

Atomistic Investigation of High Temperature Material Behavior

A Thesis

Presented to

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University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Mechanical Engineering

by

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May 2014

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Abstract

High temperature mechanical behavior of materials is of critical importance in a variety of contexts: next-generation reentry vehicles, hyper sonic flights, nuclear plants, engines, among many others. Creep is the dominant failure mechanism for materials used in such applications. Atomistic design of next-generation ultra-high-temperature ceramic composites as well as a thorough understanding of the various complex micro-mechanisms of creep damage using state-of-the art atomistic methods is the main goal of this dissertation. There are two challenges that need to be overcome to accomplish this endeavor. The first one is aptly amplified in a quote by Professor Nabarro (2002) “The creep rate in a land-based power station must be less than $10^{-11}s^{-1}$... The present state of knowledge reveals specific questions that call for experimental investigation. Theory will contribute, but atomic computation, with a time scale of $10^{-11}s$, will not handle processes that take $10^{11}s$ ”.

The other is that for the materials of interest, the so-called ultrahigh-temperature ceramics (ZrB_2 and HfB_2), atomistic potentials are not available. No type of atomistic methodology (molecular dynamics, Monte Carlo) can proceed without this. Furthermore, since oxidation and various related chemical reactions play a key role in the damage of such materials at high temperatures, the atomistic potential must be able to account for reactions. First-principle calculations are indeed possible without an empirical force field but such computations present severe limitations of the size scales they can access and of course, the enormous difficulty of modeling finite temperatures.

In short, in this dissertation, I will focus on two aspects that can potentially pave the way for modeling high temperature behavior of ceramics: development of ReaxFF potentials for ZrB_2 / HfB_2 using quantum chemistry tools and implementation of algorithms that allow access to time scales relevant to creep deformation and damage.

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Chapter 1

Introduction

1.1 High temperature mechanical behavior: creep deformation and damage

Creep damage is defined as the progressive (time-dependent) reduction in the ability of materials to resist stress. At stresses far lower than the yield stress, provided that the temperatures are “high” enough, time-dependent deformation ensues leading eventually to fracture and hence failure. This mode of deformation and damage is of critical importance in all scenarios where materials are subjected to temperature above half the melting temperature. As example, SnPb eutectic solder is used extensively in electronics. The melting temperature of this material is low enough that it even creeps at room temperature. Accordingly, reliability of our electronics devices depends on the design against creep. Airplanes, engines, nuclear reactors among many others are engineering situations where creep is the dominant failure mechanism.

Figures 1.1 and 1.2 show possible micro structural deformations that occur during creep, and how they affect the macro scale behavior properties. Vacancies are common defects that exists in any crystal. However, both the concentration of these vacancies, and their mobility increase exponentially with the temperature. The formation of voids is therefore, very common at temperatures higher than $0.5T_h$. The

nucleated voids or cavities can form anywhere in the structure. However, they do energetically prefer to nucleate at the grain boundaries, triple junctions, and second phase particles. Once nucleated, these voids grow, coalesce and eventually form cracks that propagate to fail the material. During this process, the microscopic state of the material is quite complex. Any macroscopically applied stress is redistributed due to grain boundary and volume diffusion and grain boundary sliding. The latter can lead to high stress concentrations when the sliding boundaries impinge upon second phase particles. These stresses, in turn, may be relaxed by diffusion. The primary mechanisms for void growth on the grain boundaries are diffusion and dislocation glide-climb in the adjacent crystal.

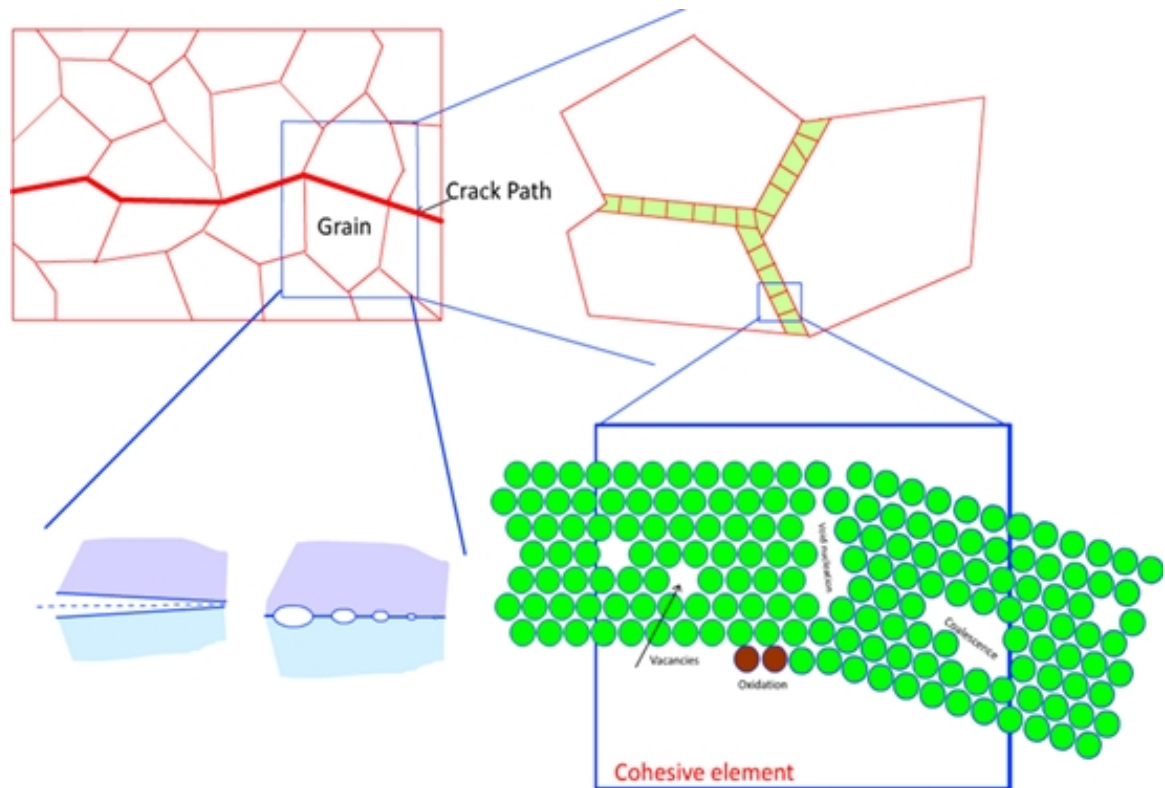


Figure 1.1: A schematic showing the outline of different micro mechanics models

While the general picture of creep deformation and damage is understood, despite many decades of research, several open questions still remain. For example, in modeling grain boundary sliding, as will be explained in later chapters, atomistic and some macroscopic aspects of various creep micromechanisms still remain poorly understood e.g. grain boundary sliding constitutive law, void nucleation rates among others.

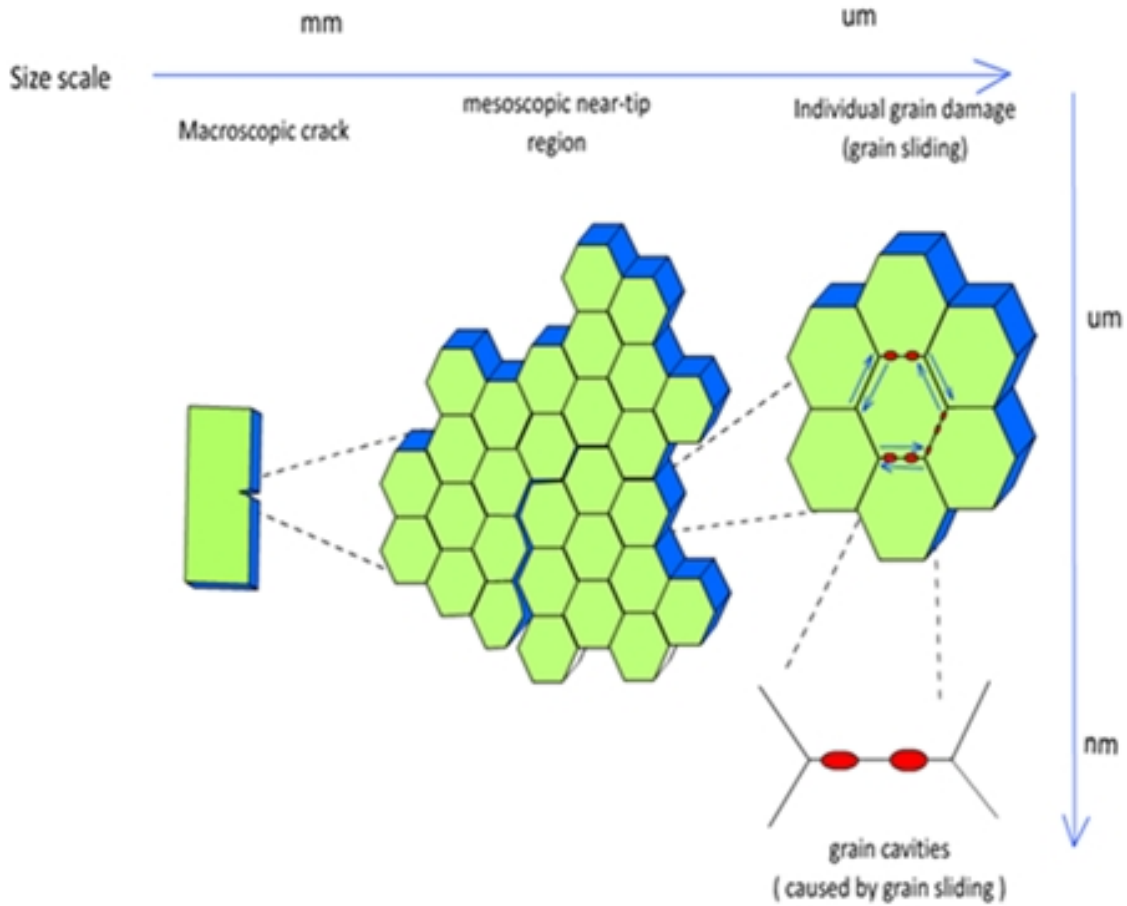


Figure 1.2: Schematic of creep damage across various length scales

1.2 Ultra high temperature materials: properties and applications

Driven by the “need for speed” in new potential aerospace applications, researchers have shown a lot of interest in Ultra High Temperature Ceramics (UHTCs) for what they offer of a unique combination of excellent mechanical and thermal properties ([1], [2], [3]). UHTCs are typically Borides, Carbides, and Nitrides of the transition metals (group 3 to 12). However, early transition metals (group 3-4) are generally preferred because of their higher melting and oxidation temperatures. For instance, Hafnium Di-Boride (HfB_2) and Zirconium Di-Boride (ZrB_2), which are the materials of interest in this work, are preferred over others because of their outstanding properties (high melting temperature, stable oxides, high young modulus, ...).

1.2.1 Properties

There are different properties, based on which, materials can be characterized. For instance, materials with higher Young moduli are stronger, those with higher melting temperatures are more resistant to extreme heat, and those with lower thermal conductivity can serve as better insulators to extreme environment.

In table 1.1, we collect some of the significant mechanical and thermal properties for different UHTCs and metals. Aluminum (Al), Copper(Cu), and Gold (Au) are added to the table to highlight the difference between metals and UHTCs.

Table 1.1: Mechanical and thermal properties for some UHTCs and metals

Material	Young Modulus [Gpa]	Melting T.[°C]	Thermal Exp. [°C ⁻¹]	Thermal Conduct. [Wm ⁻¹ K ⁻¹]	Mohse Hardness
HfB ₂	530	3380	7.6	104	8-9
ZrB ₂	500	3245	8.3	60	8-9
TiB ₂	551	3225	7.7	25	8-9
TaB ₂	257	3040	8.4	36.2	8-9
Al	70	660	23.1	237	2.75
Cu	120	1080	16.5	401	3.0
Au	79	1060	14.2	318	2.5

* Data collected from [4], [5], [6], and [7]

Table 1.1 shows clearly that all UHTCs are characterized by high strength and hardness (above 8 on the Mohrs hardness scale) due to the strong covalant bonds present between their elements. They also exhibit much higher melting temperatures than metals (above 3000 °C), lower thermal expansion coefficients (6 to $8.5 \cdot 10^{-6} \text{ K}^{-1}$), and lower thermal conductivity, which enables them to serve as coating materials. Despite all these interesting thermo-mechanical properties, these materials are still unsuitable for many refractory applications because of their susceptibility to oxidation at high temperatures [8], [9] [10] [11] [12] [13] [14].

These properties, although presented for a small set of materials, present the general trend for this class of ceramics (Borides, Carbides, and Nitrides). However, each group of these have some specific properties due to the chemical and structural differences between atoms: In fact, borides, for instance, and more specifically ZrB₂ and HfB₂, are the most promising materials, and those attracting most of the interest ([15], [16]). They benefit from the very strong bonding between Boron atoms as

well as strong metal to Boron bonds. Their HCP structure, where layers of B atoms are connected in Graphene-like rings, and alternating with metal sheets give them a high but anisotropic strength as single crystals. Compared to other classes of UHTCs, Borides exhibit higher thermal conductivity ($75 - 105 \text{ Wm}^{-1}\text{K}^{-1}$) [17] [18] and lower coefficients of thermal expansion ($5 - 7.8 \cdot 10^{-6} \text{ }^\circ\text{K}^{-1}$) and improved oxidation resistance. Carbides, in general, tend to have higher melting point and young modulus than other ceramics because of their covalent Carbon networks ($3980 \text{ }^\circ\text{C}$ for TaC). However, they are much more brittle and more susceptible to oxidation. Nitrides, such as HfN, have similarly strong covalent bonds and are of critical importance in the microelectronics industry, but their refractory nature makes them especially difficult to synthesize and process.

1.2.2 Applications

Thanks to the excellent properties discussed above, UHTCs are used in a wide range of applications. For instance, they are being investigated as possible thermal protection systems (coatings for materials subjected to high temperatures) [19], as blades for reactor turbines, or even as high temperature shielding for hyper-sonic vehicles [20]. The surfaces of these vehicles experience extreme temperatures (higher than 2500°C), and a strong flow of oxidizing plasma. Such conditions makes the current generation of thermal protection system materials unable to withstand the considerably higher forces and temperatures, and thus limit the design of orbital re-entry bodies and hyper-sonic vehicles to UHTCs [21] [22].

Hafnium and Zirconium Di-Borides, specifically, are developed for this purpose (to handle the excess of forces and temperatures). They are also widely used in boiling water reactor fuel assemblies due to their strong corrosion resistance.

In a nutshell, UHTCs, and specifically ZrB_2 and HfB_2 -studied in this work- are prospective materials for all applications requiring both thermal resistance and mechanical strength. However, the major challenge this class of materials is facing is its susceptibility to oxidation. Indeed, significant efforts are underway to find possible oxidation enhancements for Di-Borides (by adding different kinds of impurities). Such a development, will allow UHTCs to be more useful in the various aforementioned approximations.

1.3 Outline of the dissertation

Following is the outline of the dissertation. In chapter 2, we present the detailed development of reactive force fields for ZrB_2 and HfB_2 . It will be shown that the developed potential allows accounting for chemical interactions with Oxygen (O), Carbon (C), Silicon (Si), and Tungsten (W). Illustrative examples are given related to extracting diffusion properties and ion bombardment.

In chapter 3, we explain one possible (and promising) methodology to account for long-time effects in atomistic simulations.

In chapter 4, we provide the first example of the use of the long-time-scale atomistic methods. Specifically, we derive the constitutive law for grain boundary sliding.

We choose Al for this illustration since other works have performed conventional MD calculations for this material to achieve the same goal.

In chapter 5, we attempt to settle a long standing controversy regarding void growth: can voids grow via shear loop emission?

In chapter 6, we return to one of the key motivating materials and study grain boundary sliding in ZrB_2 and then diffusion in chapter 7.

Finally, and before the concluding chapter, we investigate one of the key phenomena in creep for UHTCs (diffusion) in chapter 7. We use some electronic calculations to explain the different diffusion mechanisms in pure and doped ZrB_2 .

Chapter 2

ZrB₂ and HfB₂ reactive potential

2.1 Introduction

Molecular Dynamics (MD) are the most frequently used atomistic simulation approach. In the context of N-body system, the coordinates and velocities of atoms are determined by numerically solving the Newton's equations of motion (equation 2.1) for the whole set of particles. Forces between particles and potential energy are defined by inter atomic force fields. These force fields (or potentials) do entirely define the function, $V(x)$, and allows the MD to yield the trajectories.

$$m_i \cdot \frac{d^2 x_i}{dt^2} = - \frac{dV(x_1, x_2, x_3 \dots)}{dx}. \quad (2.1)$$

While there is no exact analytic expression for $V(x)$, much work have been done to find reasonable models. Each model only works for the specific range of materials it was designed for. For example, one of the simplest models is the Lennard-Jones potential which only has three parameters and is useful to predict well interactions between pairs of neutral atoms or molecules. If this potential is used for ZrB₂ for example, it will poorly predict most of the properties. Other potentials like Tersoff, Stillinger Weber, and EAM are used. e.g. EAM is designed for metals, Tersoff is useful for covalent materials ...

One class of the potentials is called reactive (or bond order potentials). It also contains Finnis-Sinclair and Tersoff potentials, and provides the advantage of considering the strength of bonds between two atoms to be variable, and dependent on the local environment, which allows us to model reactions more easily.

In this chapter, we develop the so-called ReaxFF potential [23] for ZrB_2 and HfB_2 . The developed potential will also account for reactions with some elements of interest like Silicon, Carbon, Oxygen, and Tungsten.

2.2 Theoretical formulation

The energy of the atomistic system is divided into different partial energy contributions [23] as illustrated in the following equation :

$$\begin{aligned}
 E_{system} = & E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{tors} + E_{pen} + E_{C_2} \\
 & + E_{triple} + E_{conj} + E_{H-bond} + E_{vdwaals} + E_{coulomb},
 \end{aligned} \tag{2.2}$$

where the different energy contributions, respectively, stand for : Bond energy, lone pair energy, over-coordination energy, under-coordination energy, valency energy, torsion energy, penalty energy, C_2 correction energy, triple bond energy, conjugation energy, Hydrogen bond correction energy, Van Der Waals energy, and coulomb energy. Although we have the most general energy expression, it is always useful to look closer to each contribution, and neglect the terms that are not relevant for our

specific problem. The formulation can then be simplified, and useless calculations can be avoided. For that purpose, the energy expression can be simplified to :

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{vdwaals} + E_{coulomb}. \quad (2.3)$$

The contribution of each of these partial energies will be detailed in equations (2.4) to (2.37).

2.2.1 Bond order

The main difference between reactive and non reactive potentials is the concept of bond orders, which evaluate the degree of connection between two atoms. In regular potentials, the value of the bond order is an integer (0 if the atoms are not connected, 1 if it is a simple bond, 2 if it is a double bond, and 3 if it is a triple bond). However, in the ReaxFF potential, it's rather a real number ranging from 0 to 3 (0 is the limiting case where the atoms are very far from each others). Its expression is a function of the inter atomic distances r_{ij} , and is given by equations (2.4), (2.5), (2.6), and (2.7) as follows:

$$BO'_{ij} = BO'^{\sigma}_{ij} + BO'^{\pi}_{ij} + BO'^{\pi\pi}_{ij}, \quad (2.4)$$

$$BO'^{\sigma}_{ij} = \exp \left[P_{bo1} \cdot \left(\frac{r_{ij}}{r_0^{\sigma}} \right)^{P_{bo2}} \right], \quad (2.5)$$

$$BO'^{\pi}_{ij} = \exp \left[P_{bo3} \cdot \left(\frac{r_{ij}}{r_0^{\pi}} \right)^{P_{bo4}} \right], \text{ and} \quad (2.6)$$

$$BO'^{\pi\pi}_{ij} = \exp \left[P_{bo5} \cdot \left(\frac{r_{ij}}{r_0^{\pi\pi}} \right)^{P_{bo6}} \right]. \quad (2.7)$$

The contribution of each type of bonding (σ , π , and $\pi\pi$) varies from 0 to 1 and is added separately to the total bond order, which is calculated between each pair of atoms regardless of the connectivity. P_{bo1} , P_{bo2} , P_{bo3} , P_{bo4} , and P_{bo6} are to be fitted against Quantum Mechanics data later.

2.2.2 Bond order correction

From the equations above, the calculated bond orders only depend on inter-atomic distances between each pair. Obviously, the picture is more complicated than that: The connectivity between two C atoms distant by 2 Å , for example, should be different if they are put in different environments. The bond order correction is then needed to slightly modify the previous result. The following equations ((2.8) to (2.18)) present the mathematical formulation of the correction:

$$\Delta'_i = -Val_i + \sum_{j=1}^{neighbors(i)} BO'_{ij}, \quad (2.8)$$

$$\Delta_i^{boc} = -Val_i^{boc} + \sum_{j=1}^{neighbors(i)} BO'_{ij}, \quad (2.9)$$

$$BO_{ij}^{\sigma} = BO'_{ij}{}^{\sigma} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}), \quad (2.10)$$

$$BO_{ij}^\pi = BO_{ij}'^\pi \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}), \quad (2.11)$$

$$BO_{ij}^{\pi\pi} = BO_{ij}'^{\pi\pi} \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_1(\Delta'_i, \Delta'_j) \cdot f_4(\Delta'_i, BO'_{ij}) \cdot f_5(\Delta'_j, BO'_{ij}), \quad (2.12)$$

$$BO_{ij} = BO_{ij}^\sigma + BO_{ij}^\pi + BO_{ij}^{\pi\pi}, \quad (2.13)$$

$$f_1(\Delta'_i, \Delta'_j) = \frac{1}{2} \left[\frac{val_i + f_2(\Delta'_i, \Delta'_j)}{val_i + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} + \frac{val_j + f_2(\Delta'_i, \Delta'_j)}{val_j + f_2(\Delta'_i, \Delta'_j) + f_3(\Delta'_i, \Delta'_j)} \right], \quad (2.14)$$

$$f_2(\Delta'_i, \Delta'_j) = \exp(-P_{boc1} \cdot \Delta'_i) \cdot \exp(-P_{boc1} \cdot \Delta'_j), \quad (2.15)$$

$$f_3(\Delta'_i, \Delta'_j) = -\frac{1}{P_{boc2}} \cdot \ln \left(\frac{1}{2} \cdot [\exp(-P_{boc2} \cdot \Delta'_i) + \exp(-P_{boc2} \cdot \Delta'_j)] \right), \quad (2.16)$$

$$f_4(\Delta'_i, BO'_{ij}) = \frac{1}{1 + \exp(-P_{boc3} \cdot (P_{boc3} \cdot BO'_{ij} \cdot BO'_{ij} - \Delta_i'^{boc}) + P_{boc5})}, \text{ and} \quad (2.17)$$

$$f_5(\Delta'_j, BO'_{ij}) = \frac{1}{1 + \exp(-P_{boc3} \cdot (P_{boc3} \cdot BO'_{ij} \cdot BO'_{ij} - \Delta_j'^{boc}) + P_{boc5})}, \quad (2.18)$$

where Δ_i is an over-coordination variable showing how much the atom is over or under coordinated. If Δ_i is positive, the specific atom is, then, making more bonds ($\sum_{j=1}^{neighbors(i)} BO'_{ij}$) than it should (val_i). The correcting functions f_1 , f_2 , f_3 , f_4 , and f_5 decrease the value of the bond orders to relax the over-coordination. If Δ_i is negative, the specific atom is making less bonds than it should, and the correcting functions increase the value of the bond orders to relax the under-coordination. After correcting the bond orders, we calculate separately the different types of energy of the system (bond energy, over-coordination energy, under-coordination energy, valence energy, Van Der Waals energy, and coulomb energy).

2.2.3 Bond energy

Equation (2.19) is used to calculate the bond energy. The shape and value of the energy is mainly dictated by the choice of the parameters P_{pb1} and P_{pb2} , and have the form of equation 2.19 and figure 2.1:

$$E_{bond} = -D_e^\sigma \cdot BO_{ij}^\sigma \cdot \exp \left[P_{be1} \left(1 - (BO_{ij}^\sigma)^{P_{be2}} \right) \right] - D_e^\pi \cdot BO_{ij}^\pi - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}. \quad (2.19)$$

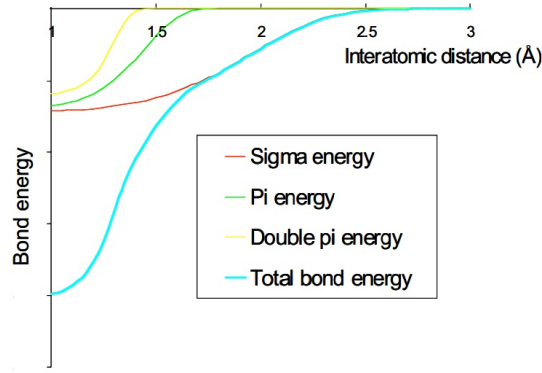


Figure 2.1: Bond energy profile

2.2.4 Over-coordination energy

Even after the bond order correction, which aims to remove the over-coordination or under-coordination of the system, the system might not fully converge to the real valency. Therefore, an over-coordination penalty energy is imposed to the system to ensure further convergence. The form of the energy presented in the following equations ((2.20) to (2.22)) quickly vanishes to 0 when Δ_i is negative or positive and

small:

$$\Delta_i = -val_i + \sum_{j=1}^{neighbors(i)} BO_{ij}, \quad (2.20)$$

$$\Delta_i^{lpcorr} = \Delta_i - \frac{\Delta_i^{lp}}{1 + P_{ovun3} \cdot \exp \left(P_{ovun4} \cdot \left[\sum_{j=1}^{neighbors(i)} (\Delta_j - \Delta_j^{lp}) (BO_{ij}^{\pi} + BO_{ij}^{\pi\pi}) \right] \right)}, \quad (2.21)$$

$$E_{over} = \frac{\sum_{j=1}^{nbonds} P_{ovun1} \cdot D_e^{\sigma} \cdot BO_{ij}}{\Delta_i^{lpcorr} + Val_i} \cdot \Delta_i^{lpcorr} \cdot \left[\frac{1}{1 + \exp \left(P_{ovun2} \cdot \Delta_i^{lpcorr} \right)} \right]. \quad (2.22)$$

Based on the above equations, a typical over-coordination energy should look like figure 2.2.

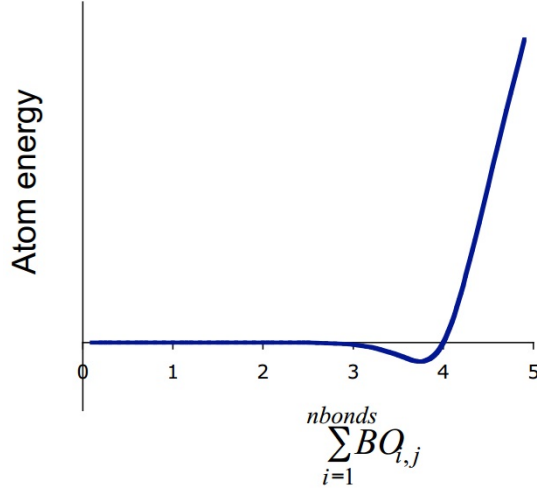


Figure 2.2: Over-coordination energy profile

2.2.5 Under-coordination energy

The under-coordination energy is only meaningful when two atoms have π or $\pi\pi$ bonds. The choice of the parameters P_{ovun2} , P_{ovun5} , P_{ovun6} ensures that the energy

vanishes when $\Delta_i > 0$. Its expression is given by:

$$E_{under} = -P_{ovun5} \cdot \frac{1 - \exp(P_{ovun6} \cdot \Delta_i^{lpcor})}{1 + \exp(P_{ovun2} \cdot \Delta_i^{lpcor})}. \quad (2.23)$$

2.2.6 Valence energy

The valence energy is a penalty added to the system if the equilibrium angles are not satisfied. E_{val} (given by equation (2.24)) vanishes when angles are equal to Θ_0 and takes positive values otherwise. The shape and the amplitude of this function is determined by the set of parameters $P_{val1} - > P_{val10}$, and is in general similar to figure 2.3, while the following equations show the expression of the valence energy contribution:

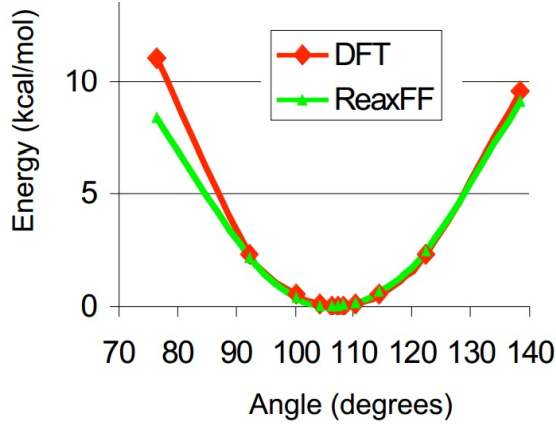


Figure 2.3: Valence energy profile

$$E_{val} = f_7(BO_{ij}) \cdot f_7(BO_{jk}) \cdot f_8(\Delta_j) \cdot (P_{val1} - P_{val1} \cdot \exp(-P_{val2}(\Theta_0(BO) - \Theta_{ijk})^2)), \quad (2.24)$$

$$f_7(BO_{ij}) = 1 - \exp(-P_{val3} \cdot BO_{ij}^{P_{val4}}), \quad (2.25)$$

$$f_8(\Delta_j) = P_{val5} - (P_{val5} - 1) \cdot \frac{2 + \exp(P_{val6} \cdot \Delta_j)}{1 + \exp(P_{val6} \cdot \Delta_j) + \exp(-P_{val7} \cdot \Delta_j)}, \quad (2.26)$$

$$SBO = \sum_{n=1}^{neighbors(j)} (BO_{jn}^{\Pi} + BO_{jn}^{\text{III}\Pi}) + (1 - \prod_{n=1}^{neighbors(j)} \exp(-BO_{jn}^8) (-\Delta_j^{angle} - P_{val8} \cdot n_{lp,j})), \quad (2.27)$$

$$\Delta_j^{angle} = -val_j^{angle} + \sum_{n=1}^{neighbors(j)} BO_{jn}, \quad (2.28)$$

$$\begin{aligned} SBO_2 = 0 & & SBO < 0 \\ & = SBO^{P_{val9}} & 0 < SBO < 1 \\ & = 2 - (2 - SBO)^{P_{val9}} & 1 < SBO < 2 \\ & = 2 & SBO > 2, \text{ and} \end{aligned} \quad (2.29)$$

$$\Theta_0(BO) = \Pi - \Theta_{0,0} \cdot (1 - \exp[-P_{val10} \cdot (2 - SBO)]). \quad (2.30)$$

2.2.7 Van Der Waals energy

In addition to bonded interactions, non-bonded interactions are also accounted for in the reactive potential : Repulsive interactions at short inter-atomic distances (or Van Der Waals forces) are given by equation (2.34). Where the taper correction, given by equation (2.31), is used to smooth the transition and to avoid energy discontinuities

when atoms jump off the cut-off radius. The taper expression is given by :

$$Tap = Tap_0 + Tap_1.r_{ij}^1 + Tap_2.r_{ij}^2 + Tap_3.r_{ij}^3 + Tap_4.r_{ij}^4 + Tap_5.r_{ij}^5 + Tap_6.r_{ij}^6 + Tap_7.r_{ij}^7, \quad (2.31)$$

$$Tap_0 = 1,$$

$$Tap_1 = 0,$$

$$Tap_2 = 0,$$

$$Tap_3 = 0,$$

$$Tap_4 = -\frac{35}{R_{cut}^4},$$

$$Tap_5 = -\frac{84}{R_{cut}^5},$$

$$Tap_6 = -\frac{70}{R_{cut}^6}, \text{ and}$$

$$Tap_7 = -\frac{20}{R_{cut}^7}. \quad (2.32)$$

While the Van Der Waals energy is given by:

$$f_{13}(r_{ij}) = [r_{ij}^{P_{vdw1}} + (\frac{1}{\gamma_w})^{P_{vdw1}}]^{\frac{1}{P_{vdw1}}}, \text{ and} \quad (2.33)$$

$$E_{vdw} = Tap.D_{ij}.[\exp(\alpha_{ij}.[1 - \frac{f_{13}(r_{ij})}{r_{vdw}}])]. \quad (2.34)$$

2.2.8 Coulomb energy

Coulomb energy is the second type of non-bonded interactions in ReaxFF potential. In contrast to Van Der Waals, the Coulomb energy is a long range interaction, and its expression is given by equation 2.35. The following expression shows how a shielding factor (γ_{ij}) is used to avoid divergence for small distances:

$$E_{coulomb} = Tap. \frac{q_i \cdot q_j}{[r_{ij}^3 + (\frac{1}{\gamma_{ij}})^3]^{\frac{1}{3}}}. \quad (2.35)$$

Typical Coulomb and Van Der Waals energy profiles are shown in figure 2.4.

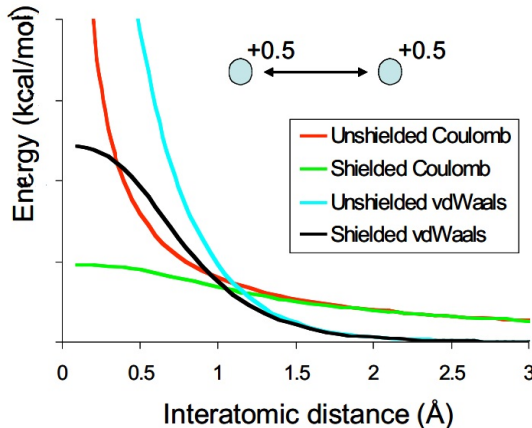


Figure 2.4: Coulomb and Van Der Waals energy profiles

2.3 Training set and weights

The quality of any potential is, in general, defined by three properties : The choice of the training set, the accuracy of Quantum Mechanics (or experimental) data, and the accuracy of the fitting procedure.

The first crucial step in developing a good potential is, then, choosing the best, and more exhaustive training set. Although the main materials of interest for our problem are ZrB_2 and HfB_2 , they will not be the only species appearing in the potential. In fact, these materials are in general associated with other atomic species: For instance, SiC is often added to these ceramics (appears as grains in ZrB_2 lattice). Tungsten, as well as Oxygen are also interacting species (generally present at the surfaces and grain boundaries).

In order for the potential to be able to well predict these interactions, a wide training set defining the behavior of all these materials should be considered :First, properties of the pure materials in their most common crystalline structure (Zr, Hf, B, Si, C, O, W) are studied: Equations of state, dissociation curves, defect energies and surface energies calculations are performed. Each of these properties have a special role in making the potential accurate and reliable. In fact, if we ignore the errors resulting from the fitting procedure, the potential should be able to predict flawlessly all the training set data. Other properties are not guaranteed to be well predicted. However, if the main physical phenomena is well described, all emerging properties should follow. For example, if the potential makes a good estimate of the stacking fault energies, it should follow that dislocation nucleation is well described. If vacancy formations and migration energies are well defined by the potential, all diffusion properties will follow as well.

For our case, the equations of state are important to fit the lattice constant, the binding energy, and the bulk modulus of the material(obtained by deriving the

equation of state twice) and are given by equation 2.36. If the equations of state are well fitted, so will be all these properties.

The dissociation curves are also important because they define energetically how two atoms form or break a bond, since we aim to study interactions, this will be an important feature. Defect energies (or vacancy formation energies) are important to define the diffusion properties of the materials. Surface energies dictates the energy of voids and allows us to model simulations with less than ideal coordination.

Now, it is necessary to specify the weight of every property in the error function that will be minimized. This choice is subjective, but, it is guided by our choice of “how much do we care about each property”. For the reasons explained above, we do chose the weights as appears in figure 2.5. It is important to remember here, that these weights are those for pure crystals, and not the final weights.

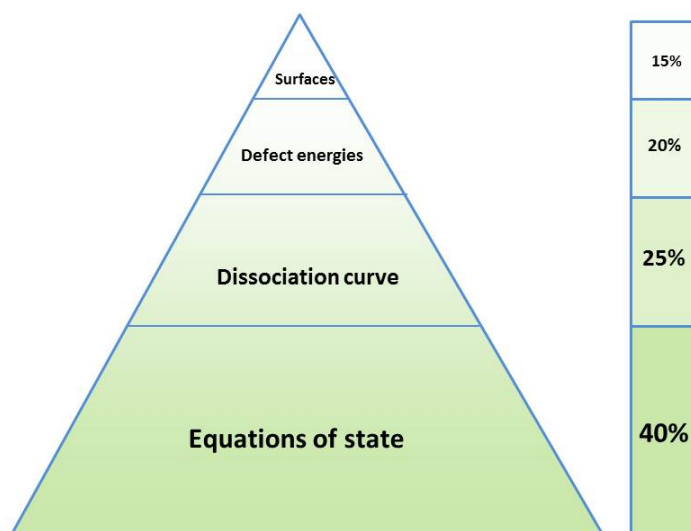


Figure 2.5: Error function weight for pure crystals

All the properties defined above, are for sure important, but are not enough to characterize our reactive potential. In fact, compound elements (ZrB_2 for example) do have Zr-B bonds in addition to Zr-Zr and B-B, which cannot be characterized only by means of pure crystals.

Since seven atom species are present in our potential, a full characterization of all possible reactions requires the identification of 7 atomic properties (Zr, Hf, B, Si, C, O, W), 28 different bond properties (Zr-Zr, Zr-Hf, Zr-B, Zr-Si, Zr-C, Zr-O, Zr-W, Hf-B, Hf-Si, Hf-C, Hf-O, Hf-W, B-B, B-Si, B-C, B-O, B-W, Si-Si, Si-C, Si-O, Si-W, C-C, C-O, C-W, O-O, O-W, W-W), and about 200 angle properties (Zr-Zr-Zr, Zr-Zr-B, ...). However, it is not practically possible to include that large number of Quantum Mechanics data points. A wise choice should then be done to decide which properties to simulate.

We, then, consider only the commonly known alloys (ZrB_2 , HfB_2 , ZrC, HfC, ZrO_2 , HfO_2 , SiC, B_2O_3 , ZrW, HfW). These compounds, although they do not present an exhaustive list of the possible reactions, they do provide descent knowledge about the most important bonds. Other bond properties will be extrapolated as will be shown in the following sections.

In addition to equations of state, dissociation curves, defect energies, and surface energies, other properties are only significant in alloys, and thus are added to the training set. In fact, the heat of formation of alloys such as ZrB_2 is a fundamental property that defines the energetics of ZrB_2 formation. The charge distribution is also important in defining the Coulombic interactions and is only significant in compound

structures (all charges are zero in pure crystals). The weights of these properties are summarized in figure 2.6.

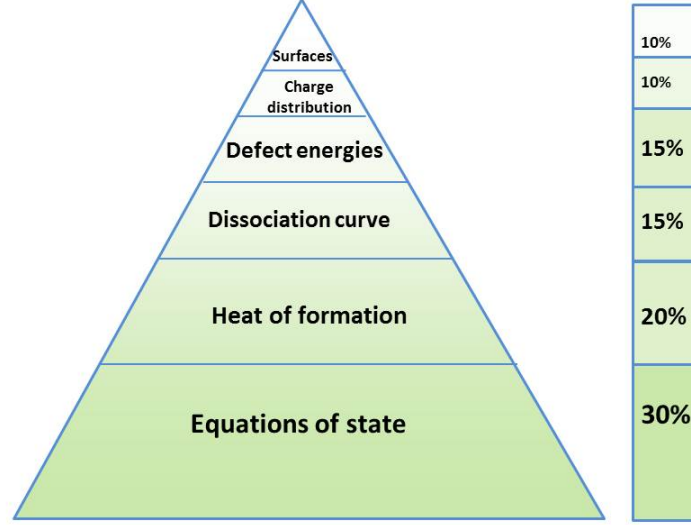


Figure 2.6: Error function weight for alloys

Combining these two sets, our final training set is composed from both pure crystals, and alloys. The final weights are presented in table 2.1.

Table 2.1: Final weights for the error function

property	weight (pure)	weight (alloy)	total weight
Equations of state	20	15	35
Dissociation curve	12.5	7.5	20
Defect energies	10	7.5	17.5
Surface energies	7.5	5	12.5
Heat of formation	—	10	10
Charge distribution	—	5	5

2.4 Quantum calculations

To generate our training set, we need to collect reliable data either from quantum calculations or experiments. In general, experimental results are more accurate, and should be chosen over the quantum calculations if available. However, since we do not have these experimental results for all materials, we chose to be consistent and run our quantum calculations to obtain all properties. We, then, use the VASP package [24] to generate our training set. We do also make sure, that for every type of simulation, the results are convergent with respect to the number of K-points.

2.4.1 Equations of state

Equations of state are of fundamental importance in defining the strength and equilibrium properties of materials. In fact, equation 2.36 shows how to extract the bulk modulus from a volume expansion equation of state, as

$$E = E_0 + \frac{9}{8}B_0V_0 \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right)^2, \quad (2.36)$$

where, E_0 is the total cohesive energy, B_0 the bulk modulus, V_0 the equilibrium volume, and V the volume of deformed state.

If we consider the absolute energies, these curves can also provide us with the cohesive energy, and equilibrium volume of the materials. For clarity, we normalize the equations of state with respect to the equilibrium volume and cohesive energy, and we present the relative energy of the lattice with respect to $(\delta = \left(\frac{V_0}{V}\right)^{2/3} - 1)$ to extract

the bulk modulus. Cohesive energies and equilibrium volumes of the structures are then presented separately.

Figures 2.8, 2.7, 2.9, and 2.10 present the equations of state of the pure elements and some of the possible compounds, while table 2.2 summarizes the obtained binding energies, bulk modulus, and lattice parameters.

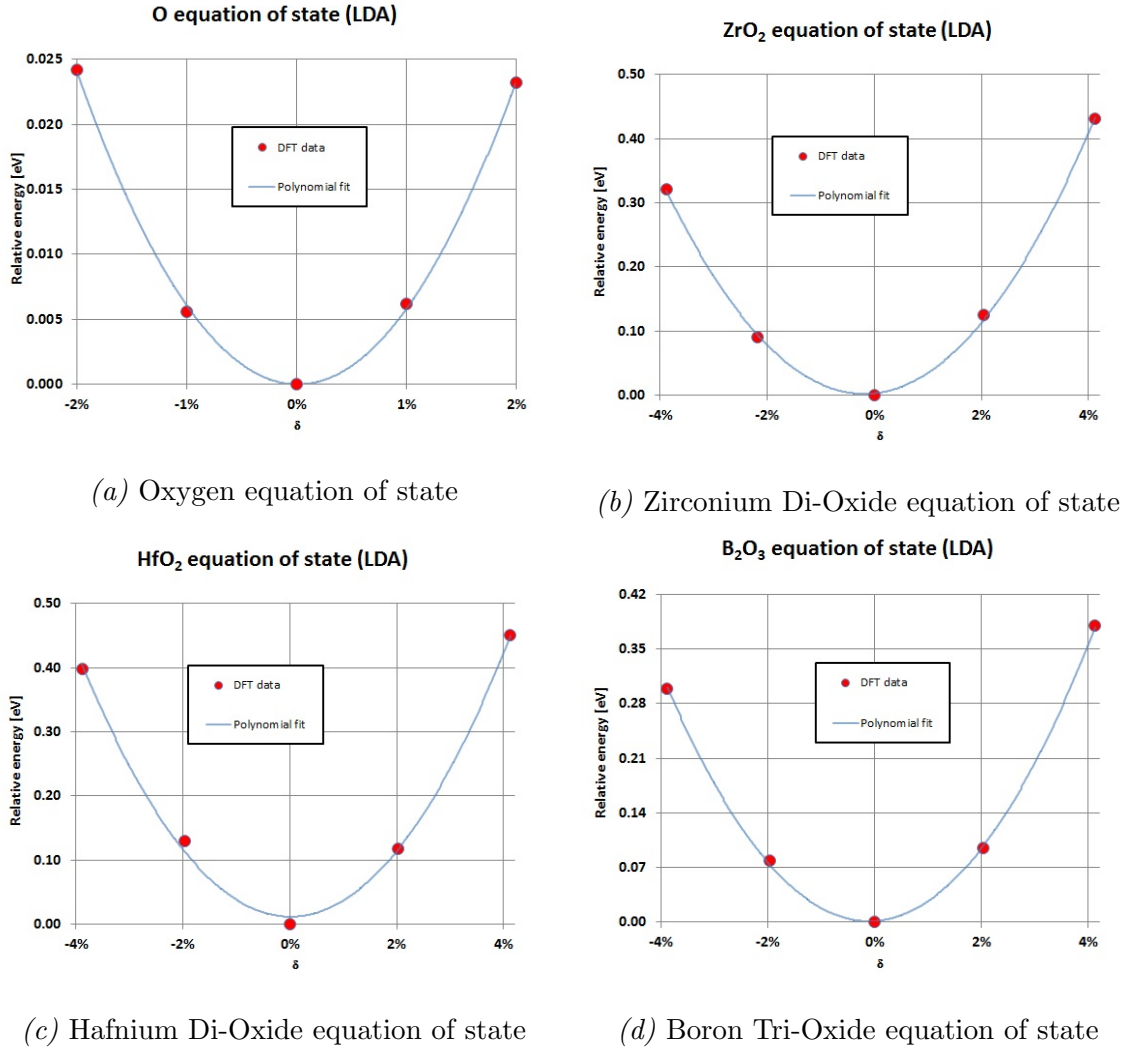
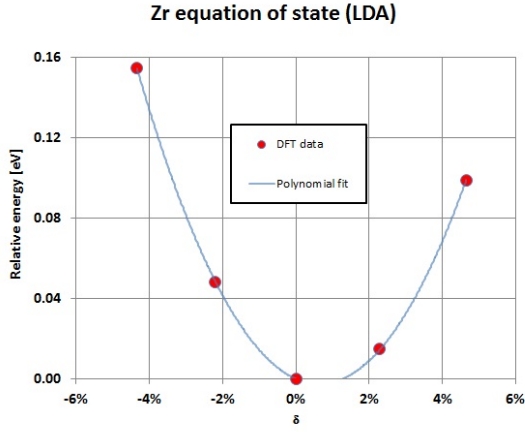
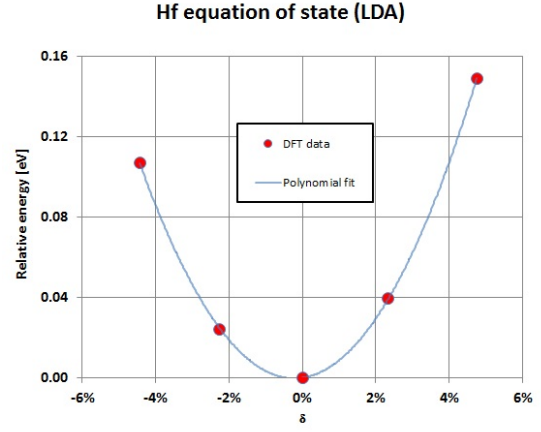


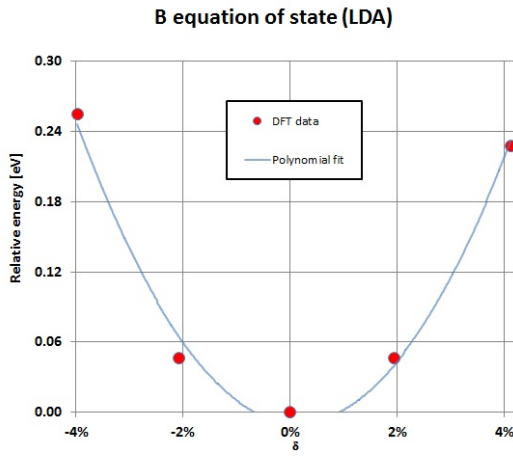
Figure 2.7: Oxygen, and Oxides equations of state



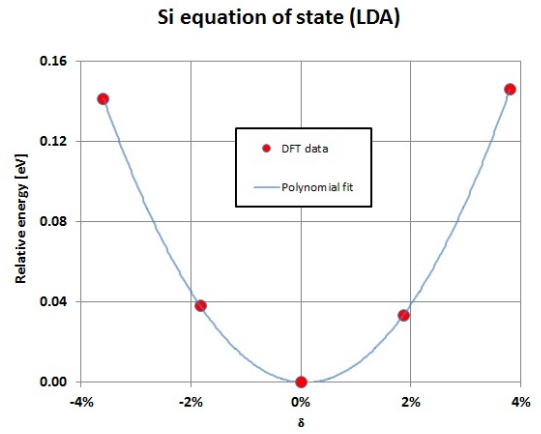
(a) Zirconium equation of state



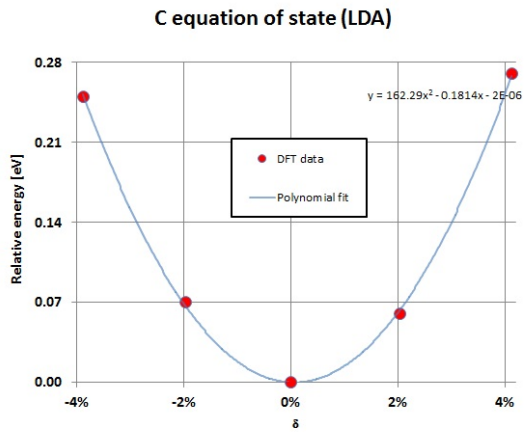
(b) Hafnium equation of state



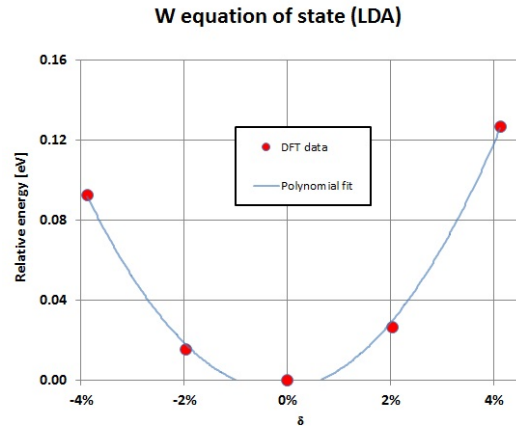
(c) Boron equation of state



(d) Silicon equation of state

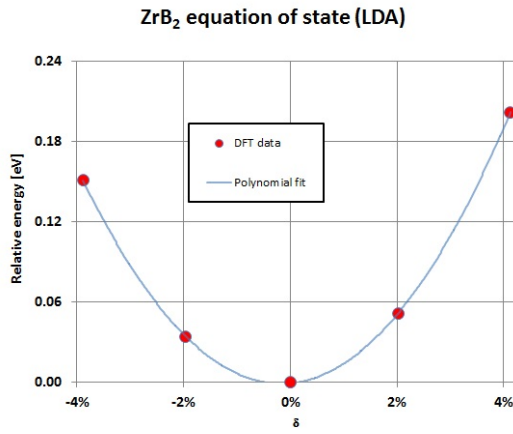


(e) Graphite equation of state

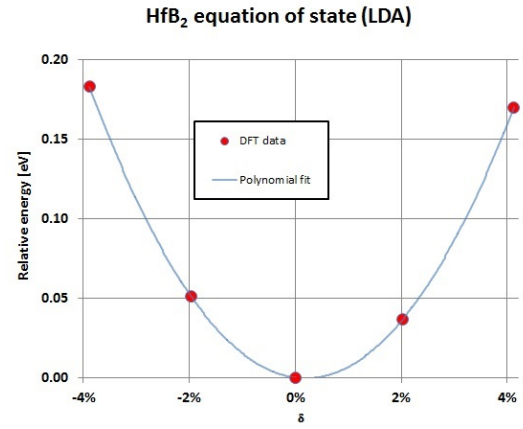


(f) Tungsten equation of state

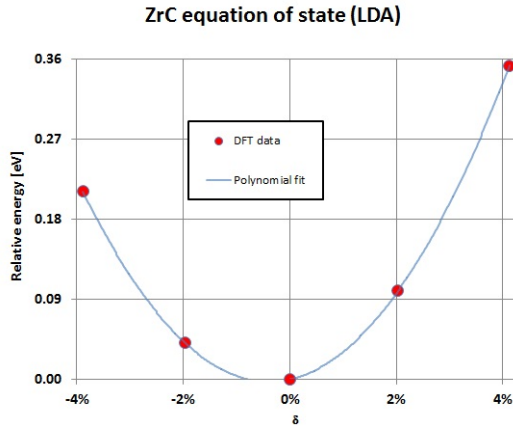
Figure 2.8: Pure elements equations of state (Zr, Hf, B, C, W, and Si)



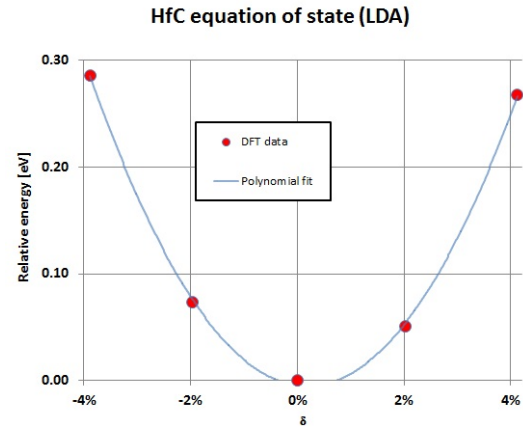
(a) Zirconium Di-Boride equation of state



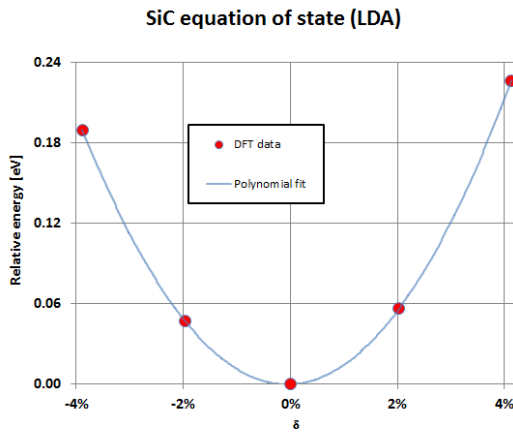
(b) Hafnium Di-Boride equation of state



(c) Zirconium Carbide equation of state

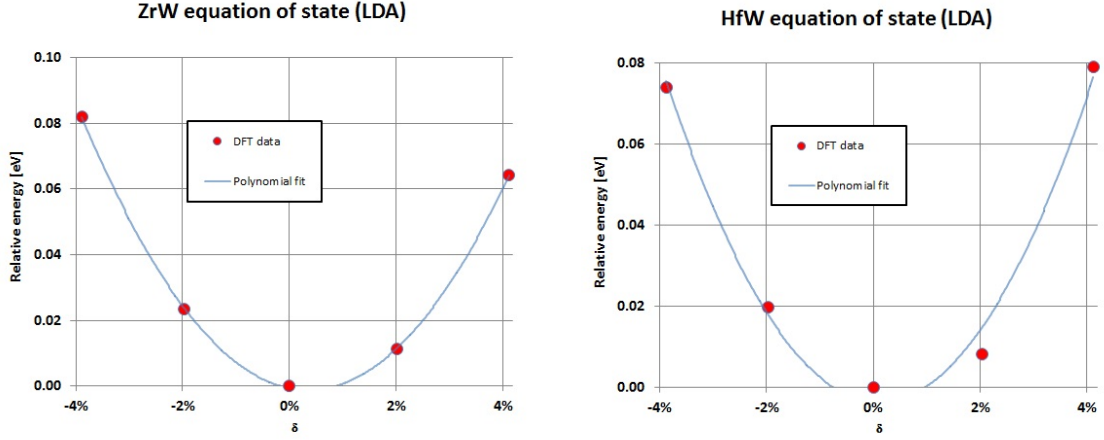


(d) Hafnium Carbide equation of state



(e) Silicon Carbide equation of state

Figure 2.9: Borides and Carbides equations of state



(a) Zirconium Tungsten equation of state (b) Hafnium Tungsten equation of state

Figure 2.10: Tungstates equations of states

Table 2.2: Properties summary for pure elements and alloys

entity	structure	atoms	lattice constant[Å]	binding energy [eV]	bulk modulus [Gpa]
Zr	sc	4	4.45	-7.36	93.60
Hf	sc	4	4.36	-6.73	115.99
B	hex.	36	4.85 — 12.43	-7.34	255.42
Si	dc	8	5.41	-5.20	94.73
W	bcc	2	3.18	-10.11	324.75
C	c	8	4.23 — 2.44 — 6.23	-8.84	207.02
O	—	2	—	-1.85	—
ZrB ₂	c	6	3.13 — 5.43 — 3.51	-8.28	262.81
HfB ₂	c	6	3.09 — 5.36 — 3.46	-8.38	273.75
ZrC	c	8	4.65	-9.01	248.08
HfC	c	8	4.58	-9.24	260.35
SiC	c	8	4.33	-7.32	227.83
B ₂ O ₃	hex	15	4.31 — 8.30	-7.79	223.84
ZrO ₂	c	12	5.06	-8.70	255.36
HfO ₂	c	12	4.98	-8.97	298.81
ZrW	bcc	2	3.30	-8.53	182.05
HfW	bcc	2	3.27	-8.70	203.03

The used structures for our simulations are the most common structure for each material, although the crystalline structure may not seem in agreement with what is commonly known. In fact, for simplicity reason (of the fitting procedure), we

choose to convert the structures, when possible to cubic systems. For example ZrB_2 crystallizes in HCP structure, but can be converted to a cubic system as shown in figure 2.11. Similar changes are made for HfB_2 , C, B ...

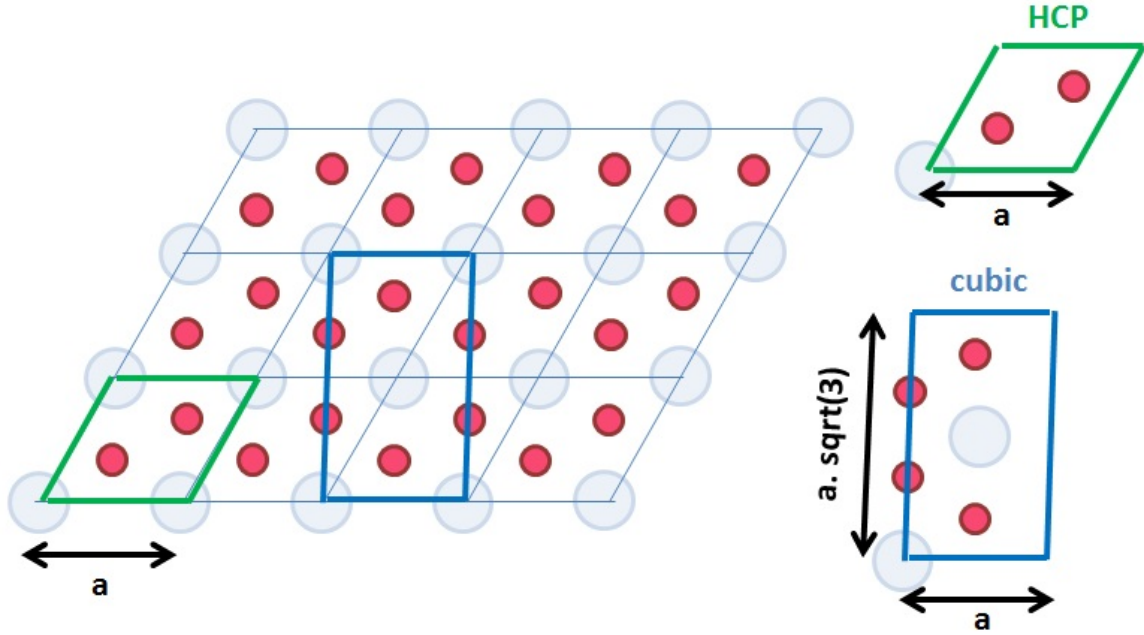


Figure 2.11: ZrB_2 conversion : hcp to cubic

2.4.2 Crystal dissociation curve

The dissociation curves are important in estimating the exact bond distances and energies for breaking and formation. It is important to note that these Quantum Mechanics calculations are not straight forward: Since the electronic shell is not fully filled in dimers, spin polarized calculations have to be done.

Figure 2.13 show the binding energy per atom with respect to inter-atomic distance for the pure elements in our potential, while figures 2.12, 2.14, and 2.15 describe the dissociation for binary elements. Oxygen dissociation is also added (but, since

Oxygen is present in gas phase and no crystalline structure is possible, we only consider an O_2 molecule dissociation).

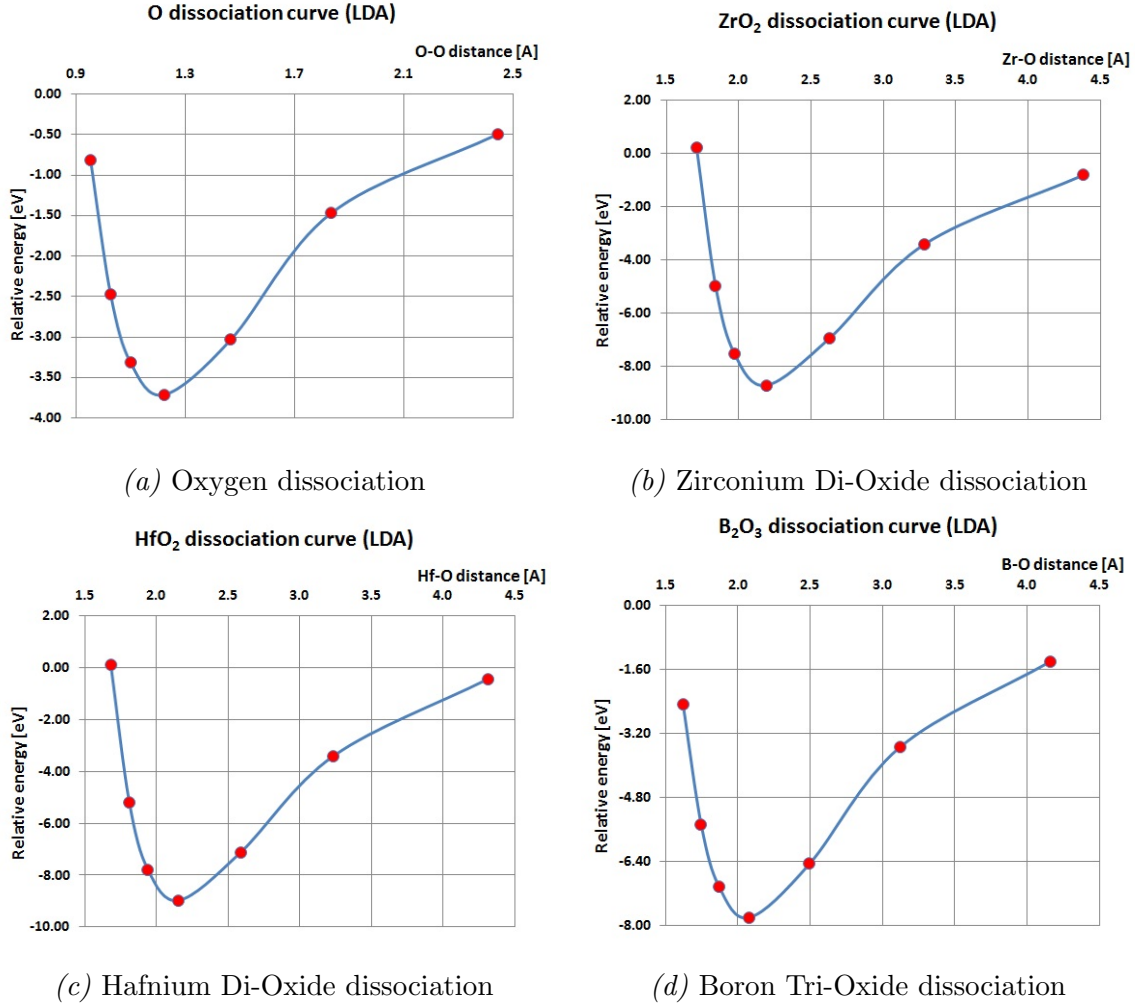
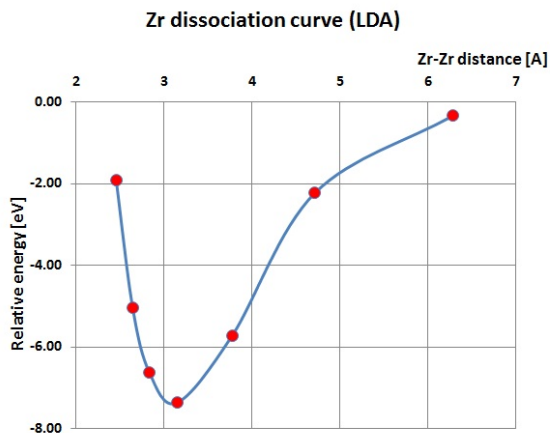
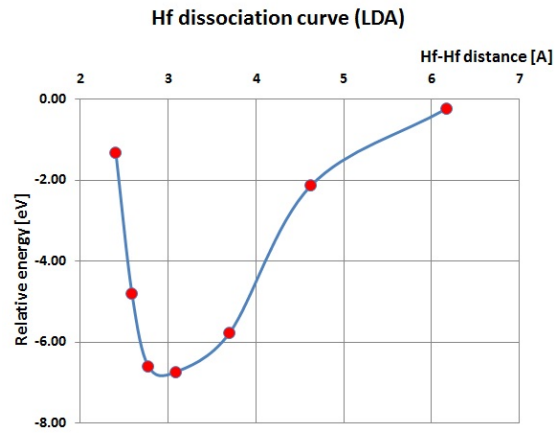


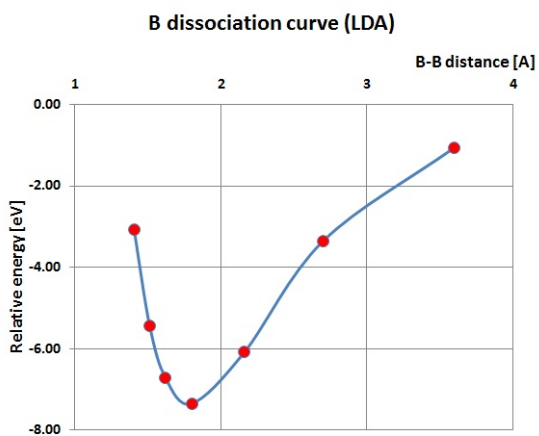
Figure 2.12: Oxygen and Oxides dissociation curves



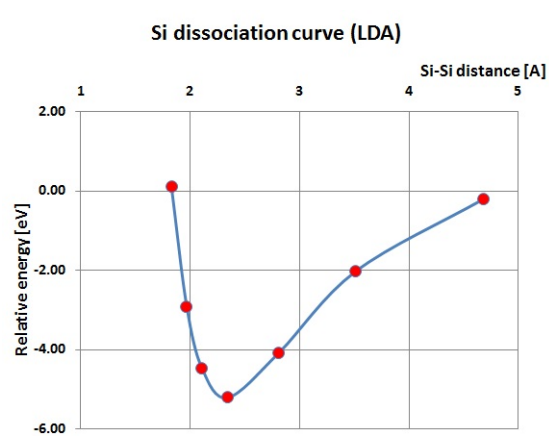
(a) Zirconium dissociation



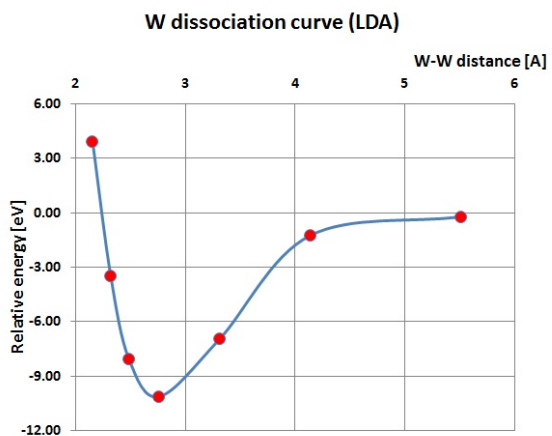
(b) Hafnium dissociation



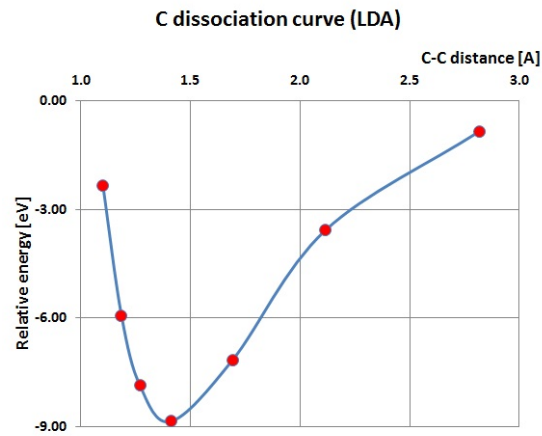
(c) Boron dissociation



(d) Silicon dissociation

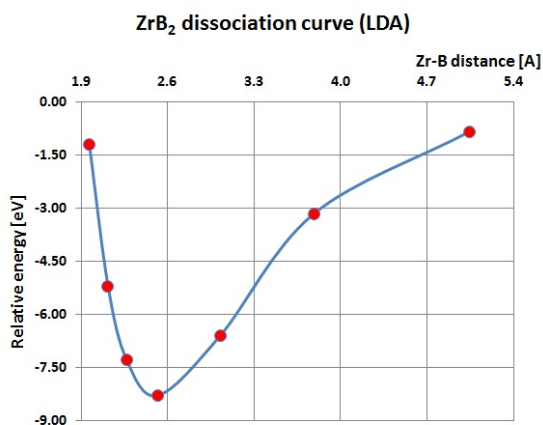


(e) Tungsten dissociation

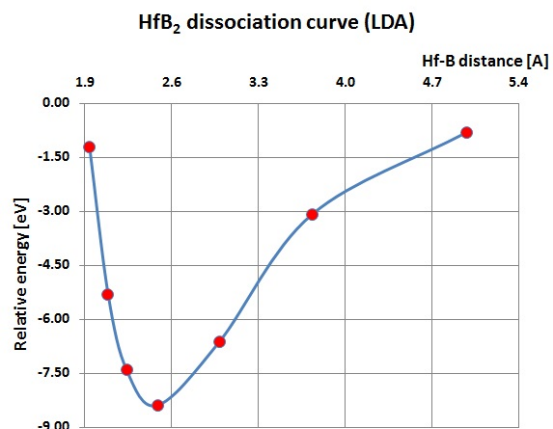


(f) Graphite dissociation

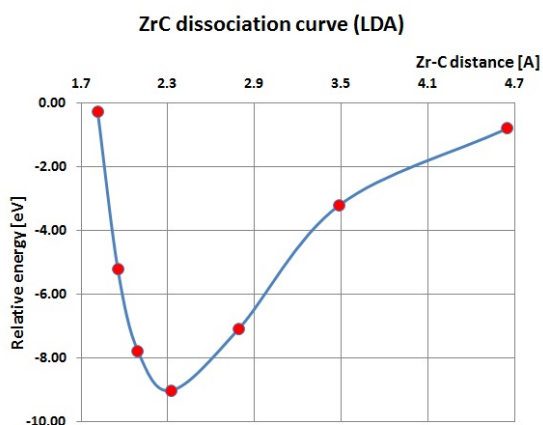
Figure 2.13: Pure elements dissociation curves



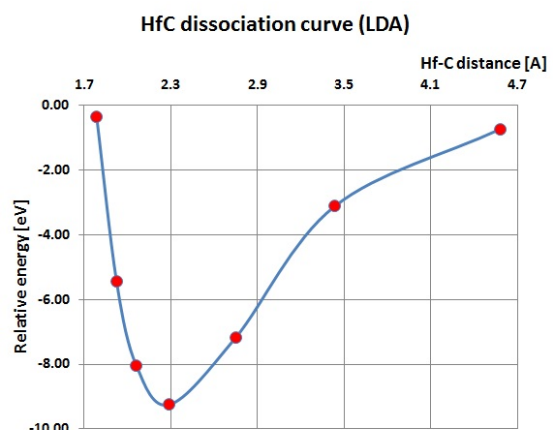
(a) Zirconium Di-Boride dissociation



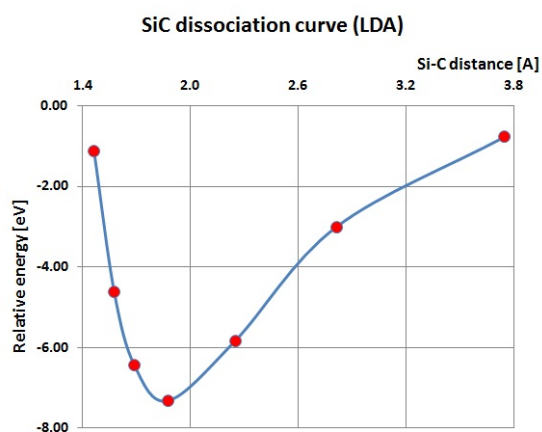
(b) Hafnium Di-Boride dissociation



(c) Zirconium Carbide dissociation



(d) Hafnium Carbide dissociation



(e) Silicon carbide dissociation

Figure 2.14: Borides and Carbides dissociation curves

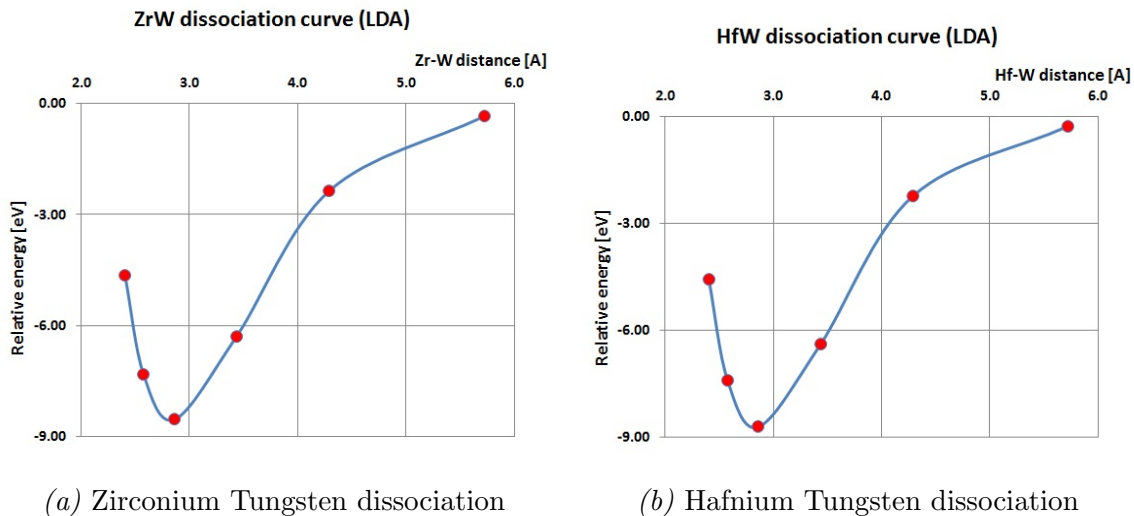


Figure 2.15: Tungstates dissociation curves

2.4.3 Mulliken charge distribution

Charge distribution is an important property in reactions, which is only relevant for binary elements (because all atoms in pure crystals have the same electronegativity). For binary materials, the charges tend, in general, to lean toward the more electronegative atoms species. We should note here, that the electronegativity is an atomic property (presented in table 2.3), and does not depend on the crystalline structure.

Table 2.3: Electronegativity of Zr, Hf, Si, B, C, O, and W

Atom	Hf	Zr	W	Si	B	C	O
electronegativity	1.3	1.4	1.7	1.8	2.0	2.5	3.5

Electronegativity, in general, increases from left to right and from bottom to top on the periodic table. That explains why Oxygen is the most electronegative element

in our list. Table 2.4 shows how the charges are distributed for some binary materials.

Table 2.4: charge distribution for alloys

alloy	atom	charge
ZrB ₂	Zr	+0.50
	B	-0.25
HfB ₂	Hf	+0.44
	B	-0.22
SiC	Si	+0.35
	C	-0.35
ZrC	Zr	-0.29
	C	+0.29
HfC	Hf	-0.02
	C	+0.02
ZrO ₂	Zr	-1.12
	O	+0.56
HfO ₂	Hf	-1.20
	O	+0.60
ZrW	Zr	+0.11
	W	-0.11
HfW	Hf	+0.09
	W	-0.09

2.4.4 Surface energies

Physically, the surface energy quantifies the disruption of atomic bonds that occur when a surface is created. Since the surface energy depends on the orientation of the crystal, it will also indicate which surface is most likely to be created (the orientation with the lowest surface energy). Mathematically it is given by

$$\gamma = \frac{E_{slab} - E_{bulk}}{2A}. \quad (2.37)$$

In principle, calculating an accurate surface energy does require surface relaxation (sometimes, even a reconstruction and neutralization with H atoms is required). However, in this work, we only calculate single point energies based on bulk coordinates (we only remove the periodicity for the surface in question). On the one hand, getting the correct surface structures for many structures is tricky, and requires a large unit cell and long computational time. On the other hand, although the calculated surface energies won't be exact, this won't decrease any of the accuracy of the potentials since we will be fitting the same configuration and we will be comparing energies of similar structures. Figures 2.16, 2.17, 2.18, 2.19, and 2.20 present surface energies obtained for pure crystals, Borides, Carbides, Oxides, and Tungstates.

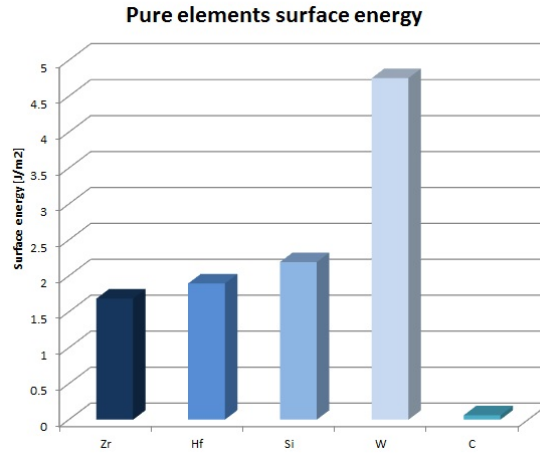


Figure 2.16: Pure elements surface energies

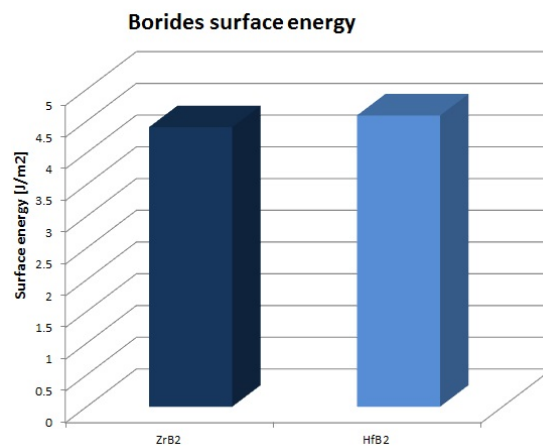


Figure 2.17: Borides surface energies

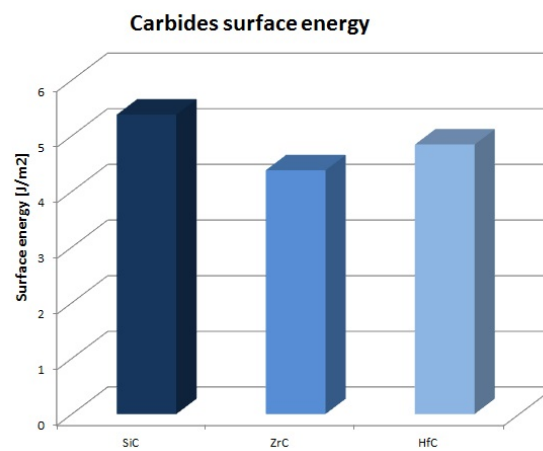


Figure 2.18: Carbides surface energies

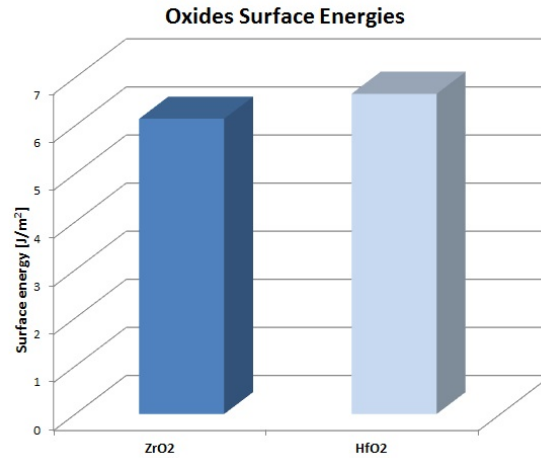


Figure 2.19: Oxides surface energies

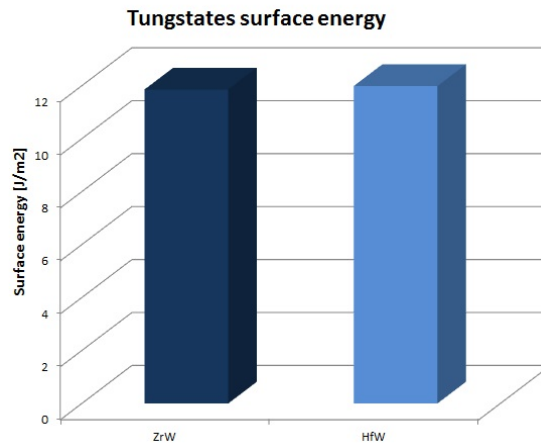


Figure 2.20: Tungstates surface energies

2.4.5 Heats of formation

Heat of formation (HOF) of a compound describes the difference between energy states of the compound and the pure elements. This physical property is different than the reaction activation energy (HOF describes the difference between initial and

final energies, while activation energy reflects the barrier between them). Figure 2.21 presents the different values for the formation energies.

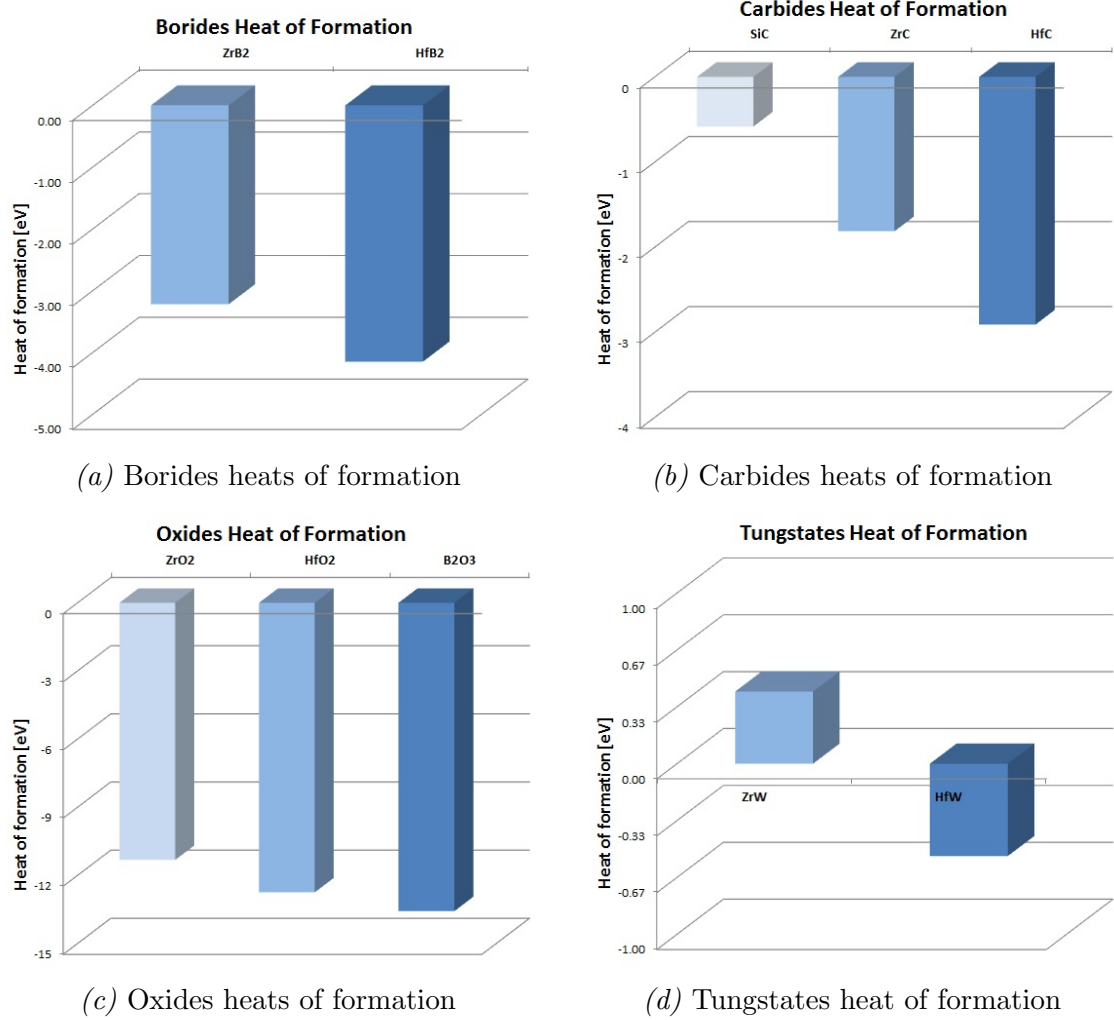


Figure 2.21: Heats of formations for carbides, borides, oxides, and tungstates

Some conclusions can be drawn from these figures: Oxides have very high heat of formation energies, they are easy to form and they are stable. Tungstates have very low heats of formation (sometimes positive) because the simulated structures does not reflect the real structures (in reality Zirconium Tungstate, and Hafnium Tungstate are present in more complex structures $\text{Zr}(\text{WO}_4)_2$ and $\text{Hf}(\text{WO}_4)_2$) and with much lower

energies), but for our purpose, we are fitting energies to energies of similar structures, so it is not important whether these structures are the lowest energy structures or not. Zirconium and Hafnium Di-Borides have fairly high formation energies (3 to 4 eV) while Carbides have relatively low heats of formation (1 to 3 eV).

2.4.6 Intrinsic defect energies

Defect energies (or Vacancy Formation Energies), are needed for accurate modeling of diffusion related processes. For pure elements, VFE are of a single kind, however, for compounds, two or more vacancy formation energies may exist (one for each element). Table 2.5 summarizes our calculations for the defect energies for pure elements while table 2.6 summarizes the VFE for binary alloys.

Table 2.5: Vacancy formation energy for pure elements

Atom	Bulk energy	energy with defect	number of atoms	vacancy formation energy
Zr	-293.83	-282.46	32	2.19
Hf	-339.70	-326.85	32	2.23
Si	-47.57	-38.50	8	3.12
C	-80.95	-63.55	8	7.28
W	-224.71	-206.92	16	3.74

Table 2.6: Vacancy formation energy for compounds

Crystal	Bulk energy	number of atoms	Atom	energy with defect	defect energy
ZrB ₂	-99.34	12	Zr	-85.40	5.66
			B	-88.20	2.86
HfB ₂	-100.55	12	Hf	-86.62	5.55
			B	-89.42	2.76
ZrC	-72.09	8	Zr	-55.48	7.59
			C	-61.12	1.95
HfC	-73.97	8	Hf	-57.06	7.65
			C	-62.57	2.15
SiC	-55.52	8	Si	-45.37	5.83
			C	-46.97	5.13
ZrO ₂	-104.42	12	Zr	-80.41	15.3
			O	-94.19	1.52
HfO ₂	-107.62	12	Hf	-83.02	15.6
			O	-96.93	1.72
ZrW	-159.47	16	Zr	-147.31	2.19
			W	-148.83	0.67
HfW	-167.41	16	Hf	-155.12	1.82
			W	-156.40	0.54

2.5 Fitting procedure

Four types of parameters are to be fitted in this potential : General parameters, atomic parameters (valence, electronegativity, ...), bond parameters (amplitude, equilibrium distance, decay speed, ...), and angular parameters (equilibrium angle, ...). For each of these, we need to provide an initial guess (reasonable enough) to help the fitting code converge within a reasonable time.

General parameters are easy to provide since most of the previously developed ReaxFF potentials do have similar (or close parameters). Table A.2 provide a list of these parameters with a small description, and their values.

Atomic properties are also easy to provide because of two reasons. First, some atomic properties are available from previous works (Silicon properties from lithium silicon potential [25], Oxygen properties from Hydrocarbon potential [26]). These parameters are fitted using an available fitting code and provide the values of parameters in Table A.3. a description of these parameters is given in A.1.

Bond properties are probably the most important and are those who define the behavior of the bond (length, strength, nature ...). Each of these properties is described in table A.4, and the final values of the parameters are given in A.6 and A.5. It is important to note that for the bond parameters we do not have initial guesses, we suppose that the value of a parameter is the average of its values for pure elements (for example, if a parameter P_0 has a value of 3 for Zr-Zr bond, and a value of 4 for B-B bond, we will assign a value of 3.5 for this parameter in the Zr-B bond.

Angular terms are less important for most materials and do represent the variation in strength of the bonds with respect of the angles between atoms (table A.7)

2.6 Results and applications

After providing the initial guess, a code developed by Van Duin [26] is used to fit the parameters. An estimate of the averaged errors is presented in table 2.7, while two MD applications are performed to verify the performance of the potential.

Table 2.7: Estimation of the error (percentage)

parameter	eq. of state	dissociation	Defect E.	Surface E.	HOF	charge
Zr	05	12	09	12	—	—
Hf	04	08	05	04	—	—
B	08	14	*	*	—	—
C	03	07	00	10	—	—
Si	02	07	00	04	—	—
W	07	06	05	12	—	—
O	10	15	—	—	—	—
ZrB ₂	09	11	21	10	—	—
HfB ₂	05	07	13	14	00	09
SiC	12	05	17	05	00	05
ZrC	03	04	22	04	01	03
HfC	07	04	04	07	01	11
ZrO ₂	12	10	25	08	00	05
HfO ₂	11	09	11	14	00	05
B ₂ O ₃	14	12	*	*	03	09
ZrW	02	06	06	06	12	10
HfW	04	11	11	09	15	22

*: not calculated

2.6.1 Ion bombardment

The above developed ReaxFF is a reactive empirical bond order potential that is able to model the formation and dissociation of bonds by using the bond order concept. It has been parameterized to model atomic reactions. Thus, in order to

illustrate the potential and investigate its ability to capture physical phenomena that are not included in the training set, we performed MD simulations of B bombardment on Zr crystal (figure 2.22).

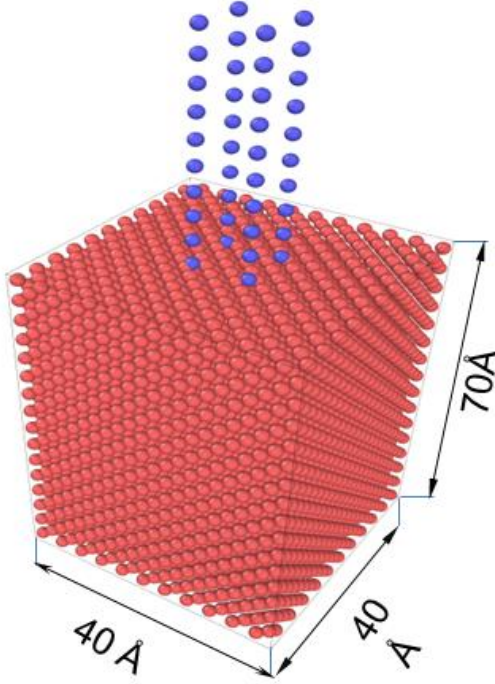


Figure 2.22: Ion bombardment simulation setup

A bulk of $40\text{\AA} \times 40\text{\AA} \times 70\text{\AA}$ (4690 atoms) of Zr was used as a substrate, and a beam of B was bombarded at room temperature onto the Zr bulk. A total of 200 B atoms were bombarded with a velocity of $2.1 \text{ \AA} / \text{s}$ and a time step of 0.2 fs. Figure 2.23 illustrates clearly that the potential faithfully created atom connectivity between B and Zr atoms.

During the ion-bombardment process, the B atoms injected into the Zr crystal create a disordered state. Under “ideal” conditions, HCP structure of ZrB_2 is expected in the regions of interaction. However, the kinetics of such a phase formation is very

slow at room temperature. Therefore, during the ion-bombardment process, when the Zr matrix loses its cubic structure and is not able to navigate the high-energy barriers to the HCP structure, a (meta stable) amorphous state is induced.

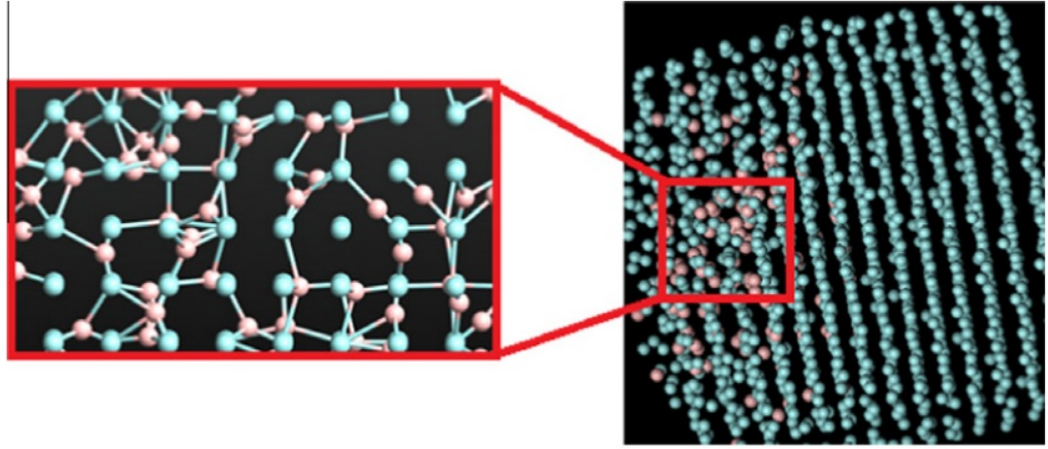


Figure 2.23: Snapshot of the samples after the atom bombardment

A standard way to characterize the amorphous state is by tracking the changes in the radial distribution functions (RDFs), the bond angle distributions (BADs), and the average internal energy (U). A combination of these three analyses will confirm the creation of ZrB_2 amorphous phase around the bombardment zone.

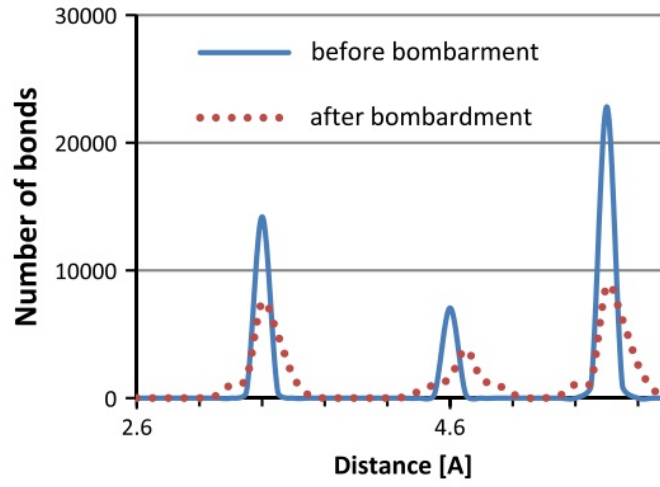
To investigate this further, we used the same sample (1372 Zr atoms with 200 B atoms). After the relaxation of the sample at room temperature, the average distances, angles, and energies are investigated. Figure 2.24a clearly shows the presence of different peaks associated with first, second, and third neighbors that dominate the structure of the system. However, unlike a perfect crystal, close to the neighbor distances, some atoms are placed at non-ideal distances because of the injection of B interstitials into the bulk. The first neighbor is placed at 3.21 Å in the original

structure and retains the same average configuration in the bombarded structure. However, a wider range of distances ($3 \text{ \AA}$ to $3.5 \text{ \AA}$) is observed. This confirms the presence of the ZrB_2 amorphous phase. Investigation of the angle distribution reveals the same trend as the RDF analysis (figure 2.24b). Since the bond angle distribution of an amorphous phase is different than that of a crystal phase by the presence of off-equilibrium angles (meta-stable states), the distributions are wider than for pure Zr.

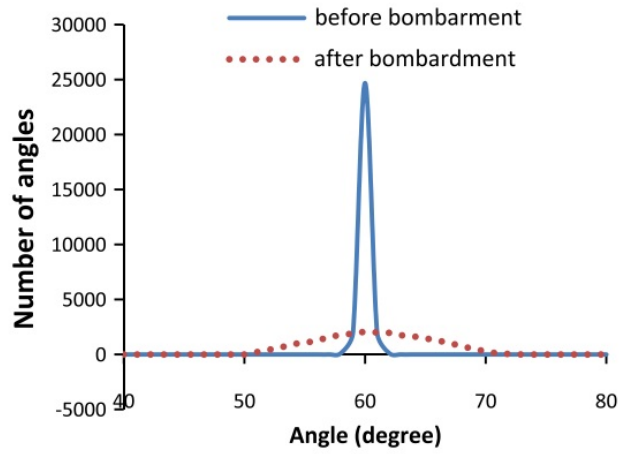
Calculating of the internal energy of the system is another way to verify the amorphization of the material: internal energy for amorphous materials is in general higher than that of a crystalline material with the same number of atoms. During the MD simulation, the internal energy per atom increased from -74.12 to -77.14 kcal/mol. This increase is associated with the amorphization of the ZrB_2 bulk.

2.6.2 Layers reaction

The purpose of this work is to observe reactions between Zr and B layers and to study the relevant properties: reaction barriers, temperature dependence, and reaction rates. The model that we have consists of one layer of Zr ($20 \text{ \AA}$ thick), and one layer of B ($12 \text{ \AA}$ thick) distant by $2 \text{ \AA}$ (figure 2.25). By letting the system relax the reaction begins in the surface, and we observe collective motion of Zr and B atoms to form an amorphous state at the boundary. This reaction, even though more realistic, does not allow us to extract the real energy barriers because of the collective motion (figure 2.25).



(a) Radial Distribution Function for pure Zr bulk (solid) and Zr bulk after B bombardment (dashed)



(b) Bond Angle Distribution function for pure Zr bulk (solid) and Zr bulk after B bombardment (dashed)

Figure 2.24: Analysis of both bond lengths and angles for the bombarded system

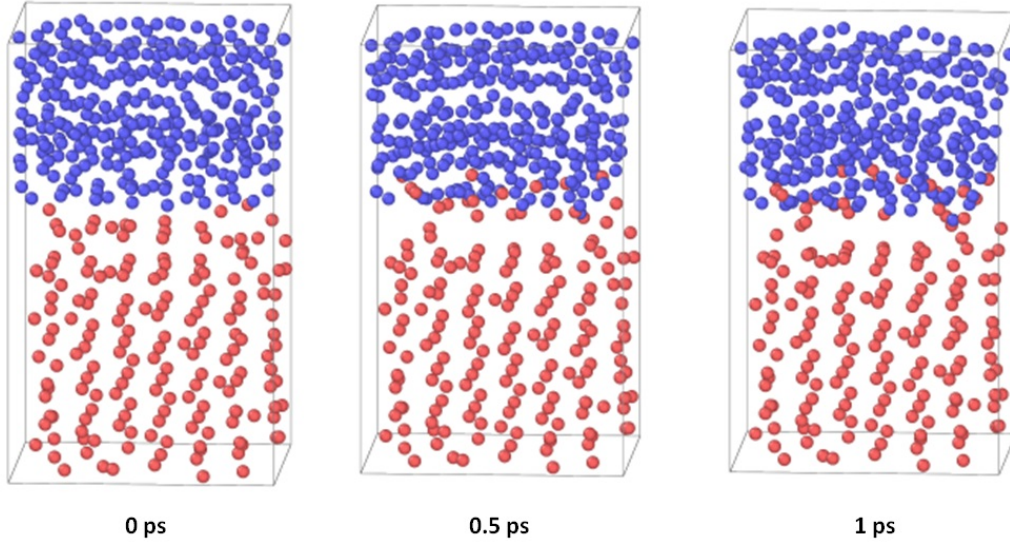


Figure 2.25: Collective motion during reaction (50K)

The above presented result confirms that a reaction is taking place between Zr and B atoms, and that ZrB_2 (in amorphous state) is formed. But, It is very hard to interpret quantitatively the energy barriers and reaction paths because of collective motion. In fact, Zr, and B atoms on both surfaces move at the same time toward each others making the apparent energy barriers insignificantly high (because the barriers are associated with collective atoms motion).

To solve this problem, we assume that the reaction environment does not affect much the barriers. We, then, freeze all atoms during the reaction except one (allowing one atom to react at a time). Once the atom settles in its new minimum energy configuration in the surface, we release the second atom, then the third ... until a reasonable number of atoms have reacted. We then extract the barriers that every

atom crossed, and we average them. For that purpose we use a slightly smaller structure, having 3 layers (figure 2.26).

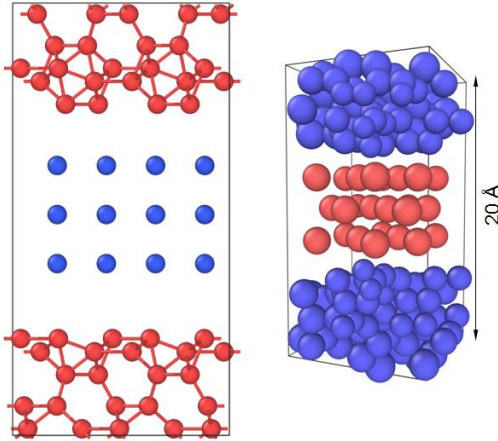


Figure 2.26: Initial setup of the layers

Using this configuration, the reaction occurs step by step until satisfaction, and the energy barriers can be easily recorded. The final state is shown in figure 2.26, and the average energy barriers are found to be around 0.91 eV (ranging from 0.5 eV to 2 eV).

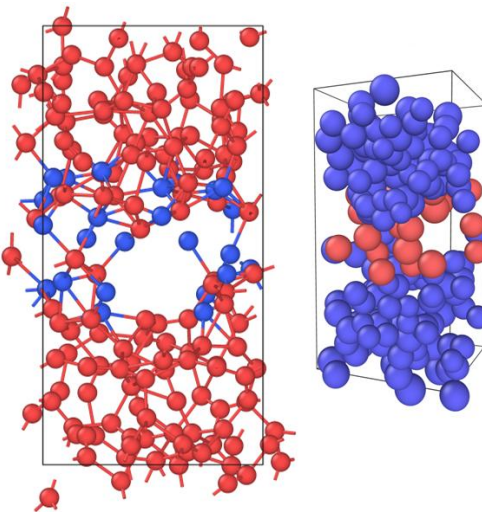


Figure 2.27: final reaction of the layers

2.7 Conclusion

We have developed a reactive force field for ZrB_2 and HfB_2 that will pave the way for accurate finite temperature atomistic simulations of these important ceramic compounds. Most of the possible reactants were also included in the potential to ensure a wider range of use. This objective was achieved by generating a substantial training set of Quantum Mechanics data for a wide variety of structures and energetic situations relevant to high temperature behavior (surface energies, heat of formations, charge distributions, dissociation curves...). The potential should, then, predict well a wide range of simulations for different purposes. It can even be adjusted if needed by adding some Quantum Mechanics points relevant to the studied physical phenomena into the training set. The surface and bulk energetics of the potential compare very well with density functional calculations. A simple ion-bombardment molecular dynamics simulation, predicated on the developed potential, confirmed the ability of the potential to model the formation and reaction of the expected bonds. An amorphous state was formed in the bombarded zone and was captured by means of radial distribution and bond angle distribution analysis.

Chapter 3

Atomistic simulations and the time scale barrier: a new approach

3.1 Introduction

Atomic simulations have become more and more omnipresent in the last two or three decades, and are playing a critical rule in understanding material behavior. This is due to two reasons: On the one hand, advances in computers' speed, memory, and storage are allowing atomic simulation to be used in new fields, previously inaccessible because of computing limitations [27]. On the other hand, the accuracy of the simulation results has encouraged many researchers to complement experiments with this approach.

Moreover, atomic simulations, and more specifically Molecular dynamics (MD) can be useful, at time, to replace expensive or dangerous experiments [28]. MD can, as well, explore and calculate at length and time scales not easily accessible by experiments [29], [30]. Samples, input loads, and measurements are much more flexible in simulations, as well: One can change the size or the shape of the sample in few minutes without the need to re-manufacture.

However, MD has two main limitations that severely limits its capabilities :

(i) Small length scale: each mole of material has about 10^{23} atoms. With the most powerful supercomputers, MD can barely reach 10^{10} atoms [31](the equivalent

of few hundreds nanometers configurations). Moreover, knowing that many materials have grain sizes of micrometers, their correct structures can never be duplicated by MD. However, most of the simulations use grain sizes easily accessible by the available computing power. This length scale limitation is also valid for any physical property. This shortcoming is generally overcome by parallelising the space domain over different processors [32]. However, this solution is not very efficient because the computation time does not vary linearly with the size (the number of processors does).

(ii) Short time scale: MD simulations are based on solving the set of Newton's equations of motion at different time steps. The typical Debye frequency for most materials is about 10^{13} Hz [33], which require at least 10^{-15} s intervals to accurately perform the numerical integration schemes. For instance, a million iterations will be equivalent only to 1 ns in experimental time, making the strain rates extremely high and nonphysical. A typical tensile test strain rate would be around 10^{-7} to 10^2 for experiments [34] [35], while around 10^8 to 10^{10} for MD simulations [36]. Molecular Dynamics, then, cannot provide trustful insights on time dependent phenomena (creep rates, sliding velocities, void nucleation rates ...).

The same time scale limitation can be explained from a different perspective : Knowing that most of the interesting dynamics requires the passage of the system from a local minimum to another through an infrequent rare event, the system should remain in some energy basin for a long time (millions or billions of MD time steps

depending on the energy barrier). Obviously, such a rare event cannot be accessible in MD simulations.

Different attempts have been made to address this time scale limitation, and several solutions have been proposed (often called accelerated molecular dynamics). Examples include meta-dynamics [37], hyper-dynamics [38], parallel replica dynamics [39], temperature accelerated dynamics [40], activation relaxation technique and others [40].

3.1.1 Parallel replica dynamics

This method is the most accurate, and the simplest, but not the most promising. It's based on running, in parallel, several replicas of the systems in different processors. All the replicas are independent, but once the required transition happens in some processor P_0 , all processors are stopped and all replicas are reassigned to the new configuration obtained after the transition. The enhancement achieved by this method is linear in the number of processors (if you have 10^{-6} probability to cross a barrier with one processor, you will have $n.10^{-6}$ probability if you have n replicas).

3.1.2 Hyper-dynamics

The hyper-dynamic approach is based on modifying the potential surface $V(r)$ of the system, by adding a positive bias potential $\Delta V(r)$ inside the wells, (figure 3.1).

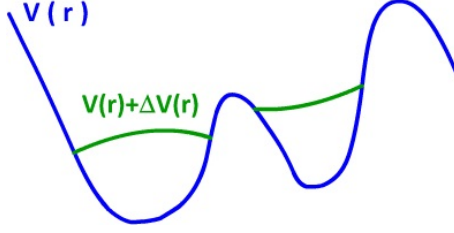


Figure 3.1: Schematic of the hyper-dynamic method : a bias potential $\Delta V(r)$ is added to the well to decrease the activation energy

Knowing that the probability of escape from a potential well is exponential to the barrier, we can easily see how much effective this method is. However, it is a challenging task to derive the bias potential. On the one hand, it should be zero at all the dividing surfaces (which are not known). On the other hand, the system must still obey the Transition State Theory for dynamics on the biased potential. However, if such a bias potential is constructed, we obtain a trajectory that evolves correctly from state to state at an accelerated pace. The average boost provided by hyper dynamics is given by equation 3.1:

$$boost_{Hyperdynamics} = \frac{t_{hyper}}{t_{MD}} = \langle \exp\left(\frac{\Delta V(r)}{K_b.T}\right) \rangle_b, \quad (3.1)$$

where the $\langle \rangle_b$ indicates an average over the trajectory on the biased potential.

3.1.3 Temperature accelerated dynamics

In the temperature-accelerated dynamics method (TAD), we do not speed up the simulation by adding a biasing potential, but rather by increasing the temperature. By doing so, transitions occur more rapidly and the dynamics of the system are called

“thermally accelerated”. While the obtained rates do not reflect the real dynamics at the original temperature, an extrapolation back to the temperature of interest is performed. The TAD method is less accurate than the previous two methods because it relies on the Harmonic Transition State Theory (explained later in this chapter) which is acceptable for limited applications. The TAD method often gives substantially more boost than hyper-dynamics or parallel-replica dynamics, and the obtained trajectory is allowed to wander on its own to find each escape path (exactly like the previously explained methods).

Many other methods and algorithms have been developed to address, the same issue ([40] have presented a very good review on all these methods). Nevertheless, the above presented remain the most effective and commonly used.

In the present work, we chose one of the hyper dynamics variants (called Autonomous Basin Claim) to accelerate the dynamics of the problem. The Nudged Elastic Band, Finite Temperature String, Kinetic Monte Carlo, and Transition state theory were used afterward to enhance the results and provide trustful and accurate results. The next section provides the readers with a detailed description of all the used tools involved in this work.

3.2 How to cross the time scale barrier ?

3.2.1 Autonomous Basin Climb

The Autonomous Basin Climb method was first developed and used by S. Yip and A. Kushima ([41], [42], [43], [44]) and is based on the following concept:

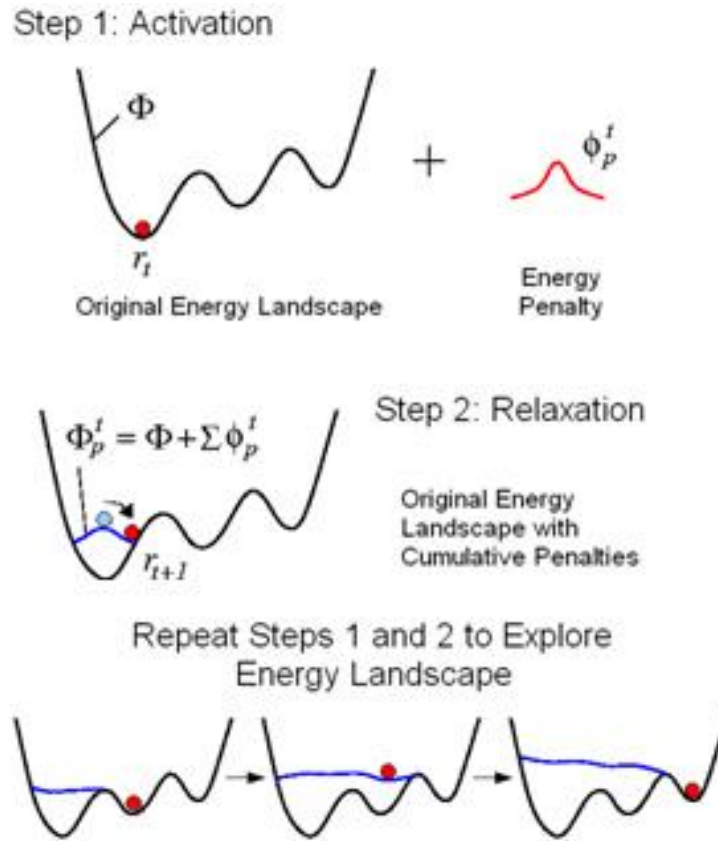


Figure 3.2: Schematic of concept of ABC

1- We start from an initial configuration R_0 stable under the applied boundary conditions of the problem. If the initial configuration is not a local minimum

(not a stable configuration), we apply a minimization to drive the system to a local minimum).

2- a Gaussian penalty function centered at the local minimum and given by equation 3.2 is added to the system. The amplitude and spread of the penalty are defined by W and σ and their values depend on the studied problem. (figure 3.2, step 1):

$$pE = W.exp(\frac{-\Delta R}{\sigma^2}), \quad (3.2)$$

where W and σ are parameters.

3- when the penalty is added, the configuration R_0 is no longer a local minimum, the structure is again minimized (to R_1) (figure 3.2, step 2).

4- an iterative process is repeated on 2 and 3 until the system crosses this barrier and reaches an other well (this state is captured by finding that the total potential energy at R_n ($E + pe$) is not different than E (figure 3.2, step 3)

The power of the ABC resides in its ability to find a path based on the real dynamics of the system, the more time ABC is simulated, the more the energy landscape is sampled, the more configurations on the path we have.

However, it is important to note that ABC always over estimates the energy barriers (because the system might be stuck in some artificial local minimums higher than the saddle point before converging to the new energy well). Consequently, a wise decision would be to use the power of each method and only get the list of

configurations on the needed path from ABC. An other method (NEB) will then be used to exactly obtain the energy barriers

3.2.2 Nudged Elastic Band

NEB (or Nudged Elastic Band) is a powerful tool to identify the lowest energy path for a rearrangement of a group of atoms from one stable configuration to another. It has been widely used to find barriers for reactions, and collective atom motion in MD and DFT calculations.

The method consists in starting from a set of replicas linearly interpolated from an already known initial and final state (as a first guess of the Minimum Energy Path [MEP]). Each image is connected to its two neighbors by a spring force. The energies of the replicas are then minimized to generate the final MEP. The total energy (that has to be minimized) consists of normal, and tangential parts (eq 3.3,3.4, and 3.5) as follows:

$$F_i = F_i^t + F_i^n, \quad (3.3)$$

$$F_i^t = K_{i+1} \cdot (R_{i+1} - R_i) - K_i \cdot (R_i - R_{i-1}), \text{ and} \quad (3.4)$$

$$F_i^n = -\text{Grad}V(R_i). \quad (3.5)$$

As a limit case scenario, we can think of a very weak chain of springs: Half of the replicas will converge back to the initial image, while the rest will converge to the final state. The system will have then coincident replicas (which is not helpful for our

purpose). By increasing the spring forces, we ensure that all replicas do reproduce a path by allowing them to go to the lowest possible energy state that the spring will allow. In this work, we use the initial and final replicas (provided by the ABC), and we use the NEB to find the exact barrier.

3.2.3 Finite Temperature String

The Finite Temperature String method (or FTS) is an algorithm that has the same objective as NEB (to find the energy barrier and path between 2 known states). This method is mainly used for the study of rare events such as conformational changes of macro molecules, nucleation events during phase transitions, or chemical reactions that occur within a long timescale. The barriers between different conformations in such processes are very high compared to the thermal fluctuations, and they do require an unusually high thermal fluctuation to jump over these barriers. The method samples the energy landscape and determines the iso-probability surfaces for the transition. Upon weighting these surfaces by the equilibrium probability distribution, we obtain an effective transition pathway (a tube in configuration space inside which conformational changes occur with high probability). A detailed explanation of the FTS process can be found in [45].

3.2.4 Kinetic Monte Carlo

Kinetic Monte Carlo (or KMC) is a computer simulation approach that finds the time evolution of processes. Without going into general algorithmic details, we only present the way KMC is applied for atomistic simulations.

By using the ABC and NEB, the obtained result is a path sequence with a barrier estimate for each transition. We made here, a very important assumption: We assumed that the configuration will always cross the lowest barrier, and that the ABC will always provide the lowest barrier.

These assumptions are not necessarily correct: On the one hand, the Autonomous Basin Climb is an approximate method (while accumulating the penalty energies, the code can oversee a barrier of 2 eV and goes to a barrier of 2.5 eV just because of some numerical artifacts). On the other hand, even if the code works perfectly, and crosses the 2 eV barrier, we do not know for sure that it should have done that from a physical viewpoint. In fact, jumping from a state to an adjacent state is a probabilistic event that follows the Boltzmann distribution. Therefore, an accurate calculation of the path should be done by calculating the jump probabilities.

KMC is a tool, that when applied to atomistic simulations can help us do so. a simple example is shown below to explain : suppose a potential energy landscape that only have 5 local minimums. The barriers for each possible jump is presented in table 3.1

Table 3.1: Barriers between states

state	1	2	3	4	5
1	-	0.6	0.5	0.7	0.7
2	0.9	-	0.8	1.1	0.6
3	0.5	0.4	-	0.7	0.6
4	0.9	0.6	0.7	-	1.2
5	0.8	0.7	0.9	0.5	-

If we suppose that the system always chooses the lowest energy barrier, the system will follow the following path : 1 $\rightarrow$ 3 (0.5 eV), 3 $\rightarrow$ 2 (0.4 eV), 2 $\rightarrow$ 5 (0.6 eV), 5 $\rightarrow$ 4 (0.5 eV). To use the KMC, we start by converting the barriers matrix into a jump probability matrix following the Boltzmann distribution:

$$k_{AB} = \nu * \exp\left(\frac{-\Delta E}{K_b.T}\right). \quad (3.6)$$

Supposing that $T = 750K$, we obtain table 3.2

Table 3.2: jump frequencies between states

state	1	2	3	4	5
1	-	$9.3 \cdot 10^8$	$4.4 \cdot 10^9$	$2.0 \cdot 10^8$	$2.0 \cdot 10^8$
2	$9.0 \cdot 10^6$	-	$4.2 \cdot 10^7$	$4.1 \cdot 10^5$	$9.3 \cdot 10^8$
3	$4.4 \cdot 10^9$	2.110^{10}	-	$2.0 \cdot 10^8$	$9.3 \cdot 10^8$
4	$9.0 \cdot 10^6$	$9.3 \cdot 10^8$	$2.0 \cdot 10^8$	-	$8.6 \cdot 10^4$
5	$4.2 \cdot 10^7$	$2.0 \cdot 10^8$	$9.0 \cdot 10^6$	$4.4 \cdot 10^9$	-

Now once we have the jump frequencies, we can convert them into jump probabilities by dividing each jump frequency by the sum of all the possible jumps starting from that configuration (table 3.3). We then obtain table 3.3:

Table 3.3: jump probabilities between states

state	1	2	3	4	5
1	-	16%	77%	3%	3%
2	1%	-	4%	0%	95%
3	17%	79%	-	1%	4%
4	1%	82%	17%	-	0%
5	1%	4%	0%	95%	-

Obviously, since the process is probabilistic, the obtained result won't be the same each time we run the KMC. For example, from the previous example, we obtain these following paths from two separate runs

$$\begin{aligned}
 &1 \text{ --- } > 2 \text{ --- } > 5 \text{ --- } > 4 \text{ --- } > 2 \text{ --- } > 5 \text{ --- } > 4 \text{ --- } > 3 \text{ --- } > 1 \text{ --- } > 3, \\
 &1 \text{ --- } > 3 \text{ --- } > 2 \text{ --- } > 5 \text{ --- } > 4 \text{ --- } > 2 \text{ --- } > 5 \text{ --- } > 2 \text{ --- } > 3 \text{ --- } > 5.
 \end{aligned}$$

3.2.5 Transition State Theory

Transition State Theory is based on the fact that the rate at which a system transitions across a dividing surface can be exactly expressed as the average absolute value of the velocity of the system normal to the dividing surface weighted by the equilibrium probability that the system resides on the dividing surface [46]. Mathematically, that can be translated to equation 3.7:

$$k_{ab}[S] = \sqrt{\frac{k_B T}{2m\pi}} Z_a^{-1}, \quad (3.7)$$

where $K_{ab}[S]$ is the transition rate across the dividing surface S , k_B is the Boltzmann constant, T is the temperature, m is the effective mass, and $V(x)$ is the potential energy in the R configuration.

The TST formulation is, in its most general form, extremely accurate for the systems where the potential wells are bigger than the thermal fluctuations, Which covers a very wide range of applications. However, In general, the calculation of the partition function is computationally very expensive, and becomes practically impossible for more than few atoms. The dividing surfaces S are also very hard to obtain in a $3N$ dimensional space.

For that reason, less demanding versions of TST using relaxed assumptions have been developed. Although less accurate, these variations of the original method are more accessible and useful for practical purposes.

Variational TST (or VTST) assumes that the dividing surface is the one minimizing the total frequency transition of the system given by :

$$\nu = 2k_{ab}[S]Pa[S], \quad (3.8)$$

where $Pa[S]$ is the probability that the system resides in state a . To solve this highly non-linear minimization problem, the dividing surface is obtained by an iterative process (from which the “Variational” notation comes).

Alternatively, PTST assumes that a potential energy ridge S exists between the two states, and considers that ridge to be the dividing surface. Harmonic TST

(or HTST), assumes that both wells and saddle points are locally quadratic, which physically equates to assume that material properties are temperature independent. This, surely is a crude assumption, but it allows to remove the integral from the partition function and convert it to an easily calculable entity (eq. 3.9) as

$$k_{ab}[S] = \sqrt{\frac{k_B T}{2m\pi}} Z_a^{-1}, \quad (3.9)$$

where $\nu_i^{initial}$ (respectively ν_i^{saddle}) represents the i_{th} normal frequency of the system at the bottom of the well (respectively, at the saddle point).

Simple Harmonic TST (or SHTST) is the most simplistic TST model. It assumes that all normal frequencies are equal to the debye frequency of the material. The transition rate can, then, be given by eq 3.10:

$$k_{ab} = \nu e^{-\frac{\Delta V}{k_B T}}. \quad (3.10)$$

Chapter 4

Grain boundary sliding mechanisms

4.1 Introduction

At low enough temperatures (low compared to half the homologous temperature) crystalline materials exhibit irrecoverable deformation provided the imposed mechanical stresses exceed the so-called yield threshold [47]. For all practical purposes, this deformation is considered to occur instantaneously. At high temperatures, however, even at stresses well in the elastic regime, irrecoverable deformation occurs gradually over an extended period of time. At the micro scale, this time-dependent deformation is predicated on several viscous processes such as grain boundary and volume diffusion, grain boundary sliding, dislocation glide-climb, void nucleation, void growth and others ([48] [49] [50] [51]). These micro mechanisms exhibit characteristics relaxation times that range from seconds to years (depending on the level of applied stress and temperature). This “creeping” deformation behavior is the predominant cause of failure in materials that are subject to high temperature environment: ice glaciers, nuclear reactors, air crafts, electronics among others ([52] [53] [54]), e.g. Sn-Pb alloys are extensively used in electronics and the melting temperature of this class of alloys is low enough that at even room temperature, creep eventually (in conjunction with other factors) leads to failure [54].

It is now well recognized that grain boundary sliding (GBS) is a key deformation and damage mechanism in creep [55]. Grain boundary sliding is the phenomenon of relative sliding of crystalline interfaces or grains in a slow viscous manner upon application of a macroscopic stress. The sliding is accommodated by grain boundary diffusion, volume diffusion and in the case of metals, dislocation glide/climb within the adjacent grains.

Although work on grain boundary sliding dates back more than sixty years, some of the first quantitative studies on this are those by Raj and Ashby [56] who presented an analytical study of this phenomenon based on accommodation by grain boundary and volume diffusion. This most widely used paradigm indicates a linear dependence between strain and sliding rate with the absence of any threshold stress. Extensive theoretical and experimental literature now exists which outline a number of (sometimes) contradictory observations. For example, Chauhan et. al. [57] studied the problem from the experimental side, and used an ultra-fine grained Al alloy (300 nm grain size) and observed qualitatively a threshold stress for grain boundary sliding. The proposed value of threshold was found to be about 10 Mpa (23 times lower than the yield strength of the experiment). For further details, the reader is referred to the review article by Langdon [58]. Despite the extensive focus on this phenomenon, several issues still remain open or at least, relatively unsettled, e.g. (i) In case of diffusion dominated creep, is the stress-sliding rate relation linear, as predicted by Raj and Ashby [56]? (ii) Is there a threshold stress for grain boundary sliding? (iii) What is the qualitative form of the constitutive law for grain boundary sliding?

Given the advent of computational power and the concomitant development in atomistic simulation methods, that is a logical route to take to answer the aforementioned questions and in general clarify the atomistics of grain boundary sliding. To that end, Qi and Krajewski [59], in a nice work, carried out a molecular dynamics study of a shear test on an Al bicrystal. This study was carried out at 750 °K to investigate the effect of applied force and grain boundary mis-orientation on sliding. A linear relationship between constant sliding velocity and applied stress was observed, although the linear fit had positive intercepts indicating a critical value of applied stress below which no sliding was perceived. In other words, their work appears to confirm the linear relation between stress-sliding albeit a sharp threshold stress is predicted (around 0.2 GPa for the material simulated), which is about 10 times lower than the yield strength for the 6nm grain size used in the simulation [60].

While the work by Qi and Krajewski provided important insights, there is a fundamental limitation of classical molecular dynamics methodology that has prompted us to reexamine this problem with alternative approaches. As is well known, classical molecular dynamics can only handle time-scales of the order of a few pico to nanoseconds. While this is sufficient for several classes of problems, it is a serious deficiency when it comes to the study of creep related phenomena, where the relaxation times are in seconds and sometimes years. In other words, in classical molecular dynamics, the applied strain rate is several orders of magnitude faster than typical grain boundary sliding rates thus preventing for simulations to truly capture the time-dependent nature of the irreversible creep deformation process.

In this Chapter, we employ a sequence of methods to extract a realistic constitutive law for grain boundary sliding and answer some of the questions raised in the preceding paragraphs. We choose Al bi-crystal as a model material system albeit our approach can be repeated for any material. One motivation for choosing this particular system is that conventional molecular dynamics based results by Qi and Krajewsky [59] are already available, thus facilitating a comparison. Our work is paved by the recent success of the potential energy surface sampling approach (the so-called autonomous basin climbing algorithm [41]). Yip and co-workers have confirmed its applications to several time-dependent problems such as viscosity of supercooled liquids, creep relaxation of metals, and void nucleation rates ([42] [43] [61]).

4.2 Grain boundary formation

We start the study by duplicating the same structure and boundary conditions used in [59] (figure 4.1). The sample consist of two grains (6nm x 4nm x 2nm each) juxtaposed along the x direction with a mismatch of about 25.2°. Both grains have a common z axis oriented along the $\langle 1 \ -1 \ 0 \rangle$ directions, while the x and y directions are oriented along $\langle 110 \rangle$ and $\langle 001 \rangle$ for the first grain (blue), and along $\langle 332 \rangle$ and $\langle 1 \ 1 \ -3 \rangle$ for the second grain (green). These orientations insure a mismatch angle of about 25.2°.

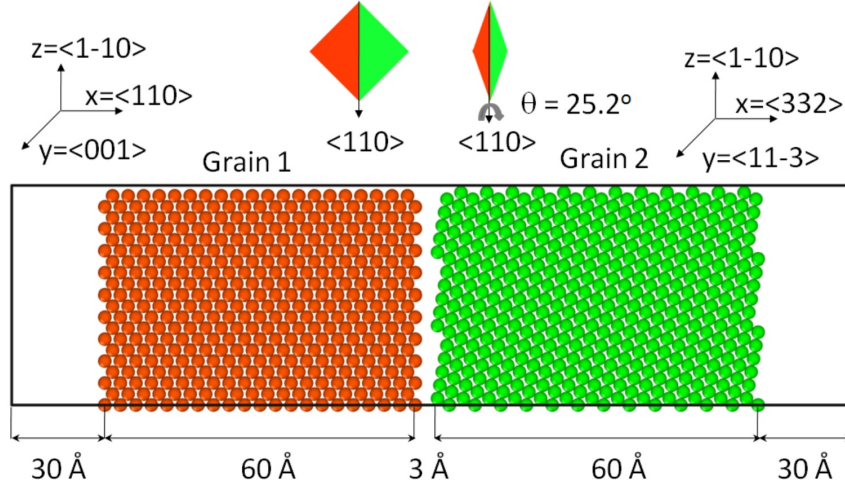


Figure 4.1: Schematic for the Aluminum grains' size and orientations

It is important to note that if we use periodic boundary conditions, 2 grains will be formed (one at the interface, and one at the boundary of the simulation cell). We, then, create a 3nm vacuum from each side of the box to ensure that the grains only interact to form one grain boundary. The periodicity along y and z directions are conserved to simulate infinite grain interfaces (figure 4.2).

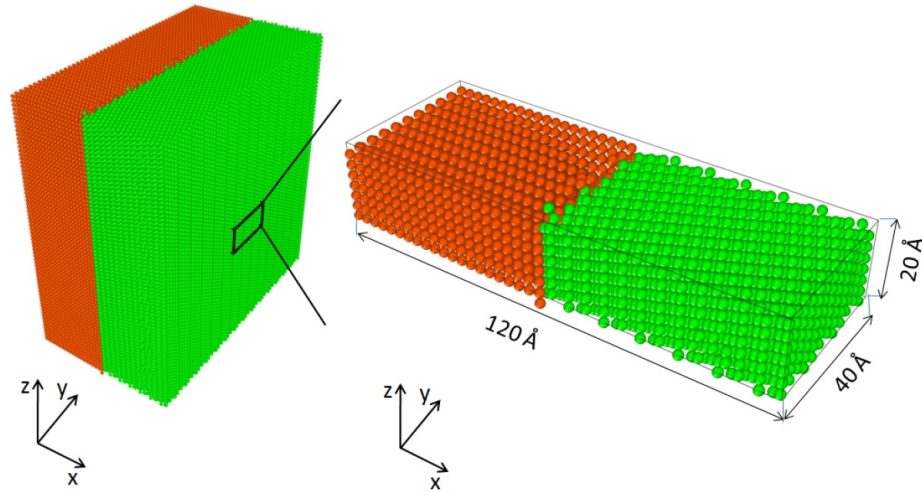


Figure 4.2: Multi-scaling schematic : using a 6 nm sized grains to model an infinite bi-crystal

By having the 2 grains closely juxtaposed, a simple NPT relaxation at finite temperature allows the atoms to freely move and fill the interface in the lowest possible energy configuration. The relaxation was performed at room temperature for about 1 ns, and the grain boundary was formed successfully (figure 4.3).

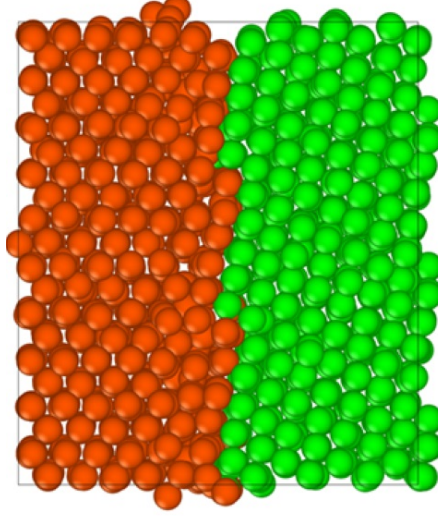


Figure 4.3: Snapshot of the Aluminum grain boundary after relaxation

The grain boundary energy of the formed interface was calculated using equation 4.1

$$\gamma_{GB} = \frac{E_{sample} - (E_{slabs} + n.E_{atom})/2}{A}, \quad (4.1)$$

where E_{sample} is the energy of the bi-crystal, E_{slabs} is the sum of the energies of both grains if they were separated by a vacuum, E_{atom} is the binding energy per atom calculated on an Aluminum bulk, n is the total number of atoms, and A is the area of the grain boundary ($\Delta y.\Delta z$). The obtained grain boundary energy was $\gamma_{GB} = 0.580 J/m^2$, which compares well with Qi et. al. [59] ($0.548 J/m^2$).

After forming the boundary at 300°K, we rise the temperature to 750°K (0.8 the homologous temperature of Aluminum) to reach the creep deformation regime. This temperature rise was performed at a slow rate under NPT conditions. Once the ultimate temperature was reached, we relax the structure again at constant temperature and pressure for 50 ps to remove any residual stresses. Finally, we minimize the whole structure using the conjugate gradient method to ensure that the configuration lies in a perfect local minimum.

Figure 4.3 shows the initial structure of the grain boundary interface prior to applying any shear stress. This configuration, is then loaded by 2 opposite forces on both sides to simulate the shear (as shown in figure 4.4) : The displacements at the two ends of the system are constrained in both x and y direction to avoid dangling atoms (5 Å from each side), a load on the z direction is then applied at an adjacent region from both sides of the grain (20 Å from each side), and the largest region is kept free of any boundary condition to allow the grain boundary stress to be relieved freely during the sliding without over constraining the problem (35 Å from each side). The corresponding shear stress along the grain boundary is obtained by equation 4.2

$$\tau = \frac{f.n}{A}, \quad (4.2)$$

where τ is the shear stress, f is the applied force per atom, and n is the number of atoms in the moving zone.

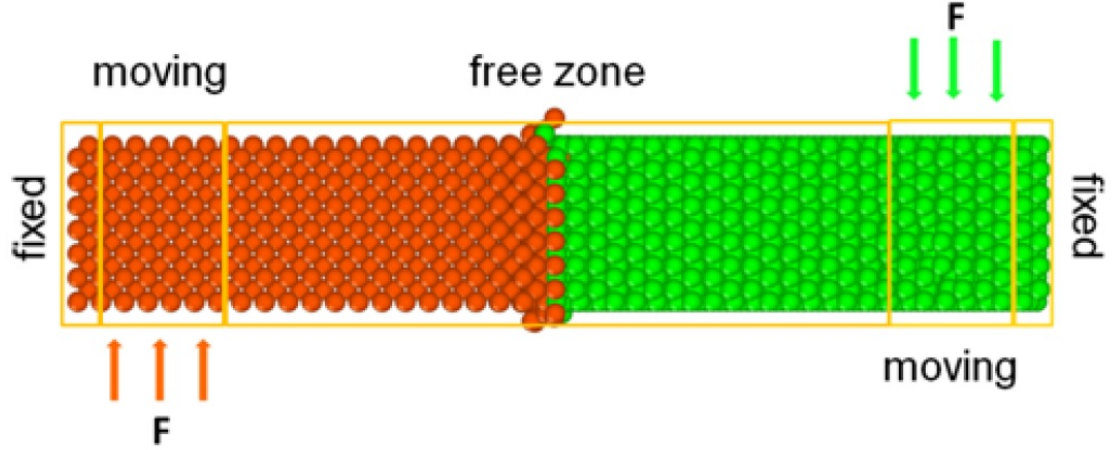


Figure 4.4: Boundary conditions for the grain boundary sliding problem

4.3 Procedure

Having defined all the boundary conditions of the problem, we now discuss the procedure we follow to obtain the correct dynamics of the problem. The first step consists in sampling the potential energy surface under the applied shear stress. This is done using the Autonomous Basin Climb (ABC) algorithm developed by Kushima and Yip et al. ([41], [42], [43], and [44]), and based on the meta-dynamics concept introduced in 2002 by Laio and Parinello [62]. The strength of this method lies in its ability to find the final state without prior knowledge. Through a series of iterations, the Algorithm moves the system from one energy basin to an other via a series of small activation and relaxation steps, to finally output a list of stable configurations that the system visited successively under given boundary condition (e.g. shearing in the present case).

The process starts from the local minimum configuration obtained after the grain boundary formation. Then, a 3N dimensional Gaussian penalty function $E_p(r)$, centered at the minimum configuration, is added to the system, as

$$E_p = W.exp \left[-\frac{(r - r_0)^2}{2.\sigma^2} \right], \quad (4.3)$$

where r and r_0 are respectively, the atomic configuration, and the minimized configuration with all previous penalties at any iteration. W is a parameter and defines the amplitude of the gaussian (in eV), while σ determines its width. Once the penalty function is added, the minimum configuration transforms into a saddle point because of the gaussian nature of the penalty, the system is, then, again relaxed and a penalty energy centered at current position is added. This process is repeated till the accumulation of the penalty energies is enough to make the system cross the easiest barrier and reach a new basin. Following this process, the algorithm “explored” a small part of the potential energy topography on the the path of the sliding, and allowed us to obtain the local minimums that the system should visit when the shear is applied. The ABC method do also provide an approximation of the transition barrier by identifying the configuration with the highest penalty energy inside the well as the saddle point. This assumption always over-estimates the barriers, and is not, in general, accurate. Repeating this procedure further, will allow us to explore and sample more and more the path and obtain the needed configurations (which will be used later to extract the jump rates using the Transition State Theory).

We should allude, at this point, that the choice of these parameters is crucial, and should be carefully adjusted in accordance with the physics of the problem. For example, if we suspect the problem to have barriers of around 1 eV, choosing $W = 5$ will not make any sense because the algorithm will cross the barrier in one iteration and might even jump to a further local minimum without seeing the closer ones. However, if we chose a $W = 0.01$ for the same problem, the algorithm will be stuck forever trying to fill the well.

Gathering the configurations on the path of the sliding, and an approximation of the barriers from ABC, can provide - by itself - some insight of the mechanisms during the mechanical load, but, it is not the fine purpose of this study. In fact, to retrieve the correct transition rates, the collection of the exact barriers is crucial.

4.4 Results and discussion

At an applied stress of 170 MPa, the mechanism for accommodation of grain boundary sliding appears to be grain boundary diffusion as evident from the atomistic pictures of the grain boundary interface on xy projection, as shown in figure 4.5. We observe no evidence of dislocation based accommodation and this may be anticipated given the extremely small sizes of the grains.

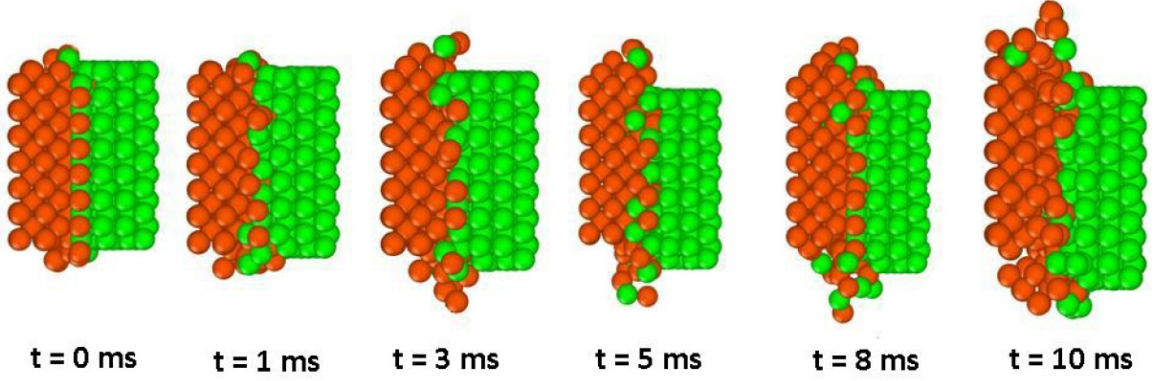


Figure 4.5: Snapshot of the grain boundary at different instants during the sliding

Since the penalty energies added to the system are cumulative, the potential topography might be biased in some areas, which can lead to a lack of accuracy in the configurations of the obtained minima. The obtained barriers are in general overestimated because of the nature of the algorithm. To increase the accuracy of our simulations, the structures of the bi-crystal corresponding to the obtained minima are extracted and then minimized individually using conjugate gradient iteration technique. Nudged Elastic Band (NEB) simulation between these minima is performed in a sequential order of time of evolution with 24 replicas between each consecutive minima. The sliding path and energy barriers are then obtained accurately.

Like the ABC method, the output of the NEB simulation is an ordered sequence of minima and saddle points on the sliding trajectory. However, the barriers and the configurations are not approximate at this level 4.6. The time corresponding to each transition event is then calculated using the harmonic transition state theory (equation 4.4) as

$$t_{A \rightarrow B} = \left(\nu \cdot \exp \left[-\frac{\Delta E_{A \rightarrow B}}{K_b \cdot T} \right] \right)^{-1}, \quad (4.4)$$

where ΔE is the energy barrier between A and B, ν is the characteristic frequency factor approximated to $10^{13} Hz$, T is the temperature, and K_b is the Boltzmann Constant. Having the transition time needed to cross each barrier on the path 4.7 and the sliding distance at each configuration, 4.8 the sliding rate can be obtained by mean of a linear interpolation of the time dependent sliding 4.9.

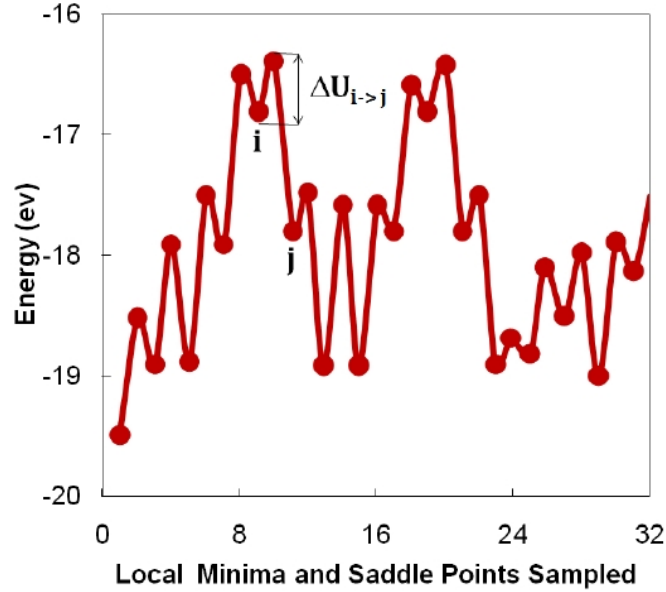


Figure 4.6: Energy of transition between local minima from NEB

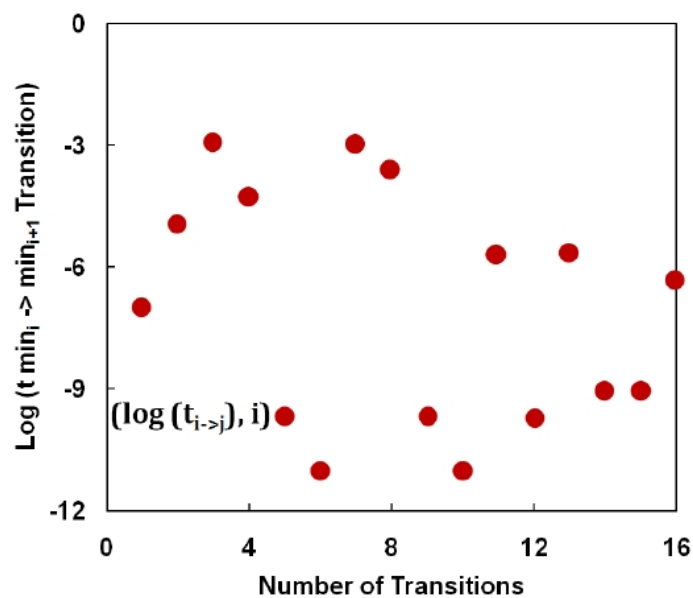


Figure 4.7: GB sliding for every transition between successive minima

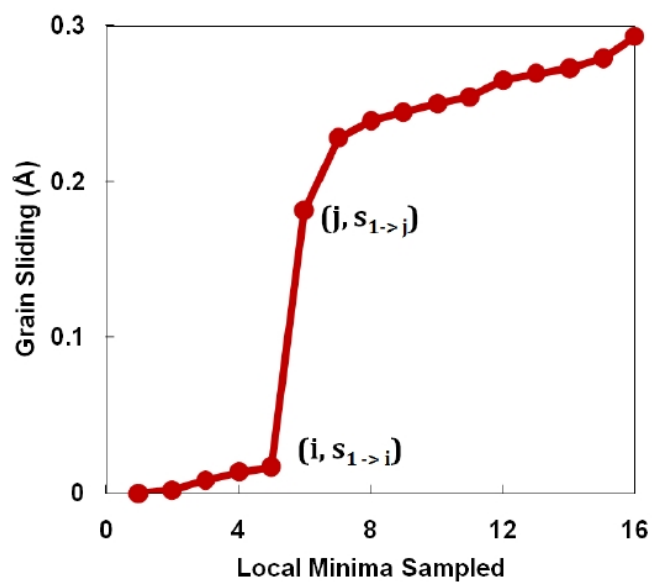


Figure 4.8: Time for barrier transition (used in the calculation of time by Transition State Theory)

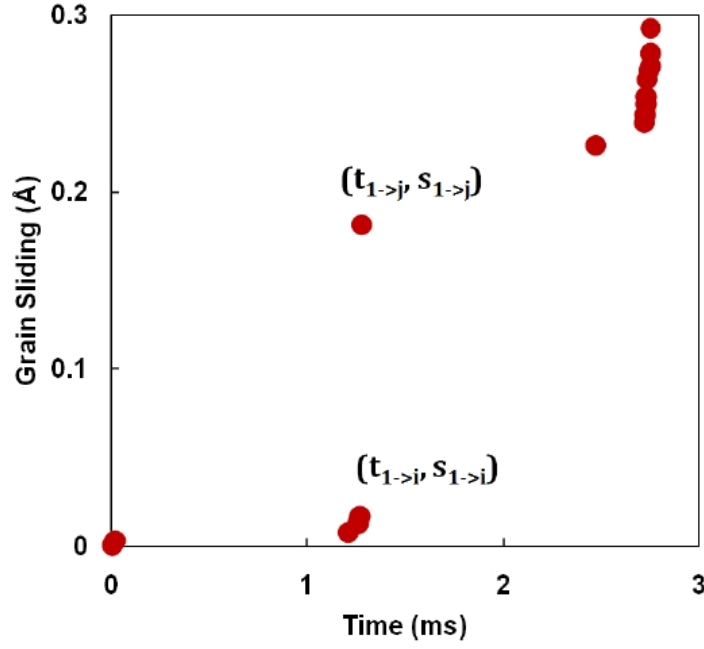


Figure 4.9: Grain boundary displacement as a function of time (by correlating sliding to time for transition)

The points i and j correspond to the same pair of minima in all the plots. 4.8 shows non-uniform sliding for different transitions and this is due to non-continuous sliding of the grain boundary. Larger obstacles can make the system deform slower over many transitions and there may be a sudden sliding after the obstacle is overcome. In the current study, a comparison between our constitutive equation and those found by [59] are presented in 4.10.

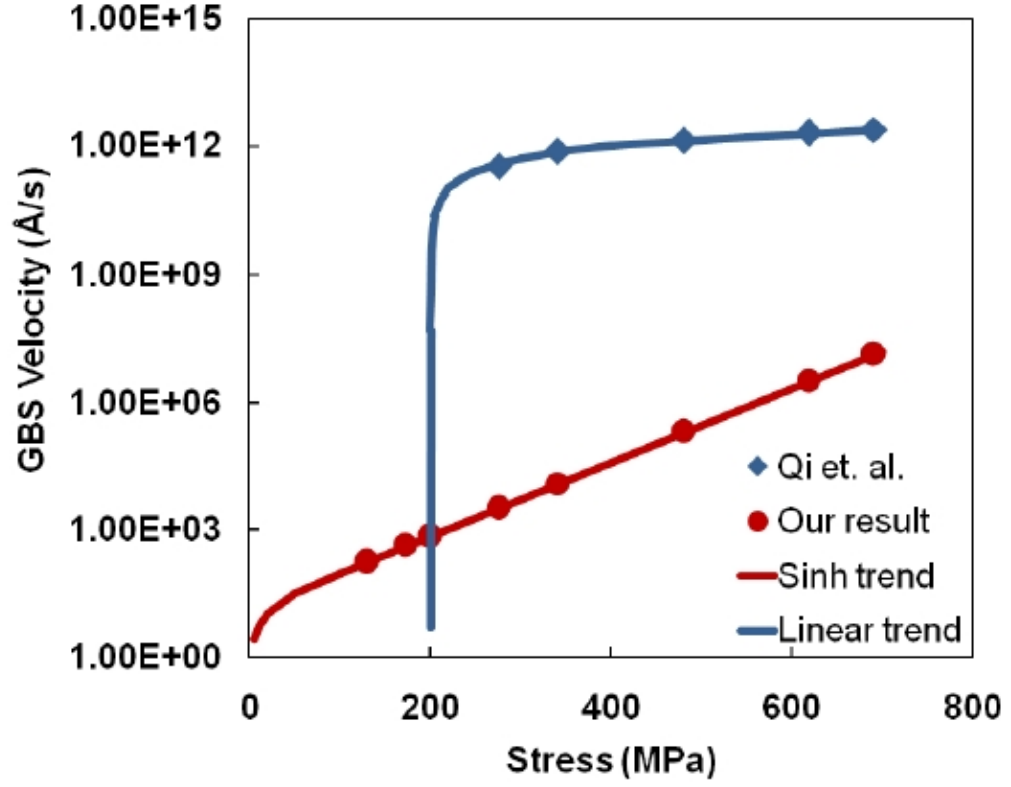


Figure 4.10: A plot of grain boundary velocity against corresponding applied shear stress

The constitutive equation showing the dependence of sliding rate with applied stress is given in equation 4.5 as

$$\dot{s} = C \cdot \sinh\left(\frac{\tau}{A \cdot \tau_{yield}}\right), \quad (4.5)$$

where $\dot{s}$ is the grain boundary velocity in Å/s, and τ is the shear stress in MPa. Here, A is a material constant and τ_{yield} is the yield strength of material. For the present case, we found $C = 27$.

Figure 4.10 suggests that a threshold may exist for grain boundary sliding, but it is well below that estimated from atomistic simulation using molecular dynamics and is quite low (and we may claim that practically speaking there is no threshold for grain boundary sliding). For getting an exact value of threshold stress ABC simulation needs to be done at lower stress close to the yield point value for aluminum using more computational resources for quick convergence. If the time corresponding to a sliding of 1.5% strain is in hours, then we can conclude that for all realistic engineering applications, that value is the threshold stress.

This combination of the used algorithms (ABC, NEB, and HTST) is surely an improvement against conventional MD, our results can be improved further. The accuracy of barrier estimation can be improved by using the finite temperature string method, which is more suitable for high temperature problems. The assumptions inherent in simple harmonic approximation for transition state theory may be relaxed as well, and a more realistic sliding path can be generated using Kinetic Monte Carlo. However, for the specific purpose of this paper, where no complex dislocation motion or grain rotation is observed, we believe that, certainly qualitatively, our results are reasonable. Future work is anticipated that will employ some of these aforementioned refinements and investigate cases where dislocation accommodation is evident.

Chapter 5

ZrB₂ grain boundary sliding

5.1 Introduction

Due to the importance of ZrB₂ for high temperature applications, we now, repeat the grain boundary sliding study for this material.

HCP systems (like ZrB₂), have a wider range of grain boundary types because of the anisotropy: The same misfit angles lead to different grains depending on the direction. A study on some of these types of GB and their properties are described in [17].

The strength of a grain boundary is mainly defined by it's associated energy: a higher grain boundary energy generally signifies a more disordered interface. For these reasons, boundaries orthogonal to [0001] directions are in general (depending on the angle) less energetic than those in other planes.

5.2 Grain boundary formation

We chose to study two types of grain boundaries shown in figures 5.1 and 5.2. The grain boundary along the x axis is formed by combining grain 1 and 2, while the grain boundary along the z axis is formed by combining grain 1 and 3.

1. Grain 1 has 2577 atoms (945 Zr 1632 B) and is oriented along $\langle 110 \rangle$ (x), $\langle -110 \rangle$ (y), and $\langle 001 \rangle$ (z).

2. Grain 2 has 2529 atoms (945 Zr 1584 B) and is oriented along $\langle 1 - 10 \rangle$ (x), $\langle 110 \rangle$ (y), and $\langle 001 \rangle$ (z).
3. Grain 3 has 2424 atoms (840 Zr 1584 B) and is oriented along $\langle 1 - 10 \rangle$ (x), $\langle 110 \rangle$ (y), and $\langle 001 \rangle$ (z).

These orientations ensure a misfit of 30 °around the z axis for both cases. For the 3 grains, the size of the sample is the same (30Å x 30Å x 30Å), but since the orientations are different, the number of atoms is, as well.

Zirconium (red) and Boron (blue) are always present in different z planes. Each Zirconium atom have 6 Zirconium neighbors in the same plan (figure 5.2), while each Boron have three neighbors. The orientation of the grains is 60 degree periodic (a mismatch of 60 deg, will be equivalent to no mismatch).

A small gap of 2 Å was left for the atoms to give them some freedom to form the new bonds at the boundary, and the grain boundary energy is computed for both structures. Figures 5.1 and 5.2 show the two different ways a grain boundary can be formed with two similar grains.

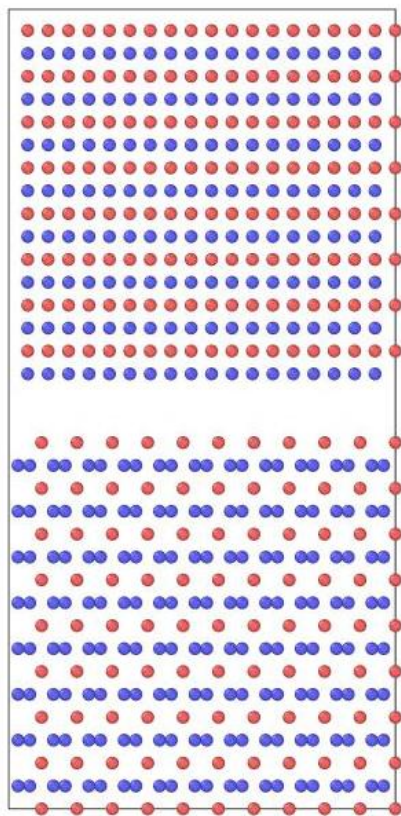


Figure 5.1: ZrB_2 grain boundary along the z axis

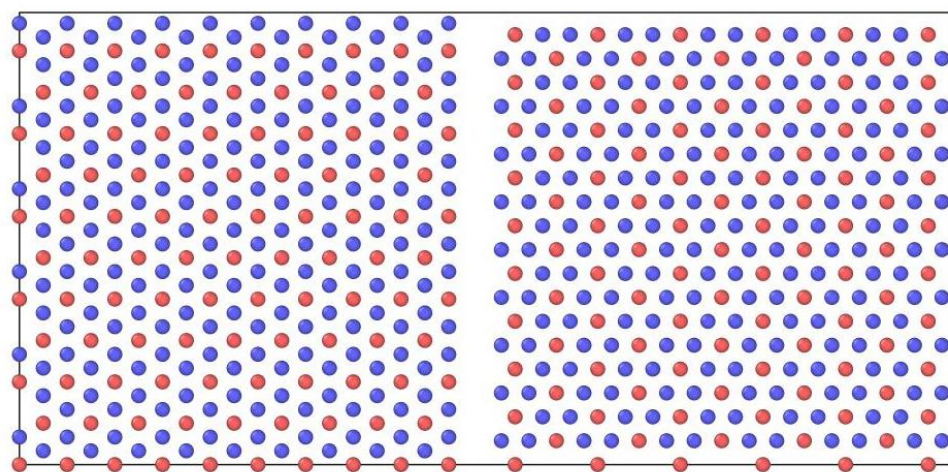


Figure 5.2: ZrB_2 grain boundary along the x axis

To form the final grains, a NPT relaxation was performed (to allow the system to change its volume). After 1ns, the grains are fully relaxed and the internal stress is found to be very close to zero.

The grain boundary energy is defined for ZrB_2 the same way it is defined for Aluminum. (equation 4.1). It is important to mention that it is more challenging to obtain the correct energetics of the system, because boundaries are less organized, and take much longer to equilibrate.

Calculating the bulk energies for the 3 grains is, then, not straight forward because of the HCP structure of ZrB_2 crystal. In fact, when using an orthogonal box, the hexagonal structure of ZrB_2 makes the edges of the box irregular, and thus causes the bulk energy calculation to be incorrect. To turn around this problem, we use a different approach to calculate the bulk energy of each grain: We use non-orthogonal boxes having 30° tilt to match the HCP structure. This way, all the boundaries are smooth and the potential energy can be associated with the bulk energy. The energy per atom is then calculated and the total energy of each grain is estimated by multiplying the energy per atom by the number of atoms.

Table 5.1: Energy per atom for ZrB_2

Potential	Airebo	Tersoff
Total Energy	-28283	-21346
number of atoms	3000	3000
Energy/atom	-9.4276	-7.1154

Figure 5.3 shows, as an example, how is the first grain non orthogonal box oriented.

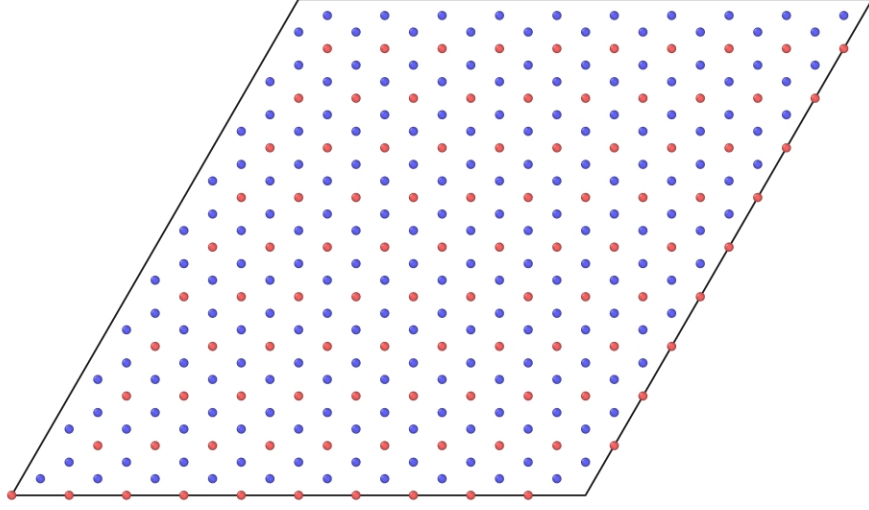


Figure 5.3: Non orthogonal ZrB_2 box

Using table 5.1 , the bulk energies of the 3 grains is obtained. The slab energies (needed to calculate the grain boundary energy) are calculated using a NPT simulation for 1 ns followed by a conjugate gradient minimization. Using the obtain values, we calculate the grain boundary energy (table 5.2). After making sure the grain boundary energy is correct, and that the grain boundary is correctly formed, we take a closer look at the boundary.

Table 5.2: Grain boundary energy for ZrB_2

Potential	Airebo	Tersoff
Grain 1	-24295	-18336
Grain 2	-23842	-17995
Grain 3	-22852	-17247
Slab 1 (x)	-22019	-17708
Slab 1 (z)	-23282	-17925
Slab 2	-21736	-17328
Slab 3	-21116	-16882
GB 1 (x)	-45766	-35562
GB 2 (z)	-45635	-35096
GBE1 [Jm^{-2}]	3.20	2.16
GBE2 [Jm^{-2}]	2.27	1.68

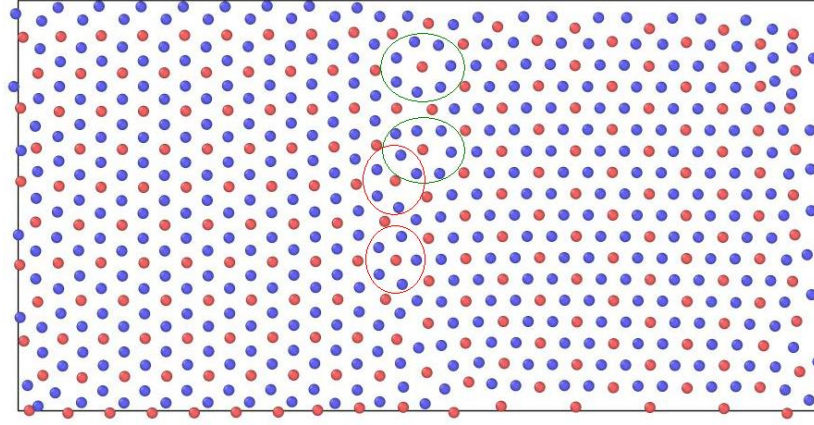


Figure 5.4: ZrB_2 grain boundary formed along the x axis

We can clearly see the alteration of the grain: The 6 Boron atoms ring that the Zirconium atoms used to sit in between (for a top view of the structure is biased, they were deformed to 7 and 5 atoms rings (highlighted in green and red). In the Zirconium plane, the same phenomena was observed. This alteration is a typical grain boundary deformation mechanism observed in most materials having ring-like structures (Graphene for example). Figure 5.4 clearly shows this alteration.

5.3 Procedure

After forming both grain boundaries, and checking their corresponding energies, we chose to run our ABC simulations for the grain formed along the x axis because it is closer to what is observed experimentally. The simulation set up we performed is very similar to the Aluminum grain boundary sliding simulation. After we created the grain boundary, we divided each grain into 3 parts : a free zone toward the boundary to make sure atoms are free to slide without over constraints (417 atoms from each side), a moving zone in the middle, where we applied the shear load (800 atoms from each side), and a fixed zone at the edge to ensure the stability of the simulation (1336 atoms from each side). Figure 5.5 shows the simulation set up explained above.

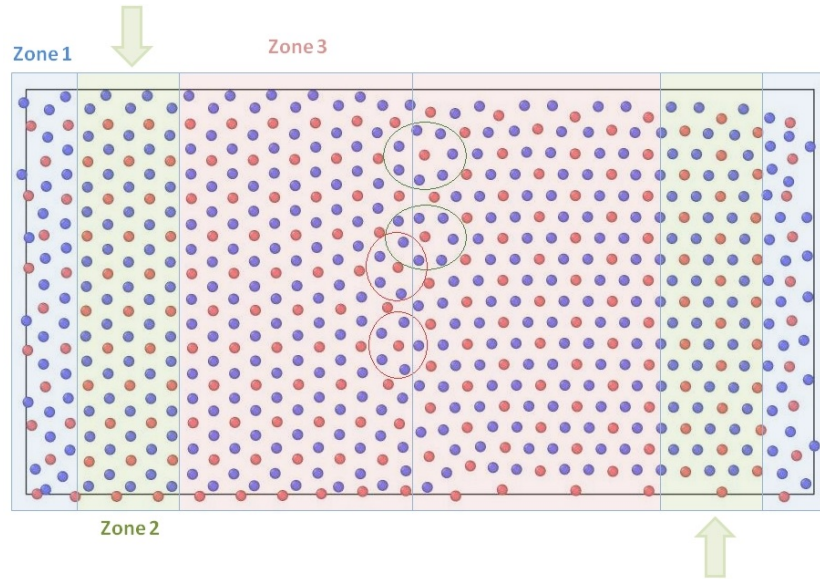


Figure 5.5: ZrB₂ grain boundary formed along the x axis

5.4 Results and discussion

We now run now our ABC simulations to observe qualitatively and quantitatively the grain boundary sliding mechanisms. By running the simulations, we found that the grains slide the same way Aluminum grains does. To conclude, we again do not observe any dislocation based defects. Diffusion is found to be the dominant physical phenomena happening at the boundary. If we use a bigger sample, we might give enough space for the system to nucleate dislocations. Similar to Aluminum, Zirconium Diboride have a much lower threshold stress than what MD simulations predict.

Chapter 6

Void growth mechanisms

6.1 Introduction

The study of the nucleation and growth of voids in metals is of great interest for the understanding of failure under mechanical loading. For this reason, void growth has been studied extensively in the past three decades from a continuum mechanics standpoint. Experimental, computational, and analytical research has been devoted to analyze void growth and coalescence in different materials and under various loading conditions.

Interestingly, it has been first found by Stevens et. al. [63], that voids experiencing a high strain rate tensile load grow by dislocation mechanisms and that diffusion does not contribute because of the short time scale the phenomena take. Since void growth is in general associated with large strain rates, it cannot be accomplished by vacancy diffusion since there is no sufficient time for diffusive mass transport.

MD simulation by Traiviratana [64] on metals indicate that these dislocations were generated at the void surface after a critical shear strain have been reached. However, the geometric nature of these dislocations is still a controversial matter(prismatic loop or shear loop). The difference between these two kinds of dislocation loop emissions is that prismatic loops have a burgers vector not in the plane of the loop, in contrast with shear loops which have burgers vector lying in the loop plane. Lubarda

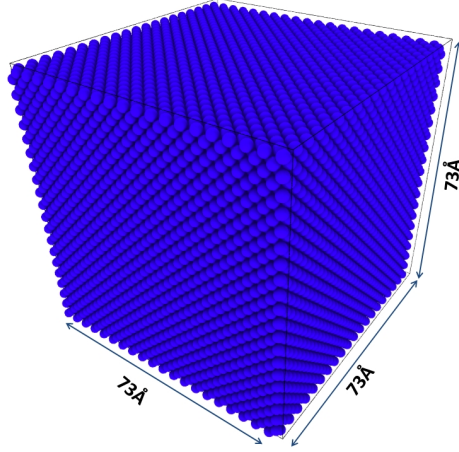
et al. [65] and Traiviratana et al. [64] have proposed that both prismatic and shear dislocation loop emissions from void surfaces when experiencing high stress concentrations serve as a vehicle to transport atoms away from void surfaces resulting in further growth. Recently, Traiviratana et. al [64] have been challenged by Bulatov et al. [66] about the nature of the dislocation loops. they claim that shear loops do not contribute in void growth. other authors also share the same point of view and consider prismatic loop as the unique mechanism for growth [67] [68].

There is an apparent disagreement between two groups of researchers on this issue. And in this work, we try to observe the nature of the dislocations loops and verify the geometry they are presented in.

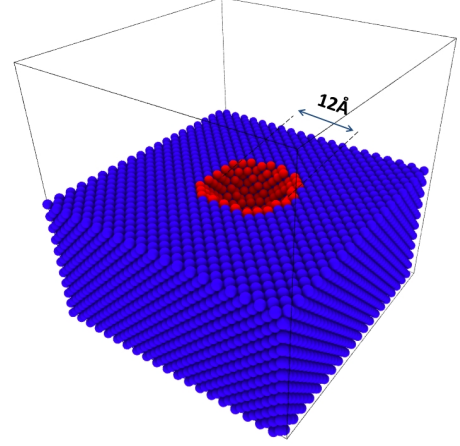
6.2 Void growth atomistic simulations

Since we don't know in advance which structure and void size will be enough to get the needed space for the dislocations to nucleate and move freely, we model 3 different structures with voids. We use Copper as a matrix, and we generate 3 cubic structures presented in table 6.1.

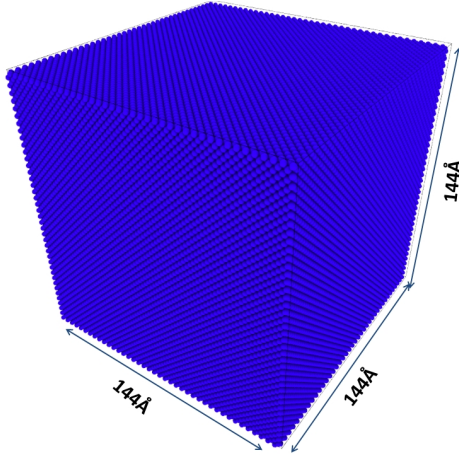
The 3 structures are shown in figures 6.1a to 6.1f where the blue and red color coding are based on the centro symmetry parameter. The atoms close to the void are, then, shown in different colors since they have lower coordination numbers.



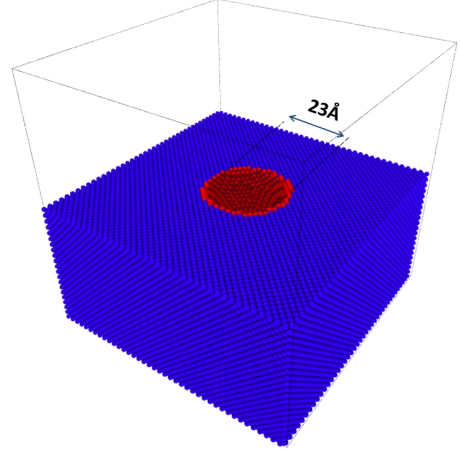
(a) First sample schematic



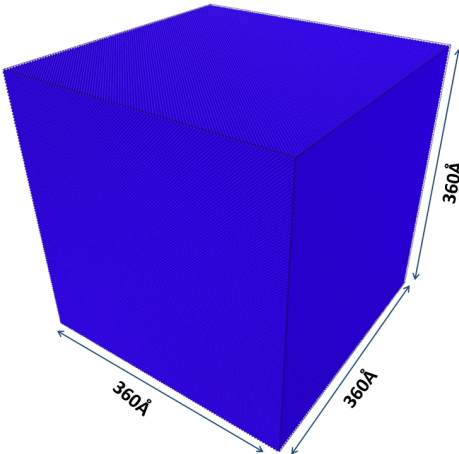
(b) Sliced view for the void in the first sample



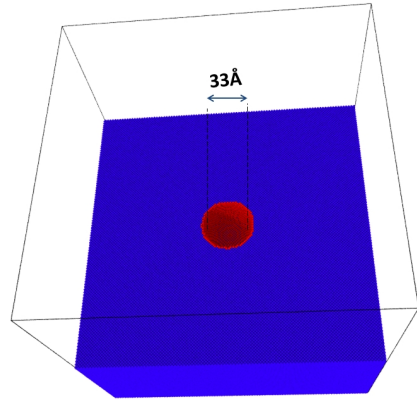
(c) Second sample schematic



(d) Sliced view for the void in the second sample



(e) Third sample schematic



(f) Sliced view for the void in the third sample

Figure 6.1: Schematics and void sliced views in different samples

Table 6.1: Samples used for Void growth simulations

	Sample 1	Sample 2	Sample 3
dimension [nm]	7.21	14.42	36.05
dimension [lattices]	20	40	100
number of atoms	32000	256000	4000000
void diameter [nm]	1.08	2.16	3.24
void fraction	0.78%	1.39%	0.30%

In order to excite the void, we apply a tensile stress on both edges of the structure (around $0.0001 \text{ eV}/\text{\AA}$ per atom, or 13 Mpa). What we should expect is either the collapse or the growth of the void. We should also expect the nucleation of some dislocations either from or toward the void. To visualize our structures, we use the OVITO software and we filter the atoms using the centro symmetry parameters to observe the dislocations.

Figures 6.2 and 6.3 show how does the dislocations nucleate and propagate for the two first samples. Qualitatively, we observe 4 dislocations emerging from the void. These extra half planes are clearly shown in figure 6.2. Figure 6.3, however, show a different aspect of these dislocations: By changing the centro symmetry filter, we are able to observe the so-called dislocations loops emerging from the void.

Quantitatively, to calculate the dislocation velocities, we just compute the distance traveled, and the number of MD steps that the simulation took. The dislocation velocity is expressed as

$$V_{dislocation} = \frac{d}{nb_{steps} \cdot t_{step}}, \quad (6.1)$$

where nb_{steps} is the number of steps the dislocation needed to cross the structure, and t_{step} is the MD time step (1fs). Table 6.2 summarizes the dislocation velocities for the different samples.

Table 6.2: Dislocation velocities in Cu

	d [Å]	nb_{steps}	t_{step}	V_d
sample 1	44	500	10^{-15}	$8800m.s^{-1}$
sample 2	88	950	10^{-15}	$9260m.s^{-1}$
sample 3	160	1850	10^{-15}	$8650m.s^{-1}$

The observed dislocations from previous figures are of prismatic nature. After they reach the edges for the first time, a series of other edge dislocations start nucleating from the surface. They move toward the center of the sample(the void), and get pinned when they get close enough to the void.

To calculate the void size is a very tricky operation since the shape might change to either an elliptic or irregular shape. To circumvent this problem, and calculate accurately the size of the void after each step, we use the following procedure:

1. We export the atoms coordinates to Matlab.
2. We ID the atoms at the edge of the void by mean of centro symmetry parameters.
3. We delete all other atoms (from all steps).
4. We fit their coordinates to an ellipsoid using Matlab predefined functions.
5. We calculate the inside volume of the ellipsoid.

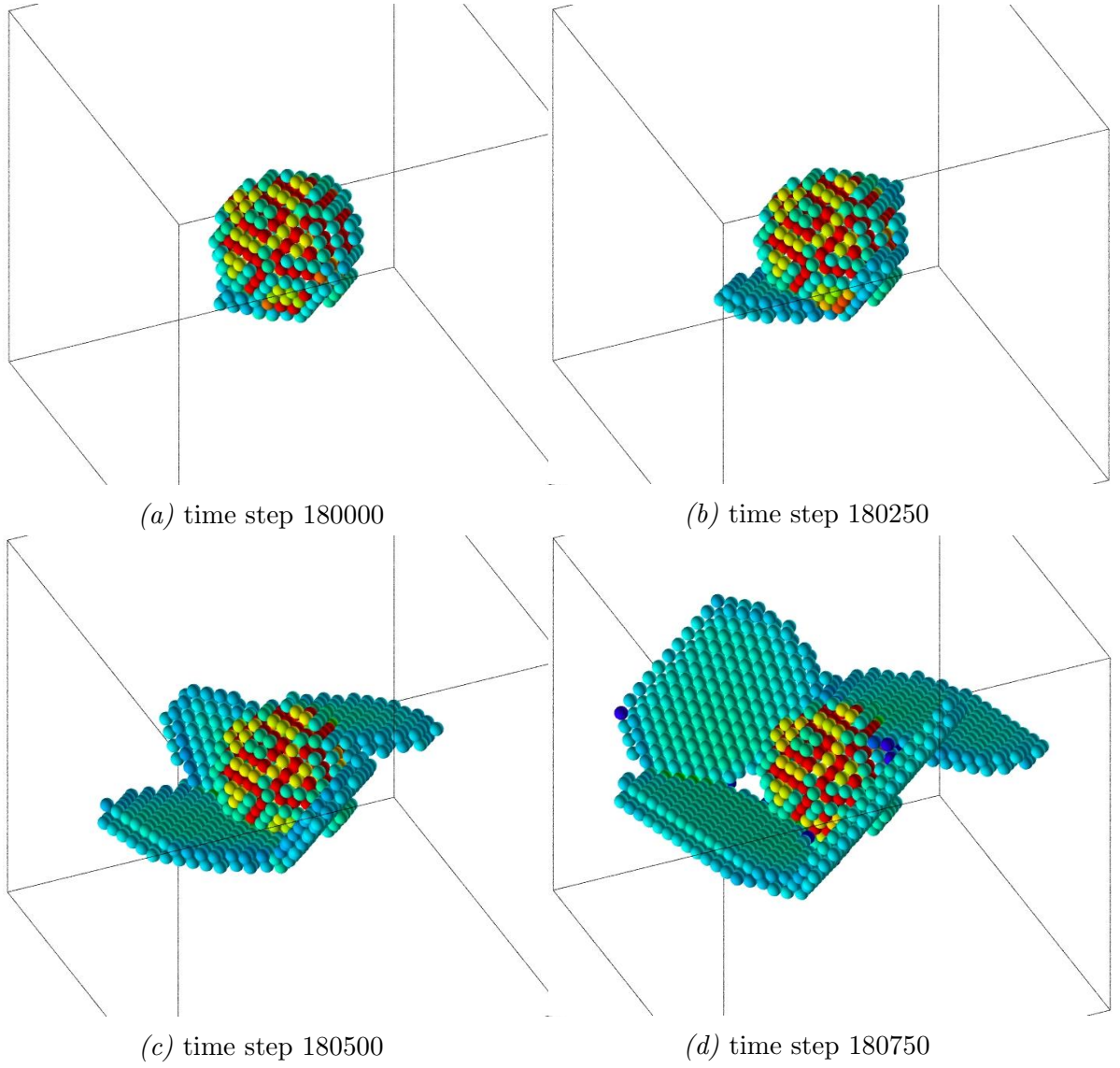
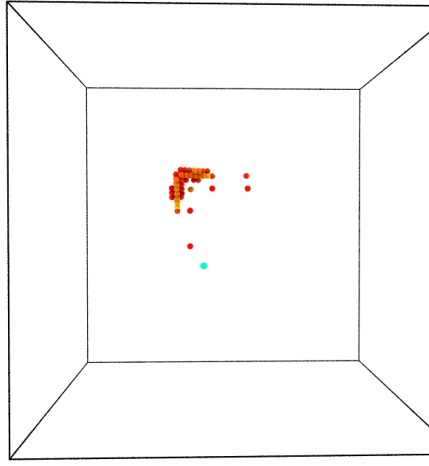
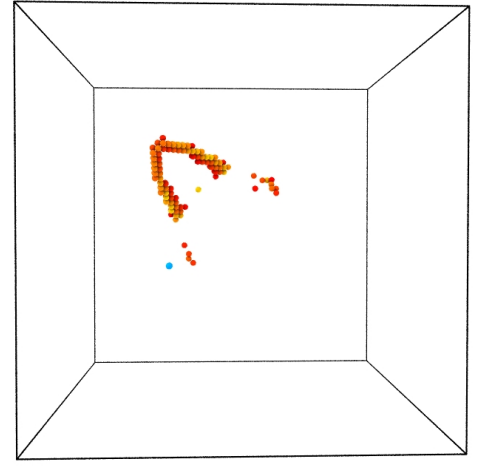


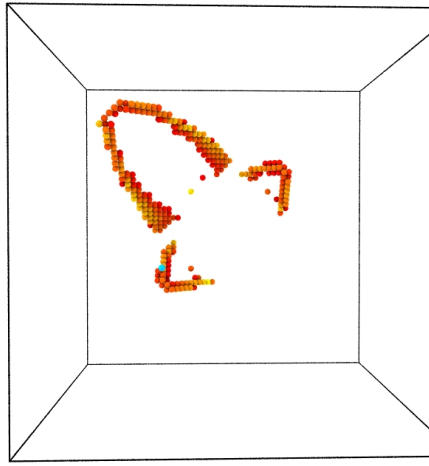
Figure 6.2: Dislocation nucleation and motion snapshot for the first sample



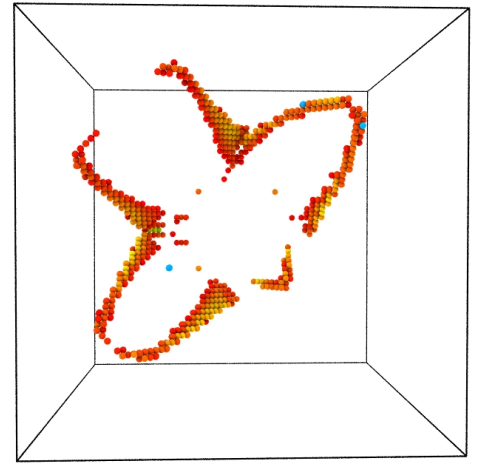
(a) time step 240000



(b) time step 240250



(c) time step 240500



(d) time step 240750

Figure 6.3: Dislocation nucleation and motion snapshot for the second sample

We should note here that we didn't observe a noticeable growth in volume for the void. This can be either due to the inaccuracy of calculating the void or to the short time scale we could reach (the void just grow by few burgers vectors).

Chapter 7

Diffusion and impurity characterization for ZrB_2

7.1 Introduction

A very important feature in understanding creep mechanisms in UHTCs is diffusion. Diffusion can, in general, be calculated by computer simulations using different ways: Molecular Dynamic calculations -for instance- is one of the most popular ways that can help understand vacancy diffusion rates by averaging the square displacements of the atoms [69], [70]. This process is, more or less, straight forward, and the diffusion constant is directly deducted from the MD simulation using equation (7.1):

$$\langle x^2 \rangle = q_i \cdot D, \quad (7.1)$$

where $\langle x^2 \rangle$ is the mean square displacement, q_i is a numerical constant which depends on the dimensionality: $q_i = 2, 4$, or 6 , for $1, 2$, or 3 dimensional diffusion, and D is the diffusion constant.

However, such a property strongly depends on the potential used (which may in some cases have a poor prediction of the activation barriers and the melting temperature), and the obtained result is not often accurate. In fact, to obtain acceptable results, the potential should be extremely precise in catching the correct

vacancy/interstitial energies, migration energies, and the entropy of the vacancies (which is harder to obtain).

An alternative way to work around the strong requirements of the potential is Quantum Calculations. Quantum Mechanics are known to be accurate, and more fundamental (have very little approximations compared to MD). However, they are much more computationally expensive, making the modeling of thousands of atoms and directly obtain the mean square displacements impossible.

Therefore, the obtaining of the correct diffusion constant goes through the calculation of different physical properties that can be combined to obtain the diffusion constant. Three main properties are to be calculated: the vacancy formation energy, The vacancy migration energy, and the entropy associated with the vacancy formation. The total diffusion is then given by:

$$D = a^2 \cdot \nu^* \cdot \exp\left(\frac{-\Delta S_f}{K_B}\right) \cdot \exp\left(-\frac{\Delta H_f + \Delta H_m}{K_B \cdot T}\right). \quad (7.2)$$

The above equation can be much more complicated if there are multiple diffusion paths or diffusing species. This can be observed, for example, for amorphous structures [71] or in alloys or structures with many present different atom types [72]. In the following sections, each term in equation (7.2) is calculated separately, while in the final section, we will summarize, and present the final diffusion properties.

7.2 Diffusion in pure ZrB₂

7.2.1 Free atoms energy

The first step in calculating the different terms in equation (7.2) from Quantum Mechanics calculations is to get the correct free atom energies: These energies will be subtracted later from the total energy to obtain the potential energy that characterizes the bonds between atoms, as shown in equation (7.3):

$$E_{pot} = E_{tot} - E_{atom}. \quad (7.3)$$

The VASP package [24] was used to run all our simulations (including obtaining the free atom energies), and the GGA (Generalized Gradient Approximation) [73], known to be more accurate in estimating bond energies, was chosen. It is important to mention that other, more accurate, functional approximations exist [74] [75], but are more computationally expensive, and thus, were not used.

Since obtaining the correct energetics of the atoms is primordial, we used two different methods: single atom calculation, and crystal calculation. The first -classical- method consists in placing one atom in a large box, and calculating the energy of the system. A spin polarized calculation is necessary in this case : the code recalculates the electronic structure and spin orientations for the single atom electrons. However, depending on the atom type, the convergence of the calculation may require a larger or smaller box size to eliminate the wave functions overlap (because of the

periodicity). This can be observed especially for the Zirconium atom, where a full convergence was not achieved (7.1). In our example, the box size was varied from 4Å to 20Å to visualize the convergence, and the results are presented in figure 7.1 and table 7.1.

Table 7.1: Zr,Hf,W,and B atom energies (in eV) for different size boxes

Box size (Å)	4	6	8	10	12	16	20
Zr	-4.93	-2.40	-2.14	-2.14	-2.23	-2.37	-2.14
Hf	-5.89	3.60	-3.29	-3.29	-3.29	-3.52	-3.52
B	-0.84	-0.35	-0.32	-0.32	-0.32	-0.32	-0.32
W	-5.65	-4.64	-4.63	-4.63	-4.63	-4.63	-4.63

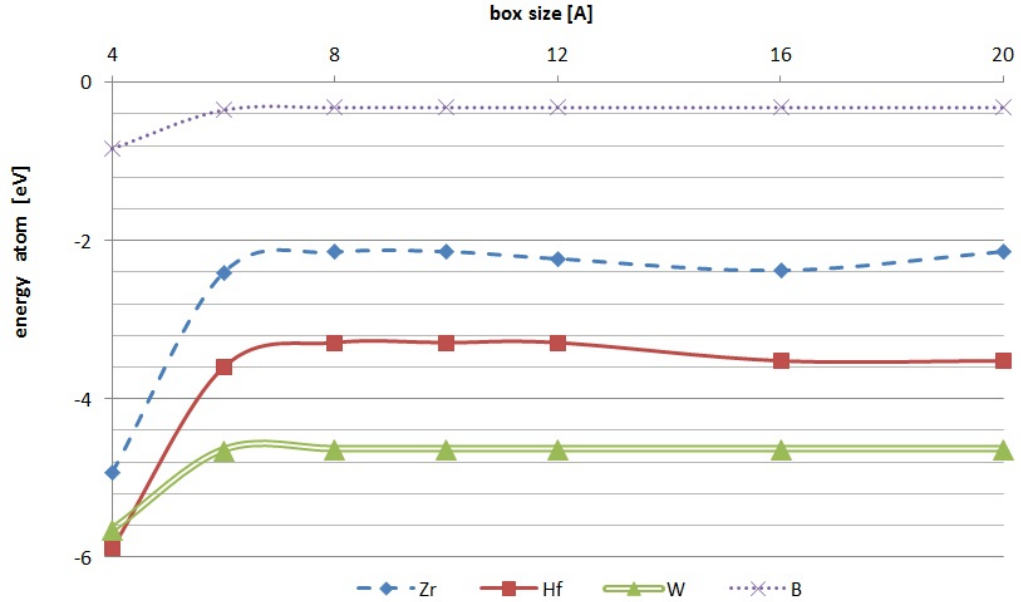


Figure 7.1: Convergence of the energies of the single atoms as function of the box size

The above obtained results -coming from a quantum calculation- can be considered accurate and trustful. However, they depend on the used pseudo-potential approximation. Different algorithms (LDA, GGA, HYBRID, ...) do provide in gen-

eral results that are up to 30% different. This incertitude can be accumulated in a large sample leading to non-correct diffusion constants. Therefore, we used a second method, that eliminates any effect for the pseudo-potential approximation, providing a more accurate estimate of the energies.

The second method is based on using the binding energies of the most stable crystalline structures for the different species. The concept of this method is simple : The binding energy (available experimentally) E_{bind} , is deducted from the total energy E_{tot} to obtain the free atom energy E_{atom} . This second methods is more accurate because of two main reasons: First, crystal calculations are more accurate using the VASP package (this is the case for most Quantum Mechanics software). Second, the artifact of the functional approximation will disappear since we are scaling our energies to experimental binding energies. Equation 7.4 gives the atom energy as function of the binding and total energies,expressed as

$$E_{atom} = \frac{E_{tot}}{n} - E_{bind}, \quad (7.4)$$

where E_{tot} is the total energy calculated for the bulk structure, n the number of atoms in a unit cell, and E_{bind} is the binding energy per atom. Table 7.2 present the atom's energies obtained using this method.

It's clear from tables 7.1 and 7.2, and from figure 7.2 that the energies of the free atoms are consistent using both methods (maximum error of 0.5 eV). However, for the reasons explained earlier, we believe the second method is more accurate, and

Table 7.2: Zr,Hf,W,and B atom energies using the binding energy method

Atom type	n	E_{tot}	E_{bind}	E_{atom}
Zr	4	-33.92	-6.25	-2.23
Hf	4	-39.43	-6.40	-3.45
B	36	-238.67	-5.81	-0.81
W	2	-25.94	-8.90	-4.07

thus will be used in the remaining of this work to calculate the potential energies of the different configurations.

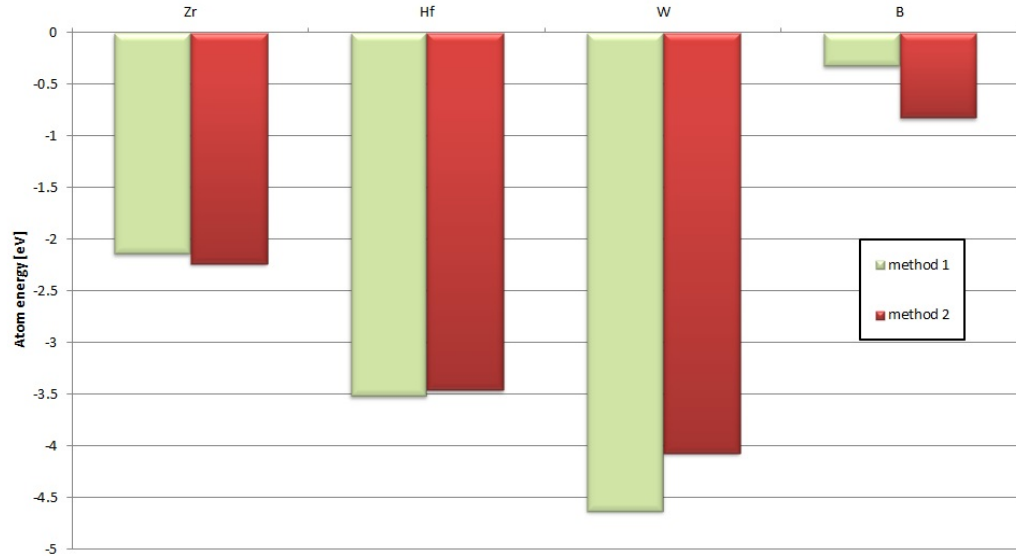


Figure 7.2: Comparison between atom energies obtained by both methods

7.2.2 Structure relaxation

After defining each atom energy, we can obtain the potential energy of each system by performing a bulk VASP energy calculation, and subtracting the energies of the free atoms ([76], [77]). The different vacancy formations energies have to be

calculated following equation 7.5

$$V_f = E_{bulk} \cdot \frac{n-1}{n} - E_{vac}, \quad (7.5)$$

where E_{bulk} is the energy of the original system, E_{vac} the energy of the system with one vacancy, and n the total number of atoms. Since the systems of interest for our study are ZrB_2 and HfB_2 , we start by optimizing the structures and lattice constants to ensure exact E_{bulk} energy calculation. These exact parameters are computed and presented in figure 7.3 and table 7.3.

Figure 7.3: Equations of state for ZrB_2 and HfB_2

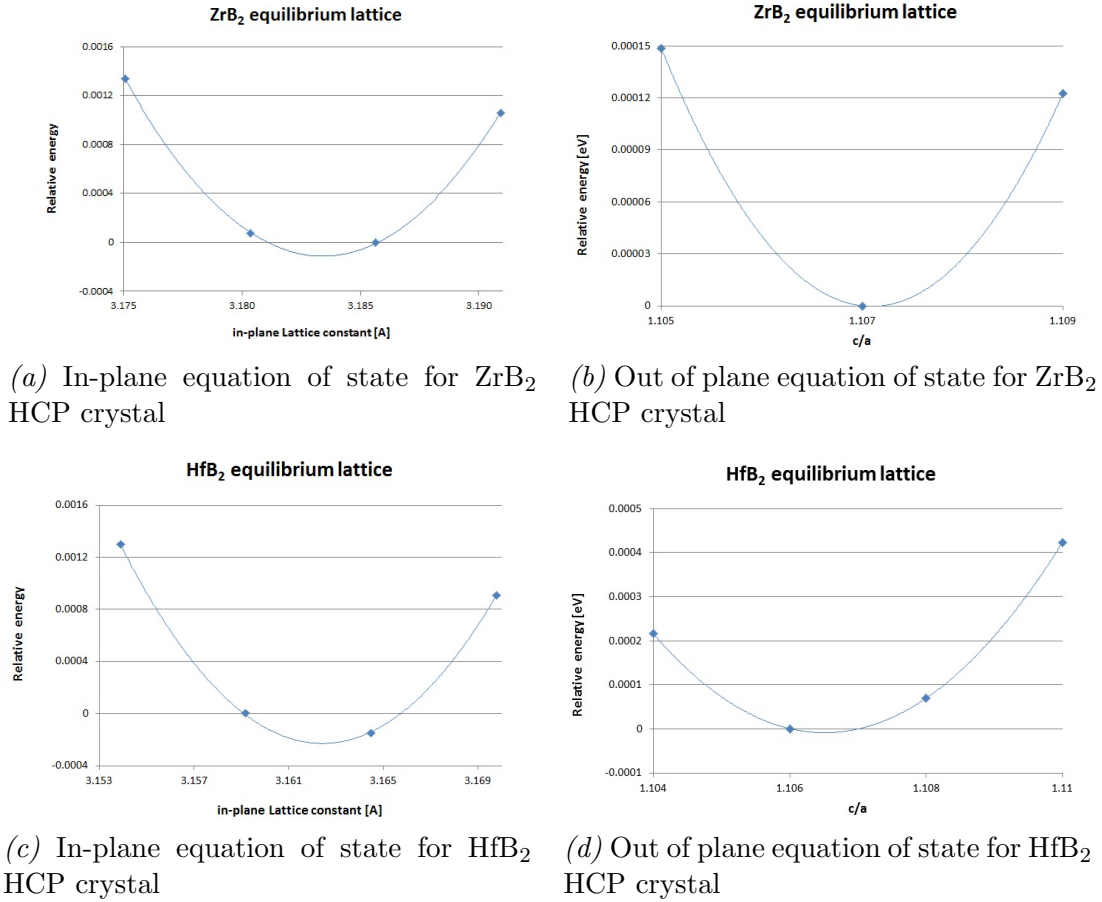


Table 7.3: ZrB₂ and HfB₂ structures

structure		a	c	c/a	E/lattice
ZrB ₂ (our work)	HCP (P6/mmm 191)	3.183	3.523	1.107	-20.93
ZrB ₂ ([78])	HCP (P6/mmm 191)	3.170	3.533	1.114	—
HfB ₂ (our work)	HCP (P6/mmm 191)	3.163	3.500	1.107	-21.21
HfB ₂ ([79])	HCP (P6/mmm 191)	3.141	3.470	1.105	—

Now that we have optimized our structures, it is time to start investigating the diffusion terms, one by one. We will then start by the vacancy formation energy, the migration energy, and the entropic change. Finally we will gather all the information and summarize the diffusion rates.

7.2.3 Vacancy formation energy

The first term in equation 7.2 is the vacancy formation energy, which is a measure of the energy loss accompanied with creating a vacancy. It can be also viewed as a measure of the strength of atomic bonds directly bonded to a specific atom (the stronger the bonds are, the higher the energy required to remove the atom is).

To create the vacancies, we start from the -previously- obtained optimal geometries : We create an HCP bulk containing 24 atoms (2x2x2 lattices), and we remove separately a Boron atom, a Zirconium atom (or Hafnium), and a ZrB₂ tri-atom (or HfB₂). After relaxing the structures with vacancies, we obtain the required vacancy formation energies using equation 7.5.

From the results presented in Table 7.4, different conclusions can be found:

Table 7.4: Vacancy formation energies in ZrB_2 and HfB_2

structure	E[eV]	Vacancy energy[eV]
ZrB_2	-167.45	
$\text{ZrB}_2 - \text{V}(\text{Zr})$	-155.75	4.72
$\text{ZrB}_2 - \text{V}(\text{B})$	-158.13	2.34
$\text{ZrB}_2 - \text{V}(\text{ZrB}_2)$	-137.67	8.85
HfB_2	-169.73	
$\text{HfB}_2 - \text{V}(\text{Hf})$	-158.13	4.52
$\text{HfB}_2 - \text{V}(\text{B})$	-160.42	2.23
$\text{HfB}_2 - \text{V}(\text{HfB}_2)$	-139.64	8.87

- Because the structure of ZrB_2 and HfB_2 are very similar and the atomic properties of Zr and Hf are also similar, the vacancy formation energies in ZrB_2 and HfB_2 are very close (maximum difference of 0.2 eV).

- Boron atoms are the smallest and the lightest atoms, they have the lowest binding energy, and they are only bonded to 3 other Boron atoms. Thus, they are the easiest to remove. However, Zirconium atoms are bigger, heavier, strongly bonded, and have six immediate Zirconium neighbors (figures 7.4 and 7.5). It follows that the Boron vacancy formation energy is much lower than the Zirconium (or Hafnium).

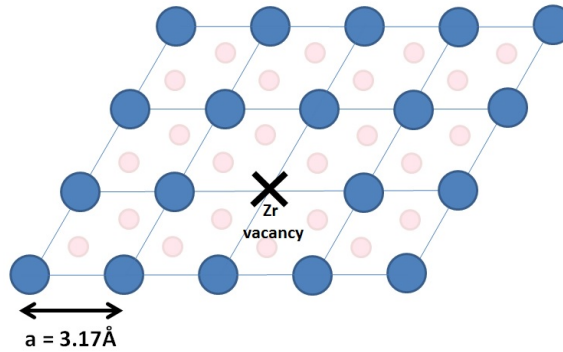


Figure 7.4: Zirconium vacancy

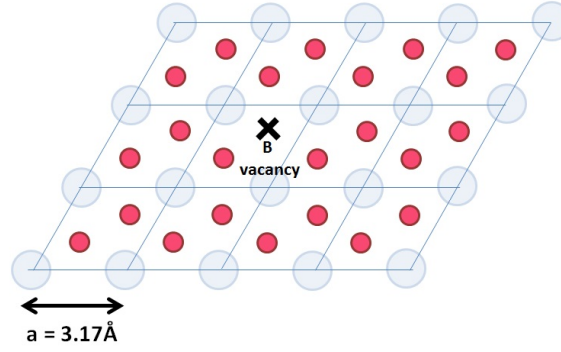


Figure 7.5: Boron vacancy

It also follows from equation 7.6 that the concentration of Boron vacancies is higher for any given temperature, (figure 7.6).

$$C_v = \exp\left(\frac{-\Delta H_f}{K_B \cdot T}\right). \quad (7.6)$$

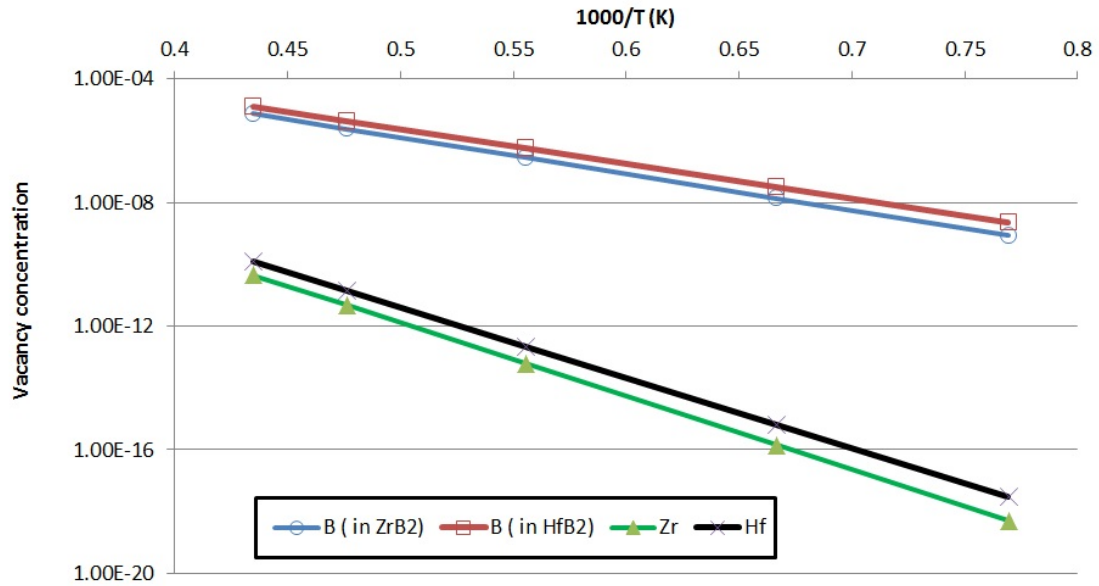


Figure 7.6: Vacancy concentration of different atomic species at high temperatures

7.2.4 Vacancy migration energy

The vacancy migration energy is defined as the barrier that the configuration needs to cross to move the vacancy from one site to an other (figure 7.7). The higher the barrier is, the more difficult the vacancy can move, and the lower the diffusion constant is. Unlike the vacancy formation, different vacancy migration energies can be associated with a single vacancy: In fact, once the vacancy is present, it can follow different paths. For example, Boron vacancies can either move to a neighbor Boron site on the same basal plane, or can cross the basal plane to move to the Zirconium plane. Depending on the barrier it needs to cross, only one path will be favorable because of the exponential nature of the diffusion expression.

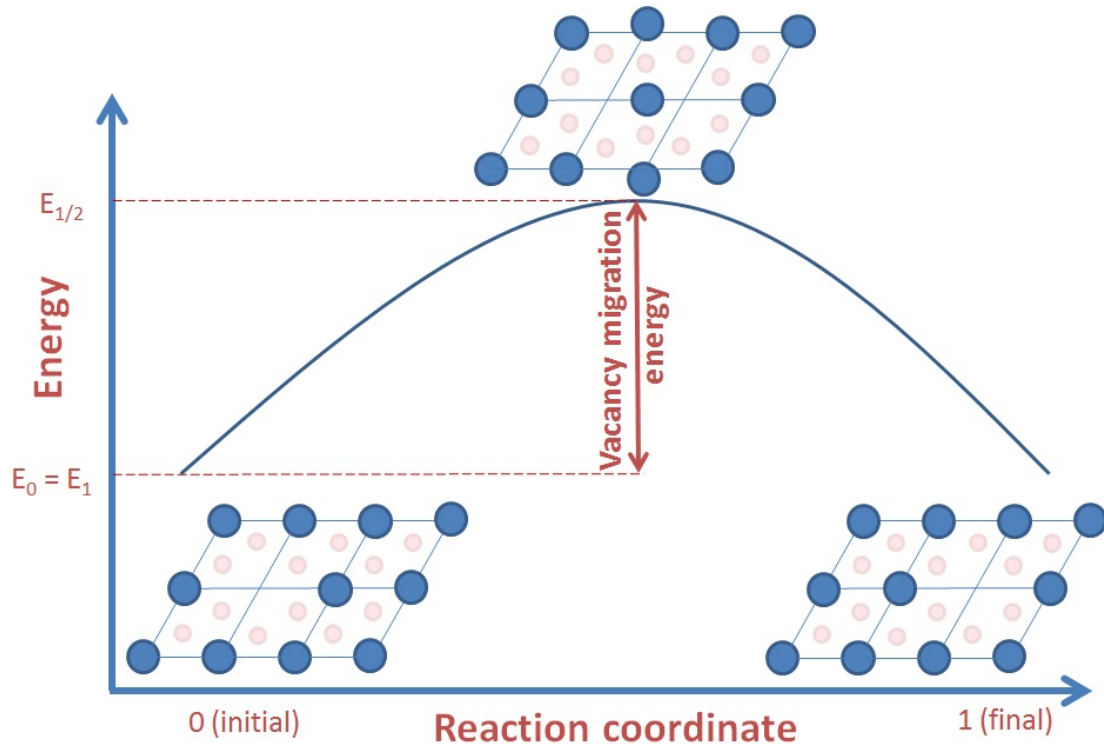


Figure 7.7: Vacancy migration energy cartoon

In principle, we should only study the migration energies of Boron vacancies because other types of vacancies are less likely to exist (Zr vacancies are 10^6 to 10^{12} times less probable to exist, while ZrB_2 vacancies are 10^{15} to 10^{30} times less probable to exist depending on the temperature). However, we present in this section the migration energies of all different types of vacancies in ZrB_2 to achieve a full characterization of the problem (HfB_2 will have similar diffusion properties).

The Nudged Elastic Band method (described previously) is used for this purpose: The same samples are used, and the initial and final states are associated with systems having neighbor vacancies (figure 7.7). After relaxing both structures, NEB is run to find the minimum energy path between these two configurations. The path energies of the Boron and Zirconium vacancies are presented in figure 7.8 and table 7.5.

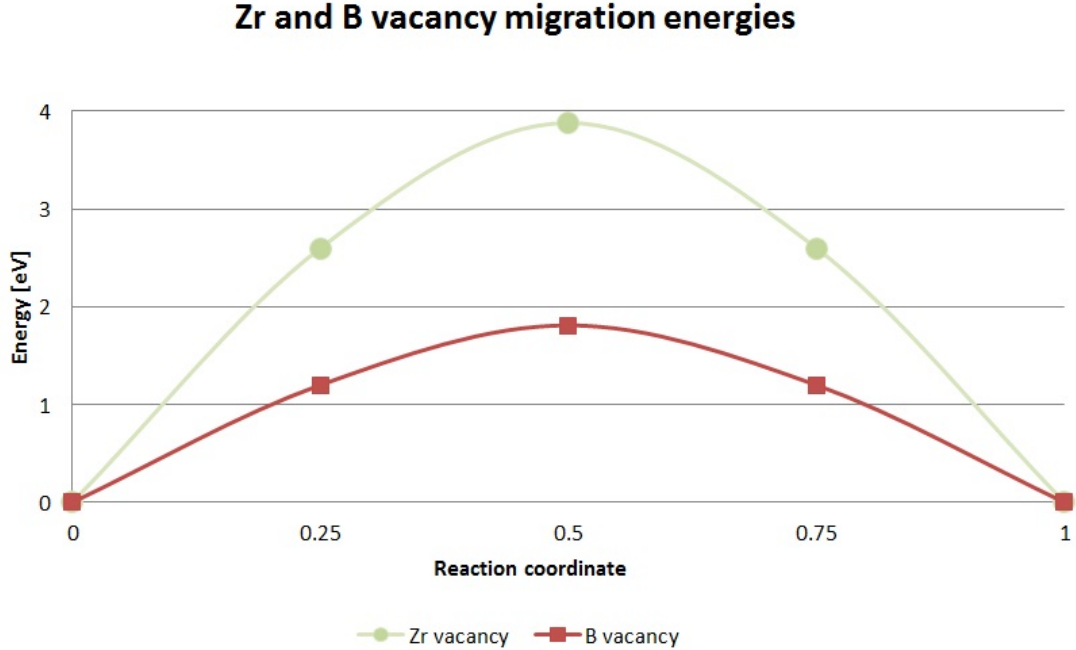


Figure 7.8: Vacancy migration energies for Zr and B atoms

Table 7.5: Vacancy migration energies in ZrB₂ and HfB₂

structure	migration energy [eV]
V(B) in ZrB ₂	1.81
V(Zr) in ZrB ₂	3.88

In binary HCP structures where Boron settles in parallel -graphene like- sheets (like ZrB₂ and HfB₂), it is very hard for Boron vacancies to jump over the metal layers. The metal vacancies are also less likely to cross the Boron layers because of the large migration energies associated with these paths. Consequently, the diffusion of both species in crystalline ZrB₂ occurs in the basal planes. Moreover, analyzing the values of the migration energies (table 7.5), we can easily conclude that the Boron atoms are more likely to move than the Zirconium atoms.

7.2.5 Entropy variation

The third term in defining the diffusion constant is the entropy change. The presence of a vacancy is always associated with a change in the entropy of the system. This change is a key factor in determining the diffusion prefactor, shown in equation 7.7:

$$D_0 = a^2 \cdot \nu^* \cdot \exp\left(\frac{-\Delta S_f}{K_B}\right). \quad (7.7)$$

The entropy of a system can be obtained by integrating its density of state. Such a calculation is performed using VASP, and the entropy of the different systems is presented in table 7.6. Once again, the similarity between ZrB₂ and HfB₂ is astonishing.

Table 7.6: Entropy variation for different systems

configuration	DOS	$S[K_b]$	$\Delta S[K_b]$	$a[A]$	$D_0[m^2s^{-1}]$
ZrB ₂	172	5.147	—	—	—
ZrB ₂ - V(B)	158	5.062	-0.085	3.18	$9.30 \cdot 10^{-8}$
ZrB ₂ - V(Zr)	168	5.124	-0.024	1.84	$3.30 \cdot 10^{-8}$
ZrB ₂ - V(ZrB ₂)	150	5.011	-0.137	3.18	$8.83 \cdot 10^{-8}$
HfB ₂	154	5.037	—	—	—
HfB ₂ - V(B)	142	4.956	-0.081	3.16	$9.22 \cdot 10^{-8}$
HfB ₂ - V(Hf)	150	5.010	-0.026	1.83	$3.25 \cdot 10^{-8}$
HfB ₂ - V(HfB ₂)	134	4.897	-0.139	3.16	$8.70 \cdot 10^{-8}$

The Boron vacancy in both structure is not associated with much entropy variation, however the other types of vacancy are more entropically unfavorable.

7.2.6 Diffusion constants

After gathering the results from all previous sections, we have now, all the ingredients to calculate the diffusion constants in ZrB₂. Qualitatively, it is the Boron specie that dominates the diffusion. Being smaller and lighter, with lower binding energies, Boron vacancies can nucleate orders of magnitude more often than Zirconium vacancies. Moreover, they can migrate easily with a barrier of less than 2eV inside the Boron basal plane. If Boron tries to move out of plane, it will face a much larger barrier because it will have to brake strong Zr-Zr bonds to sit in between. In the Zirconium plane, the atoms are much heavier and bigger, the bonds are stronger (every Zr is bonded to six other atoms), and the distance the vacancy needs to cross is larger. This makes the diffusion inside the Zirconium plane very hard and energetically expensive. Quantitatively, table 7.7 presents a summary of the data collected

through the previous sections for Zr, Hf, and B vacancies, while figure 7.9 shows the total diffusion between 1300K and 2300K.

Table 7.7: Zirconium, Hafnium, and Boron vacancy properties

atom	formation E. [eV]	migration E. [eV]	total barrier [eV]	prefactor [m^2s^{-1}]
Zr	4.72	5.22	9.94	$3.30 \cdot 10^{-8}$
Hf	4.52	5.22 *	9.74	$3.25 \cdot 10^{-8}$
B (in ZrB_2)	2.34	1.81	4.15	$9.30 \cdot 10^{-8}$
B (in HfB_2)	2.23	1.81*	4.04	$9.22 \cdot 10^{-8}$

* : approximated to be the same as in ZrB_2

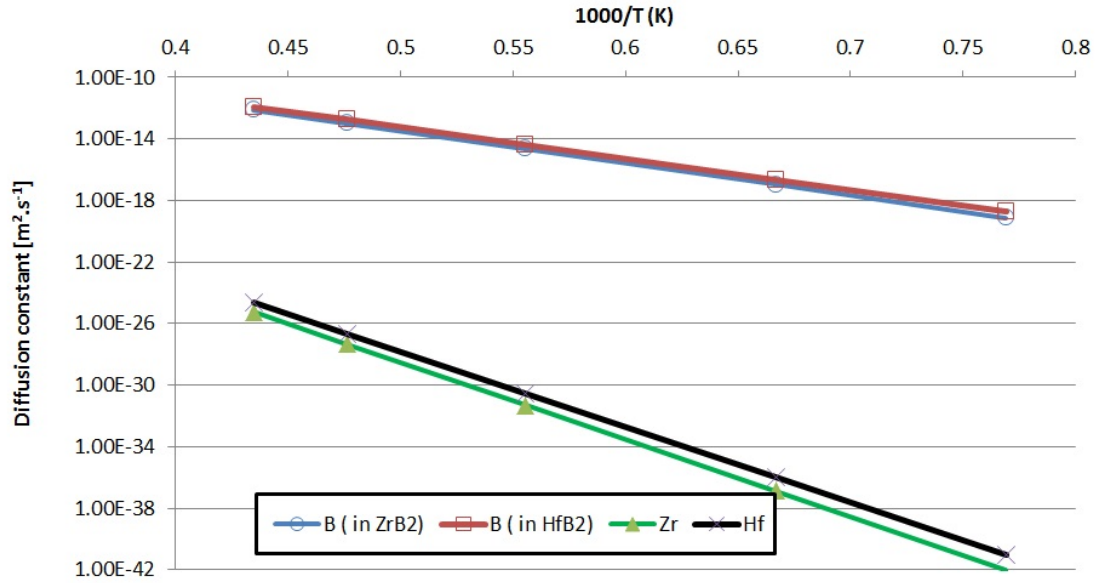


Figure 7.9: Diffusion coefficients for B, Hf, and Zr atoms in ZrB_2 and HfB_2

7.3 Effect of presence of Tungsten as impurity

It has been observed by several studies ([80], [81] ...) that the presence of impurities in UHTCs do have in general an important role. Specifically, Tungsten is

believed to have a very important role in changing creep properties. In fact, one of the dominant creep mechanisms in ZrB_2 multi-grain systems is grain boundary rotation. This phenomena tends to reduce when Tungsten is doped into the system. A possible explanation is that when Tungsten is added, it diffuses into the grain boundaries accommodating for the residual stresses. If Tungsten diffuses in ZrB_2 faster than Boron, this can explain and validate the experimentally observed results.

7.3.1 Tungsten in ZrB_2 : interstitial or substitute ?

For the purpose of finding the effect of Tungsten, we start by identifying the way it can be present in a ZrB_2 lattice: Substituting one of the atoms, or sniffing into an interstitial site (in the Zr plane, in a B plane, or in a plane in between). The accommodation with the lowest energy would be the one that Tungsten would prefer to settle in.

Physically, that would depend on the atomic physical properties : If the size of the impurity is reasonably similar to the matrix atoms, a substitution would be favorable. But, if the size of the impurity is fairly small, it will try to find its way inside the lattice without kicking out any atom.

From results presented in table 7.8, we clearly see that the W atom is relatively big and that its properties are quiet similar to Zr and Hf, but different than B. Thus, we should expect a very high interstitial energy and small Zr (or Hf) substitution energy.

Table 7.8: Atomic properties for Zr, Hf, B, and W

Atom	atomic radius [pm]	inter-atomic distance [pm]
Zr	206 [82]	320*
Hf	208 [82]	315*
B	87 [82]	185*
W	193 [82]	274*

* : DFT calculation result

Table 7.9 validates our previous conclusions, and shows the different substitution and interstitial energies. If the substitution is the favorable mechanism, the Tungsten atoms should substitute those of similar atomic radii and inter-atomic distances (table 7.8). If the interstitial is the favorable mechanism, the Tungsten, will in general try to find the largest empty site it can fit in (in between the planes can be a favored spot). Moreover, since the Zirconium atom size is very close to Tungsten, the substitution mechanism is dominant. This can be seen from the huge difference in the energetics of the different configurations.

Table 7.9: Tungsten substitution/interstitial energies

configuration	Energy [eV]	Subst./Int. Energy [eV]
ZrB ₂	-167.68	—
W substituting Zr	-168.17	-0.49
W substituting B	-162.64	+5.05
W interstitial in Zr plane	-164.76	+9.51
W interstitial in B plane	-164.91	+9.37
W interstitial in between planes	-165.68	+8.63

To seek the effect of the Tungsten doping, we investigate both direct and indirect effects : The direct effect (covered in the next section) is the contribution of Tungsten

diffusion into the overall diffusion, while the indirect effect (covered in the following section) is the effect of the presence of Tungsten in changing the Boron and Zirconium diffusion properties.

7.3.2 Tungsten diffusion constant in ZrB_2

To find the Tungsten diffusion properties, we calculate its vacancy formation and migration energies, and the entropy variation in a ZrB_2 with 4% molar W. A sample of 24 total atoms is considered, where only 1 Tungsten atom is substituting a Zirconium atom (7 Zr, 16 B, 1 W). Such a composition have around 4.2% W. Table 7.10 presents vacancy formation and migration energies of Tungsten (and a comparison with Zr and B vacancies) while 7.11 shows the diffusion prefactor for the three species.

Table 7.10: Vacancy formations and migration energies

atom	formation Energy [eV]	migration Energy [eV]	total barrier [eV]
Zr	4.72	5.22	9.94
W	4.15	6.51	10.66
B	2.34	1.81	4.15

Table 7.11: Entropy variation for Tungsten vacancy

configuration	DOS	S	ΔS	a	D_0
ZrB_2 (with W)	176	5.170	—	—	
ZrB_2 - V(B)	171	5.141	-0.029	1.84	$3.29 \cdot 10^{-7}$
ZrB_2 - V(Zr)	160	5.075	-0.095	3.18	$9.20 \cdot 10^{-7}$
ZrB_2 - V(W)	154	5.036	-0.134	3.18	$8.84 \cdot 10^{-7}$

From the results presented in the above tables, it is clear that Tungsten diffuses slowly in the ZrB_2 lattice. and that its diffusion constant is comparable with Zirconium. The hypothesis of W diffusing to accommodate for the grain boundary rotation is then to be removed. However, The impurity atom might have an indirect effect (the presence of W may increase the diffusivity of the other species in the compound).

7.3.3 Effect of Tungsten on Boron and Zirconium diffusion constants

To find out about the effect of Tungsten, we need to re-calculate the Zirconium and Boron diffusion properties (formation, migration, entropy) in the ZrB_2 4% W. A sample of 24 atoms (16 B, 7 Zr, 1 W) is considered. Table 7.12 shows the B vacancy formation and migration energy with and without the presence of W.

Table 7.12: Boron vacancy energies with and without Tungsten

atom	Vac. form. Energy	Vac. mig. Energy	total activation barrier
B in ZrB_2	1.81 eV	2.34 eV	4.15 eV
B in ZrB_2 (4 % W)	1.80 eV	1.65 eV	3.45 eV

The above presented table shows clearly that Tungsten stimulates the Boron atoms to diffuse more: Although the vacancy formation energy did not change, the migration energies dropped significantly allowing the Boron atoms to move more freely.

7.4 Conclusion

The presence of Tungsten does not have much of a direct effect at low concentrations. At about 4% molar, the diffusion of Tungsten doesn't reach anywhere near Boron diffusion because it will be present in the Zirconium planes which does not contribute much in the diffusion. However, the presence of Tungsten effects the Boron vacancy migration energy (dropping it from 2.34 eV to 1.65 eV) and make Boron more favorable to move, thus, increasing the Boron diffusion by 2 orders of magnitude at 2000K.

It is important to mention that all the obtained results are for bulk diffusion, and that grain boundary diffusion was not considered. However, although we didn't notice any clear effect on bulk diffusion when Tungsten is present, it is still likely that Tungsten will diffuse through the grains affecting directly the overall grain boundary diffusion since grain boundaries are, in general, known for attracting the impurities.

Chapter 8

Conclusions and future work

8.1 Conclusions

In this dissertation, we tried to investigate different aspects of Ultra High Temperature Ceramics creep properties, by implementing a new atomistic approach that is able to simulate creep mechanisms.

1. Since we used atomistic simulations, we had to start by developing a new inter-atomic potential for ZrB_2 and HfB_2 . We chose the so-called “ReaxFF” potential, because of its ability to simulate bond formation/breaking, and to simulate reactions. We, chose Zirconium and Hafnium Di-Borides as example UHTCs and we incorporated in the potential the ability to react with Silicon, Carbon, Oxygen, and Tungsten.

2. We, then, presented a full methodology to overcome the classical time scale issues that Molecular Dynamics have. First, we implemented the Autonomous Basin Climb method, which served to explore the energy landscape of the system under a specific load. Then, we used the Nudged Elastic Band, the Kinetic Monte Carlo, and the Transition State Theory methods to estimate the exact paths and time needed for any physical phenomena to happen.

3. We used the developed methodology to comment on some open problems in time dependant mechanisms : We obtained a real time scale grain boundary sliding

constitutive law, and we determined that a small threshold stress do prevent the grains from sliding because of built static friction.

4. Since it is well known that diffusion is one of the key features in determining creep properties, we characterized diffusion in ZrB_2 . We, then, found that Boron is the dominant specie in diffusion, and that it diffuses much faster than Zirconium. The presence of Tungsten as impurity was also found to stimulate the Boron vacancies to nucleate more and move faster, allowing the system to have faster diffusion.

At the end, we do not claim that, in this dissertation, we present the magic solution to any time dependent problem, but we believe we present a reasonable approach that can be used to overcome the MD time scale limitation. The methodology is very powerful in the sense that it can be applied to any physical problem with a reasonable number of atoms. However, there still exist several limitations, that future research should be dedicated to refine.

8.2 Possible Future Work

Although this dissertation presents the solutions for some creep related properties, a wide spectrum of enhancements can emerge from this work:

A larger training set for the ZrB_2 system can be generated with better fitting accuracy can provide us with a potential that would be more efficient for reactions. Including dislocation energies and enhancing the surface calculations can also improve the quality of the developed potential.

The whole combination of algorithms, can be properly coded in an automated way to ease its use. On the other hand a more sophisticated coding would allow us a better paralellisation, and would allow us to investigate larger systems. Replacing the Nudged Elastic Band by the Finite Temperature String, and the Harmonic Transition State Theory by the Variational Transition State Theory should also enhance the accuracy of our results.

The Grain Boundary Sliding simulations we performed can also be made more realistic by studying realistic grain sizes. Unfortunately, for the time being, we can only simulate a small number of atoms using our methodology.

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Chapter A

ReaxFF parameters

Table A.1: Description of atomic parameters

parameter	description
cov.r	σ covalant radius
cov.r2	π covalant radius
cov r3	$\pi\pi$ covalant radius
valency	Valency of the atom
nb. el	number of valence electrons
a.m	Atomic mass
Rvdw	Van Der Waals radius
Evdw	Van Der Waals dissociation energy
gammaavdW	Van Der Waals shielding
val1	valence energy parameter
val3	valence energy parameter
val4	valence energy parameter
ov/un	OOver/under coordination
gammaEEM	EEM shielding
alpha	Van Der Waals parameter
chiEEM	EEM electronegativity
etaEEM	EEM hardness
Eunder	Under coordination energy
13BO1	Bond order correction
13BO2	Bond order correction
13BO3	Bond order correction
Elp	Lone pair energy

Table A.2: Description of general parameters

parameter	suggested value	description
P_{ovun3}	50.0000	Over coordination parameter
P_{ovun4}	9.8407	Over coordination parameter
P_{coa1}	21.2839	Valency angle conjugation parameter
P_{trip2}	3.0000	Triple bond stabilization parameter
P_{trip3}	6.5000	Triple bond stabilization parameter
P_{ovun5}	0.9782	Under coordination parameter
P_{trip4}	1.0250	Triple bond stabilization parameter
P_{ovun6}	6.3452	Under coordination parameter
P_{ovun7}	11.6274	Under coordination parameter
R_{cut}	10.0000	Upper Taper-radius
P_{val1}	33.8667	Valency under coordination
P_{val2}	88.6186	Valency angle/lone pair parameter
P_{val3}	1.0563	Valency angle
P_{val4}	2.0384	Valency angle parameter
P_{val5}	7.5203	Double bond/angle parameter
P_{val6}	0.3989	Double bond/angle parameter: overcoord
P_{val7}	3.9954	Double bond/angle parameter: overcoord
P_{coa2}	2.1645	Conjugation
γ_{vdw}	1.4553	!vdWaals shielding
P_{val5}	2.8921	Valency angle conjugation parameter
P_{ovun1}	7.1783	Over coordination parameter
P_{ovun2}	1.4473	Over coordination parameter
P_{val6}	3.1353	Valency/lone pair parameter
P_{coa3}	1.6052	Valency angle conjugation parameter

Table A.3: Initial values for atomic parameters

parameter/specie	Zr	Hf	B	C	Si	W	O
cov.r	2.6153	2.5844	1.6831	1.3817	2.2977	2.3101	1.2450
cov.r2	*	*	1.0000	1.1341	1.2962	2.0154	1.0548
cov.r3	*	*	*	1.2114	*	1.9777	0.9094
valency	4.0000	4.0000	3.0000	4.0000	4.0000	4.0000	2.0000
nb. el	4.0000	4.0000	3.0000	4.0000	4.0000	4.0000	6.0000
a.m	91.244	178.49	10.811	12.000	28.060	183.90	15.999
Rvdw	2.3435	2.3435	1.6500	1.8903	1.8550	2.0511	2.3890
Evdw	0.2201	0.2201	0.0500	0.1838	0.2176	0.1526	0.1000
gammavdW	47.463	47.463	2.3847	2.1346	5.1210	11.241	13.845
gammaEEM	0.6797	0.6797	1.0000	0.7807	0.5947	0.8474	1.0898
alfa	11.258	11.258	9.0923	9.7558	11.714	10.211	9.7300
chiEEM	-1.000	-1.000	5.6220	5.9895	4.2033	2.1454	8.5000
etaEEM	7.8853	7.8853	7.4077	6.0000	5.5558	6.2584	8.3122
Eunder	-5.000	-5.000	0.1000	34.935	21.711	4.2140	37.500
Eover	0.0000	0.0000	80.000	79.558	139.39	0.0000	116.07
Elp	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

* : property was not considered in the study

Table A.4: Description for bond parameters

parameter	description
Edis1	σ bond dissociation energy
Edis2	π bond dissociation energy
Edis3	$\pi\pi$ bond dissociation energy
P_{be1}	Bond energy
P_{be2}	Bond energy
kov	Over coordination penalty
P_{bo1}	Bond order parameter 1
P_{bo2}	Bond order parameter 2
P_{bo3}	Bond order parameter 3
P_{bo4}	Bond order parameter 4
P_{bo5}	Bond order parameter 5
P_{bo6}	Bond order parameter 6
ovcorr	Over coordination BO correction

Table A.5: Initial values for alloys bond parameters

bond	E_{dis1}	E_{dis2}	E_{dis3}	P_{be1}	P_{be2}	P_{bo1}	P_{bo2}	P_{bo3}	P_{bo4}	P_{bo5}	P_{bo6}
Zr-B	192.4	0.000	0.000	0.168	0.014	-0.12	11.77	-0.20	15	-0.20	15
C-O	106.4	153.4	56.58	0.637	0.443	-0.13	5.640	-0.33	09	-0.33	19
Zr-Hf	75.60	0.000	0.000	-0.22	0.387	-0.10	7.341	-0.20	15	-0.20	15
Zr-C	115.1	49.59	39.00	-0.49	0.400	-0.44	7.033	-0.10	08	-0.10	08
Zr-Si	78.53	0.000	0.000	-0.17	0.437	-0.11	8.341	-0.20	15	-0.20	15
Zr-O	110.3	72.50	25.00	0.037	0.521	-0.11	6.920	-0.15	12	-0.15	22
Zr-W	87.08	0.000	0.000	-0.22	0.387	-0.10	7.341	-0.20	15	-0.20	15
Hf-B	76.82	0.000	0.000	0.355	0.365	-0.09	7.961	-0.20	15	-0.22	15
Hf-C	118.6	49.59	39.00	-0.49	0.400	-0.44	7.033	-0.10	08	-0.10	08
Hf-Si	82.05	0.000	0.000	-0.17	0.437	-0.11	8.341	-0.20	15	-0.20	15
Hf-O	110.6	72.50	25.00	0.012	0.496	-0.11	6.420	-0.15	12	-0.15	22
Hf-W	90.60	0.000	0.000	-0.22	0.387	-0.10	7.341	-0.20	15	-0.20	15
B-C	116.3	49.59	39.00	0.081	0.379	-0.43	7.653	-0.10	08	-0.12	08
B-Si	79.75	0.000	0.000	0.405	0.415	-0.10	8.961	-0.20	15	-0.22	16
B-O	108.3	72.50	25.00	0.592	0.474	-0.10	7.040	-0.15	12	-0.17	22
B-W	88.30	0.000	0.000	0.355	0.365	-0.09	7.961	-0.20	15	-0.22	15
C-Si	121.5	49.59	39.00	-0.44	0.450	-0.45	8.033	-0.10	08	-0.10	08
C-W	130.1	49.59	39.00	-0.49	0.400	-0.44	7.033	-0.10	08	-0.10	08
Si-O	113.5	72.50	25.00	0.062	0.546	-0.12	7.420	-0.15	12	-0.15	22
Si-W	93.53	0.000	0.000	-0.17	0.437	-0.11	8.341	-0.20	15	-0.20	15
O-W	122.1	72.50	25.00	0.012	0.496	-0.11	6.420	-0.15	12	-0.15	22

Table A.6: Initial values for pure elements bond parameters

bond	E_{dis1}	E_{dis2}	E_{dis3}	P_{be1}	P_{be2}	P_{bo1}	P_{bo2}	P_{bo3}	P_{bo4}	P_{bo5}	P_{bo6}
Zr-Zr	72.08	0.000	0.000	-0.22	0.387	-0.10	7.341	-0.20	15	-0.20	15
B-B	74.53	0.000	0.000	0.935	0.344	-0.08	8.581	-0.20	15	-0.25	16
C-C	158.2	99.18	78.00	-0.77	0.414	-0.77	6.726	-0.20	01	-0.25	01
O-O	142.2	145.0	50.00	0.250	0.605	-0.12	5.500	-0.10	09	-0.10	29
Si-Si	84.98	0.000	0.000	-0.12	0.487	-0.12	9.341	-0.20	15	-0.20	16
Hf-Hf	79.12	0.000	0.000	-0.22	0.387	-0.10	7.341	-0.20	15	-0.20	15
W-W	102.1	0.000	0.000	-0.22	0.387	-0.10	7.341	-0.20	15	-0.20	15

Table A.7: Description for angular parameters

parameter	description
Θ_0	180 °- (equilibrium angle)
K_a	1 st force constant
K_b	2 nd force constant
P_{conj}	Valence conjugation
P_{v2}	Under coordination
K_{penal}	Penalty energy
P_{v3}	Energy/bond order

