been investigated using a MD simulation. The MEAM potential was used to described the interatomic interactions. W nanoparticles melt at a temperature that is lower than the bulk melting temperature. The result of our present calculations shows the melting temperature to be approximately a decreasing function of the inverse radius. We found that W nanoparticle melting is preceded by surface melting effects of its outer skin, similar to the melting of spherical clusters of many other elements.
9.1 Introduction

Sintering is a heating process that leads particles to bond together. A significant strengthening and improved material properties are the advantages. The sintering temperature could be far below the melting temperature of constituents. Bonding becomes evident in the atomistic scale when a neck grows between adjacent particles. Fundamentally the process is due to large atomic motions over the neck regions. Also, the reduction in surface energy is another driving force for this mechanism. The surface-to-volume ratio increases with a decrease of the particle size, and surface energy per unit volume increases with the inverse of the particle size. Hence, smaller particles have more specific surface areas and their surface reactivity is higher than for larger particles. And accordingly they sinter faster. Nevertheless, much of the free surface energy is needed to overcome the grain boundary energy. So as neck growth removes surface energy, grain boundary energy adds up. In order to continue the process, the decrease of surface energy has to be greater than the increase of the grain boundary energy.

There are several reasons to conduct this research to find the mechanisms of this phenomenon by atomistic simulations. For example how the driving forces influence this
mechanism, the path of the atomic vibrations, how the atomic motion and how the geometry of the system affects the driving forces. The sintering mechanism is usually a diffusion process; it is either surface diffusion or volume diffusion. Typically surface diffusion takes place along the grain boundary and volume diffusion takes place through the crystalline lattice. Heating causes atomic vibrations, and atomic bonds lengthen at high temperature; in addition to the curvature of the system and surface reactivity, sintering occurs. At high temperature, more atoms have energy equal to or above that required to break their neighboring bonds and to move to the new site. The minimum energy that an atom needs to move is called the activation energy. One statistical concept popularly known as the Arrhenius theory depicts as

\[
\frac{N}{N_0} = \exp\left(-\frac{Q}{RT}\right)
\]  

(9.1)

This describes the population ratio of atoms that have diffused at a particular temperature, where \(N/N_0\) is the ratio of the number of moving atoms to the total number of atoms, \(Q\) is the activation energy, \(R\) is the ideal gas constant, and \(T\) is the absolute temperature. The activation energy depends on the material and strength of the atomic bonds. Sintering is faster as the temperature approaches the melting point, since near the melting temperature atoms already have enough energy to break the bonds and move freely.

At high temperatures, the jumping atoms do not have any knowledge of where to go so they simply wander. This random process occasionally results in atoms landing at the bond between particles where they help reduce surface area and surface energy. After that, it is quite unfavorable for the atoms to move away, since it would increase energy.
Sintering is a collection of a large number of atomic jumps, of which a small fraction of those jumps lead towards the growth of the sintering bonds, and reduction of the surface energy. The role of heating is to increase the total number of atomic jumps. Because to obtain considerable sintering bonding, one must have a large number of atomic jumps. This statistical process involves a large number of atom vibrations, typically $10^{14}$ Hertz.

There are few bulk observables required to quantify the sintering process. Neck growth is such an aspect. A fundamental measure of sintering is the neck-size ratio $\frac{X}{D}$, defined as the ratio of neck diameter ($X$) and the particle diameter ($D$). Surface area declines rapidly during sintering and is usually measured as $\Delta S/S_0$, the ratio of change in surface area to the original surface area.

Table 9.1 lists various material properties of tungsten. Tungsten, tungsten alloys, and tungsten compounds occupy unique positions in materials science. Most uses derive from combinations of the high density, hardness, melting temperature, elastic modulus, and conductivity in conjunction with the low thermal expansion. These unique properties combine to support applications ranging from home lighting to thermonuclear fusion first-wall protection [97, 187]. Global tungsten consumption has reached about 40 million kg per year.

Tungsten is the logical first choice for a full model of nanoscale powder processing. It is an established material that is traditionally fabricated using sintering. The unique properties of tungsten are well recognized in a diversity of applications. With nanoscale tungsten powders available at reasonable costs, it is clear that new thinking is required on how to balance size-dependent advantages against temperature-dependent limitations. The
Table 9.1 Different bulk properties of tungsten (W).

<table>
<thead>
<tr>
<th>Property</th>
<th>tungsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>W</td>
</tr>
<tr>
<td>Atomic number</td>
<td>74</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Body centered cubic (BCC)</td>
</tr>
<tr>
<td>Standard Atomic weight</td>
<td>183.84 g/mol</td>
</tr>
<tr>
<td>Density near room temperature</td>
<td>19.25 g/cm³</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>3695 K</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>52.31 kJ/mol</td>
</tr>
<tr>
<td>Heat Capacity ($C_v$)</td>
<td>24.27 J/mol/K at 25°C</td>
</tr>
<tr>
<td>Heat conductivity</td>
<td>173 W/m/K at 300 K</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>4.5 m/K at 25°C</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>411 GPa</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.28</td>
</tr>
</tbody>
</table>
Hall-Petch effect (hardness increases in proportion to the inverse square-root of grain size) suggests that significant opportunity exists if nanoscale powders could be consolidated to full density with minimized coarsening.

Tungsten and tungsten carbide were some of the first widely available nanoscale materials [147, 187]. In spite of nanoscale powder availability, uses have lagged because of rapid micro-structure coarsening when processed in standard sintering cycles. Some novel, but expensive, consolidation processes have been used to lower the densification temperatures as a means to reduce grain growth [10, 13, 73, 78, 73, 154]. The few successes to date are in applications for small components that require small particles, such as in printed circuit drills [52]. That application relies on 200 to 300 nm WC-Co powders to fabricate 70 nm diameter drills. Unfortunately, there is difficulty in processing tungsten-based materials to grain sizes below 200 nm [115, 153, 165, 186]. Although there is much interest in nanoscale micro-structures, calculations suggest that abnormal grain growth is a fundamental limitation [65].

The production of smaller grain size products would be beneficial, but the difficulty is due to the current processing route [79]. It is important to recognize that processing involves both size-dependent (compaction) and temperature-dependent (phase transformation) parameters, and that sintering is sensitive to both. For example, a popular cemented carbide composition is WC-10Co-0.5VC (wt.%). The VC is an effective grain-growth inhibitor [183] that segregates to the WC interface during heating [98]. At the sintering temperature, it slows grain growth by annihilation of surface reaction sites on WC and by lowering the WC solubility in Co. The standard approach inherently leads to a nonuni-
form VC distribution in the starting micro-structure. Regions far from the VC grain-growth inhibitor coarsen three to five times faster [65, 173]. Consequently, substantial and nonuniform grain growth is detected as low as 1150°C, prior to diffusional homogenization of the VC, and leading to well-documented problems with nanoscale WC-Co-VC [52, 65, 173]. Other thermochemical reactions require high temperatures independent of the micro-structure scale [3, 160, 163, 164]. Hot isostatic pressing, spark sintering, and microwave sintering give densification with reduced grain growth, but with a loss of temperature-dependent adjustments, so the product is not much improved [1, 10, 13, 165]. These conflicts between size-dependent events and temperature-dependent events create micro-structure imbalances that result in reduced sintered properties. Several other tungsten materials have been processed in the nanoscale size range - including pure W [63, 165], W-Cu [81, 103, 104, 122, 151, 188, 189], W-Ni-Fe [41, 81], and W-Y [9]. Many properties would improve with a small grain size, including strength, hardness, and wear resistance [52, 112, 146]. Abrasive wear rates fall exponentially as the hardness increases [147], and fracture toughness increases with a high hardness [161]. One option is to adjust the powder chemistry prior to consolidation, possibly by coating the powders with nanoscale films of activators, grain-growth inhibitors, or liquid-phase formers [43, 78, 84, 179].

Nanoscale W powders have some processing attributes that scale with particle size, while others are only temperature-dependent. Accordingly novel consolidation cycles need to be created to adapt to the differing sensitivities. For example, 20 nm tungsten sinters to near full density at temperatures below 830°C [35], but oxide reduction that is a part
of sintering in hydrogen is delayed to higher temperatures [160]. Likewise, nanoscale WC-Co compositions sinter densify far below the liquid formation temperature, but the change in temperature-dependent solubility relations make carbide stoichiometry control difficult. In the W-Cu system, a small grain size will improve arc erosion behavior in electrical contacts, but oxide reduction is incomplete prior to densification, so the material lacks adequate conductivity. Thus, nanoscale tungsten-based materials need to be reassessed for a balance between thermodynamics and processing. It is the contention here that modeling provides a means to identify processing cycle options customized to nanoscale tungsten-based materials. Data on powder characteristics, sintering response, and product properties exist for tungsten powders [5, 8, 13, 84, 90, 97, 136, 138, 139, 160, 171, 178, 187]. Likewise, processing models are known with regard to compaction and sintering [49, 50, 129]. Recent research has assembled the processing models into a model customized for the consolidation of nanoscale tungsten powders, determined using existing data. Accordingly, predictions can now be made for product properties as functions of the starting powder and processing conditions. This procedure allows examination of opportunities as a guideline to future research.

9.2 Results and Discussion

All the molecular dynamics simulations we carried out using a Modified Embedded Atom Method (MEAM) potential for tungsten. First we tested our potential results
with DFT or experimental results. Once we obtained a compelling match, we ran sintering simulations for various external conditions.

Table 9.2  W MEAM potential parameters used for simulations.

<table>
<thead>
<tr>
<th></th>
<th>$E^0$</th>
<th>$r^0$</th>
<th>A</th>
<th>$\alpha$</th>
<th>$\beta^{(0)}$</th>
<th>$\beta^{(1)}$</th>
<th>$\beta^{(2)}$</th>
<th>$\beta^{(3)}$</th>
<th>$t^{(0)}$</th>
<th>$t^{(1)}$</th>
<th>$t^{(2)}$</th>
<th>$t^{(3)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.66</td>
<td>2.74</td>
<td>0.98</td>
<td>5.63</td>
<td>3.98</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>3.16</td>
<td>8.25</td>
<td>-2.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 9.2 shows the potential parameters we used for all the molecular dynamic simulations for sintering. The screening parameters $C_{\text{max}}$ and $C_{\text{min}}$ are kept in their usual values 2.8 and 2.0 respectively.

9.2.1 Lattice Constant

In Fig. 9.1, we calculated the total energy of system as we changed lattice constant of tungsten crystal unit cell. The unit cell is cubic and contains BCC structure of tungsten atoms. The total number of atoms in this unit cell is big enough (128) to simulate thermal effect. Optimum lattice constant of BCC tungsten crystal was determined from Fig. 9.1.

The calculated lattice constant is 3.165 Å, which is the same as the experimental lattice.

1 Calculations were done using present MEAM parameters in comparison with DFT calculations. $B_0$ is the bulk modulus (GPa); $C_{11}$, $C_{12}$, $C_{44}$ are the elastic constants (GPa); $E(100)$, $E(110)$, $E(111)$ are surface energies of corresponding surfaces (J/m²); $\Delta E$s are the structural energy differences (eV/atom).

2 $E^0$ is the sublimation energy, $r^0$ is the equilibrium nearest neighbor distance, $A$ is the scaling factor for the embedding energy, $\alpha$ is the exponential decay factor for the universal energy function, $\beta^{(03)}$ are the exponential decay factors for the atomic densities, $t^{(03)}$ are the weighting factors for the atomic densities, $C_{\text{max}}$ and $C_{\text{min}}$ screening parameters are 2.8 and 2.0, respectively.
Table 9.3  Calculated physical properties of W in bulk.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DFT</th>
<th>Expt.</th>
<th>MEAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_0)</td>
<td>330</td>
<td>314</td>
<td>270</td>
</tr>
<tr>
<td>(\frac{(C_{11} - C_{12})}{2})</td>
<td>190</td>
<td>163</td>
<td>160</td>
</tr>
<tr>
<td>(C_{44})</td>
<td>280</td>
<td>163</td>
<td>160</td>
</tr>
<tr>
<td>(E(100))</td>
<td>7.81</td>
<td>5.98</td>
<td></td>
</tr>
<tr>
<td>(E(110))</td>
<td>6.39</td>
<td>5.66</td>
<td></td>
</tr>
<tr>
<td>(E(111))</td>
<td>7.19</td>
<td>5.03</td>
<td></td>
</tr>
<tr>
<td>(\Delta E_{bcc-fcc})</td>
<td>0.494</td>
<td>0.325</td>
<td></td>
</tr>
<tr>
<td>(\Delta E_{bcc-hcp})</td>
<td>0.397</td>
<td>2.168</td>
<td></td>
</tr>
</tbody>
</table>
constant. This is because of the fact that one of the MEAM potential fitting parameters for BCC tungsten is its lattice parameter.

![Graph showing relaxed energy variation with lattice parameter.](image)

**Figure 9.1** Relaxed energy variation with lattice parameter.

For bulk tungsten in BCC structure, $E$ versus $a$ from MEAM, predicts the lattice parameter of 3.165 Å compared to the experimental 3.16 Å

Fig. 9.2 shows one nano-size tungsten particle which was built using the optimum lattice constant. The radius of the particle is 10 nm. Total number of atoms is 33079.

### 9.2.2 Melting Response of Crystal to Various Size of Nanoparticles

We increased the temperature of the system with a constant heating rate with a No¨se-Hoover thermostat. The time for one molecular dynamic step is 0.004 picoseconds. We run 5000 steps at each data point of temperature.

Fig. 9.3 shows the melting response of the crystal and various size of nanoparticles from atomistic molecular dynamic simulations. In the constant heating process, the slope of the linear region corresponds to the specific heat of the solid or liquid. The jump from
Figure 9.2  Particle preparation for atomistic simulation.

Nano tungsten powder sintering; model for single tungsten particle (BCC, 10 nm, 33079 atoms).

Figure 9.3  Melting response of crystal and various nanoparticles.

Phase transitions for only 8–12 nm nanoparticles are shown here.
one linear region to another clearly shows the melting response of the bulk or the nanoparticles. In the figure, the crystal absorbs latent heat around 4500K and goes through a phase transition from solid to liquid. The accepted melting temperature of tungsten crystal in the literature is 3683.15 K. The calculated melting temperature (4000 K) is quite close, but is a little bigger than the experimental melting temperature due to superheating.

A small size nanoparticle has a bigger ratio of surface area over volume. The energy along the y-axis represents energy per atom. The percentage of number of surface atoms in a small nanoparticle is big and surface atoms have higher energy than do bulk atoms. Therefore the smaller the nanoparticle is, the bigger the energy per atom is. The crystal is an extreme case of big nanoparticles.

In this picture, comparing melting temperature of different sizes of nanoparticles seems to be difficult. Theoretically a smaller size of nanoparticle has a lower melting temperature than a big size of nanoparticle because the surface atom’s binding energy is low. The melting temperatures of nanoparticles are quite low compared to crystal bulk, which is an extreme of a big nanoparticles. We can make sure that the smaller the nanoparticle is, the lower is the melting temperature.

9.2.3 Iso-thermal Sintering

We maintained constant temperature to study the sintering process at various different temperatures using a Nosé-Hoover thermostat. In this iso-thermal sintering simulation, the time for one molecular dynamic step is 0.004 picoseconds. Around 2000K, it
illustrates the solid-state sintering process. Around 3500K, it illustrates the liquid-state sintering process.

Fig. 9.4 shows an iso-thermal sintering process at 3500K using two 10 nm nanoparticles. At this high temperature, the crystal structure ruptures in a few picoseconds. It is around 200 pico seconds for the two nano particles collapse into one particle. When we used smaller temperature, the full sintering time goes up.

Fig. 9.5 shows displacement vectors in cross section in an iso-thermal sintering process. At 2000 K, at the beginning the core of the nano particle maintains its original crystal structure and only surface atoms contribute to the sintering process. It is hard to define surface diffusion or grain boundary diffusion or volume diffusion mentioned before in the literature for our simulation results. We can not say that there is grain boundary diffusion because the atoms in the grain boundary do not seem to move a lot. The surface atoms a little bit away from the neck area have some movement, but there are no consistent movements. It is hard to say that there is surface diffusion. For the volume diffusion, there is some positive movements. The crystallized atoms are released and move towards the neck area. It’s quite close to volume diffusion, but not what people expected before.

At 3000K it resembles liquid-state sintering even though it is quite below the melting temperature.

Fig. 9.6 shows dimensional change and neck growth, shrinkage and densification. In order to estimate shrinkage and densification, we measured the distance between two nano particle centers (D1), and the distance between the left end of left nano particle and the right end of right nano particle (D2), which are shown in the figure. We assumed that
Figure 9.4  Snapshots of the two nanoparticles at different times

At 3500 K temperature. The snapshots are taken at 0, 5, 15, 20, 30 and 50 ps.
Figure 9.5 Displacement vector through cross section at 2000 K.

The width of the surface premelt increases with time.
Figure 9.6  Variations of observables in sintering.

Dimensional change and neck growth (upper left), shrinkage (upper right) and densification (lower).
each nano particle maintains a perfect sphere during the sintering process and calculated neck growth from D1 and D2. Shrinkage is calculated using the following formula:

$$\frac{\Delta L}{L_0} = \left( \frac{X}{2D} \right)^2$$  \hspace{1cm} (9.2)

where $L$ is the distance between the two nanoparticle’s centers, $X$ is the neck size and $D$ is the width of a nanoparticle. Sinter density is defined in the following equation.

$$\rho_s = \frac{\rho_G}{\left(1 - \frac{\Delta L}{L_0}\right)^{\frac{3}{2}}}$$  \hspace{1cm} (9.3)

where $\rho_G$ is the initial density before sintering, so called green density. Sinter density is calculated from shrinkage.

In the shrinkage graph, the shrinkage increases linearly and at around 100 picoseconds the shrinkage rate is very high. We need further investigation for this high rate of shrinkage.

For densification, we assumed different green densities, depending on the packing method (simple cubic, BCC and FCC) of nanoparticles. Here again around 100 picoseconds the densification rate suddenly increases.

### 9.2.3.1 Sphericity

Fig. 9.7 shows sphericity during an iso-thermal sintering process at various temperatures. The sphericity is a measure of how spherical an object is.

Wadell defined in 1932 the sphericity, $\phi$, of a particle as the ratio of the surface area of a sphere to the surface area of the particle: $\phi = \frac{\pi^{\frac{3}{2}} (6V_p)^{\frac{2}{3}}}{A_p}$ where $V_p$ is volume of
Figure 9.7 Observation of densification using sphericities.

For iso-thermal sintering at various temperatures.

the particle and $A_p$ is the surface area of the particle. The sphericity is a good measure to characterize the sintering process. We defined sphericity in our model as the following.

The mass distribution tensor $M_{\alpha\beta}$ is defined in continuum mechanics as follows for two particles $\alpha$ and $\beta$,

$$M_{\alpha\beta} = \int \rho(r)(r_\alpha - R_\alpha)(r_\beta - R_\beta) d^3r$$  \hspace{1cm} (9.4)

$$R = \frac{\int \rho(r)r d^3r}{\int \rho(r) d^3r}$$  \hspace{1cm} (9.5)

where $R$ is center of mass, $r$ is the position coordinates for atoms and $\rho$ is density.

In discrete systems

$$M_{\alpha\beta} = \sum_i n_i (r_{i\alpha} - R_\alpha)(r_{i\beta} - R_\beta)$$  \hspace{1cm} (9.6)
where $R_\alpha = \frac{\sum m_i r_{i\alpha}}{\sum m_i}$ is center of mass of $\alpha$ component and $m_i$ is mass of an atom $i$. Diagonalization of mass distribution tensor gives three principal values $M_1, M_2$ and $M_3$ where $M_1 \geq M_2 \geq M_3$. We can define our sphericity

$$s = \frac{(abc)^{1/3}}{a}$$  \hspace{1cm} (9.8)$$

where $a^2 = M_1/M$, $b^2 = M_2/M$ and $c^2 = M_3/M$.

In Fig. 9.7, as temperature increases, the sintering speed increases. The forms of the graphs at each temperature are similar so that we fit the general form of graph, which is probably an exponential form, and we could determine the sintering coefficient which will help to determine the optimum temperature and elapsed time for sintering with high densification and low grain growth.

9.2.3.2 Sintering Mechanism

Our Two-particle sintering model is that bulk transport processes change the compact density by removing mass from the particles and redepositing that mass to form the neck. The result is powder compact shrinkage. Early in sintering, the particle approach is related to the neck size as follows:

$$S = \frac{\Delta L}{L_0} = \frac{X^2}{4D_1^2}$$  \hspace{1cm} (9.9)
where the shrinkage $S$ is the compact length change $\Delta L$ divided by the initial length $L_0$. Because of shrinkage, the compact densifies from the fractional initial density $\rho_0$ to the fractional sintered density $\rho$ according to the relation

$$\frac{\rho}{\rho_0} = \frac{1}{(1 - S)^3}$$  \hspace{1cm} (9.10)

Initial stage sintering models generally trace their origin to the calculations of Frenkel for viscous flow sintering of two equal-sized spheres. The Frenkel model suggested a relation between neck size and sintering time. It was followed by the Kuczynski model and many related treatments of this core problem. Although most solutions are based on several approximations, still there is a consistent finding that links the neck-size ratio $X/D$ to a kinetic term $B$, isothermal time $t$, and particle size $D$ as follows [49]:

$$\left(\frac{X}{D}\right)^n = \frac{Bt}{D^m}$$ \hspace{1cm} (9.11)

The exponent $n$ depends on the sintering mechanism and typical values are tabulated below.

The particle size exponent $m$ is known as the Herring scaling law exponent. The neck size is given by the diameter $X$ of the neck bonding the particles together, $D$ is the sphere diameter, $t$ is the isothermal sintering time, $B$ is the kinetic term treated below where temperature $T$ enters in an exponential form as associated with the mass transport process delivering neck growth

$$B = B_0 exp\left(-\frac{Q}{RT}\right)$$ \hspace{1cm} (9.12)
Table 9.4  Initial stage sintering models required to calculate Activation energies

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>n</th>
<th>m</th>
<th>$B_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscous flow</td>
<td>2</td>
<td>1</td>
<td>$3 \frac{\gamma_{SV}}{(2\eta)}$</td>
</tr>
<tr>
<td>plastic flow</td>
<td>2</td>
<td>1</td>
<td>$9 \pi(\gamma_{SV} D_\nu/b^2) / (RT)$</td>
</tr>
<tr>
<td>evaporation-condensation</td>
<td>3</td>
<td>2</td>
<td>$(\pi/2)1/2(3P\gamma_{SV}/\rho T^2)3/2(M/RT)$</td>
</tr>
<tr>
<td>lattice (volume) diffusion</td>
<td>5</td>
<td>3</td>
<td>$80 D_\nu\gamma_{SV} / (RT)$</td>
</tr>
<tr>
<td>grain-boundary diffusion</td>
<td>6</td>
<td>4</td>
<td>$20 \delta D_b\gamma_{SV} / (RT)$</td>
</tr>
<tr>
<td>surface diffusion</td>
<td>7</td>
<td>4</td>
<td>$56 \delta D_s\gamma_{SV} / (RT)$</td>
</tr>
</tbody>
</table>

where $B_0$ depends on collection of material, crystal structure, geometric constants and transport mechanism, $R$ is the ideal gas constant, $T$ is the absolute temperature, and $Q$ is an activation energy associated with the atomic transport process. The activation energy depends on the dominant mechanism. The values of $n$, $m$, and $B$ also depend on the mechanism of mass transport as described Table 9.4. In the Table 9.4, $\gamma_{SV}$ is the solid-vapor surface energy, $\eta$ is the viscosity, $D_\nu$ is the volume diffusivity, $b^2$ is the Burger’s vector, $V$ is the molar (atomic) volume, $P$ is the vapor pressure, $\rho$ is the theoretical density, $M$ is the molecular weight, $\eta$ is the diffusion layer width or thickness, $D_b$ is the grain-boundary diffusivity, and $D_s$ is the surface diffusivity.

Dimensional Changes: Based on the simulation results, Figure 9.8 shows dimensional changes such as $D_1$, $D_2$, $X$, and $\rho$ during isothermal sintering process.
Figure 9.8  Sintering behavior in isothermal sintering.

Growth of neck angle (top-left), densification (top-right) and characteristic dimensions (D1-D2) (bottom).
Apparent Activation Energy: We obtained the apparent activation energy based on Equations 9.11 and 9.12 for the two-particle neck growth model in isothermal sintering as follows:

1. First, we obtained the slope $B$ at each isothermal temperature using the following equation as shown in Figure 9.9

$$\frac{X^n}{D^{n-m}} = Bt = \left[ B_0 \exp\left( -\frac{Q}{RT} \right) \right]$$  

(9.13)

2. From the $B$ value obtained by Step 1, we obtained the slope $Q$ using the following equation as shown in Figure 9.9

$$\ln B = \left( -\frac{1}{RT}Q + \ln B_0 \right)$$  

(9.14)

From the isothermal sintering simulation results at 2000, 2500, 3000, and 3500 K, we calculated the sintering activation energies based on the above model, as listed in Table 9.4. For five different diffusion processes, the sintering phenomenon with time ($t$) and logarithmic kinetic term with respect to $-\frac{1}{RT}$ are shown in Figure 9.9 and Figure 9.10.

The calculated activation energies are low compared with reference values [48] in Table 9.5. The difference reflects several issues, such as the lack of a grain boundary due to the perfect alignment of crystalline structures between the two particles. The calculated activation energy is the lowest for viscous or plastic flow, which may reflect the dominance of the premelting layer.

Densification Behavior: Based on the simulation results, Figure 9.11 shows shrinkage and densification during an isothermal sintering process.
Figure 9.9 Calculations for activation energies.

For viscous or plastic flow (top) with $R^2=0.9423$, evaporation-condensation (middle) with $R^2=0.9722$, and lattice or volume diffusion (bottom) with $R^2=0.9572$. 
Figure 9.10 Calculations for activation energies.

For grain-boundary diffusion (top) with $R^2=0.9247$ and surface diffusion (bottom) with $R^2=0.9045$. 
9.2.4 Effects of Pressure and Crystal Misalignment

Pressure Effect: We simulated isothermal simulations with various pressures from 50 to 200 MPa. Figure 9.11 shows neck growth and densification with various temperatures and pressures. Pressure enhances neck growth and densification.

Misalignment Effect: We simulated isothermal simulations with various misalignments in crystal orientation between the two particles, represented by rotations of 15° and 30°. Figure 9.12 shows neck growth and densification with various temperatures and misalignment. Misalignment reduces neck growth and densification, and therefore enhances the activation energy.

Table 9.5 Activation energies from the simulations at different misorientations.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Activation energy</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0°</td>
<td>15°</td>
</tr>
<tr>
<td>Viscous or plastic flow</td>
<td>49</td>
<td>110</td>
</tr>
<tr>
<td>evaporation-condensation</td>
<td>72</td>
<td>136</td>
</tr>
<tr>
<td>lattice (volume) diffusion</td>
<td>115</td>
<td>192</td>
</tr>
<tr>
<td>grain boundary diffusion</td>
<td>142</td>
<td>224</td>
</tr>
<tr>
<td>surface diffusion</td>
<td>158</td>
<td>253</td>
</tr>
</tbody>
</table>

In Table 9.5 the activation energies are shown. It is evident from the Table that with an increase in the misalignment, the activation energy increases significantly. To
Figure 9.11  Sintering behavior during pressure assisted sintering.

Growth of necksize and densification at 2000 K (top) and at 50 MPa pressure (bottom).
Figure 9.12  Sintering behavior during different misalignment.

Growth of necksize and densification at 2000 K (top) and at 30° misalignment (bottom).
get comparable values in activation energies, we believe that we need to model the grain boundary effect close to realistic systems. Furthermore, it is also evident that the surface diffusion is the most predominant flow mechanism in sintering.

### 9.3 Conclusions

We made atomistic level simulations using the molecular dynamic method and the modified embedded atom method to simulate powder sintering process of crystalline tungsten materials. We calculated melting points of the crystal and of various sizes of tungsten nanoparticles. We calculated expected shrinkage of tungsten powder in an isothermal sintering process. We calculated the densification profile with respect to sintering time in an iso-thermal sintering process. We employed the sphericity concept to describe the sintering process in terms of densification. We modeled sintering at different temperatures, pressures and also at different rotation angles (misalignment) between the particles. We found surface diffusion with higher misalignment is the most predominant flow mechanism in sintering.
10.1 Summary

During this study, several achievements were made. Using DFT, it has been shown that Al is not a good candidate to be substituted to increase the magnetization of magnetic material barium hexaferrite. For future purposes to evaluate the candidacy of another element/material, it would be a good idea to test the substitutional defect formation energy. It is general practice to mix a few weight percentage of vanadium-carbide (VC) with tungsten-carbide (WC) while generating WC nanoparticles to create more grains inside the nanoparticles. During the adsorption/desorption study of W/C atom adsorption on WC(0001), it has been revealed that a VC layer on top of the WC, inhibits W/C atom adsorption. In another DFT application, we found how barium (Ba) atoms can diffuse inside hematite to form barium hexaferrite. It is interesting to note that the theoretical diffusion barrier closely matches with the experimentally found temperature regime (corresponding to the diffusion barrier) where diffusion is successful. To probe several atomistic phenomena such as melting or grain boundaries, it is important to have a reliable potential for the single crystal or alloy material. It has been found that how vanadium (V) affects pure iron (Fe) with a developed MEAM potential. Several structural, physical and thermal
effects have been studied with different % of V doping. Molecular dynamics simulations of calcium (Ca) single crystals were performed with a developed MEAM potential to test the ability of the new potentials to quantitatively reproduce the macroscale behavior of real materials. Thermal activity, such as surface melting or premelting of nanoparticles, and sintering simulations have been studied using W nanoparticles. Simulation of sintering has been studied using several external conditions, such as temperature, pressure and grain boundary.

10.2 Impact

It has already been shown that MEAM provides a single universal formalism for classical atomistic simulations of a wide range of elements and their alloys. This work presents a contribution to the task of bridging quantum-mechanical and classical atomistic scale simulations. Information from *ab initio* electronic structure calculations was used to construct parameters of semi-empirical MEAM potentials for large-scale atomistic simulations of alloys. The new MEAM models were constructed to exactly reproduce the equilibrium lattice parameters, cohesive energies, heats of formations, and bulk moduli of the single elements in their ground state crystal structure and the alloys in the reference structure from *ab initio* electronic structure calculations. To test the transferability of the model, the energies of vacancies, substitutional, and interstitial defects, surface formation, and stacking faults were obtained. The results of the new MEAM models compare well to those from other published inter-atomic potentials.
10.3 Future Direction

Classical MD simulations provide a model of a physical system at the atomistic level. They are limited by the achievable accuracy on one side, and by the time duration and size scale of a simulation on the other side. The problem of the low accuracy of classical MD simulations can be addressed by the development of new, more elaborate models that provide better representation of a physical system and the phenomena in question. In order to improve the accuracy of classical MD simulations, Fe-V inter-atomic potential was developed. The original inter-atomic potentials, introduced by Lennard-Jones, included only two-body terms. They provided a realistic model of noble gases characterized by van der Waals forces. In order to model elements with metallic bonds, the potential has to include many body terms. MEAM potentials, used in this work, and multiscale MEAM potentials provide a general framework able to represent systems with directionally-dependent covalent bonding. However, their accuracy improvements come at the expense of increased computational requirements. The development of new, more general and more accurate inter-atomic potentials is one way to increase the reliability of MD simulations. The other way to obtain a more realistic representation, characteristic for every scientific discipline that involves modeling of the physical system, is to bridge the resolutions and scales of models at different levels.

Inter-atomic potentials are empirically constructed to reproduce properties of an atomic system in a specific domain. If the atomic system remains in the domain for which potentials have been designed, calculations are expected to provide reliable results. If atoms in some region are far from the domain the potential was designed for, it is desirable
to use a more detailed model for that region. If a large number of atoms in the modeled atomic system acts as a homogeneous block, i.e. the atoms undergo uniform deformation, it is desirable to model such a block of atoms as a continuum element. Thus the restriction of the MD simulation size can be relaxed. The use of finite element analysis (FEA) to model a uniform block of atoms allows us to reduce the computational requirements of a simulation and allow us to increase the size of a modeled system for multiscale modeling.
REFERENCES


[101] B.-J. Lee, M. Baskes, H. Kim, and Y. Koo Cho, “Second nearest-neighbor modified embedded atom method potentials for bcc transition metals,” *Phys. Rev. B*, vol. 64, no. 18, Oct 2001, p. 184102, Fe potential is modified by UCSD School of engineering and M. I. Baskes. This work is still unpublished. V potential is the same as reported in this paper.


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