INVESTIGATION OF THE STABILITY OF C15 LAVES PHASE STRUCTURES IN BCC IRON BY MOLECULAR DYNAMICS METHOD

by

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Abstract

Radiation damage can significantly alter a material’s strength, ductility, plasticity and stability. Thus, the radiation resistance of the selected structural materials is the primary concern in the design of advanced nuclear reactors. Body-centred cubic (bcc) iron-based alloys are important structural materials. Recently, a new class of interstitial clusters which present a structure of C15 Laves phase has been theoretically predicted in bcc iron. These nano-sized C15 clusters in bcc iron are expected to be highly stable and immobile, and may grow by the capture of self-interstitial atoms (SIAs), then transform into <100> loops. However, these C15 clusters have never been identified experimentally. In this thesis, molecular dynamic (MD) simulations were explored to investigate the stability of perfect C15 Laves phase structures made of iron atoms and with or without point defects, as well as the stability of nano-sized C15 clusters embedded in bcc iron with point defects nearby. The absence of nano-sized C15 Laves phase structures in experimental observations can be therefore interpreted.

In this work, in first-ever simulations, two empirical Fe-Fe potentials were tested and the Ackland-2004 potential was demonstrated to be suitable. Periodic boundary conditions (PBCs) were used along three axes. For the perfect C15 Laves phase structures made of iron, calculations were performed on the total potential energy, temperature dependence of elastic constants and elastic moduli, as well as the process of phase transformation at 300K. For interactions between perfect C15 Laves phase structures and their internal point defects, the formation energies of vacancies and SIAs, phase transformation temperature, and the process of phase transformation at 300K were simulated. Furthermore, radial distribution function (RDF) calculations were used to check stability and structural changes between 0K and 300K. For interactions between nano-sized
C15 clusters and nearby external point defects, the process of phase transformation at 300K was also simulated.

The simulation results suggest that pure C15 Laves phase structure can remain stable up to about 425K. The presence of internal point defects will cause a decrease of phase transformation temperatures to below 260K. With increasing temperatures, perfect C15 Laves phase structures that contain internal point defects will transform into imperfect bcc structures. At 300K, the presence of nearby external vacancies will induce a recombination of the same number of SIAs from nano-sized C15 clusters, therefore possibly eliminating the C15 clusters; meanwhile, nearby external SIAs will induce the nano-sized C15 clusters to rearrange into 1/2<111> loops. As a conclusion, perfect C15 Laves phase structures with internal point defects are likely unstable at the temperatures higher than 260K, thus they may not remain to be observed at room temperature during irradiation.
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<th>Description</th>
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<tbody>
<tr>
<td>A-vac</td>
<td>Type-A atom vacancy</td>
</tr>
<tr>
<td>B-vac</td>
<td>Type-B atom vacancy</td>
</tr>
<tr>
<td>BCC</td>
<td>Body centered cubic</td>
</tr>
<tr>
<td>CNA</td>
<td>Common neighbor analysis</td>
</tr>
<tr>
<td>Cu</td>
<td>Coper</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EAM</td>
<td>Embedded atom method</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FDM</td>
<td>Finite difference method</td>
</tr>
<tr>
<td>FS</td>
<td>Finnis-Sinclair potential</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary</td>
</tr>
<tr>
<td>I\textsubscript{2}C\textsuperscript{15}</td>
<td>C15 cluster (12 interstitials sharing 10 lattice sites)</td>
</tr>
<tr>
<td>I\textsubscript{4}C\textsuperscript{15}</td>
<td>C15 cluster (18 interstitials sharing 14 lattice sites)</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>MEAM</td>
<td>Modified embedded atom method</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>MS</td>
<td>Molecular statics</td>
</tr>
<tr>
<td>NPT</td>
<td>Fixed numbers of atoms, pressure and temperature ensemble</td>
</tr>
<tr>
<td>PBC</td>
<td>Periodic boundary condition</td>
</tr>
<tr>
<td>PKA</td>
<td>Primary knock-on atom</td>
</tr>
<tr>
<td>RDF</td>
<td>Radial distribution function</td>
</tr>
<tr>
<td>SIA</td>
<td>Self-interstitial atom</td>
</tr>
<tr>
<td>SIA^A_Dumbbell</td>
<td>Type-A dumbbell</td>
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<tr>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>SIA^B_Dumbbell</td>
<td>Type-B dumbbell</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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</table>
List of Symbols

\( a \)  
Acceleration

\( a_B \)  
Bohr radius

\( e \)  
Electronic charge

\( E_f \)  
Formation energy

\( E \)  
Young’s modulus

\( F \)  
Force

\( F(r) \)  
Local electron density radial function

\( G \)  
Shear modulus

\( H \)  
Heaviside function

\( K \)  
Kelvin

\( r \)  
Cut-off radius

\( r_{ij} \)  
Interatomic distance of atom i and atom j

\( T \)  
Time

\( T_{tr} \)  
Phase transformation temperature

\( U(r_{ij}) \)  
Pair potential

\( v \)  
Velocity

\( Z_A \)  
Atomic number of atom A

\( \rho_i \)  
Local electron density

\( \varepsilon_0 \)  
Permittivity of free space
Chapter 1

Introduction

The success of nuclear technology would depend critically on the behavior of materials in the intense radiation fields in reactors [1].

--- Fermi Enrico (1901-1954)

With the development of nuclear technology, nuclear power has become a widely used and trustworthy energy source. In 1946, Fermi first recognized that the irradiation of structural materials significantly impacts reactor efficiency. In 2004, Butler proposed that understanding and controlling the behavior of materials is the primary challenge of promising advanced reactor design concepts [2]. For a reactor, changes to material behavior is mainly caused by high-energy particles displacing atoms from their original lattice sites. In 1946, Winger verified that energetic incident neutrons would dislodge atoms from their regular lattice sites, thus changing the physical and mechanical properties of affected materials [3]. Unfortunately, it was evidenced in experiments that most of these changes were detrimental. So the influence of high-energy radiation (neutrons, gamma rays, nuclear reaction fragments) on the materials in fission and fusion reactors is referred to as "radiation damage". Radiation damage impacts such things as the strength, ductility, plasticity and stability of materials used in reactors and their equipment. The reactor environment, such as working temperature, neutron energy spectrum, irradiation dose, and
stress state will significantly determine the radiation-damaged behavior of the materials. Therefore, it is necessary to study the effects of radiation on these materials in order to develop radiation-resistant alloys [4-6].

As nuclear reactor engineering requires structural materials with a high tolerance for radiation, their microstructure evolution is of great concern, especially the radiation resistance of the required materials. Bcc iron has been the focus of study, with increasing attention being paid in particular to iron-base alloys, which serve as structural materials in nuclear reactors. Point defects or point defect clusters, which are made of vacancies and self-interstitial atoms (SIAs), are produced in bcc iron under irradiation; their evolution and performance remain to be fully understood. Experimentally, vacancy clusters form not only planar loops and voids, but also stacking fault tetrahedra (SFT) in face-centred-cubic (fcc) metals and alloys [7,8]. Single SIA’s were studied using density functional theory (DFT), finding that the <110> SIA dumbbell has the lowest formation energy and the most stable SIA configuration [9]. This is only for iron, while other bcc transition metals will form a <111> crowndion [10]. Dumbbells can be accumulated into bundles, forming small dislocation loops. However, SIA clusters in metal can only produce nanometer-size planar loops [11]. The Burgers vector of these loops in bcc iron observed by transmission electron microscopy (TEM) are either 1/2<111> in general or <100> at high temperatures (1185K) [12-14], which means the observed ratio of these two dislocation loops mainly relies on the irradiation temperature and neutron fluence. Further, molecular dynamics (MD) shows that 1/2<111> loops have less migration energy and may be absorbed by other defects, which implies that they would not accumulate into high densities. Recently, a new
mechanism was provided that immobile $<100>$ loops can be formed out of two interacting $1/2<111>$ loops [15].

In $\alpha$-iron, when an energetic incident particle or primary knock-on atom (PKA) initiates a cascade, most of the self-interstitial atoms (SIAs) formed single defects or glissile clusters as well as sessile clusters as an aftermath of the collision cascade. The thermal stability of a diverse size and number of sessile clusters depend on their cascade atom energy and irradiation temperature [16]. Some sessile clusters grow from catching mobile species that collide with each other, which consequently prevent the organization of a stable glissile loop. It is possible that when the defects have the same number of atoms, a more three-dimensional structure is adopted [17]. In 2000, D.J. Bacon [17] reported the two versions of sessile di-interstitials shown in Figure 1: (a) a triangular configuration with three atoms sharing the same site; and (b) 12 atoms sharing 10 lattice sites. These highly symmetric three-dimensional clusters can grow larger by capturing single SIAs. A new class of interstitial clusters in bcc iron has been proposed for different size ranges from single point defects to nano-metric clusters. These clusters have a particular metastable crystal structure that corresponds to the C15 Laves phase structure. Laves phase forms the largest group of intermetallic phases [18]. There are three general types of Laves phase structure: hexagonal MgZn$_2$ (C14), cubic MgCu$_2$ (C15) and di-hexagonal MgNi$_2$ (C36) [19]. The only difference in these three structures is their stacking sequences. Laves phases are attractive in structural applications because of their high strength at high temperatures and lower ductile-brittle transition temperatures. The C15 Laves phase, as an AB$_2$ topologically close-packed structure, impacts the stability of the crystal structure [20,21].
The specific details of the C15 Laves phase structure will be described in Chapter 4, Section 1.

Figure 1. Two versions of metastable di-interstitials created in cascade simulations of α-iron. (a) Three atoms in a \{111\} plane sharing one lattice site, (b) 12 atoms sharing 10 lattice sites. The large grey spheres indicate interstitial atoms, the small grey spheres indicate lattice sites (vacancies).

In 2012, M.C. Marinica [22] viewed the three-dimensional defect structure in Figure 1(b) as a kind of C15 Laves phase cluster in bcc iron named \( I^C_{2} \). DFT simulations show that this new class of interstitial clusters with C15 Laves phase structures in bcc iron can be formed directly from a displacement cascade and grow by capture SIAs. These clusters indicate lower energies, higher stability and immobility for C15 aggregates \( (I_4^{C15}, I_6^{C15}, I_8^{C15}) \) than the most stable cluster formed by parallel dumbbells [22]. These new clusters represent a turning point for predicting microstructural evolution in irradiated iron-base alloys.
Studies on the stability of C15 cluster structures in iron have been reported by L. Dézerald [23]. The C15 structure is found to be mechanically and dynamically stable according to the calculations of the energy-volume curve and phonon dispersion of bulk C15, which means this structure will not suffer deformation, such as a collapse at larger SIA cluster sizes. Then, using DFT, C15 structures were compared with ring and loop configurations of various cluster sizes, and it is suggested that C15 structures formed by 4 and 8 interstitials in bcc iron have the lowest energy among all known configurations.

The next question is whether C15 clusters at larger sizes remain stable under irradiation. Y. Zhang reported that MD simulation shows only C15 clusters within a certain size range offer a higher stability than loops [24]. If the cluster size is beyond a critical size (20-30 SIAs), C15 clusters easily grow by the capture of small sized SIAs and then may transform to <100> and 1/2<111>loops. Moreover, a new citation reveals that the 1/2<111>loops turn into <110> loops. On the other hand, based on analytical theory proposed by Bacon and Scattergood (1982), J. Dérès reported that the dislocation unpinning from nano-sized irradiation defects in bcc iron [25] reveal that C15 clusters have stronger pinning strength than other types of defect below 17 SIAs. This is to say that the C15 clusters below that critical size are the most stable interstitial defects in bcc iron. However, the C15 clusters have similar pinning strengths to other defect types above 17 SIA. Thus, C15 clusters may contribute to irradiation hardening in iron base alloys.

Predictions show that C15 Laves phase structures may exist in bcc iron under irradiation. If C15 Laves phase exists in a non-simulated environment, the tiny defects in bcc iron cannot be easily seen as voids and loops, and also in C15 clusters. However, this special C15 structure in bcc iron has not yet been observed in experiments. Because the
existence of C15 Laves phase structures will affect material behavior/performance - such as the dynamic and mechanical properties of bcc iron - it is important to answer the question: Why haven’t C15 Laves phase structures been observed experimentally?

In this thesis, molecular dynamic (MD) simulations were employed to investigate the stability of perfect C15 Laves phase structures made of iron atoms with or without point defects, as well as the stability of nano-sized C15 clusters embedded in bcc iron with external point defect nearby. The thesis will also consider the above open question.

1.1 Thesis outline

Chapter 1 introduces the basic theory related to the C15 Laves phase structures in bcc iron.

Chapter 2 briefly presents and discusses the MD simulation method and related analysis techniques.

In Chapter 3, in first-ever simulations, two empirical Fe-Fe potentials (FS-1993 and Ackland-2004) are tested and compared with the experimental data. FS-1993 empirical is re-optimized for the whole potential function continuity using the least squares method.

In Chapters 4 to 7, MD simulations of the stability of perfect C15 Laves phase structures made of iron atoms and with or without point defects, as well as the stability of nano-sized C15 clusters in bcc iron with point defects nearby are given. For the perfect C15 Laves phase structures made of iron, calculations were performed of the total potential energy, temperature dependence of elastic constants and elastic moduli, as well as the process of phase transformation at 300K. For interactions between perfect C15 Laves phase structures and their internal point defects, the formation energies of vacancies and SIAs,
phase transformation temperature, and the process of phase transformation at 300K were simulated. Furthermore, radial distribution function (RDF) calculations were used to confirm stability and structural changes between 0K and 300K. For interactions between nano-sized C15 clusters and nearby external point defects, the process of phase transformation at 300K was also simulated.

Finally, the concluding remarks are shown in Chapter 8. The particular process of the phase transformation at 300K offers a possible answer why nano-sized C15 Laves phase structures in bcc iron have never been reported experimentally.
Chapter 2

Molecular Dynamic Simulation

Molecular Dynamic (MD) simulation has been in development since the 1950s. In 1957 Alder and Wainwright used MD simulation to investigate the phase diagram of a hard sphere system and began calculating the macroscopic properties of materials [26]. In 1960, Gibson researched irradiation damage for crystal, which was the first time MD was applied in materials science [27]. A further milestone for materials science in MD simulation was the Parrinello-Rahman algorithm, which was related to the relaxations not only for particles in the system but also for the system volume [28]. By putting forward and developing many-body potentials, the MD method began to be implemented in semiconductor and metal systems. However, we found these potentials could not model electronic properties. In order to have a more accurate calculation of semiconductor and metal, Car and Parrinello combined Electron Theory with the MD method to propose the First Principle method in 1985 [29]. Moreover, MD can also be used to deal with organic matter and chemical reactions. In 1991, Cagin and Pettie created the grand canonical ensemble [30] for MD method that was easy to solve adsorption problems. Nowadays, MD can be widely applied in fields such as condensed matter physics, materials science, nanoscience, nuclear engineering, biochemistry and drug design.

In this chapter, the MD simulation method is explained first, and then empirical potential, MD algorithms, and the multi-step method are discussed. At last, the related analysis techniques used in the present work are briefly introduced.
2.1 Molecular Dynamic (MD) simulation method

Simulations act as a bridge to connect theory and experiment. MD simulation is the equivalent to a real experiment; a “digital experiment”. Classical MD uses classical dynamics, ie Newton’s law, to describe the evolution of position $\vec{r}$ and velocity $\vec{v}$ of each particle. The state of the system constituted by N atoms and a unique point in the 6N dimensional phase space consisted of 3N positions and 3N velocities.

Assuming the mass of $i$th atom is $m_i$, the position is $\vec{r}_i$, the displacement of atom $i$ and $j$ is $r_{ij} = |\vec{r}_i - \vec{r}_j|$, the interaction potential of atom $i$ and $j$ is $\phi(r_{ij})$, the total potential energy of the N atoms system is:

$$U(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \sum_{i=1}^{N} \sum_{j=1}^{N} \phi(r_{ij})$$  \hspace{1cm} (2-1)

Depending on the classical mechanics, the force of atom $i$ in the system is the negative gradient of potential energy:

$$\vec{F}_i = -\nabla_i U = -\left( \vec{i} \frac{\partial}{\partial x_i} + \vec{j} \frac{\partial}{\partial y_i} + \vec{k} \frac{\partial}{\partial z_i} \right) U$$  \hspace{1cm} (2-2)

Based on Newton’s law, the acceleration of atom $i$ can be written as:

$$\vec{a}_i = \frac{\vec{F}_i}{m_i}$$  \hspace{1cm} (2-3)

As the initial velocity of atom $i$ is $\vec{v}_i^0$, the initial position is $\vec{r}_i^0$, the time integration of Newton’s law can predict the position and velocity of atom $i$ after the time $t$, where

$$\frac{d^2}{dt^2} \vec{r}_i = \frac{d}{dt} \vec{v}_i = \vec{a}_i$$  \hspace{1cm} (2-4)
\begin{align*}
\vec{v}_i &= \vec{v}_i^0 + \vec{a}_i t \\
\vec{r}_i &= \vec{r}_i^0 + \vec{v}_i^0 t + \frac{1}{2} \vec{a}_i t^2
\end{align*}

The main task for Molecular Dynamic simulation is to solve the classical Newton’s equation. At first, the total potential energy of the system can be calculated by the position of each atom. The force and acceleration of each atom can then be predicted by setting $t = \delta t$ to a very short time interval. This procedure can be repeated until the position and momentum of all the atoms is known at every moment, which means the trajectory of atoms in the phase space can be tracked. Due to this ability to track trajectory at all times, the MD method does not have random factors. In microcosmic physical systems, the motion of atoms can be described by Newton’s equation. The intrinsic kinetics of the movement of each atom depends on Hamiltonian or Lagrangian mechanics. The energy of an atomic system can be treated within the frame of quantum mechanics; Lagrangian mechanics are convenient to treat the evolution of many-body interactions. The properties of the system, such as total energy, temperature, pressure and relaxation volume can be obtained based on classical statistical mechanics.

### 2.2 Empirical potentials

In the conservative system studied here, the force can be calculated from the potential energy, which depends on the relative positions of all particles in the system. Generally, in order to save computational time in MD calculations, the empirical potential is usually used as effective potential by setting a cutoff distance time [31]. There are several basic potential types commonly used in MD simulations for metallic systems: pair potential, Finnis-
Sinclar (FS) potential or embedded atom method (EAM). In this thesis, the FS and EAM type potential is used for Fe-Fe. These two potentials will be revisited in later sections.

### 2.2.1 Pair potential

Pair potential assumes that the interaction of atoms is only based on the position of every two atoms. When calculating the force between two atoms, we don’t need to concern ourselves about other atoms. The pair potential $U(r_{ij})$ has a strong repulsive interaction at short interatomic distances, changes to an attractive interaction at intermediate separations, and then finally has no interaction at longer distances. Therefore, the pair potential is usually written into two parts: the short strong repulsive $U_R$ and long attractive $U_A$ interactions as a function of interatomic distance $r_{ij}$. The Lennard-Jones potential is an example pair potential that describes inert gas or neutral molecule interactions, and can be written as:

$$U(r_{ij}) = U_R + U_A = 4\varepsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

Where $\varepsilon$ and $\sigma_{ij}$ are the free parameters which refer to properties of the material. In early years, the MD method was mainly used to simulate liquid and inert gases. Then some typical pair potentials were developed, such as the Lennard-Jones (LJ) potential [32], Morse potential [33] and Born-Mayer (B-M) potential [34]. LJ potential is used to calculate the binding energy, the equilibrium lattice constant and the bulk modulus of inert gases in solid state [35]; Morse potential is often used for determining the interaction of cubic metal atoms [36,37] and Covalent bonding atoms [38]; B-M potential was based on Morse
potential, which is suitable for studying the basic properties of ionic crystals, like NaCl and KBr [35].

### 2.2.2 Many-body potential

Although pair potentials are still useful for a basic understanding of material properties, the agreement between their simulations results and experiments can only be qualitative at best. They are physically justified for inert elements and some interactions between inert gas and metals if no important bonding features are involved in these interactions. Pair potentials do not have environment dependence and cannot account for any directional nature of the bond. Therefore, it is known that the total energy resulting from pair potential is only a part of a metal’s total energy. To correct this discrepancy, one method is to add a density-dependent but structurally-independent term to describe the total bonding energy [39]. The potential corrected with this method cannot be used in lattice defect studies because the assumption of homogeneous density is not correct. A second method is to include a many-body term in the potential energy, which will lead to a "many-body" potential such as the embedded atom method (EAM) and Finnis-Sinclair (FS) potentials.

Using the density functional theory (DFT) [40], Dew and Baskes first proposed the embedded-atom method in 1984 [39]. Later the EAM potential was improved to characterize the interactions of bcc or fcc transition metals and their alloys [41-43]. Assuming one given atom is embedded into uniformly distributed electrons, the EAM potential can be considered as the energy that relates to the local electron density by the DFT [40,44]. Basically, the total electron density near a given atom is the sum of the
electron densities of this atom and its surrounding atoms. Thus, the total potential can be divided into two parts: one part is the pair potential of two-body interactions and the other is the embedded energy of the many-body interaction. The total energy of the system with \(N\) atoms can be described as:

\[
U_{EAM} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \varphi_{ij}(r_{ij})
\]  \hspace{1cm} (2-8)

\[
\rho_i = \sum_{j \neq i} f_j(r_{ij})
\]  \hspace{1cm} (2-9)

Where the first term \(F_i(\rho_i)\) on the right side is the embedded energy, the second term \(\frac{1}{2} \sum_i \sum_{j \neq i} \varphi_{ij}(r_{ij})\) is the two-body interaction. \(\rho_i\) is the local electron density around atom \(i\). \(r_{ij}\) is the interatomic distance between atom \(i\) and atom \(j\). \(f(r)\) is the local electron density radial function. \(F, \varphi,\) and \(f\) refer to the different metal models used.

The EAM potential is suitable for calculating most properties of bcc and fcc metals because the properties of their alloys can be calculated directly by using the simple metal potential. Subsequently, Baskes proposed the modified embedded-atom method (MEAM) [45] and EAM-LJ potential [46] to make up the disadvantages of traditional EAM potential.

In 1984, based on the second-moment approximation of the tight-binding scheme potential (TB-SMA), Finnis and Sinclair proposed the FS potential as a new empirical many-body potential [47]. Using the FS potential, many scholars fitted the bcc or fcc metal potential and also explored physical properties such as defects, phase transformation and diffusion of pure metals and alloys. For example, Finnis and Sinclair built the FS potential for metals like Ni, Ta, C, W and Fe [47]. Ackland focused on the properties of point defects
and surface and grain boundaries of noble metal alloys and the noble metals Cu, Ag, Au and Ni [48,49]. Then, in 1994, Calder developed the FS potential to calculate large defects like clusters and displacement cascades for Fe-Fe [50]. Recently, Rudd researched void growth in bcc metals by using FS potential [51]. In this thesis, one potential used for the properties of C15 Laves phase structures in pure Fe is the Calder FS potential. Compared to the EAM potential function, the embedded function of FS potential has a square root dependence. The expression of total energy of the system with \( N \) atoms is:

\[
U_{\text{FS}}(r_{ij}) = \frac{1}{2} \sum_{i \neq j = 1}^{N} V_{ij}(r_{ij}) - \sum_{i = 1}^{N} \left[ \sum_{j \neq i = 1}^{N} \phi_{ij}(r_{ij}) \right]^{1/2}
\]  

(2-10)

Where the first term on the right is the repulsive interaction of the pair potential and the second term is the attractive interaction of the many-body potential. \( r_{ij} \) is the interatomic distance between atom \( i \) and atom \( j \). The function \( V_{ij} \) and \( \phi_{ij} \) only depend on the distance \( r_{ij} \). The two-body term have the form of 3rd-order knot functions

\[
V_{ij}(r_{ij}) = \sum_{a=1}^{N} p_a [H(r_a - r_{ij})](r_a - r_{ij})^3
\]

(2-11)

\[
\phi_{ij}(r_{ij}) = \sum_{b=1}^{M} q_b [H(r_b - r_{ij})](r_b - r_{ij})^3
\]

(2-12)

Where \( p_a \) and \( q_b \) are the knot coefficients, \( r_a \) and \( r_b \) are knot points. \( M \) and \( N \) the number of knots used in the functions. \( H \) is the Heaviside function

\[
H = \begin{cases} 
1 & x < 0 \\
0 & x \geq 0 
\end{cases}
\]

(2-13)
While cascade collision may slightly expand the distance between two atoms in the system, the potential of the system was mainly contributed to by the repulsive term of the pair potential $V_{ij}(r_{ij})$. So FS potential needs to be remodeled to accurately describe the interaction of atoms, especially for the repulsive term of the pair potential. In order to accurately adjust the interaction of atoms as Cu-Cu, Fe-Fe and Cu-Fe under irradiation damage process, universal screened Coulomb function [52] was used instead of the repulsive term of the pair potential in FS potential function:

$$V_{ij}(r_{ij}) = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{ij}} \psi(X), \quad r_{ij} \leq r_1;$$

(2-14)

$$\psi(X) = 0.1818 \exp(-3.2X) \pm 0.5099 \exp(-0.9423X)$$

$$+ 0.2802 \exp(-0.4029X) + 0.02817 \exp(-0.2016X);$$

(2-15)

$$X = \frac{r_{ij}}{a_s};$$

(2-16)

$$a_s = 0.44267 a_B / \left( \frac{Z_A^{2/3} + Z_B^{2/3}}{2} \right)^{1/2};$$

(2-17)

Where $a_B$ is the Bohr radius, $e$ is the electronic charge and $\varepsilon_0$ is the permittivity of free space. $Z_A$ and $Z_B$ are the atomic number of atom A and B, $\psi(X)$ is the screen function. $r_{ij}$ is the interatomic distance between atom $i$ and atom $j$, $r_1$ is the fitted parameter.

Therefore, when the distance of two atoms satisfies $r_{ij} \leq r_1$, the repulsive term of pair potential is represented by universal screened Coulomb function. However, when $r_{ij} \geq r_2$ and $r_2 > r_1$, the repulsive term of pair potential $V_{ij}(r_{ij})$ was represented by the 3rd-order knot functions. In order to ensure the potential function itself and its first
derivative are continuously at the knot $r_1$ and $r_2$, and simple interpolation function $V_{ij}(r_{ij})$ is used. In addition, the value of fitting parameters $r_1$ and $r_2$ should make the second derivate of $V_{ij}(r_{ij})$ as smooth as possible. So when the value of $r$ is between $r_1$ and $r_2$, $V_{ij}(r_{ij})$ is shown as:

$$V_{ij}(r_{ij}) = \exp\left(c_0 + c_1 r_{ij} + c_2 r_{ij}^2 + \cdots + c_n r_{ij}^n\right), \quad r_1 < r_{ij} < r_2 \quad (2-18)$$

Where $r_{ij}$ is the interatomic distance between atom $i$ and atom $j$, $c_0, c_1, c_2, \ldots, c_n$ are the fitting parameter.

In reality, the potential is very complicated. The potential is always called the empirical potential, and potential functions are always defined as piecewise functions in a different range of distance. So the potentials need to be fitted within the whole range of distance, especially at the boundary points.

### 2.3 Numerical algorithms

Before computer simulation became available, people used mathematical analytic methods based on statistical theory to comprehend the structures and properties of many-body systems affected by interatomic forces. However, when the interatomic forces became more complex, it was not only hard to solve the statistical mechanics equations, but also hard to find the numerical solution. The molecular dynamic method can numerically solve and analyze the deterministic motion equations of many-body systems. Furthermore, the molecular dynamic method can also yield information about trajectories, structures and dynamics on the atomic scale, and, by using statistical theory, predict
material behavior at a nanometer scale. So numerical algorithms are very important for MD simulations. The MD method can be seen as an initial value problem, and can mainly use the finite difference method (FDM) to discretize the motion equation to finite difference equations. Computational Mathematics has already made many algorithms used for MD simulations; the common methods are the Verlet algorithm [53] and Gear method [54]. In this thesis, the 3rd-order predictor-corrector Gear method is used as the algorithm to solve the simultaneous differential equations.

In classical mechanics, the motion trajectory of atoms should be continuous with time dependence. The positions, velocities and accelerations can be obtained by a time $t$ dependent Taylor series expansion:

$$
\vec{r}^p(t + \Delta t) = \vec{r}(t) + \Delta t\vec{v}(t) + \frac{1}{2}\vec{a}(t)(\Delta t)^2 + \frac{1}{6}\vec{b}(t)(\Delta t)^3 + \cdots \tag{2-19}
$$

$$
\vec{v}^p(t + \Delta t) = \vec{v}(t) + \Delta t\vec{a}(t) + \frac{1}{2}\vec{b}(t)(\Delta t)^2 + \cdots \tag{2-20}
$$

$$
\vec{a}^p(t + \Delta t) = \vec{a}(t) + \Delta t\vec{b}(t) + \cdots \tag{2-21}
$$

$$
\vec{b}^p(t + \Delta t) = \vec{b}(t) + \cdots \tag{2-22}
$$

Where the superscript refers to the predicted value. The $r$, $v$ and $a$ represent position, velocity and acceleration of the atom respectively, $b$ is the third derivative of the position with regard to time. The initial position and velocity of each particle are usually given as constants [55] and we can obtain the predicted values for position, velocity, and acceleration. So this algorithm really depends on the first predicted value. The Gear algorithm provides the correction term based on a predicted acceleration $\vec{a}^p(t + \Delta t)$ and a
certain acceleration \( \vec{a}^c(t + \Delta t) \) which can be known by the certain position and force calculated at the time \((t + \Delta t)\):

\[
\Delta \vec{a}(t + \Delta t) = \vec{a}^c(t + \Delta t) - \vec{a}^p(t + \Delta t)
\]

(2-23)

Therefore, the new corrected position, velocity and acceleration are:

\[
\Delta \vec{r}(t + \Delta t) = \vec{r}^c(t + \Delta t) - C_0 \vec{r}^p(t + \Delta t)
\]

(2-24)

\[
\Delta \vec{V}(t + \Delta t) = \vec{V}^c(t + \Delta t) - C_1 \vec{V}^p(t + \Delta t)
\]

(2-25)

\[
\Delta \vec{a}(t + \Delta t) = \vec{a}^c(t + \Delta t) - C_2 \vec{a}^p(t + \Delta t)
\]

(2-26)

\[
\Delta \vec{b}(t + \Delta t) = \vec{b}^c(t + \Delta t) - C_3 \vec{b}^p(t + \Delta t)
\]

(2-27)

Where \( C_0=1/6 \), \( C_1=5/6 \), \( C_2=1 \) and \( C_3=1/3 \) are the coefficients given by Gear [55].

### 2.4 Multi-step methods for C15 Lave phase MD simulations

Length and time scales are the two typical limitations of MD applications in large systems and long-time processes. In this thesis, periodic boundary conditions (PBC) will be widely used. Due to the limited calculation efficiency of the MD method, the largest number of atoms that can be reached in the simulation system is around \( 1 \times 10^8 \). Generally, the PBCs should be in full space to eliminate the effect of surfaces on the state [55]. For instance, we can roughly calculate the volume of pure Fe consisting of \( 1 \times 10^8 \) atoms. The lattice parameter of pure Fe is about 2.8665 Å, and each unit cell has two Fe atoms. So the volume of \( 1 \times 10^8 \) atoms of Fe in the simulation box is 0.00118 \( \mu m^3 \). This means the real size of the simulated box is only in a 0.1 \( \mu m \) scale, although a massively parallel computation was applied. Thus, the PBCs should be used in simulation systems with a limited number of atoms, instead of the large numbers of atoms found in real systems. The 2D PBC diagram is shown in Figure 2. The simulation box is the shaded part in the center.
The other 8 boxes, A to H, are the periodic mirror images of the simulation box. The interactions of atom 1 are not only with other atoms in the simulation box, but also with the 8 periodic mirror images, as shown in Figure 2. The limiting conditions make the total number of atoms and the density in the simulation system remain constant. Also, the position of the boundary no longer has any substantial effect on the simulation system. In order to reflect the real macro system, limited simulation boxes are used to build a quasi-infinite volume. Therefore, the simulation box we used to set the C15 Laves phase structure should be large enough to avoid interaction with its periodic mirror images.

![Figure 2. The periodic boundary conditions shown in a 2D diagram [55].](image)

In addition, when only bcc iron is involved, a time step of fs (10^{-15}s), which is appropriate to simulate the large atomic mass, is usually used to obtain the motion equations for the C15 Laves phase structure. The total number of steps is reliant on the time it takes for the system to return to equilibrium. The multiple-step algorithm can be summarized as follows:
(1). Initialize the initial position and velocity for each bcc Fe atom to make the C15 Laves phase structure, with each atom having 6N (N is the number of atoms) variables;

(2). Set the required temperature, pressure and boundary conditions, and then choose the reasonable thermodynamic ensemble;

(3). Compute all forces and solve the equations of motion;

(4). Repeat n total time steps until the system re-reaches equilibrium;

(5). Average after n total time steps to print the properties of the interest.

Step (3) is the most time-consuming step of the whole simulation process. In MD simulations, there are many algorithms that can be used for greater efficiency in the multi-step method; the selection of the algorithm is dictated by the needs of the research. In this thesis, the Gears method is used to accelerate the computational efficiency of short-range and long-range forces. Step (5) refers to the statistical analysis; this average minimizes the calculation errors. The n total time steps not only depend on the state of system but the physical properties of interest [56].

2.5 Analysis techniques

MD simulation directly obtains the time-dependent trajectory of all atoms; the quantities of atom trajectory mainly contain position and velocity. However, when discussing thermodynamic and kinetic material behavior, some macroscopic physics quantities such as energy, temperature, pressure must be researched. These can be gained by using the microscopic results obtained by MD simulation to analyze the system’s macroscopic properties. Moreover, focusing on the different simulation objects, the atom
In order to systematically distinguish the local atomic environment, the common neighbor analysis (CNA) is used to analyze the atoms in pure C15 and C15 Laves phase structures with defects from a matrix-perfect bcc Fe lattice [57]. The CNA is based on the geometry of the local atomic environment, which means the position of each atom relative to its surrounding coordination is very important. The geometry of the local atomic environment, in our case, is a crystal lattice environment, which is a uniform structure of metals such as fcc, bcc and hcp. The CNA method also can be described as the decomposition of the radial distribution function (RDF) [57]. The first peak of the RDF refers to the nearest neighbors. The distance between each ‘bonded’ pair of atoms can be defined as $r < r_c$, where $r_c$ is the position of first minimum of the RDF. Each pair of atoms is defined by a set of three indices, $jkl$ [57]. This algorithm was updated to research the MD results, which were simulated at different finite temperatures. The thermal fluctuation affects the position of each atom because of the different finite temperature relaxations. In this way, the thermal fluctuations can be used to determine $r_c$ as the critical value to determine if the bonding between two atoms will occur. The value of $r_c$ can be seen as a length that is slightly larger than the first nearest neighbor peak. In this thesis, the value of $r_c$ is between the first and second nearest neighbor of bcc iron. By using CNA, the three indices $jkl$ are defined as follows [57]:

- $j$: the number of neighbors common to both atoms;
- $k$: the number of bonds between these common neighbors;
$l$: the number of bonds in the longest continuous chain formed by the $k$ bonds between common neighbors.

Three indices $jkl$ of fcc and hcp structure are shown in Figure 3. The local geometrical environment can be distinguished after illustrating the specified $jkl$ of each pair of atoms and the coordination number of nearest neighbor distance.

**Figure 3.** Illustration of the classification of pairs of atoms according to their local environment, which in CN analysis is characterized by the three indices $jkl$ [57].
Chapter 3

Interaction Potential of Fe-Fe

3.1 The verification of Fe-Fe potential

Potential, which describes the interaction of atoms, plays an important role in MD simulation. The interactions of atoms fundamentally control the structure of materials, intrinsic mechanics and electromagnetic properties. Therefore, whether the potential can truly correspond to the experimental results will determine the success or failure of MD simulations. The correct potential is determined via a two part process. One part focuses on the specific object, because potentials are divided into many different forms for different cases. Each potential has its own limitations and scope of application, and potentials must truly describe the specific interaction of atoms during simulation. So the form of the selected potential should be suited for the specific case. The second part of the process is to verify that selected potential can correctly embody the interaction of atoms, which means the fitted properties of the selected potential and experiment values should be as similar as possible. Thus, the correctness of the selected potential should be verified before MD simulation.

In previous literature, two main empirical potentials have been used to calculate the properties of self-interstitial clusters (C15 type) \[58,59\] and C15 Laves phase structures \[60-62\] in bcc Fe. The Calder and Bacon-1993 empirical potential \[63\], which is good for calculating displacement cascades in Fe, is an FS potential. The Calder and Bacon-1993 empirical potential has been abbreviated to FS-1993 in this thesis. Second, the EAM
potential by Ackland-2004 [64], is good for calculating radiation damage and point defect properties in Fe. Both empirical potentials have already been fitted and used for researching properties of C15 interstitial clusters in bcc Fe.

In this thesis, Ackland-2004 and FS-1993 empirical potentials were verified and calculated before MD simulations occurred using the energy minimization method [65] to optimize the simulation system. In order to avoid the existence of high energy effects in the simulation system, the starting point of the simulation should be the structure with the lowest energy state. The principle of energy minimization method makes the lattice parameter of a specific lattice structure vary within a certain range. The method can also calculate the potential energy, which corresponds to the range of the lattice parameter at 0K. Therefore, the lattice parameter with the minimum energy state can be obtained, which can determine the minimum energy simulation structure. In my work, the energy minimization method was used to verify the availability of Ackland-2004 and FS-1993 empirical potentials in bcc Fe. The potentials and their first and second derivatives were obtained in bcc iron at 0K in order to study the continuity of these two empirical potentials. Through calculation, the potentials themselves and the first derivative of the potentials were proven to be continuous. However, the second derivative of the functions of the original FS-1993 empirical potential was not completely continuous at three boundary points \((x = 0.0305nm, x = 0.062nm \text{ and } x = 0.235053nm)\) of the given range [63]. The plot is shown in Figure 4. These discontinuities may cause unreliable results when calculating the
properties of pure bcc Fe and C15 Laves phase structures in bcc Fe. Consequently, the FS-1993 empirical potential needs to be re-optimized.

**Figure 4.** The Ackland-2004 and FS-1993 empirical potentials change with atomic distance in bcc Fe at 0K. The partially enlarged detail shows FS-1993 empirical potentials discontinuous at x=0.0305nm, x=0.062nm and x=0.235053nm.

### 3.2 Re-optimized the FS potential

The suitable potential function can be chosen according to the specific case; the parameter of this potential should be fitted first and then used in MD simulations. The original method for the fitting process is the least squares method, which makes the fitting properties as approximate to the experimental data as possible. In most cases, the experimental data refer to static properties, such as the lattice parameter, elastic constants,
vacancy formation energy, binding energy and so on. But here, all these static properties have been fitted already.

The original FS-1993 empirical potential consists of four piecewise functions [63]:

\[ x \leq 0.0305\text{nm}: \]
\[ V(x) = \frac{Z^2 e^2}{4\pi\varepsilon_0 x} \psi(x); \]  \hspace{1cm} (3-1)

\[ 0.0305\text{nm} \leq x \leq 0.062\text{nm}: \]
\[ V(x) = \exp(9.7262382 + 18.058868x - 2674.88847x^2 + 23381.5021x^3); \]  \hspace{1cm} (3-2)

\[ 0.062\text{nm} \leq x \leq 0.235053\text{nm}: \]
\[ V(x) = 7069.7203\exp(-43.991821x); \]  \hspace{1cm} (3-3)

\[ x \geq 0.235053\text{nm}: \]
\[ V(x) = \text{Finnis -- Sinclair function} \]  \hspace{1cm} (3-4)

My work is to use the method of least squares [66] to re-optimize the original FS-1993 empirical potential itself and the first and second derivative of the potential functions to be continuous and smooth everywhere, especially at the three points of discontinuity \( (x = 0.0305\text{nm}, x = 0.062\text{nm} \text{ and } x = 0.235053\text{nm}) \). Each function should be continuous at their given range. Equation (3-2) and (3-3) include these two points of discontinuity, so they need to be fitted. Although equation (3-4) has the discontinuity point as well, it can be used directly as a known potential function.

MATLAB was used to achieve the potential function curve fitting. The least squares method minimizes the sum of the squares of the errors made in the results of every equation
When the functions share the same boundary point, the potential function should be continuous both from the left and the right at this point. The equation (3-2) and (3-3) as the interpolation function were showed in the Chapter 3 equation (2-18). Although there are four high order terms for the equation (3-2) and two high-order for the equation (3-3), they are not enough to accurately make the potential function continuous. In order to improve the precision of the interpolation functions, two more higher-order terms for equation (3-2) and one more higher-order term for equation (3-3) were added as follows:

\[
V(x) = \exp(c_0 + c_1 x + c_2 x^2 + \cdots + c_5 x^5), \quad 0.0305nm \leq x \leq 0.062nm; \quad (3-5)
\]

\[
V(x) = a_0 \exp(a_1 x + a_2 x^2), \quad 0.062nm \leq x \leq 0.235053nm; \quad (3-6)
\]

Where \(c_0\) to \(c_5\), \(a_0\) to \(a_2\) are the fitting parameters. Each fitting parameter needs to be calculated by the method of least squares. At the boundary point \(x = 0.235053nm\), the value of potential energy itself \(V\) and its first and second derivative (\(V'\) and \(V''\)) can be obtained by the equation (3-4). Because of the continuity of the potential, these three values can be plugged into equation (3-6) itself and its first and second derivate. Then the three fitting parameters and three new values \(V_1(x), V_1(x)'\) and \(V_1(x)''\) can be solved. In the same way, \(c_0\) to \(c_5\) can be solved by using the equation (3-1) and (3-6) at the boundary points \(x = 0.0305nm\) and \(x = 0.062nm\). An example solution of equation (3-6) using MATLAB code is given in Appendix A. Thus, the updated FS-1993 potential \(V(x)\) are shown as:

\(x \leq 0.0305nm:\)
\[ V(x) = \frac{Z^2 e^2}{4\pi \varepsilon_0 x} \psi(x); \] (3-1)

0.0305nm \leq x \leq 0.062nm:

\[ V(x) = \exp(162.67298 - 1924.33065x + 9373.61374x^2 - 22067.97689x^3 \]
\[ + 244882.71641x^4 - 10790.60754x^5) \text{eV}; \] (3-7)

0.062nm \leq x \leq 0.235053nm:

\[ V(x) = 8.4962196\exp(-0.677592x - 0.3652877x^2)\text{eV}; \] (3-8)

\[ x \geq 0.235053nm: \]

\[ V(x) = \text{Finnis – Sinclair function} \] (3-4)

**Figure 5.** The FS-1993 empirical potential was re-optimized at the original discontinuous points (a) \(x=0.0305nm\), (b) \(x=0.062nm\) and (c) \(x=0.235053nm\) to make the potential continuous.
After re-optimizing the FS-1993 empirical potential, the continuity of the potential function around the three discontinuous points can be verified. The plot shows the distance dependence of potential curves around the three discontinuous points, which contrast between the original and re-optimized FS-1993 empirical potential in Figure 5. The curve is optimized, but it is not necessary to make the first-order and second-order derivative very smooth because they have no effect on calculating the elastic constants $C_{11}$ and $C_{44}$.

3.3 Fitting details: elastic constant $C_{11}$ and $C_{44}$

The elastic constant and the elastic modulus are two of the most basic physical properties for a crystal. One standard way to estimate if a many-body potential can correctly describe the interaction of atoms is to verify whether the elastic properties can be calculated by this potential and whether the results fit the experimental data.

Thermal fluctuation formulas were used to calculate the thermodynamic properties of the given models by using a fixed numbers of atoms, fixed pressure and fixed temperature (NPT) ensemble. The statistical mechanical formulas were used for calculating the elastic constants in NPT simulations as follows:

The force on atom $a$, $F_a$, can be obtained from the potential energy $E_{pot}$ given in Eq.:

$$F_a = -\frac{\partial E_{pot}}{\partial x_a}, \quad (3-9)$$

Which yields,

$$F_a = -\sum_{\substack{b=1 \ b \neq a}} \left[ \frac{\partial F_b}{\partial \rho_a} \frac{\partial \rho_a^{at}}{\partial r_{ab}} + \frac{\partial F_b}{\partial \rho_b} \frac{\partial \rho_b^{at}}{\partial r_{ab}} + \frac{\partial \phi_{ab}(r_{ab})}{\partial r_{ab}} \right] \hat{r}_{ab}, \quad (3-10)$$
Where \( \hat{r} \) describes a unit vector along \( r \), \( \phi_{ab}(r_{ab}) \) is the two-body interaction potential evaluated at the interatomic distance \( r_{ab} \), \( \rho_a \) is the electron density at atom site \( a \) due to all other atoms in the system

\[
\rho_a = \sum_{\substack{b=1 \\ b \neq a}} \rho_b^{at}(r_{ab}),
\]

(3-11)

The microscopic stress tensor can be obtained from the virial theorem and has the form [67-69]:

\[
P_{ij} = \frac{1}{V} \left[ \sum_{a=1}^{N} \frac{p_{ai} p_{aj}}{m_a} - \sum_{a,b=1}^{N} \frac{\left( F'_a \rho_{a}^{at} + F'_b \rho_{b}^{at} + \phi'_{ab} \right) x_{abi} x_{abj}}{r_{ab}} \right] + \frac{2 N k_B T}{V_0} \left( \frac{\delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk}}{r_{ab}} \right)
\]

(3-12)

Where \( V \) is the volume of the system, \( p_{ai} \) is the \( i \)th Cartesian component of the momentum of particle \( a \), and \( x_{abi} \) is the \( i \)th component of the relative position vector of atoms \( a \) and \( b \).

As we all know, the elastic constants \( C_{ijkl} \) is a second-order fourth-rank tensor. The components of tensors are not very complex, so linear Hooke’s law is used in the calculation process. Strain does not have a large effect on elasticity, which makes \( C_{ijkl} \) widely used in the description of the mechanical properties of materials. The elastic constants \( C_{ijkl} \) can be determined by using fluctuation formulas [47-49]:

\[
C_{ijkl} = -\frac{V_0}{k_B T} \left( \langle P_{ij} P_{km} \rangle - \langle P_{ij} \rangle \langle P_{km} \rangle \right) + \frac{2 N k_B T}{V_0} \left( \delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk} \right)
\]

(3-13)

\[
+ \left( \langle B_{1ijkl} \rangle + \langle B_{2ijkl} \rangle + \langle B_{3ijkl} \rangle \right),
\]

Where \( T \) is the temperature of the system, \( k_B \) is the Boltzmann constant, \( P_{ij} \) are components of microscopic stress tensor, \( \delta \) is strain fluctuations. The first term is the fluctuation term,
while the second term is temperature correction term. The third term consists of three Born terms which were given by [47-49]:

\[
B_{1ijkm} = \frac{1}{V_0} \sum_{a,b=1}^{a<b} \left( \phi''_{ab} - \phi'_r \right) \frac{x_{abi}x_{abj}x_{abk}x_{abm}}{r_{ab}^2},
\]

\[
B_{2ijkm} = \frac{1}{V_0} \sum_{a,b=1}^{a\neq b} \left( \rho'' b - \rho'_r \right) \frac{x_{abi}x_{abj}x_{abk}x_{abm}}{r_{ab}^2},
\]

\[
B_{3ijkm} = \frac{1}{V_0} \sum_{a=1} F''_a g_{aij} g_{akm},
\]

And \( g_{aij} \) is shown as

\[
g_{aij} = \sum_{b=1}^{b\neq a} \frac{\rho'' b x_{abi}x_{abj}}{r_{ab}}.
\]

### 3.4 Fitting results and comparison with experimental data

In the present work, the equations in the former section were used to calculated elastic constant \( C_{11} \) and \( C_{44} \) by Ackland-2004 and updated FS-1993 empirical potentials in bcc iron. These elastic constants as the function of the temperature were plotted every 100K, starting from 0K to 500K. For the experimental elastic constant, the data from experiment one were reported by D. J. Dever in 2000 [70], other more recent data, from experiment two were given by Adams et. al. in 1972 [71]. The experimental and theoretical results will be compared in order to find a better potential for our simulations.
Figure 6 (a) and (b) show the temperature dependence of elastic constant $C_{11}$ and $C_{44}$ obtained with the two given potentials as well as the two experimental datasets of bcc iron. One point of concern is that each empirical potential as a model is not able to exactly match all the behavior of the materials. The current research focus of empirical potentials is how to use Fe-Fe potential to reflect iron properties at high temperatures. So far, the reported Fe-Fe potentials are all fitting the properties at 0K or room temperature. For high temperatures, especially higher temperature calculations, the Ackland-2004 potential reflect the closest trend of experimental data of all empirical potentials. For the plot about $C_{11}$ and $C_{44}$, all the data shows the same gradually decreasing trend until the temperature reaches 500K. The Ackland-2004 potential will be influenced by magnetic disturbances at around 500K such that the Ackland-2004 simulation value of $C_{44}$ changes slightly more than the experimental data, however, the value of the FS-1993 calculation is much lower than others. In this thesis, the difference between the Ackland-2004 simulation value and the experimental value of $C_{44}$ can be accepted because to some extent the Ackland-2004 potential reflect the best variation trend of iron properties from 0K to 500K. In summary, the Ackland-2004 empirical potential is closest to the experimental conditions and will be used to study the stability of perfect C15 Laves phase structures made of iron atoms.
Figure 6. Comparison between experimental and theoretical data for temperature dependence of elastic constant $C_{11}$ (a) and $C_{44}$ (b) values of bcc Fe.
3.5 Summary

An appropriate empirical potential is the one that best conforms to the experimental data potential through MD and MS calculations. A.F. Calder-1993 and Ackland-2004 empirical potentials have already been used to calculate some properties of the C15 Laves phase structure in bcc iron. However, when repeating the calculation, the A.F. Calder-1993 empirical potential was found not completely continuous in three points. For this reason, the least square method was used to re-optimize the A.F. Calder-1993 potential. After calculating the elastic constant of perfect bcc iron by using these two potentials and comparing their data with the experimental data, we found that the Ackland-2004 potential is better fitting for the experimental data and can be used in the following calculations.
Chapter 4

The stability of perfect C15 Laves phase structure

For this chapter, MD simulation was used to research the stability of perfect C15 Laves phase structures made of iron atoms. The MD simulation was performed using Fortran 90 codes. The simulation cell was a 4×4×4 perfect C15 Laves phase structure of 1536 atoms. When calculating this model, Ackland-2004 empirical potential, discussed in Chapter 3, Section 3.1, was used to describe the interaction of Fe-Fe atoms. While focusing on temperature fluctuations, the energy and position of each atom in perfect C15 Laves phase structures may change, so the temperature dependence of elastic properties and phase transformation are the main criteria to study the stability of the structures. Through analysis of the simulation results, the phase transformation temperature can be determined. Unless otherwise indicated, this chapter and subsequent chapters all use Ackland-2004 empirical potential and NPT ensemble.

4.1 The simulation Model

The C15 Laves phase structure is a Frank–Kasper phase structure and has topologically close-packed organization. Generally, the C15 Laves phase structure has an AB₂ cubic structure and can be seen composed of two substructures. The larger A atoms have a diamond cubic structure, while the smaller B atoms can form four regular tetrahedral structures. For example, MgCu₂ is one of the typical C15 Laves phase structures. A atoms occupy the site of Mg, B atoms occupy the site of Cu. The projection of the C15 structure on the basal (XY) plane is shown in Figure 7 [72]. In Figure 7, each shaded atom, which
represents the A atom, has four nearest neighbor A atoms at a distance of $\sqrt{3}a/4$ and twelve nearest neighbor B atoms at a distance of $\sqrt{11}a/8$. Each white atom, which represent B atom, has six nearest neighbor B atoms at a distance of $\sqrt{2}a/4$ and six nearest neighbor A atoms at a distance of $\sqrt{11}a/8$ [72].

![Diagram](image)

**Figure 7.** A projection of cubic C15 (MgCu$_2$) structure on the basal (XY) plane is shown in a unit cell with lattice parameter $a$, where the number is the Z coordinate of the atoms. Shaded atoms indicate A atoms, blank atoms indicate B atoms [72].

A 4x4x4 simulation box of a perfect C15 Laves phase structure was built of bcc iron, with a total of 1536 atoms. Larger simulation models were tested to ensure that defect properties did not measurably change. Periodic boundary condition is used during the whole calculation. This size of simulation box is enough to avoid the interaction with its periodic mirror images. By minimizing the energy at 0K, the lattice parameter and potential energy corresponding to each atom in the minimum energy system can be obtained. The lattice parameter for perfect C15 Laves phase structures at 0K is 6.663309Å. There are only
two kinds of potential energies in the system which belong to the two different types of atom shown in Table 1. The potentials were obtained at 0K after relaxing the whole system.

**Table 1.** The potential energy of A and B atoms in pure C15 Laves phase structures at 0K.

<table>
<thead>
<tr>
<th>Atomic species</th>
<th>A atoms</th>
<th>B atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ep(eV)</td>
<td>-4.25312</td>
<td>-3.62368</td>
</tr>
</tbody>
</table>

A atoms have lower potential energy than B atoms. Figure 8 is a three-dimensional representation of a perfect C15 Laves phase structure in a unit cell on the basal (XY) plane under the minimum energy system at 0K. The shaded part in Figure 8 is a regular tetrahedron structure formed by four red atoms which represent the position of B atoms. There are a total of four regular tetrahedrons in one unit cell. The blue spheres represent the position of A atoms.

**Figure 8.** Atomic projection of three-dimensional structure of a perfect C15 Laves phase structure on the basal (XY) plane in a unit cell. The blue spheres represent A atoms and the red spheres represent B atoms.
4.2 Temperature dependence of elastic constants and elastic moduli

The elastic constants were determined by performing an iterative computation which minimizes the error between the measured and calculated frequencies. The elastic constants $C_{11}$, $C_{12}$ and $C_{44}$, which depend on thermal fluctuation, can be calculated by using the equation (3-13). For the simulation of a perfect C15 Laves phase structure in bcc iron, the simulation box was assumed homogeneous and isotropically symmetric. So only two independent elastic moduli, $C_{11}$ and $C_{44}$, are required to fully define the elasticity of the system. These two elastic moduli can be used to compute shear modulus $G$ and Young’s modulus $E$:

Shear modulus: $G = C_{44}$

Young’s modulus: $E = C_{44} \frac{3C_{11} - 4C_{44}}{C_{11} - C_{44}}$

The shear modulus can measure the stiffness of the material and will be affected by many factors, such as melting temperature and pressure. Typically, the value of the shear modulus of bcc iron at room temperature is 52.5GPa [73]. Young’s modulus, as a mechanical property of linear elastic solid materials, is also a measure of the stiffness of solid materials. Young’s modulus focuses on the relationship between stress and strain. The elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ as a function of temperature, and two elastic properties, Young’s and shear moduli, also as a function of temperature, were obtained with the Ackland-2004 empirical potentials, plotted in Figure 9. It is assumed that the crystal directions have no effect on Young’s modulus. In order to study the variation trend of the elastic constants and elastic moduli affected by the temperature, the average value of the data was collected incrementally every 25K until a major change was detected.
Figure 9. Elastic properties of a perfect C15 Laves phase structure calculated using Ackland’s potential. (a) Elastic constants $C_{11}$, $C_{12}$ and $C_{44}$; (b) shear and Young’s moduli.
Figure 9(a) shows the temperature dependence of elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. If the temperature is higher than 425 K, elastic constant $C_{44}$ of the structure decreases rapidly. $C_{11}$ increases gradually from 0K to 450K. $C_{12}$ has a slight decrease after 425K. Figure 9(b) shows the temperature dependence of Young’s modulus and shear moduli. Young’s modulus and shear moduli were calculated by equation (4-3) and (4-4). We can see after 425K, both moduli decreased rapidly. Therefore, the relationship between stress and strain in the system has already changed. Usually, the shear modulus and the Young’s modulus of a material should decrease with increasing temperature, but in this case, both moduli gradually increased from 0K to 425K. Considering this from an MD perspective, perfect C15 Laves phase structures are not stable as bcc iron. With each temperature change, energy minimization should be performed in the whole system to find the stable state. Higher temperatures may cause the atoms to move with greater ease into a more stable structure after relaxation. This is one explanation for the positive correlation between temperature and elastic properties. Experimentally, this situation has already happened in a C15 Laves phase compound Hf$_{25}$V$_{60}$Nb$_{15}$. F. Chu found the anomalous elastic properties of Hf$_{25}$V$_{60}$Nb$_{15}$ in 1994, finding that the shear modulus and Young’s modulus increase in conjunction with temperature at temperatures between 0K and 300K [74]. Also, K. Foster found that temperature dependences of shear modulus and Young’s modulus of the C15 Laves phase material TaV$_2$ were anomalous with increasing temperature within the range of 0K to 345 K [75]. So the result in this thesis is plausible.

Figure 9(b) illustrates a plummet of both shear modulus and Young’s modulus values after 425K. This means that if the temperature is over 425K, the stiffness of the structures will change. In these conditions, the whole system may no longer be stable and may not
maintain its original structure. Some atoms will jump to other positions to make the whole system stabilize by returning to minimum energy. At this stage, phase transformation may happen and perfect C15 Laves phase structures can be proven to be in a metastable phase. Thus, perfect C15 Laves phase structures in bcc iron can exist at room temperature.

The phase transformation process for a perfect C15 Laves phase structure around the possible phase transformation temperatures has been given in Figure 10. Comparing the perfect C15 Laves phase structure at 0K with the structure at 400K, only a small change is seen in Figure 10(a) and (b). In general, structural changes affect the performance of materials. However, the small structural changes seen here will not affect the performance of the perfect C15 Laves phase structure because the whole system readily reaches a stable state at 400K via a small number of atomic movements. Correspondingly, Figure 9 indicates the elastic properties of the perfect C15 Laves phase structure could keep gradually increasing from 0K to 400K. The C15 Laves phase structure is a metastable structure; phase transformation will happen if the temperature is high enough to induce a

![Figure 10](image)

**Figure 10.** The atomic projection of phase transformation for a perfect C15 Laves phase structure around the phase transformation temperature after relaxation on the basal (XY) plane. (a) is the original structure relaxed at 0K; (b), (c), (d) show the transient states of the structure at 400K, 425K and 450K after relaxation.
loss of stability within the structure. From Figure 10(c), we see that the bulk of the atoms displace and the original structure is not stable at 425K. Figure 10(d) illustrates that all the atoms in the system are disordered at 450K in the process of finding a new stable state, which causes the distinct decreases in elastic properties shown in Figure 9. Comparing the changes of elastic properties with structural changes around the possible phase transformation temperatures, we can see that 425K is the phase transformation temperature for perfect C15 Laves phase structure.

Each second-order fourth-rank tensor $C_{ijkl}$ contains a thermal fluctuation term, a temperature correction term and three Born terms, which have already been discussed in Section 3.3. The $P_{ij}$, which restores force from atomic displacement, relates to the thermal fluctuation term. The three Born terms contribute to the temperature dependence of elastic constants. From Figure 9 we can see that the temperature dependence of $C_{44}$ has the most effect on the elastic properties of perfect C15 Laves phase structures, so the three Born terms $B1_{C_{44}}$, $B2_{C_{44}}$, $B3_{C_{44}}$ and the microscopic stress tensor $P_{44}$ are analyzed under different temperatures. All three of these Born terms refer to Ackland-2004 potential. $B1$ and $B2$ terms are pair terms of this potential and $B3$ focuses on the curvature of the potential function [69]. Figure 11 shows how these four terms vary at different temperatures when the perfect C15 Laves phase structure is in a stable state. Since the structure is stable below 425K, the chosen temperatures are every 100K from 0K to 400K. The timestep is every 100 fs from 10000 fs to 15000 fs to ensure whole system stability within the minimum energy state. Figure 11(a)-(c) shows the temperature dependence of $B1_{C_{44}}$, $B2_{C_{44}}$, $B3_{C_{44}}$. These values of the three Born terms at 0K can be seen as a standard reference. Then, the values of the three Born terms from 100K to 400K all vibrate near an average
value, which keeps steadily rising. These results fit with the plotted trend of $C_{44}$ in Figure 9(a). From Figure 11(d) we can see that the value of $P_{44}$ vibrates around 0 GPa, which means the system has almost no external forces and the temperature dependence of elastic constants are not being affected by the thermal fluctuation term. It is proven that the three Born terms primarily contribute to the temperature dependence of the elastic constant $C_{44}$.

**Figure 11.** The temperature dependence of microscopic stress tensor $P_{44}$ and three Born terms $B1_{C44}$, $B2_{C44}$, $B3_{C44}$ of a perfect C15 Laves phase structure in a stable time period. The temperatures are chosen every 100K from 0K to 500K. The time is from 10000fs to 15000fs.
and the elastic constants mainly refer to the potential energy. Thus, it is seen that Ackland-2004 potential is an adequate tool for calculating the temperature dependence of elastic constants of perfect C15 Laves phase structures made of iron atoms.

4.3 Phase transformation at 300K

The previous work in this thesis focused on calculating the elastic properties in order to study the stability of pure C15 Laves phase structures under different temperatures. In this section, the changes to perfect C15 Laves phase structures will be studied, since they directly show the morphology of perfect C15 structures and thus enable us to observe the occurrence of phase transformation. Previous TEM experiments have never observed any C15 Laves phase structures in bcc Fe. So 300K and a 4×4×4 simulation box were chosen to simulate the variation of the structure, seen in Figure 12. Figure 12(a) shows the original morphology of the perfect C15 Laves phase structure at 0K in the minimum energy state, (b) to (d) show the transient state when the temperature is kept at 300K. From plot (b) to (c) we find that the structure did not change a lot, the atoms only vibrate within a very tiny area. The process from plot (c) to (d) is relaxation, where the structure goes to the minimum energy state again and has almost same morphology as seen in plot (a). Plot (d) indicates that type-A atoms are more stable and have higher potential energy than type-B atoms. So phase transformation does not happen when the perfect C15 Laves phase structure stays at 300K. This result will be compared to the stability of perfect C15 Laves phase structures containing internal defects in the next two chapters.
Figure 12. The atomic projection of phase transformation of the perfect C15 Laves phase structure at 300K on the basal (XY) plane. (a) shows the original structures relaxed at 0K; (b), (c), (d) show the transient state of the structures at the given time of relaxation. The blue spheres represent A atoms and the red spheres represent B atoms.

4.4 Summary

For perfect C15 Laves phase structures made of iron atoms, the temperature dependence of elastic constants and elastic moduli keep gradually increasing until the temperature goes up to 425K. When higher than 425K, the structures may suffer a phase transformation and the atoms in the whole system may become disordered. The study of the morphology of the structures at 300K indicates that phase transformation may not happen at room temperature. Thus, pure C15 Laves phase structures should be observed in the experiment at room temperature. But why C15 Laves phase structures in bcc iron have
never been seen through TEM is still a question. Focusing on the stability of pure C15 Laves phase structures made of iron atoms and with point defects, as well as that of nano-sized C15 clusters with nearby point defects in bcc iron, the next three chapters will explore the possible answer.
Chapter 5

The stability of C15 Laves phase structure with vacancies

The results in Chapter 4 show that perfect C15 Laves phase structures made of iron atoms are stable at 300K. In this current chapter, the same method and model are now used to study how vacancy, as one of the primary point defects of materials, affects the stability of C15 Laves phase structures. Type-A and Type-B vacancies are added into perfect C15 Laves phase structures to calculate formation energy, temperature dependence of phase transformation and relaxation evolution, and the comparison of radial distribution function (RDF) at 0K and 300K. Particularly, the process of the phase transformation is most important. The main purpose of this chapter is to study how the two types of initial vacancies affect the stability of perfect C15 Laves phase structures in bcc iron. Whether the structures will remain unaffected by internal vacancies at 300K, or whether phase transformation will take place, their morphologies will be described below.

5.1 The simulation model

In Chapter 4, the simulation box has already been built and there are only two types of atoms made of iron in the perfect C15 Laves phase structures. So vacancy as an important point defect was designed using these two types of atoms as well. The removal of one type-A atom creates a vacancy, referred to in this thesis as a type-A atom vacancy, or A-vacancy; removal of one type-B atom creates a vacancy, referred to in this thesis as a type-B atom vacancy, or B-vacancy. In order to compare the results easily, the size of simulation box is still 4×4×4, which is the same as the perfect C15 Laves phase structure.
model. For each type of vacancy, 5 different positions were chosen for the following calculations, and they all show the same trend in the results. Figure 13 shows the typical example two basic vacancies on the basal (XY) plane within perfect C15 Laves phase structures. The red solid sphere indicates that the atom at the C15 lattice site was removed. Plot (a1) and (a2) shows the three-dimensional perfect C15 Laves phase structures with both types of vacancies (A and B) in a unit cell. Plot (b1) and (b2) describe the morphology of relaxed system at 0K containing a vacancy, and the locally enlarged part of the vacancy.

**Figure 13.** Vacancy-containing C15 Laves phase structures on the basal (XY) plane. (a1), (a2) are the three-dimensional representations of two types of vacancies (A and B) within a C15 Laves phase structure in a unit cell; (b1), (b2) are representations of two types of vacancies (A and B) within a C15 Laves phase structure in a relaxed simulation box.
From the relaxed system, it is evident that the A-vacancy-containing C15 Laves phase structure shows a similar morphology to the perfect C15 Laves phase structure with no vacancies. However, the atoms surrounding the B-vacancy move slightly to minimize the system’s energy.

5.2 Formation energy

Formation energy is one of the basic properties used to analyze material characteristics. From the results from Figure 13(b1) and (b2), whether or not the vacancy formation energy shows a similar variation pattern needs to be verified. When calculating formation energy, the system should be in its minimum energy state. That means the total energies of the perfect system and the defect system should be obtained after relaxation. Formation energy is calculated as:

\[ E^f = E^{\text{def}} - E^{\text{perf}} \cdot \frac{N_{\text{def}}}{N_{\text{tot}}} \]  

(5-1)

Where \( E^{\text{def}} \) is the total energy of the system including the defects, \( E^{\text{perf}} \) is the energy of the perfect lattice, \( N_{\text{def}} \) is the number of atoms with defects, \( N_{\text{tot}} \) is the numbers of atoms in a perfect lattice.

The total energies of perfect C15 Laves phase structures and C15 Laves phase structures containing one vacancy are relaxed for 10 ps at 0K to minimize the potential energy. The total number of the vacancy system \( N_{\text{vac}} \) is \( (N_{\text{tot}} - 1) \). Each of the 24 atoms in a C15 unit cell was individually removed, and the formation energy for the resulting vacancy was calculated. The formation energies of two types of vacancies are illustrated in Table 2. The negative value indicates that the C15 structures are more likely to form a
type-B vacancy. The formation energy of A-vacancy is higher than B-vacancy. So it is easier to form B-vacancy than A-vacancy.

**Table 2.** Formation energies $E_f$ for two types of vacancies in perfect C15 Laves phase structures at 0K.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Vacancy</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-vacancy</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>B-vacancy</td>
<td>-0.31</td>
</tr>
</tbody>
</table>

### 5.3 Temperature dependence of phase transformation

Perfect C15 Laves phase structures are stable at room temperature. However, it is not known if perfect C15 Laves phase structures containing either vacancy type are also stable at room temperature. In order to study the temperature dependence of phase transformation for C15 Laves phase structures containing one vacancy, the temperature was raised incrementally in 10K steps from 0K to seek the phase transformation temperature. Before each temperature increase, the system was relaxed at 0K to minimize energy and reduce errors. And I did 5 calculations for one condition. In Table 3, we find that the perfect C15 Laves phase structure with no defects have the highest phase transformation temperature among the three structures. The phase transformation temperature of a perfect C15 Laves phase structure containing A-vacancy is higher than the structure containing B-vacancy. The highest phase transformation temperature of perfect C15 Laves phase structures containing a vacancy is 260K. A-vacancy has a lower formation energy than B-vacancy, which means formation energy is negatively correlated with transformation temperature.
Table 3. Phase transformation temperatures \( T_{tr} \) for different C15 Laves phase structures in bcc iron.

<table>
<thead>
<tr>
<th>Structure</th>
<th>C15</th>
<th>C15+A-vacancy</th>
<th>C15+B-vacancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{tr} ) (K)</td>
<td>410</td>
<td>260</td>
<td>200</td>
</tr>
</tbody>
</table>

While it has been proven that vacancy-containing C15 Laves phase structures are not stable at 300K, study of the temperature dependence of their morphological changes is still needed. As the temperature increased from 0K to 300K, the vacancy dislodged the atoms in the whole system from their equilibrium positions. In order to better understand the phase transformation process, the simulation time was set to 1000 ps. Five different positions were chosen for each type of vacancy, then calculations were made, and the results all showed the same trend. Phase transformation for each structure at 300K is typically shown to have five stages, detailed in Figure 14. Plot (a) shows how the vacancy system in the initial state should look after relaxation at 0K. Plot (b) gives a brief illustration of the vacancy affecting the whole system, showing atom displacement in the first few picoseconds at 300K. Plot (c) shows the beginning of phase transformation. Plot (d) shows that phase transformation is complete after 960ps. Plot (e) is a relaxation process to find new equilibrium positions and make the system stable again at 1000ps. After comparing the five stages of these two C15 Laves phase structures using common neighbor analysis, it was found that vacancy-containing C15 Laves phase structures may change into imperfect bcc structures with vacancies and vacancy clusters in the final state. The positions of the vacancies and vacancy clusters can be random, changing with each timestep. Thus, vacancy-containing C15 Laves phase structures are not stable at 300K and the structures tend to reorganize into imperfect bcc iron structures.
Figure 14. Atomic projection images illustrating the phase transformation of vacancy-containing C15 Laves phase structures at 300K on the basal (XY) plane. Image (a) indicates the initial structure after relaxation; (b), (c), (d) show the transformation state of structures at the given time. Image (e) shows the final state of the structure after relaxation.

How can we ensure that vacancy-containing C15 Laves phase structures reorganize into imperfect bcc iron structures, rather than other similar structure at 300K? If the atomic arrangement of two structures are the same, we can see the two structures are the same. If two structures have the same average coordination number, they probably have the same arrangement of atoms. We can determine the distance for all atom pairs by using the radial distribution function (RDF). This means that the spatial distribution probability between a given atom and its neighbors can be derived through statistical analysis, and then the average coordination number for that atom can be determined. Thus, the radial distribution function also contributes to proof that the structure has been transformed into imperfect bcc iron.

Certain conditions, such as temperature and the presence of defects, can change C15 Laves phase structures. If some atoms in C15 Laves phase structures have moved to other positions, the new position of those atoms can be determined by the coordination number
and the distances between the target atom and nearest neighbor atoms using RDF. The new position of the target atom may influence the coordination number at different distances between the target atom and other atoms. For example, one vacancy within a C15 Laves phase structure will induce disorder in its direct vicinity. A target atom with a position near the locally disordered zone can be chosen to study the variation of the coordination number. Comparing the perfect C15 Laves phase structure with the disordered one, the number of the average near neighbor of the given atom will be different. RDF was used to calculate the distance dependence of the coordination numbers of bcc iron, perfect C15 Laves phase structures, and A-vacancy containing and B-vacancy containing C15 Laves phase structures at 0K and 300K. The impact of the presence of vacancies and of temperature on C15 Laves phase structure is analyzed and the solutions are plotted in Figure 15.

Figure 15(a) shows the distance dependence of the coordination number for these four structures at 0K. From this plot we can see that bcc iron has the highest peaks, and nanocrystallites with pure C15 Laves phase and C15 with two types of vacancies have similar peak positions. Higher peaks indicate larger coordination numbers. Compared to the pure bcc iron structure, the peaks of all three C15 structures have drifted a small distance. The coordination numbers of A-type vacancy containing C15 Laves phase structures are closer to those of C15 Laves phase structures with no vacancies, suggesting that A-vacancies have little effect on the original organization of C15 Laves phase structures at 0K. The position of the first peak of B-type vacancy-containing C15 Laves phase structures is between the two peaks of perfect C15 Laves phase structures, and the peaks of B-type vacancy containing C15 Laves phase structures are shorter than the peaks of the other structures.
Figure 15. The radius dependence coordination numbers of C15 Laves phase structures containing either A-type or B-type vacancies after relaxation at 0K (a) and 300K (b). The coordination number of bcc iron is also given as a reference standard.
Figure 15(b) plots the distance dependence of the coordination numbers of these four structures at 300K. The plot shows the peak positions of both types of vacancy-containing C15 Laves phase structures were almost same as bcc iron structure and the height of the first two peaks were almost identical. Thus, all of these structures have the same coordination numbers at the first and second nearest neighbor, which means they are the similar structure as bcc iron but not a perfect bcc structure. This suggests that phase transformation has occurred and both types of vacancy-containing C15 Laves phase structures have transformed into imperfect bcc iron structures. This plot, together with Figure 14, can analyze phase transformation. Figure 14(e2) and (e3) show that after 1000ps and relaxation, both types of vacancy-containing C15 Laves phase structures have reorganized into imperfect bcc iron structures. These two plots together can strongly support that perfect C15 Laves phase structures containing any vacancy at 300K will undergo phase transformation. However, perfect C15 Laves phase structures maintain their original organization and their atoms will have only slight vibration, as is indicated by the higher peaks at 0K than at 300K. RDF and phase transformation plotting are good tools to analyze how quantitative and qualitative changes affect the stability of vacancy containing C15 Laves phase structures at specific temperatures.

5.4 Summary

C15 Laves phase nano-crystallites with two types of vacancy is not stable at room temperature. The vacancy-1 has higher formation energy than the vacancy-2 with pure C15 Laves phase, which means vacancy-2 is easier to form than vacancy-1. Moreover, the phase
transient temperature of pure C15 with the two type vacancies indicates that the vacancy-1 has higher phase transient temperature which is still lower than room temperature. Meanwhile, pure C15 Laves phase with a vacancy at room temperature causes phase transformation which turns to be imperfect bcc Fe. The density of C15 Laves phase with vacancy and bcc iron at room temperature are pretty similar so that these C15 structures may as same as bcc iron. Radial distribution function demonstrated the same results because the coordination number of the first and second nearest neighbors are the same between C15 Laves phase with vacancy and bcc iron at room temperature.
Chapter 6

The stability of C15 Laves phase structure with SIAs

The preceding two chapters demonstrated the stability of perfect C15 Laves phase structures with and without an internal vacancy. A self-interstitial atom (SIA) is another kind of point defect that is as influential that can change the organization. In this chapter, the same research methods were applied to study how an internal SIA impacts the stability C15 Laves phase structures. The focus of the research for this chapter is on the formation energy, temperature dependence of phase transformation and relaxation evolution, and the comparison of radial distribution functions (RDF) at 0K and 300K. These results can be compared with C15 Laves phase structures and vacancy-containing C15 Laves phase structures.

6.1 The simulation model

The pattern of SIA can be either a dumbbell or a crowdion. The selection of the SIA depends on the type of atom. For the type-A atoms, the SIA can be built as dumbbell in the direction of <100>, <110>, <111>. At this time, the dumbbell structure also can be regarded as crowdion in these three directions. Selecting one type-A atom as the original coordinate, the general coordinates of A-type dumbbells were shown as follows: in <100> direction, only the x coordinate changes around ±2Å; in <110> direction, both the x and y coordinates changes $\pm \sqrt{2}/2 \times 6.64 \times 0.3$ Å; in <111> direction, the x, y and z coordinate changes $\pm \sqrt{3}/3 \times 6.64 \times 0.3$ Å. The direction of SIAs is different for B-type atoms. B-
type atoms form regular tetrahedrons in C15 Laves phase structures, so the directions we choose are along the three edges adjacent to the vertex of the regular tetrahedron occupied by the B-type atom. B-type atoms can also build three dumbbells or crowdions along <110>, <-101> and <0-11> directions. The B-type dumbbells are placed with one end halfway along the edge of the tetrahedron and the other extending beyond the induced vacancy. The true coordinates of each atom should be obtained after energy minimization. Figure 16 details an SIA in a C15 Laves phase structure on the XZ plane of a unit cell. The red solid

![Figure 16](image)

**Figure 16.** 3D representations of C15 Laves phase structures containing an SIA on the XZ plane in a unit cell. All (a) designations show the type-A SIAs contained in a C15 unit cell, all (b) designations show the type-B SIAs contained in a C15 unit cell. The definitions of the different dumbbells in perfect C15 Laves phase structures are given in the text.
spheres indicate that the atoms in these C15 lattice sites have been removed. The red rectangles show the dumbbells in different directions, the black and red arrows show the directions of the SIA dumbbells. Figure 16(a1)-(a3) show the type-A dumbbells in <100>, <110> and <111> directions in a unit cell, respectively, (b1)-(b3) shows the type-B dumbbells along the <110>, <-101> and <0-11> directions of three edge of the tetrahedron in a unit cell, respectively.

6.2 Formation energy

The position and direction of SIAs have an effect on their formation energies. MD simulation was used to calculate the formation energies of different types of SIA in perfect C15 Laves phase structures at 0K. After relaxation, we found that the atoms of the whole system are distributed non-uniformly and all the formation energies were negative values. This indicates that the relaxed energy is not suitable for this setting. Molecular statics (MS) simulation was chosen to study the unrelaxed energies. The unrelaxed simulation is also a process of energy minimization to ensure that each atom maintains its original direction. This process can be achieved by controlling the position of the added SIA. Equation (6-1) is the calculation formula for formation energy. Five different positions were chosen for each type of SIA for calculations, and each result shows the same trend. Table 4 shows the formation energies of different types of SIA in bcc iron at 0K. Type-A dumbbells are referred to as SIA$^{A}_{\text{Dumbbell}}$, Type-B dumbbells are referred to as SIA$^{B}_{\text{Dumbbell}}$. It is seen that the type-A dumbbells have lower formation energies than the type-B dumbbells, and the type-B dumbbells show the same formation energy in all three directions. From the prior
model we can see that the type-B dumbbells have the same coordination numbers, which may be why formation energy is the same in all three directions.

**Table 4.** Formation energies $E_f$ for different self-interstitial atom in bcc iron at 0 K.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\text{SIA}^1_{\text{Dumbbell}}$</th>
<th>$\text{SIA}^2_{\text{Dumbbell}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;100&gt;$</td>
<td>5.35</td>
<td>10.58</td>
</tr>
<tr>
<td>$&lt;110&gt;$</td>
<td>4.67</td>
<td>10.58</td>
</tr>
<tr>
<td>$&lt;111&gt;$</td>
<td>4.96</td>
<td>10.58</td>
</tr>
</tbody>
</table>

### 6.2 Temperature dependence of phase transformation

After studying the temperature-dependent stability of vacancy-containing C15 Laves phase structures in bcc iron, SIA-containing C15 Laves phase structures should be analyzed in a similar fashion. Table 5 shows the phase transformation temperature of an SIA-containing C15 Laves phase structure in bcc iron. It is evident that the phase transformation temperature of the SIA-containing structure is much lower than 300K. When these figures are compared to those in Table 3, the highest phase transformation temperature of SIA-containing C15 Laves phase structures is lower than that of vacancy-containing C15 Laves.

**Table 5.** Phase transition temperatures $T_{tr}$ for C15 Laves phase structures containing different SIAs in bcc iron.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$\text{SIA}^A_{\text{Dumbbell}}$</th>
<th>$\text{SIA}^B_{\text{Dumbbell}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;100&gt;$</td>
<td>110K</td>
<td>100K</td>
</tr>
<tr>
<td>$&lt;110&gt;$</td>
<td>140K</td>
<td>100K</td>
</tr>
<tr>
<td>$&lt;111&gt;$</td>
<td>130K</td>
<td>100K</td>
</tr>
</tbody>
</table>

| $T_{tr}$ (K) | 110K | 140K | 130K | 100K | 100K | 100K |
phase structures. Also, the $\text{SIA}^B_{\text{Dumbbell}}$ in all three directions have the same phase transformation temperature, in keeping with their matching formation energy and coordination numbers.

The phase transformation temperature of C15 Laves phase structures containing a single SIA in 3 different directions is lower than 300K. We are still concerned with how phase transformation process happens at 300K. The details of the phase transformation process at 300K are shown in Figure 17. Plot (a) show the initial structure model at 0K, where atom positions were obtained by previous calculations. This model cannot be used in the following calculation until the whole system in energy minimization. Plot (b) shows the atom positions in the real system after relaxation at 0K. The temperature of the system was then increased to 300K, and then maintained at this temperature until the system stabilized. Plot (c), (d), (e) show the transformation state of the structures in this process. The results of the last but most important step, to relax the whole system to minimize energy, is shown in plot (f). There are many vacancies and vacancy clusters in (f) because of the different structural configurations and densities between C15 Laves phase structures and bcc iron. The vacancies and vacancy clusters may exist at other positions in the final state. The final state is similar to the phase transformation of vacancy-containing C15 Laves phase structures at 300K. The structure changes from a C15 Laves phase structure containing an SIA into an imperfect bcc iron structure.
Figure 17. Atomic configurational projection showing the phase transformation of perfect C15 Laves phase structures containing different SIA at 300K on the basal (XY) plane. (a) is the model of the initial structure; (b) is the initial structure after relaxation at 0K; (c), (d), (e) show the transient state of structures at the given time at 300K. (f) shows the final state of the structure after relaxation at 300K. The red rectangular indicates the local part of a dumbbell.

The phase transformation temperature of C15 Laves phase structures containing a single SIA in 3 different directions is lower than 300K. We are still concerned with how
phase transformation process happens at 300K. The details of the phase transformation process at 300K are shown in Figure 17. Plot (a) shows the initial structure model at 0K, where atom positions were obtained by previous calculations. This model cannot be used in the following calculation until the whole system in energy minimization. Plot (b) shows the atom positions in the real system after relaxation at 0K. The temperature of the system was then increased to 300K, and then maintained at this temperature until the system stabilized. Plot (c), (d), (e) show the transformation state of the structures in this process. The results of the last but most important step, to relax the whole system to minimize energy, is shown in plot (f). There are many vacancies and vacancy clusters in (f) because of the different structural configurations and densities between C15 Laves phase structures and bcc iron. The vacancies and vacancy clusters may exist at other positions in the final state. The final state is similar to the phase transformation of vacancy-containing C15 Laves phase structures at 300K. The structure changes from a C15 Laves phase structure containing an SIA into an imperfect bcc iron structure.

As mentioned in Chapter 6, it must be confirmed that C15 Laves phase structures containing single SIAs will reorganize into imperfect bcc iron. The radius dependent coordination numbers of the final state of phase transformation at 300K using radial distribution function (RDF). Figure 18 shows the coordination number of the different SIA-containing C15 Laves phase structures at different cut-off radii at 0K and 300K. Each cut-off radius results in a different coordination number. Figure 18(a) gives all coordination numbers at 0K. The coordination numbers of the different SIA-containing C15 Laves phase structures are close to the coordination numbers of perfect C15 Laves phase structures. Figure 18(b) indicates that the peaks of the first and second coordination numbers are
Figure 18. The radius dependent coordination numbers of different SIA-containing C15 Laves phase structures after relaxation at (a) 0K and (b) 300K. The coordination number of bcc iron is also given for comparison in (b).
almost the same between SIA-containing C15 Laves phase structures and bcc iron, suggesting that the number of first and second neighbor atoms nearest to the SIA-containing C15 Laves phase structures are the same as those in bcc iron. From the third peak, the coordination number the SIA-containing C15 Laves phase structure is slightly different from that of bcc iron at the same cut-off radius, but shows a similar trend to that of bcc iron. These findings can support that the SIA-containing C15 Laves phase structure will transform into imperfect bcc iron at 300K, as proposed in Figure 17.

6.3 Summary

C15 Laves phase structures containing two types of internal SIA in three different directions are not stable at 300K. The formation energy of C15 Laves phase structures containing type-A dumbbells is lower than the structures that contain type-B dumbbells. The C15 Laves phase structures containing type-B dumbbells show the same formation energy for the dumbbells in three different directions. Moreover, the phase transformation temperature of both types of SIA-containing C15 Laves phase structures is still lower than 300K. Furthermore, all SIA-containing C15 Laves phase structures transform to imperfect bcc iron at 300K. Comparing the density and radial distribution function between SIA-containing C15 Laves phase structures and bcc iron at room temperature, the same results are demonstrated because SIA-containing C15 Laves phase structures have similar coordination numbers of the first and second nearest neighbors as bcc iron.
Chapter 7

The stability of nano-sized C15 cluster in bcc iron at 300K

While the preceding chapters have studied the stability of C15 Laves phase structures made of iron atoms and with or without point defects at 300K, this chapter will shift focus to the stability of nano-sized C15 Laves phase interstitial clusters in bcc iron with randomly-placed external point defects nearby with the model which referred to the former research in chapter 1. The following MD simulations primarily examine how these defects affect the phase transformation process of the clusters at 300K.

7.1 The simulation model

F. Gao and D. J. Bacon [16,17] firstly proposed the model of nano-sized C15 Laves phase interstitial clusters embedded in bcc iron. The simulation box of an \( L_2^{C15} \) cluster, which includes 54000 iron atoms \( = (30a)^3 \), where \( a \) is lattice parameter of iron) with metastable sessile di-interstitials (12 atoms sharing 10 lattice sites), was created. Then M.C. Marinica and L. Dézerald [22,23] reported that for the structure of small C15 clusters, the \( I_4^{C15} \) cluster (18 atoms sharing 14 lattice sites) was the most stable small sized C15 cluster in bcc iron. To create my model, structures with the lowest formation energy and the most stable configuration were selected. If the most stable nano-sized C15 cluster embedded in bcc iron become unstable when random point defects are present nearby, then there is no need to test less stable C15 clusters. Thus, the \( I_4^{C15} \) cluster will be used in this simulation.

A simulation box with 54000 iron atoms was built, and then an \( I_4^{C15} \) cluster was embedded in its center. Thus, before adding any random vacancies and interstitials, the
total number of atoms is 54004. The three-dimensional representation and a local XY basal plane projection of an I₄C₁₅ cluster in bcc iron are shown in Figure 19. The last step is to add random vacancies or interstitials close to the boundary between the I₄C₁₅ cluster and the surrounding bcc iron. The number of the random vacancies or interstitials is chosen from 1 to 8, so that the pattern change in the I₄C₁₅ cluster can be verified with greater certainty. The vacancies can be randomly added within a distance of 1 to 2 iron lattice parameters away from the I₄C₁₅ cluster. For one interstitial, DFT verifies that in bcc iron the <110> SIA dumbbell has the lowest formation energy and shows the most stable SIA configuration [9]. Thus, the interstitials are all set to randomly-placed <110> dumbbells, whose distance is also around 1-2 iron lattice parameters from the I₄C₁₅ cluster.

![Figure 19](image)

**Figure 19.** Structure of an I₄C₁₅ cluster embedded in bcc iron. (a) is the 3D structure [22]. (b) is local XY basal plane projection in the simulation box. The blue cubes and spheres at the bcc lattice sites represent vacancies, the orange and red spheres represent interstitials.

**7.2 Phase transformation at 300K**

It is not known why nano-sized C15 clusters in bcc iron have never been observed empirically. In order to answer the question, we randomly added 1 to 8 vacancies or stable
<110> dumbbells around the most stable $\text{I}_4\text{C}_{15}$ cluster and calculated at 300K. At first, all
the simulation boxes are relaxed at 0K for 10 ps in order to reach the minimized energy
state. Then, the simulation boxes are annealed at 300K for some time until the whole
system maintains a stable state. Finally, the simulation boxes are relaxed again to ensure
whole-system energy minimization. At 300K, after calculation, the phase transformation
trend for an $\text{I}_4\text{C}_{15}$ cluster randomly surrounded by 1 to 8 vacancies or stable <110>
dumbbells were the same. Two typical examples, one of an $\text{I}_4\text{C}_{15}$ cluster with 7 random
vacancies and one of an $\text{I}_4\text{C}_{15}$ cluster with 6 random <110> dumbbells nearby are given
next.

Figure 20 shows how 7 random-placed vacancies affect an $\text{I}_4\text{C}_{15}$ cluster in bcc iron.
The initial simulation box is shown in Figure 20(a), the vacancies cannot be seen because
of their positions all at the bcc lattice sites. The 7 random-placed vacancies cannot be seen
in the projection because their positions are all at the bcc lattice sites a
nd . Figure 20(b)
gives the initial simulation box after relaxation at 0K at about 10ps. These vacancies in the
bcc iron surrounding the $\text{I}_4\text{C}_{15}$ cluster draw towards the boundary between them by
capturing iron atoms. Once at the boundary, the vacancies draw atoms from the $\text{I}_4\text{C}_{15}$ cluster
so that the $\text{I}_4\text{C}_{15}$ cluster starts to break up. Figure 20 (c) to (g) describe the transient state of
the remaining atoms from the $\text{I}_4\text{C}_{15}$ cluster in bcc iron at 300K from 12ps to 350ps. In this
process, the remaining $\text{I}_4\text{C}_{15}$ cluster atoms rearrange into <111> dumbbells. Because <111>
dumbbells cannot be stable in bcc iron, the structure then transforms into imperfect bcc
iron at around 350ps. Figure 20 (f) shows the final state of the whole system after relaxation
at 300K at around 760ps. The imperfect bcc structure with several vacancies at the bcc
lattice sites has minimized energy, therefore, at 300K, the atoms from the $\text{I}_4\text{C}_{15}$ cluster in
bcc iron with 7 random vacancies nearby will recombine with the nearby vacancies until all the atoms disappear. Similarly, at 300K, $I_4^{C15}$ clusters with any random vacancies nearby in bcc iron have the same phase transformation process.

![Figure 20](image)

**Figure 20.** The atomic projection of the phase transformation process at 300K for an $I_4^{C15}$ cluster in bcc iron with 7 randomly placed vacancies nearby, in the basal (XY) plane. (a) is the model of the initial structure; (b) is the initial structure after relaxation at 0K; (c)-(g) show the transient state of structures at the given time at 300K; (h) shows the final state of the structure after relaxation at 300K. The blue spheres indicate iron base atoms, the red spheres indicate interstitials.

Figure 21 shows the phase transformation process of the $I_4^{C15}$ cluster in bcc iron with 6 randomly-placed $<110>$ dumbbells nearby in bcc iron at 300K. Figure 21(a) gives the initial simulation box, (b) shows the initial simulation box after relaxation at 0K about 10ps. It is seen that all the random-placed $<110>$ dumbbells have already transformed into the $<111>$ direction. Figure 21(c) to (d) indicates that a rearrangement of the atoms in the cluster occurs, transforming into the $<111>$ direction at 300K from 20ps to 50ps. After continuing calculation at 300K until the whole system is relaxed at around 480ps, the atoms...
from the randomly-placed $\langle 110 \rangle$ dumbbells and $I_4^{15}$ cluster move back and forth, but still maintain the $\langle 111 \rangle$ direction shown in Figure 21(e).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure21.png}
\caption{The atomic projection of phase transformation process for an $I_4^{15}$ cluster in bcc iron with 6 randomly-placed $\langle 110 \rangle$ dumbbells nearby at 300K in the YZ plane. (a) is the model of the initial structure; (b) is the initial structure after relaxation at 0K; (c)-(d) show the transient state of structures at the given time at 300K; (e) shows the final state of the structure after relaxation at 300K. The blue spheres indicate iron base atoms, the red spheres indicate interstitials.}
\end{figure}

In order to analysis the final state of the relaxed structure above, the three-dimensional image of the relaxed $\langle 111 \rangle$ atoms at 300K is separately illustrated in Figure 22 by using the software OVITO. After analysis by OVITO, Figure 22(a) and (b) show these $\langle 111 \rangle$ atoms rearrange into a loop with a Burgers vector of $1/2\langle 111 \rangle$. The $1/2\langle 111 \rangle$ loop is very stable because of its high bonding energy. Thus, external interstitials surrounding a nano-
sized C15 cluster will rearrange at the boundary between the cluster and the bcc iron, which may cause a rearrangement of the atoms in the cluster, then transforming into stable 1/2<111> loops.

**Figure 22.** The 3D image of the final state of the rearranged atoms from LiC\textsuperscript{15} cluster with 6 random <110> dumbbells nearby after relaxation at 300K. (a) and (b) indicate different perspectives of the 1/2<111> loop.

### 7.3 Summary

Nano-sized C15 clusters embedded in bcc iron with randomly-placed external vacancies nearby will not be stable at 300K. The randomly-placed vacancies will draw towards C15 clusters, and then cause the C15 clusters to disassemble and the system transform into imperfect bcc iron at room temperature. The randomly-placed nearby interstitials may cause a rearrangement of the atoms from the cluster, which will then transform into stable 1/2<111> loops. Thus nano-sized C15 clusters cannot remain long for experimental observation in bcc iron at room temperature, given that many point defects will be generated under irradiation and move around C15 clusters.
Chapter 8

Conclusions

In this thesis, molecular dynamic (MD) simulations were used to investigate the stability of perfect C15 Laves phase structures made of iron atoms and without or with point defects, as well as that of nano-sized C15 clusters with point defects nearby in bcc iron.

Ackland-2004 Fe-Fe potential and periodic boundary conditions are adopted in this simulation.

For perfect C15 Laves phase structures of iron, the total potential energy, temperature dependence of elastic constants and elastic moduli, as well as the process of phase transformation at 300K were calculated. For perfect C15 Laves phase structures with internal point defects, simulations were performed mainly on the formation energies of vacancies and SIAs, phase transformation temperature, as well as the process of phase transformation at 300K. Furthermore, radial distribution function (RDF) calculations were used to identify the stability and structural changes of perfect C15 Laves phase structures with internal point defects between 0K and 300K. From the simulation results, the following conclusions have been drawn:

1. For perfect C15 Laves phase structures, the elastic constants and elastic moduli maintain stable values until the temperature rises to 425K, and then decrease. This means that perfect C15 Laves phase structure may suffer phase transformation when the temperature goes higher than 425K, but will be phase stable at room temperature.
2. In a single C15 unit cell of 24 atoms, the atoms can be classified into two energy types. From the formation energies of vacancies and SIAs in C15 Laves phase structures, it was found that the formation energy of vacancies is lower than that of SIAs. In other words, vacancy-type defects are more readily formed in perfect C15 Laves phase structures. Furthermore, type-A vacancies have a higher formation energy than type-B vacancies in perfect C15 Laves phase structures, which means type-B vacancies are more readily formed than type-B vacancies. The formation energy of perfect C15 Laves phase structures with type-A dumbbells is lower than that of type-B dumbbells. The perfect C15 Laves phase structures with type-B dumbbells of three different directions show the same formation energy.

3. For perfect C15 Laves phase structures with simple internal point defects, phase transformation will occur at temperatures below 260K. With increasing temperature, the perfect C15 Laves phase structures with internal point defects will transform into imperfect bcc iron structures. Perfect C15 Laves phase structures with simple internal point defects are not stable at room temperature.

4. From RDF results, it is clear that the coordination number of perfect C15 Laves phase structures with simple internal point defects at 300K is similar to bcc iron at 300K. This supports the finding that perfect C15 Laves phase structures with simple internal point defects may not be stable and are likely to form imperfect bcc structures at room temperature.

For nano-sized C15 Laves phase interstitial clusters embedded in bcc iron with randomly-placed point defects near the C15 cluster, the simulation result indicates:
1. External vacancies will draw towards atoms from the C15 cluster, then C15 cluster break up and transform into imperfect bcc iron at room temperature.

2. External interstitials cause a rearrangement of the atoms in the cluster, then transforming into stable 1/2<111> loops at room temperature.

In general, C15 Laves phase structures may exist at room temperature only if they have no internal point defects, and any external point defects nearby. Therefore, nano-sized C15 clusters may not be observed in irradiated pure iron at room temperature.

**Recommended future work**

This thesis focused on C15 Laves phase clusters in pure bcc iron. However, in reality, impurities often exist in iron, such as C, Cr and Ni. Future studies may focus on how these impurities affect the stability of C15 clusters in bcc iron.
Reference


The MATLAB code for solving the equation (3-6) is given:

```matlab
function result = fpar(x)

r=2.35053;

v = 0.229628789371363;
v' = -0.549922286518945/0.229628789371363;
v'' = 1.14921016442736;

result(1) = abs(x(1)*exp(x(2)*r+x(3)*r^2)-v);
result(2) = abs(x(2)+2*x(3)*r-v');
result(3) = abs(x(1)*exp(x(2)*r+x(3)*r^2)*(x(2)+2*x(3)*r)^2+x(1)*exp(x(2)*r
+x(3)*r^2)*2*x(3)-v'');
result = result(1)*result(1)+result(2)*result(2)+result(3)*result(3);

format long
x0 = [a0, a1, a2]

option = optimset ('MaxFunEvals', 10000, 'MaxIter', 10000, 'TolFun', 1.0e-50,
'Display','iter','TolX',1.0e-25);

x = fsolve(@fpar, x0, option)
```

Results (1)-(3) are the errors of the potential itself and its first and second derivative. $V$, $V'$ and $V''$ were calculated by equation (3-4). The fitting parameters $a_0$ to $a_2$ need to be assigned individually in order to make the result ultimately approach zero. That makes the potential continuous at the boundary point.
Appendix B

The computer used for this work contains a 4th Gen Intel® Core™ i7-4600U processor operating with a maximum clock speed of 3.30 gigahertz, and has 12 gigabytes of RAM memory.

The operating system is Ubuntu 14.04, the MD simulations were written in Fortran 90. The software used to study the structural changes is OVITO 2.6.2.