COMPUTATIONAL STUDY OF HYDROGEN IN NANODIAMOND

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COMPUTATIONAL STUDY OF HYDROGEN IN NANODIAMOND

RESEARCH THESIS

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Abstract

In this study, we investigated the diffusion and effect of interstitial hydrogen atom(s) in bulk diamond and in amorphous carbon and diamond composites. The locations, electronic energy levels and motion of hydrogen are investigated through a tight binding molecular dynamics scheme.

The tight-binding method incorporates electronic structure calculations through an empirical tight-binding Hamiltonian, which bridges the gap between ab-initio calculations and an empirical classical potentials (such as Tersoff) and provides a relatively low computational workload, suitable for simulating hundreds of atoms, with high precision.

In bulk diamond, H has been found to have a sixfold degenerate site (with respect to the C-C bond) known as an ET site. The H atom gives rise to new energy states in the middle of the diamond density of states bandgap[1]. This ET site has been found to be at two-thirds of the distance between the diamond hexagonal planes, resulting in a deformation of the diamond lattice. Albeit the different chemical structure, similarities can be found to deformations in SWNT (Single Walled Nano-Tube) and MWNT due to H adsorption[2]. In samples with a surface bounded by a vacuum, the
H has been found to have a tendency to migrate to the surface layer of the diamond, resulting in a deformation of the lattice, as seen experimentally. This configuration has new energy states above and below the Fermi energy in the bandgap of the diamond density of states. This can also be correlated to hydrogenated SWNT, where a large number of states at the Fermi level are contributed by hydrogen atoms absorbed on the exterior of carbon nanotubes[3].

H₂ was shown to have little effect on the diamond lattice due to its energetic and thermodynamic stability. However we note that the final configuration of H₂ in the diamond bulk has characteristics familiar to orientational order in solid H₂.

The amorphous carbon and diamond composite is simulated by the melting of pure diamond and subsequent quenching of the sample. Then, hydrogen atoms are implanted in the diamond core, rich in sp³ bonded carbon atoms, of the relaxed sample. The local density of states (LDOS) of the sp³ rich regime show a wide bandgap, similar to the diamond bandgap. As the hydrogen concentration is increased, due to further hydrogen implants, more sp² bonds are transformed to sp³ bonds in the vicinity of the diamond core, until saturation of H in the composite is reached. This increase, stabilizes the diamond core and increases its size, resulting in the growth of the diamond regime.

In order to investigate each simulation in detail, visualizations of the samples were carried out.
List of Symbols

\( a_0 \)   Lattice constant
\( sp^2 \)   Hybridization of one \( s \) orbital with two \( p \) orbitals
\( sp^3 \)   Hybridization of one \( s \) orbital with three \( p \) orbitals
\( a - C \)   Graphite-like amorphous Carbon
\( a - C : H \)   Hydrogenated amorphous Carbon
\( ta - C \)   Diamond-like amorphous Carbon
\( g(r) \)   Radial Distribution Function (RDF)
\( \rho(r) \)   Average concentration of atoms
\( z \)   Coordination number
\( E_i \)   Energy of atom \( i \)
\( V_{ij} \)   Interaction energy between atoms \( i \) and \( j \)
\( r_i \)   Position of atom \( i \)
\( v_i \)   Velocity of atom \( i \)
\( r_{ij} \)   Distance between atom \( i \) and atom \( j \)
\( \phi_{la} \)   Atomic orbital, \( l \) located at \( \alpha \) site
\( \varphi_{la} \)   Löwdin orbital, \( l \) at site \( \alpha \)
\( \Phi_{k\alpha} \)   Bloch functions
\( U_{rep} \)   Repulsive energy
\( \Delta t \)   Time step
Chapter 1

Introduction

The diamond phase of carbon is always contaminated with hydrogen, whether it is natural or polycrystalline CVD (Chemical Vapor Depositions) diamond. Various experimental techniques are used for the observation of hydrogen in diamonds, from infrared (IR) absorption [4] through electron paramagnetic resonance (EPR) [5] and muon spin rotation ($\mu$SR) to optical measurements. However, conclusive assignment of these spectra to specific hydrogen-related structures in diamond remains to be achieved. In simulations, specific configurations can be examined in detail, thereby providing essential clues for clarification. While reading this thesis it is suggested to use the attached CD-ROM for viewing figures and movies.

1.1 Basic Properties of Carbon

Carbon is a group IV element, which is distributed very widely in nature. It is found in abundance in the sun, stars, comets, and atmospheres of most planets. Carbon is
believed to be the source of life on our planet Earth.

Carbon is found free in nature in three allotropic forms: amorphous, graphitic and diamond. Each form possesses very different physical and chemical properties, for example, graphite is soft, opaque and electrically conducting while diamond is hard, transparent and electrically insulating. It is this difference that makes carbon so fascinating and intriguing.

1.1.1 The Diamond Structure

In the diamond lattice (see figure 1.1), each carbon atom has four valence electrons spread in the \( s \) and \( p \) orbitals, the \( s \) orbital mixes with the three \( p \) orbitals (\( p_x, p_y, p_z \)) forming \( sp^3 \) hybridization (see figure 1.2), creating a strong tetrahedral structure. The four valence electrons of the carbon are equally distributed among the \( sp^3 \) orbitals, each orbital pointing to one of the corners of a tetrahedron, this tetrahedral structure gives strength and stability to the bonds. The diamond structure can be viewed as two interpenetrating FCC structures displaced by \( (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a_0 \), where \( a_0 \), the length of the cubic border, is for carbon diamond \( a_0 = 3.567\text{Å} \[6]\).

As mentioned, all valence electrons contribute to the covalent bond, hence, they are not free to migrate through the crystal, thus, diamond is a poor conductor with a band gap of 5.48eV [7].
1.1.2 The Graphite Structure

In the graphite lattice (see figure 1.3), the s orbital mixes with only two p orbitals forming three $sp^2$ orbitals pointing to vertices of a triangle in the plane (see figure 1.2). Three electrons occupy these orbitals and one electron is left in the p orbital perpendicular to the $sp^2$ plane contributing to conduction. Overlapping occurs between $sp^2$ orbitals of neighboring atoms in the same plane, and there is also overlap of their unhybridized p orbital resulting in a $\pi$ bond. The entire structure is made of sheets held together by weak Van der Waals forces, separated by a distance of 3.40Å, giving softness to the structure [8].

The stable bonding configuration of carbon at NTP (conditions when the Number of particles, their Temperature and Pressure are kept constant) is graphite, with an energy difference of $\approx 0.02eV$ per atom. Due to the high energetic barrier between the two phases of carbon, the transition from diamond to the more stable phase of graphite at normal conditions is extremely slow but, this transition can be accelerated
Figure 1.2: Schematic representation of $sp^2$ (left) and $sp^3$ (right) hybridizations

<table>
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<tr>
<th></th>
<th>Diamond</th>
<th>Graphite</th>
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<tr>
<td>Lattice constant [Å]</td>
<td>3.567</td>
<td>2.462</td>
</tr>
<tr>
<td>Density at 298K [gr/cm$^3$]</td>
<td>3.513</td>
<td>2.200</td>
</tr>
<tr>
<td>Bond Length [Å]</td>
<td>1.545</td>
<td>1.455</td>
</tr>
<tr>
<td>Band gap [eV]</td>
<td>5.48</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

Table 1.1: Properties of diamond and graphite.

under extreme conditions such as when the diamond is exposed to high temperatures. In table 1.1 some properties of diamond and graphite crystals are presented.

### 1.1.3 The Amorphous Structure

The amorphous structure is characterized by a high degree of short range order and the absence of long range order. The short range order in amorphous structures can be seen in bond length, number of nearest neighbor atoms as well as in the angle between two bonds. At a longer range, there is no periodicity in the amorphous
structure, hence its symmetry is broken, giving isotropic characteristics to the structure. Energetically, atoms in the amorphous structure are not bonded ideally, hence, the energy of the amorphous structure is higher than of a pure crystal. The method of preparation of amorphous diamond strongly affects the properties of the structure.

Two specific amorphous forms of carbon commonly appear and can be distinguished by their microscopic and macroscopic properties:

1. Diamond-like amorphous carbon, usually denoted by $ta - C$ is characterized by a mean number of nearest neighbors (or coordination number), $z = 3.5 - 3.8$, mean bond angle of $110 - 115^\circ$ and a density of $2.9 - 3.5 gr/cm^3$. This $ta - C$ is a hard, dense material mostly made of distorted $sp^3$ bonds[8].

2. Graphite-like amorphous carbon, usually denoted by $a - C$ is characterized by high percentage, $\sim 70\%$ to $\sim 98\%$, of $sp^2$ bonds hence, a mean number of
nearest neighbors, \( z = 2.9 - 3.2 \), a bond angle of around \( 120^\circ \) and a density of \( 2.0 - 2.7 \text{gr/cm}^3 \). This \( a-C \) is a soft, opaque material mostly made of distorted \( sp^2 \) bonds[9].

1.2 Basic Approaches

The ultimate goal of computer simulations is to help describe, predict and explain nature as accurately as possible in a reasonable time frame. The simulated regime can be varied according to the problem, from a numerical solution for a two-body problem to a large scale, billions of particles simulation for time scales ranging from a picosecond to several seconds. This goal can be achieved by the combination of an efficient mathematical model, a powerful hardware platform, and a refined computer graphics package for visualizations and animations.

1.2.1 Ab Initio

\textit{Ab-initio}, from Latin, 'From the beginning'. The \textit{Ab-initio} technique is based on first-principles density functional theory, without any adjustable parameters, hence, is known to be generalized, reliable and accurate. This technique involves the solution of the Schrödinger’s equation for each electron in the system, in the self-consistent potential created by the other electrons and by the nuclei. This method is known to be very expensive in terms of CPU time.
1.2.2 Monte Carlo

The *Monte Carlo* method provides approximate solutions to a variety of mathematical problems by performing statistical sampling experiments. In this method we use random moves to explore the configuration space to find out information about the space, random moves are accepted such that a different region of search space is sampled at each step.

In its statistical approach, the *Monte Carlo* simulation can be adapted to various types of ensembles, from the Grand- and Micro- Canonical ensembles to the Isotension-isothermal ensembles, each providing observable different statistical averages computed in the simulations.

1.2.3 Molecular Dynamics

*Molecular Dynamics* is a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their equations of motions in a classical many-body system. The classical contribution is that the motion of the constituent particles obeys the laws of classical mechanics, notably the Newtons equations are solved, for each atom participates in the simulation. This technique is deterministic: given an initial set of positions and velocities, the subsequent time evolution is in principle determined.
1.2.4 Potentials

Usually the potentials which are used, for both Monte Carlo and Molecular Dynamics simulations are derived directly from experimental observations (such is the case for parameters of a Lennard-Jones potential or the classical Coulomb), or by ab-initio calculations. It is desirable to reduce the computational expense for molecular dynamics simulation with a quantum mechanical potential energy function.

1.3 Nanocrystalline Diamond

Hydrogen is an ubiquitous impurity in diamond but in contrast to hydrogen in other group IV materials, the microscopic structure adopted in bulk material has largely remained elusive. There is therefore an important role for modeling to predict the properties of Hydrogen in bulk diamond.

1.3.1 The Mechanism of Diamond Nucleation

In recent years, techniques for low-pressure chemical-vapor-deposition (CVD) production of diamond have been developed to facilitate diamond growth at sub-atmospheric pressures[10, 11, 12]. Typically a hydrocarbon-hydrogen plasma is applied over a silicon substrate held at $\sim 1000^\circ$ to $1100^\circ$K while being negatively biased to $\sim 100$ to $200V$ (BEN). Diamond growth on diamond is relatively well understood and controlled, while diamond growth on silicon requires a nucleation step that is much less understood and relies largely on trial and error.
Y. Lifshitz et al. proposed a model for the mechanism of diamond nucleation from energetic species such as carbon, hydrocarbon and hydrogen which originate from the chemical vapor deposition (CVD) plasma [13]. The model is composed of 4 steps,

1. the first step is the formation of amorphous hydrogenated carbon (a-C:H) on a silicon substrate via a subplantation process, where the energetic carbon, hydrocarbon and hydrogen atoms bombard the surface and are subsequently stopped and incorporated in subsurface layers. Carbon interstitials and hydrogen atoms are provided through the subimplantation process.

2. the second stage is the precipitation of sp³ carbon clusters induced by a “thermal spike” (where energy is deposited on the carbon electrons by the energetic hydrogen atoms, consequently, the electrons transform the energy to the lattice atoms by an electron-lattice interaction leading to the increase of temperature). Most clusters are amorphous but a few are perfect diamond.

3. the third step consists of the annealing of faults in defective clusters by the incorporation of carbon “interstitials” in reactive sites and by hydrogen termination. The amorphous matrix contain ~ 20 to 30% of hydrogen.

4. the last step is the transformation of amorphous carbon to diamond at the amorphous matrix-diamond interface. This growth of the diamond clusters is typically up to several nm in size(10⁴ to 3 × 10⁴ atoms). This transformation is induced by a “preferential displacement” mechanism caused by impact of energetic hydrogen atoms.
Each step of this mechanism is supported by previously reported experiments [11] and [14] carried out using a direct-current glow discharge (DC GD) methane-hydrogen plasma on a negatively biased Si (100) at 800° to 950°C.

1.3.2 Experimental Studies

The structure and defects of nanocrystalline diamond films are studied using various complementary techniques such as NEXAFS, HR SEM, AFM, HR-TEM and XRD (refer to appendix A). NEXAFS spectroscopy is used for phase composition analysis of the nano-crystalline structures, while SEM, AFM, TEM and XRD are used for morphological and structural analysis.

In [15] nanocrystalline diamond films were obtained by plasma deposition onto p-type boron doped Si(100). The substrate temperature was kept at 880°C, the pressure of the hydrogen-methane mixture (9% $\text{CH}_4$, 91% $\text{H}_2$) was kept at 10 Torr and was biased at -500V. The films developed a characteristic gray color, brown color is obtained at short times. NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy was used to analyze the phase composition of the nanocrystalline structure and revealed a diamond phase. Additional electronic states appeared as a result of the imperfect crystalline structure of small particles as well as the large content of hydrogen in the films ($\sim 19\text{at.\%}$). Furthermore the average growth rate of the films is nearly constant and obtained a value of $\sim 1\mu\text{m/h}^{-1}$. Morphological and structural analysis were obtained by using SEM, AFM, TEM and XRD measurements. The diffraction pattern of the Si-film interface displays rings associated with graphitic
carbon where the graphitic basal planes are aligned perpendicular to the silicon substrate. Cross-sectional TEM revealed the size of the diamond crystallites to be \( \sim 5nm \) in diameter. The electron diffraction pattern obtained using XRD reveal the presence of diamond structure. The SEM and AFM microscopies do not demonstrate the real topography of the surface, the SEM demonstrate a convolution of the topography features and variations in secondary electron emission associated with heterogeneous carbon phase composition of the film. The AFM pictures are complicated by tip-surface interactions, which may result in different artifacts.

A recent study [16] used micro-Raman spectroscopy to confirm the deposition of diamond and to study the phase purity of the diamond nanocrystalline films. A first order diamond line at \( \lambda = 1334cm^{-1} \) was received for the film, a broad peak around \( 1140cm^{-1} \) suggested a small grain size or a disorder in the tetrahedrally bonded carbon network and a low board signal of \( sp^2 \) carbon-related was detected at 1400 to 1600\( cm^{-1} \).

Secondary Ion Mass Spectroscopy (SIMS) were performed by A. Hoffman et. al. [17] to profile the hydrogen concentration in nanocrystalline carbon films of a predominant diamond character. The samples were grown using a \( CD_4/D_2 \) gaseous mixture to analyze the deuterium content, since SIMS measurements can be influenced by the presence of the environmental hydrogen. Deuterium concentrations of films deposited at 880\( ^\circ C \) were found to be \( \sim 19at.% \) in the \( \sim 400nm \) close to the surface and decreases to \( \sim 5at.% \) for thickness of \( \sim 300nm \). Additional NEXAFS spectra were obtained on the samples, revealing a predominant diamond character for films deposited for 30 minutes and longer.
From the NEXAFS and SIMS results Hoffman et al [17] concluded that diamond nucleation and nanodiamond film growth occurs onto a graphitic precursor of thickness $\sim 300\text{nm}$ and that the nucleation of diamond and its growth is accompanied by an intensive hydrogen retention in the film. Higher deposition temperatures led to a decrease of hydrogen concentrations. The high amount of hydrogen in the nanodiamond film grown at $880^\circ\text{C}$ for 1 hour appears to be anomalous. These data suggest that the observed increase of hydrogen concentration is related to the diamond nucleation and growth of the nanodiamond phase.

Deposition of carbon films from methane and/or a different noble gas, such as Ar or He, resulted in a graphite or amorphous carbon deposition with only small amounts of diamond inclusions[18, 19, 20]. Gruen[21] pointed out that in such plasmas, carbon dimers, $\text{C}_2$, are formed from hydrocarbon molecules under highly non-equilibrium conditions, resulting in supersaturated carbon vapor. The $\text{C}_2$ can react, with high probability, with the methane, and form methyl-acetylene, and with a much lower probability can cause a heterogeneous nucleation on diamond nuclei on the substrate. In order to favor diamond deposition, seeding of the substrate by diamond powder must be performed before exposure to the plasma. However, the morphology and microstructure of the films deposited are completely different from the DC GD CVD method described earlier.

Several open questions still remain. Even with the state of the art experimental equipment used in [17], one cannot ascertain the exact positions of the hydrogen with
respect to the diamond nucleation sites, nor determine optimal hydrogen concentrations in the a:C/diamond composites for the growth of the nanodiamond. Moreover, it is unknown what effect the hydrogen has on the a:C/diamond composites? and it is uncertain why hydrogen is a 'key player' in the nucleation and growth of nanodiamonds?. Some of these questions will be answered in the present study from a computational viewpoint.

1.3.3 Previous Results from Atomistic Simulations

Molecular Dynamics simulation of the bombardment process during bias enhanced nucleation (BEN) phase of chemical vapor deposition (CVD) of diamond was performed by Kohary et al. [22]. Kohary used density functional based tight binding (DFTB) MD simulation to simulate realistic conditions corresponding to BEN in diamond CVD. A heated a-C:H layer was bombarded with methyl and acetylene ions of different energies.

The number of broken C-H bonds increased continuously with the bombarding energy of the projectiles, and the excess hydrogen tended to form $H_2$ molecules. The bombardment of the projectile atoms caused structural rearrangement in the substrate the total $sp^3$ content in the film increased, while the total $sp^2$ content decreased by the same magnitude. However, the role of the hydrogen in the growth of the total $sp^3$ content could not be concluded since the projectiles were hydrocarbon species and the increase in the $sp^3$ bonds can also be related to the energetic carbons. Moreover, this study cannot answer why, experimentally, when hydrogen is replaced by a different noble gas, such as Ar, the $sp^3$ content is reduced (these results, from
Hoffman et al are not yet published, and experiments are in progress).

Mehandru et al.[23] have investigated the binding and diffusion pathways for atomic hydrogen in diamond using the semiempirical atom superposition and electron delocalization molecular orbital theory. The bond-centered site has been found to be more stable than the tetrahedral and hexagonal interstitial sites due to the formation of a low-lying band-gap orbital which takes the promoted electron. According to their calculations the bond-centered hydrogen is predicted to migrate along the high-density (110) planes in the diamond lattice with an activation barrier of 1.9eV. A carbon atom vacancy is found to attract interstitial H which bind to dangling orbitals on the surrounding C atoms. These bond strengths decrease as up to a maximum of four H atoms enter the vacancy. A hydrogen atom in a vacancy is found to increase the activation energy for vacancy migration.

In Mehandru’s calculations the first and second nearest neighbor carbon atoms surrounding the BC site were completely relaxed while the position of the third shell of atoms was fixed. In equilibrium configurations, the C-C bond length containing the H atoms is found to increase by 43.5%. Calculations were also performed for a second H atom in the diamond lattice located near the one already present at the BC site. It has been found that the most stable site for the second hydrogen is the antibonding (AB) site forming a linear H-C-H-C configuration along the < 111 > direction, the BC hydrogen is now asymmetrically placed between the neighboring C atoms, being closer to the carbon located away from the AB hydrogen. The CC bond stretch has increased further by 0.07Å. To create a vacancy, a carbon atom from the center of a cluster was removed and the four nearest neighbors carbon atoms surrounding the
vacancy were relaxed and hydrogen binding to a vacancy was examined. Hydrogens were added to the cluster one at a time, in each case the positions of the H atom(s) and relaxations of the four neighboring C atoms were performed. The C-H bonds lengths were slightly different for each hydrogen, 1.08Å for the first H added to 1.00Å for the fourth and last H added. Other published work suggests otherwise and there is an ongoing debate about the H interstitial sites in diamond.

The Hydrogen Equilateral Triangle (ET) interstitial sites were discovered and studied by D. Saada[1] using tight-binding calculations. This ET site is a six fold degenerate site with respect to the C-C bond, the H at this site was found to create a dangling bond that induces an electronic energy level of $\sim 0.5eV$ above the middle of the energy gap of diamond, creating a deep donor state, the diffusion of the H between these sites are via a jump-like mechanism around the same bond.

Saada used a small supercell of 64+1 atoms and a larger 216+1 atoms samples, in contrast to Mehandru’s work, all atoms in the samples were relaxed. It has been found that the H atoms oscillates around equivalent sites (the above mentioned ET sites) of global minimum energy. The H atom was found to be bonded with one C atom, with a bond length of 1.08Å, the closest C-C bond was broken and relaxed by 43%, the distance between the H and the second nearest C was calculated to be 1.8Å. Additional H was also added to the sample at an adjacent non-occupied ET site, in this configuration the two H atoms were found to jump between equivalent ET sites. These calculations were found to be in excellent agreement with various experimental studies.
Saada’s results can associated with the experimentally found anomalous muonium, Mu*, in diamond[24]. Whereas Mehandru and others believe that the BC site is the stable site for H in diamonds despite μSR experiments[24, 25], to settle this question, further work should be done to investigate the ET site in diamonds. The work should explore the effects of higher concentrations of hydrogen (single atoms and hydrogen dimers) in the bulk diamond, as well as, various physical conditions of the samples such as boundary conditions and temperature.

1.4 Research Goal

The purpose of this study is to investigate the diffusion of hydrogen in carbon diamond including its effect on the structure of the diamond lattice. We hope to achieve new insights into the formation of the hydrogenated diamond lattice and better understanding of the processes involved in the hydrogen interstitials and hydrogen in the near-surfaces regions in diamonds. Our work will address both the electronic and mechanical structures which originate due to H migration.

Our work will focus on investigating the ET interstitial sites of hydrogen in diamonds, with a different number of hydrogens, under different temperatures and with different boundary conditions. We will enter into the scientific debate on H interstitial sites in diamonds, as we further investigate the ET site.

We will also study the effect of hydrogen on amorphous carbon/diamond composites, which relates to the ongoing experimental work on the growth of the nucleated
diamond in amorphous carbon. We will try to simulate the processes in which H participates in the growth of the nucleated Diamond in a:C, and we will try to determine from our simulations, the optimal concentration of H in the a:C which contributes to the growth.
Chapter 2

Simulation Models

There is considerable current interest in polycrystalline CVD diamond films, and as a result, efforts are needed to simulate carbon materials to complement knowledge obtained by experimental methods. There is a broad selection of techniques used to simulate carbon, varying from classical potentials such as Tersoff, through semi-classical Tight-binding or Density Functional approaches through to \textit{ab-initio} many body quantum mechanical models.

Our choice of the tight-binding molecular dynamics method for simulating carbon is a trade-off between highly sophisticated, accurate, computationally heavy methods with a very small number of atoms simulated, and the need to simulate a large number of atoms at the expense of some accuracy. By using this method we obtain a higher degree of accuracy than classical potentials, but attain relatively large sample sizes which \textit{ab-initio} simulations are incapable of performing in a reasonable time. Moreover, by simulating larger clusters we gain information about the attributes of such a sample, which in many cases cannot be inferred from a simulation of a very
small number of atoms.

2.1 Tersoff Potential for Carbon

A simple function for an interatomic potential is a sum of two-body contributions that depend on the scalar distance between the two bodies, however, this form can only be relevant for close packed structures and cannot be applied to covalent systems where at least three-body interactions must be taken into account. Hence, a suitable potential is required to deal with various applications, such as amorphous structures and other complexes, while at the same time, describing, at least, qualitatively a wide range of atomic bonding geometries, and/or other possible defects, account for \( sp \), \( sp^2 \) and \( sp^3 \) sites present in amorphous carbon structures.

In the Tersoff potential we use a two-body functional which implicitly includes an angular contribution of the force, without an explicit three-body term [26]. The potential is expressed using the following notation

\[
E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij} \\
V_{ij} = f_c(r_{ij})[A \exp(-\lambda_1 r_{ij}) - B_{ij} \exp(-\lambda_2 r_{ij})]
\]

where \( E \) is the total energy of the system, \( E_i \) is the \( i^{th} \) site energy, \( V_{ij} \) is the interaction energy between atoms \( i \) and \( j \), \( r_{ij} \) is the distance between them, and \( A, B, \lambda_1 \) and \( \lambda_2 \) are all positive parameters with \( \lambda_1 > \lambda_2 \). The first term in (2.2) is repulsive while the second term is attractive, hence, \( B_{ij} \) implicitly includes the bond order and must depend upon the local environment. \( f_c \) is a suitable, smooth, cut-off function to
restrict the range of the potential

\[
f_c(r) = \begin{cases} 
1 & r < R - D \\
\frac{1}{2} - \frac{1}{2} \sin \left( \frac{\pi}{2} \frac{r - R}{D} \right) & R - D < r < R + D \\
0 & r > R + D 
\end{cases}
\]

The parameters R and D are not systematically optimized but are chosen so as to include the first-neighbor shell only for several selected high-symmetry bulk structure, such as diamond or graphite.

As mentioned above, the \( B_{ij} \) term depends on the local environment and therefore, can accentuate or diminish the attractive force relative to the repulsive force, such that,

\[
B_{ij} = \frac{1}{(1 + \beta n \zeta_{ij}^n)^{1/2n}}
\]

\[
\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ij}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3]
\]

\[
g(\theta) = 1 + \left( \frac{c}{d} \right)^2 - \frac{c^2}{d^2 + (h - \cos \theta)^2}
\]

The \( \zeta_{ij} \) terms defines the number of nearest neighbors making the bond, taking into account the relative distance of two neighbors \( r_{ij} - r_{ik} \) and the bond angle \( \theta \). The function \( g(\theta) \) has a minimum for \( h = \cos(\theta) \), the parameter \( d \) determines how sharp the dependence on angle is, and \( c \) expresses the strength of the angular effect.

The parameters shown in table 2.1 were chosen empirically by J. Tensoff [27], with \( \lambda_3 = 0 \) for simplicitly, to fit the experimental data obtained. These parameters were previously tested and the results obtained were in good agreement with experiments and with \textit{ab-initio} calculations[28]. It was found to have the ability to distinguish
between different carbon configurations ranging from the dimer molecule to fourfold $sp^3$ bonds as well as threefold $sp^2$ bonds\cite{29}\cite{27}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ [eV]</td>
<td>1393.6</td>
</tr>
<tr>
<td>$B$ [eV]</td>
<td>346.74</td>
</tr>
<tr>
<td>$\lambda_1$ [Å]</td>
<td>3.4879</td>
</tr>
<tr>
<td>$\lambda_2$ [Å]</td>
<td>2.2119</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$1.5724 \times 10^{-7}$</td>
</tr>
<tr>
<td>$n$</td>
<td>0.72751</td>
</tr>
<tr>
<td>$c$</td>
<td>$3.8049 \times 10^4$</td>
</tr>
<tr>
<td>$d$</td>
<td>4.3484</td>
</tr>
<tr>
<td>$h$</td>
<td>-0.57058</td>
</tr>
<tr>
<td>$R$ [Å]</td>
<td>1.95</td>
</tr>
<tr>
<td>$D$ [Å]</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 2.1: Parameters for carbon atoms, for the Tersoff potential

However, in studies with the Tersoff potential it is not possible to obtain results about the electronic structure.

### 2.2 Tight-Binding Molecular Dynamics

Tight-binding molecular dynamics is an improved simulation scheme\cite{30} that has both the accuracy needed to describe complex systems, a relatively small computational workload for large-scale simulations of more than 100 atoms and can be implemented for a relatively long simulation time.
The basic idea is to derive the interatomic forces governing the time evolution directly from the electronic structure of the simulated system by the means of the Hellman-Feynman theorem, i.e., forces acting upon nuclei in the system can be calculated classically from the charge density of the molecule, and in this way, the quantum mechanical many-body nature is taken into account. In order to reduce the computational workload, the electronic structure is calculated in the framework of the semi-empirical tight-binding model, hence the solution of the electronic problem at each time-step of the simulation is much less expensive in terms of calculation time.

2.2.1 Molecular Dynamics

In *Molecular Dynamics*, the time evolution of a set of interacting atoms, is solved by integrating their equations of motion, notably Newton's law:

\[ F_i = m_i a_i \]  \hspace{1cm} (2.4)

for each atom \( i, i = 1 \ldots N \), in a system of \( N \) atoms. Here \( F \) is the force acting upon the atom with mass \( m \) and acceleration \( a \). In contrast with the *Monte-Carlo* method, molecular dynamics is a deterministic technique: given an initial set of positions and velocities, the subsequent time evolution is in principle completely determined.

2.2.2 The Tight-Binding Model

The Hamiltonian of a system of ion cores and valence electrons can be written as:

\[ H = T_i + T_e + U_{ee} + U_{ei} + U_{ii} \]  \hspace{1cm} (2.5)
CHAPTER 2. SIMULATION MODELS

where $T_{i,e}$ is the kinetic energy of ions and electrons respectively; $U_{ee}$, $U_{ei}$, $U_{ii}$ are the electron-electron, electron-ion and ion-ion interactions. For a single electron, the many-body Hamiltonian, (2.5), can be reduced to an electron moving in the average field due to other valence electrons and due to the ion fields. We can do this because electrons move $\sim 10^2 - 10^3$ faster than ions and each electron moves independently of the other electrons in the system[31], and experiences an effective interaction due to the other electrons and the ions.

We now define properties for the comprehension of the tight-binding model. Let $h$ be the reduced one-electron Hamiltonian

$$h = T + U_{ee} + U_{ei}$$

(2.6)

$|\Psi_n\rangle$ is the $n^{th}$ eigenfunction corresponding to the $n^{th}$ eigenvalue, $\epsilon_n$ such that

$$h|\Psi_n\rangle = \epsilon_n|\Psi_n\rangle$$

(2.7)

Here, we represent the wavefunctions $|\Psi_n\rangle$ as linear combination of atomic orbitals $|\phi_{\alpha}\rangle$:

$$|\Psi_n\rangle = \sum_{l\alpha} c^n_{l\alpha} |\phi_{\alpha}\rangle$$

(2.8)

where $l$ is the quantum number index and $\alpha$ labels the ions. The $c^n_{l\alpha}$ coefficients represent the occupancy of the $l^{th}$ orbital located at the $\alpha^{th}$ site. In the general case, the $|\phi_{\alpha}\rangle$ basis is not orthogonal:

$$\langle \phi_{\alpha}|\phi_{\beta}\rangle \neq 0$$

(2.9)

Substituting (2.9) into (2.7), multiplying from the left and remembering that $h$ is not necessarily diagonalized we introduce the overlapping integrals $S$ and we get the
secular problem,
\[ \sum_{i\alpha} \langle \phi_{\nu\beta} | h | \phi_{i\alpha} \rangle c_{i\alpha}^n = \sum_{i\alpha} \epsilon_n (\delta_{i\nu} \delta_{\alpha\beta} + S_{i\nu, \alpha\beta}) c_{i\alpha}^n \]  
(2.10)

From a numerical point-of-view, the secular problem (2.10) corresponds to a generalized linear problem,
\[ h c^n = \epsilon_n (S + I) c^n \]  
(2.11)

where \( I \) is the identity matrix, and \( S \) is given by
\[ S_{i\nu, \alpha\beta} = \langle \phi_{\nu\beta} | \phi_{i\alpha} \rangle - \delta_{i\nu} \delta_{\alpha\beta} \]  
(2.12)

which represents the non-orthogonal tight-binding model. The use of such model in a large-scale simulation is not numerically convenient and is very time consuming, since the evaluation of the overlapping integrals is needed at each time step of the simulation and is extremely computational workload. According to Löwdin\[32\] the non-orthogonality can be removed, by using a new set of orthogonal atomic orbitals \( |\varphi_{i\alpha}\rangle \), by doing so we reduce the secular problem to be
\[ h b^n = \epsilon_n b^n \]  
(2.13)

where \( b^n = \{\theta^a_{i\alpha}\} \) are the new coefficients of the linear combination,
\[ |\Psi_n\rangle = \sum_{i\alpha} \theta^n_{i\alpha} |\varphi_{i\alpha}\rangle \]  
(2.14)

and orthogonality,
\[ \langle \varphi_{\nu\beta} | \varphi_{i\alpha} \rangle = \delta_{i\nu} \delta_{\alpha\beta} \]  
(2.15)

Löwdin orbitals \( |\varphi_{i\alpha}\rangle \) preserve the properties of the original non-orthogonal basis \( |\phi_{i\alpha}\rangle \).

The lattice is broken into primitive cells and the position for an atom in the primitive cell \( j \) is decomposed into \( r_{jl} = R_j + r_l \), where \( R_j \) denotes the position of
the \( j^{\text{th}} \) primitive cell. When we have perfect crystals with translational symmetry, we can further enhance Löwdin equations and express our wave functions in the form of Bloch functions

\[
|\Phi_{k\alpha}\rangle = \frac{1}{\sqrt{N}} \sum_j \exp(i r_{ji} \cdot k) \varphi_{l\alpha}(r - r_{ji})
\]

(2.16)

Here we have a summation over all primitive cells \( j \) in our lattice, \( l \) is the orbital of the \( \alpha^{\text{th}} \) site and \( N \) is the total number of primitive unit cells in the crystal.

The calculation of the orthogonal tight-binding model is still computationally heavy, and some approximations must be made for the calculation to be time-effective. The off-diagonal matrix elements of \( \langle \varphi_{l'\beta}|h|\varphi_{l\alpha}\rangle \), \( l\alpha \neq l'\beta \), are the hopping integrals, and the on-site elements \( \langle \varphi_{l\alpha}|h|\varphi_{l\alpha}\rangle \), are the atomic orbital energies. In the tight-binding approach these are constants to be fitted using the following approximations:

1. We use a \textit{minimal basis set} for only the atomic orbitals whose energy is close to that of the energy bands that we are interested in\cite{33}. Hence, in the diamond simulations we used only the 2s (one orbital) and 2p (three orbitals: \( p_x, p_y \) and \( p_z \)) orbitals to describe the occupied bands.

2. We consider hopping integrals between two atoms separated by a distance shorter than a suitable cutoff. Obviously, this must be done to reduce the number of parameters to be fitted and a cut-off which includes the nearest neighbors is appropriate. However, Löwdin functions extend further than the non-orthogonal functions because the orthogonalization procedure involves orbitals from nearby atoms hence, interactions extending beyond the first nearest
neighbors have to be taken into account when an orthogonal basis is used.

Using these approximations, the off-diagonal matrix elements of the Hamiltonian are fitted to the electronic band structure of the equilibrium crystal phase. These matrix elements are known and were calculated from first principle models [34]. Sets of these hopping integrals can thus be obtained for each crystalline structure considered.

**2.2.3 Energy Calculations**

Once the single-particle energies are known by solving the secular problem given in (2.13), the total potential energy $E_{\text{tot}}$ of a crystalline system of ion cores and valence electrons can be written as

$$E_{\text{tot}} = U_{\text{ie}} + U_{\text{ii}} + U_{\text{ee}} = 2 \sum_{k,n} f_{FD}[\epsilon_n(k), T] \epsilon_n(k) + U_{ii} - U_{ee} \quad (2.17)$$

where $f_{FD}$ is the Fermi-Dirac distribution function and the $-U_{ee}$ contribution corrects the double counting of the electron-electron interactions in the first term. The sum over all the single-particle energies is commonly known as the band structure energy, $E_{bs}$

$$E_{bs} = 2 \sum_{k,n} f_{FD}[\epsilon_n(k), T] \epsilon_n(k) \quad (2.18)$$

with a factor of 2, to take into account the spin degeneracy. The last two terms appearing in (2.17) are commonly grouped together forming an effective repulsive potential $U_{rep} = U_{ii} - U_{ee}$ which is assumed to be short-ranged because of the efficient dielectric screening occurring in semiconductor materials.
2.2.4 Rescaling Functions

As mentioned, the elements of the Hamiltonian matrix are fitted to first principle calculations for different equilibrium structures [34]. To describe the properties of non-equilibrium structures, such as amorphous solids or liquids, the hopping integrals and the repulsive energy should be rescaled with respect to the interatomic distance. Generally, the equilibrium hopping integral \( \langle \varphi_{\nu\beta} | h | \varphi_{\nu\alpha} \rangle = h_{\nu\nu} \) can be written as

\[
h_{\nu\nu}(R_{\alpha\beta}) = h_{\nu\nu}^{(0)} f_{\nu\nu}(R_{\alpha\beta})
\]  

(2.19)

where \( f_{\nu\nu}(R_{\alpha\beta}) \) is a scaling function of two orbitals \( \nu \) and \( \nu' \) placed on the atoms at \( R_{\alpha} \) and \( R_{\beta} \), respectively. The constraint on this rescaling function is that \( f_{\nu\nu}(R^{(0)}) = 1 \) for \( R^{(0)} \) is the equilibrium interatomic distance. The rescaling functions proposed by Goodwin et. al. [35] for Si and later improved for Carbon by Xu et. al. [36] greatly improve the transferability of the tight binding model to structures not included in the parameterization. For the rescaling of the hopping integrals

\[
h(r) = h_0 \left( \frac{r_0}{r} \right)^n \exp \{ n \left[ -(\frac{r}{r_c})^{n_c} + \left( \frac{r_0}{r_c} \right)^{n_c} \right] \}
\]  

(2.20)

and for the repulsive potential

\[
\phi(r) = \phi_0 \left( \frac{d_0}{r} \right)^m \exp \{ m \left[ -(\frac{r}{d_c})^{m_c} + \left( \frac{d_0}{d_c} \right)^{m_c} \right] \}
\]  

(2.21)

In these Goodwin rescaling functions, the parameters \( n_c \) and \( r_c \) are the same as \( m_c \) and \( d_c \) respectively, while with the Xu functions these parameters are not necessarily the same. All the parameters appearing in the rescaling functions were obtained by fitting first-principle results of the energy versus nearest-neighbor interatomic distance for different crystalline phases, giving equilibrium sets of hopping integrals for these structures. In this way, the tight-binding model is transferable to different atomic environments.
2.2.5 Simulation Stages

During a MD (Molecular Dynamics) run we compute the interatomic forces $F_\alpha$ (where $\alpha = 1, \ldots, N_{at}$) to move atoms and to generate trajectories the phase space. They can be evaluated from the Tight-Binding Molecular Dynamics Hamiltonian $\mathcal{H}$

$$\mathcal{H} = \sum_\alpha \frac{p_\alpha^2}{2m_\alpha} + 2 \sum_n \epsilon_n f_{FD}(\epsilon_n, T) + U_{rep}$$ (2.22)

For our practical purpose in accordance with the adiabatic approximation, the electronic temperature is assumed to be zero, hence, equation (2.22) can be simplified to

$$\mathcal{H} = \sum_\alpha \frac{p_\alpha^2}{2m_\alpha} + 2 \sum_n^{(\text{occup})} \epsilon_n + U_{rep}$$ (2.23)

where $(\text{occup})$ indicates that we just use the electron energies, $\epsilon_n$ belonging to the lower half spectrum of the TB matrix (2.10).

The force $F_\alpha$ is then given by

$$F_\alpha = -\frac{\partial \mathcal{H}}{\partial R_\alpha} = -\frac{\partial}{\partial R_\alpha} \sum_n^{(\text{occup})} \epsilon_n - \frac{\partial}{\partial R_\alpha} U_{rep}$$ (2.24)

where the first term describes the attractive force and the second describes the repulsive term acting upon particle $\alpha$. $U_{rep}$ is known analytically as a short-ranged function of the interatomic distance, and hence, computed trivially. The attractive force, however, is computed numerically using the Hellman-Feynman theorem [37]. By using Eq. (2.13) and Eq. (2.19), the attractive contribution acting upon atom $\alpha$ can be calculated as

$$-\frac{\partial}{\partial R_\alpha} \sum_n^{(\text{occup})} \epsilon_n = -\frac{\partial}{\partial R_\alpha} \sum_n^{(\text{occup})} \langle \Psi_n | h | \Psi_n \rangle$$

$$= -2 \frac{\partial}{\partial R_\alpha} \sum_n^{(\text{occup})} \sum_{\gamma \beta} \langle \varphi_{\gamma \beta} | h | \varphi_{\gamma \beta} \rangle$$
\[
= -2 \frac{\partial}{\partial R_{\alpha}} \sum_{n} \sum_{\nu\gamma\beta} b_{\nu\gamma}^n b_{\nu'\gamma}^n h_{\nu\nu'}(R_{\gamma\beta}) \\
= -2 \sum_{n} \sum_{\nu\gamma\beta} b_{\nu\gamma}^n b_{\nu'\gamma}^n h_{\nu\nu'}^{(0)} \frac{\partial}{\partial R_{\alpha}} f_{\nu\nu'}(R_{\gamma\beta})
\]

(2.25)

Hence, the spectrum of the eigenvalues and eigenvectors of the Tight-Binding matrix need to be computed, respectively, the band-structure contribution to the total potential energy and the attractive contribution to the forces. The exact calculation must be done at every time-step of the simulation. Since the Tight-Binding matrix can be large, the computer memory holding the matrix must be large as well, and obviously, the simulation time might be long.

### 2.3 Simulated Annealing

Simulated Annealing is a stochastic computational technique derived from statistical mechanics for finding near-globally-minimum solutions to large optimization problems. In statistical mechanics, when a system of atoms, or molecules, is at equilibrium at a given temperature \( T \), then the probability \( P_T(s) \) that the system is in a given configuration \( s \) depends upon the energy \( E(s) \) of the configuration and follows the Boltzmann distribution:

\[
P_T(s) = \frac{\exp(-E(s)/kT)}{\sum_i \exp(-E(i)/kT)}
\]

(2.26)

where \( k \) is the Boltzmann constant.

One can simulate the behavior of a system of particles in thermal equilibrium at temperature \( T \) using a stochastic relaxation technique developed by Metropolis et al.
CHAPTER 2. SIMULATION MODELS

[38]. Suppose at time $t$, the system is in configuration $q$. A candidate $r$ for the configuration at time $t+1$ is generated randomly. The criterion for selecting or rejecting configuration $r$ depends on the difference between the energies of configurations $r$ and $q$. Specifically, one computes the ratio $p$ between the probability of being in $r$ and the probability of being in $q$:

$$p = \frac{P_T(r)}{P_T(q)} = \exp\left(-\frac{E(r) - E(q)}{kT}\right)$$  \hspace{1cm} (2.27)

If $p > 1$, that is the energy of $r$ is strictly less than the energy of $q$, then the configuration $r$ is automatically accepted as the new configuration for time $t+1$. If $p \leq 1$, that is, the energy of $r$ is greater than or equal to that of $q$, then the configuration $r$ is accepted as the new configuration with probability $p$. Thus, configurations of higher energies can be attained, which is important because otherwise the system could be stuck in a local minimum and not reach the global minimum.

Since the probability that a step is accepted is a function of the temperature $T$, one can bring the configuration after a sufficient number of trials to a local or a global minimum energy, according to the temperature schedule. Thus, on the basis of the algorithm described above, the simulated annealing technique is applied to minimize the energy of a system by suitably changing the temperature.

In studying such systems of particles, one often seeks to determine the nature of the low energy states, for example, whether freezing produces crystalline or glassy solids. Very low energy configurations are not common, when considering the set of all configurations. However, at low temperatures they predominate, because of the nature of the Boltzmann distribution. To achieve low energy configurations, it is
not sufficient to simply lower the temperature. One must use an annealing process, where the temperature of the system is elevated, and then gradually lowered, spending enough time at each temperature to reach thermal equilibrium. If insufficient time is spent at each temperature, especially near the freezing point, then the probability of attaining a very low energy configuration is greatly reduced.

In the present study, the simulated annealing technique was used to obtain an amorphous carbon sample by quenching liquid diamond (see section 4.4). The initial temperature of the sample was \( \sim 30000^\circ K \), it was then cooled at different rates down to \( 300^\circ K \) and \( 500^\circ K \).
Chapter 3

Numerical Computation Techniques

3.1 Solving the Equations of Motion

Once the potential is established at a certain time step, the interatomic forces are calculated from the electronic part of the total energy, while the atoms are considered as classical, hence, Newton equations should be solved. The coordinate and velocity are then computed by solving the following differential equations

\[ F_{ia} = m_i \frac{d^2r_{ia}}{dt^2} = -\frac{\partial E_i}{\partial r_{ia}} \]  \hspace{1cm} (3.1)

\[ v_{ia} = \frac{dr_{ia}}{dt} \]  \hspace{1cm} (3.2)

\[ a_{ia} = \frac{dv_{ia}}{dt} \]  \hspace{1cm} (3.3)

where \( i \) is the atom in consideration and \( \alpha \) is the Cartesian coordinate \( x, y \) and \( z \).

The first step is determining the neighbors of each atom considering the cut-off
used, then, the force applied by the relevant neighbors is calculated and summed over all neighbors to get the total force on the atom. Once the force is established, Newton's equations, (3.2) and (3.3), are solved.

### 3.2 Periodic Boundary Conditions

The ultimate goal of our simulations is to describe experimental results gathered by various means. Obviously, the experimental samples contain orders of $10^{24}$ atoms which cannot be described by a $10^{24}$ computerized atom model because of the heavy computational demand, there is not yet a super-computer that is capable of handling such enormous calculations in reasonable time.

In order to overcome this problem, we use *periodic boundary conditions*. When these are applied, a particle that crosses a boundary of the simulation model, is reinserted at the opposite face. The simulation box is periodically replicated in all or some directions forming a macroscopic sample (see figure 3.1). Thus, forces acting upon an atom in the outer coordinates of the simulated box are the same as if the atom was placed in the center of the box. Unless periodic boundary conditions are used, the forces near the surface may be different and may give rise to energy reflections from the boundaries.

The majority of the simulations described in the following chapter used periodic boundary conditions in every direction $(x,y,z)$. However, some were carried out with periodic conditions only in 2 directions, this was done to describe most accurately the
surface of a carbon sample that is bounded by vacuum at the non-periodic direction.

Figure 3.1: Applying Periodic Boundary conditions. When an atom crosses one face of the sample, it is reinserted at the opposite face.

3.3 Initial Configuration

Since the method is deterministic, the initial configuration and the initial velocities of the atoms play a crucial role in the simulation and will determine the nature of the motion. The initial velocities can be chosen randomly with a Maxwell distribution

\[ f(v) \sim \exp\left(\frac{mv^2}{kT}\right) \quad (3.4) \]

where \( f(v) \) is probable number of molecules with mass \( m \) having velocities \( v \) to \( v + dv \).

The velocities can be rescaled to be related to the ambient temperature \( T \) using the following relation

\[ \frac{3}{2}NkT = \sum_i \frac{m_i v_i^2}{2} \quad (3.5) \]

Here \( N \) is the number of atoms and \( k \) is the Boltzmann constant.
3.4 General Description of Software

3.4.1 OXON

The Molecular Dynamics calculations were carried out using Oxford Order N (OXON) package[39], which consists of a set of programs for carrying out atomistic static and dynamic calculations using potentials which are based on the tight-binding method. In the MD calculations, Newton’s equations of motions were solved using the predictor-corrector algorithm, using a time-step of $1.0 \times 10^{-15}$ second. Periodic boundary conditions were applied to the samples.

3.4.2 AViz

The visualizations which were essential for the development of this project were carried out with the help of the Atomic Visualization package, AViz[40], which was developed in our computational physics group. AViz is a powerful tool to help visualize the samples used in our calculations, it helped enhance 3D perception of the final positions in the samples as well as their evolution in time.

The AViz package was used extensively in all stages of the work. A visualization of our samples with color coding for different atoms helped identify bond types, interstitial sites and reorganization of the sample, different colors were also used for different bonds to highlight certain areas to help track them, at any time-frame of the simulation. Animated visualizations were also created to help understand the dynamics of the sample.
3.5 The Predictor-Corrector Algorithm

The Predictor-Corrector Algorithm is used by OXON to solve Newton’s equations, (3.1). Given atomic positions, velocities and accelerations at specific times \( t - m \Delta t \) \((m = 0, \ldots)\) the algorithm attempts to predict these quantities at a later time, \( t + \Delta t \).

The equations are solved on a step-by-step basis.

The positions and the velocities of the \( i^{th} \) atom at time \( t + \Delta t \) may be obtained by Taylor expansion about time \( t \)

\[
\mathbf{r}_i^p(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t + \Delta t^2 \sum_{m=1}^{n-1} \alpha_m \mathbf{a}_i(t + [1 - m] \Delta t) \tag{3.6}
\]

\[
\mathbf{v}_i^p(t + \Delta t) = \mathbf{v}_i(t) + \mathbf{a}_i(t) \Delta t + \Delta t \sum_{m=1}^{n-1} \beta_m \mathbf{r}_i^{(3)}(t + [1 - m] \Delta t) \tag{3.7}
\]

The force (hence the acceleration), at \( t + \Delta t \) is then computed by taking the gradient of the potential at the predicted positions,

\[
\mathbf{F}_i = - \sum_{i \neq j} \frac{\partial u(r_{ij}^p)}{\partial r_{ij}^p} = m_i \mathbf{a}_i \tag{3.8}
\]

Generally, the resulting acceleration will be different from the predicted acceleration constituting an “error signal”

\[
\Delta \mathbf{a}_i = \mathbf{a}_i(t + \Delta t) - \mathbf{a}_i^p(t + \Delta t) \tag{3.9}
\]

The \( P \) superscript describes the predicted acceleration. The next step of the algorithm is to correct the predicted values, (3.6) and (3.7), with the error signal, (3.9). The corrections are proportional to the error signal by \( \alpha_m ' s \) and \( \beta_m ' s \) coefficients. These coefficients promote numerical stability of the algorithm and depend on the order of the differential equation and on the order of the Taylor series predictor. In
Table 3.1: Coefficients of the Predictor-Corrector algorithm for n=4 for second order differential equation

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>19</td>
<td>-20</td>
<td>3</td>
</tr>
<tr>
<td>β</td>
<td>27</td>
<td>-22</td>
<td>7</td>
</tr>
</tbody>
</table>

The predictor-corrector algorithm gives accurate positions and velocities which is suitable to our “delicate” calculations, however, it is computationally expensive, requiring storage of previous calculations as well as evaluation of the interatomic forces over all atoms below the cut-off region. Some ways are implemented to save time, such as using Newton’s third law,

\[ \mathbf{F}(\mathbf{r}_{ij}) = -\mathbf{F}(\mathbf{r}_{ji}) \]  

(3.10)

decreasing the amount of computation by a factor of 2.
Chapter 4

Results

Various samples were created to study the effects of the diffusion of Hydrogen atom(s). Each sample was designed to explore different aspects of the diffusion and therefore each sample differs by one or more of the following characteristics: the size of the sample, the simulated boundary conditions, the number of hydrogen atoms simulated in the sample, the sample structure (i.e. amorphous carbon or pure diamond) and in some samples the simulation temperature was also changed. It has to be noted that the temperatures mentioned are not precise, but rather provide a hierarchy of the energetic barriers involved in the H motion in diamond. The temperatures were selected in accord with Saada et. al.[1], where only at ~ 400K the H atom starts to pull out from its initial interstitial site and by ~ 1700K the H atom diffuses between sites, experimentally this temperature correlates to the Mu-to-Mu* transitions which occur at ~ 450K in diamond. A summary of the different samples is shown in table 4.1.
<table>
<thead>
<tr>
<th>No.</th>
<th>size (unit cells)</th>
<th>Boundary Conditions</th>
<th>Number of H</th>
<th>Simulation Temperature</th>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \times 2 \times 2$</td>
<td>Periodic</td>
<td>1-6 $\times$H</td>
<td>500 to 1200$^\circ$K</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Free</td>
<td>1 $\times$H</td>
<td>500$^\circ$K</td>
<td>4.1</td>
</tr>
<tr>
<td>2</td>
<td>$3 \times 3 \times 3$</td>
<td>Periodic</td>
<td>1 $\times$H</td>
<td>500$^\circ$K</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>$2 \times 2 \times 6$</td>
<td>Periodic</td>
<td>1 $\times$H</td>
<td>500$^\circ$K</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>$3 \times 3 \times 2$</td>
<td>Periodic</td>
<td>1-3 $\times$H</td>
<td>500$^\circ$K</td>
<td>4.2</td>
</tr>
<tr>
<td>5</td>
<td>$2 \times 2 \times 2$</td>
<td>Periodic</td>
<td>1 $\times$H</td>
<td>500, 1200$^\circ$K</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ 1 $\times$H$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$2 \times 2 \times 2$</td>
<td>Free</td>
<td>1 $\times$H</td>
<td>500$^\circ$K</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ 1 $\times$H$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$2 \times 2 \times 2$</td>
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<td>2$\times$H</td>
<td>500$^\circ$K</td>
<td>4.3</td>
</tr>
<tr>
<td>8</td>
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<td>Periodic</td>
<td>2$\times$H$_2$</td>
<td>500$^\circ$K</td>
<td>4.3</td>
</tr>
<tr>
<td>9</td>
<td>$3 \times 3 \times 3$</td>
<td>Periodic</td>
<td>1-26 $\times$H</td>
<td>300, 500$^\circ$K</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of the samples created

4.1 Hydrogen Diffusion in Diamond

4.1.1 Sample Preparation

Two of the samples used for these calculations were arranged as perfect diamond crystals of a $2 \times 2 \times 2$ unit cells, i.e. 64 carbon atoms. The effect of the sample size was also checked with a $3 \times 3 \times 3$ unit cell sample, which consisted of 216 carbon atoms. A hydrogen atom was initially placed at the tetrahedral ($T_d$) interstitial site, forming a 64+1 atoms supercell and a 216+1 atoms supercell. We consider the $T_d$ interstitial site for H in diamond since other possible sites are sites of lower energy, or even of local maximum energy, as found by others[41, 42]. The results achieved from the large supercell yielded quantitatively the same results as those with the small supercell, justifying the use of the small supercell for the remaining studies.
The samples were simulated at different temperatures between 500°K and 2400°K, for a period of 20ps (for the 500°K and 800°K samples) and 32ps (for the 1200°K and 2400°K samples). The structural and electronic properties of the simulated samples were studied. We have found that these properties were altered when compared with a pure diamond sample of the same size. Our initial results, of the single H, is in full agreement with those achieved earlier by Saada et. al.[1]. Additional samples were created with up to 6 hydrogen atoms, simulated at 500°K for 20ps. The electronic structure was studied through plots of the density of states.

4.1.2 Final Configurations

As found by Saada [1], the system rapidly enters a configuration where the H atom oscillates between six ET sites, which are energetically equivalent sites are located around the C-C bond, at the corners of two equilateral triangles, which are rotated with respect to each other by 60° around the same unrelaxed C-C bond. The movement between these sites is temperature dependent. When the sample is held at temperature lower than ~ 400°K the H atom vibrates around its initial $T_d$ site, at ~ 500°K it finds its way to the nearest ET site. At temperature of ~ 800°K the H jumps between three equivalent ET sites of the same triangle (see figure 4.1), upon reaching ~ 1200°K the H atom jumps back and forth between all six ET sites around the same C-C bond (see figure 4.1).

To contribute new insights, we have performed numerous calculations regarding a single ET site of the hydrogen which was simulated at 500°K. In this configuration, the H atom is bonded to one C atom, with a bond length calculated to be 1.07Å,
Figure 4.1: 3 ET sites (left, <110> view) and 6 (right, <1\bar{1}0> view) ET sites of an H atom at 800°K and 1200°K respectively. The green spheres represent different hydrogen ET sites, and the brown spheres represent carbon atoms.

The second nearest C was calculated to be 1.78Å away, this C-C bond is broken and relaxed by 48%, in agreement with [1]. Additional distances were calculated and are shown in figure 4.2 and in table 4.2.

When looking at a diamond structure from different viewpoints, one can see two sets of adjacent hexagonal planes (at the <110> and <1\bar{1}0> views). The distance from the single H ET site, simulated at 500°K, to each of these planes was also calculated. The distances from the ET site to the planes of <1\bar{1}0> was calculated to

<table>
<thead>
<tr>
<th>Bond color</th>
<th>Blue</th>
<th>Green</th>
<th>Black</th>
<th>Red</th>
<th>Brown</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance [Å]</td>
<td>1.07</td>
<td>1.33</td>
<td>1.62</td>
<td>1.63</td>
<td>1.89</td>
</tr>
</tbody>
</table>

Table 4.2: C-H distances for the single ET site at 500°K. Refer to figure 4.2.
be 0.62Å and 1.21Å, hence, the site is located at two-thirds of the distance between planes (figure 4.3). The distance to the second planes (<110> plane) was calculated to be 0.63Å and 0.82Å (figure 4.4). When calculating the density of electronic states (DOS) for diamond with H located on the ET site and comparing it with that of diamond (figure 4.5), a new state ~ 0.5eV above the middle of the energy gap appears. Clearly, this new state is due to the H at the ET site.

As with a single H, with 6 H atoms implanted in the diamond at 500°K, 4 of the H were found to be in an ET sites surrounding 2 H forming an H-H bond, with bond length of ~ 0.65Å. Due to quick migration of two H to adjacent ET sites, each breaking a C-C bond and leaving a C vacancy. This vacancy is quickly filled with additional H, hence creating the complex were 2 H left unbonded. The remaining 2 H formed a H-H bond due to the stress caused by the other 4 H (see figure 4.6). The distance between the 4 H was ~ 1.2Å~ 2.3Å. With the Density of States (DOS)
Figure 4.3: One set of hexagonal planes at \( \{1\bar{1}0\}\) (left) and \( \{\bar{1}10\}\) (right) views, distance to the red plane is 0.62Å

Figure 4.4: Second set of hexagonal planes at \( \{1\bar{1}0\}\) (left) and \( \{\bar{1}10\}\) (right) views, distance to the yellow plane is 0.82Å
calculated, as occurred with the single H, new states emerge in the diamond bandgap below the fermi level (see figure 4.8).

We have also simulated a sample at $500^\circ K$, with a free boundary condition, i.e. with no boundaries in certain direction(s). The sample was simulated several times, each with no boundaries on a different axis ($x$-, $y$- and $z$-axis). In these simulations we have found that the system rapidly enters a configuration where the H atom is located on the C-C bond of the outer layer of the diamond sample, causing the outermost carbon to shift, and forming a 1.0 Å bond with the inner carbon, on the surface of the diamond. The DOS for this sample was also computed, and when comparing it to the pure diamond sample (figure 4.7), new states are clearly seen above the Fermi level of the diamond with H sample. In addition, note that the second bandgap of the sample decreases. Similar simulations have been performed in several different geometries and will be explained in the following section, receiving the same results quantitatively.

4.2 Hydrogen Diffusion in Semi-frozen Diamond

4.2.1 Sample Preparations

Two types of samples were created for this type of calculation. In the first, 192 carbon atoms were arranged as a perfect diamond lattice, with the 32 upper-most and 32 lower-most atoms of the sample frozen, i.e. the motion of these atoms was forbidden (see figure 4.9). Hydrogen atoms were implanted in two different initial positions. In the first, the hydrogen was placed at the $T_d$ site of the frozen diamond, and was simulated at $500^\circ K$ for 2ps. The second initial position of the hydrogen was slightly higher,
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Figure 4.5: DOS of diamond (black) and of diamond with H at the ET site (red), simulated with periodic boundaries.

Figure 4.6: <110> view of diamond lattice with 6 H atoms, simulated at 500°K
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Figure 4.7: DOS of diamond (black) and of diamond with H, without periodic boundaries

Figure 4.8: DOS of diamond (black), diamond with H (red) and diamond with 6 H (green), simulated with periodic boundaries
in the free-to-move region of the sample. As for the first sample, the simulation was at 500°K for 2ps. Although simulated for a short time, the sample achieved equilibrium.

The second type of samples were arranged with three layers containing a total of 144 carbon atoms. The first and second layers of the sample were arranged as a perfect diamond lattice and the third as vacuum, each layer being 3.55Å in height. The first and second layers consisted of 72 atoms, in the first layer the atoms were frozen and in the second layer the atoms were free to move. The initial geometry of the sample is shown in figure 4.10. Up to three hydrogen atoms were initially implanted in the samples. First, a single hydrogen atom was implanted in the $T_d$ site in the free to move region, and its diffusion simulated for 10ps at 500°K, then a second hydrogen was added to the same $T_d$ site for an additional 10ps at 500°K and then, a third hydrogen atom was added, again, to the $T_d$ site for the same period and temperature.

4.2.2 Final Configurations

For the first type of sample, with the hydrogen placed at the $T_d$ site of the frozen region, we found that the hydrogen diffused quickly to a stable location located on the boundary between the frozen and the unfrozen regions (see figure 4.9), causing a slight deformation of the unfrozen diamond lattice. In the vicinity of the H, one of the C-C bonds of the boundary between the frozen and unfrozen regions is broken (the C-C length is enlarged by 35%) causing the other C-C bonds to change, one bond is extended by 3%, causing the C to shift upwards towards the two remaining C atoms, reducing their C-C bond length by 5% symmetrically (refer to figure 4.11).
Figure 4.9: Final configuration of a semi-frozen sample type 1 (refer to text). The blue yellow and gray bonds represent a frozen bond, a semi-frozen and an unfrozen bond respectively. Be advised that the simulation is with periodic boundaries, hence the carbon of the forth layer is simulated as if it was on the left side of the column.

The H is located slightly higher, symmetrically ~ 1.8Å between all four C atoms in the xy-plane (atoms 1-4 in figure 4.11).

When the H was placed at the $T_d$ site in the free-to-move region, we find that the H quickly diffused to an ET site located above its initial position, the structural deformation of this sample is the same as for the samples described previously in section 5.1 above, where we have investigated the ET sites, i.e., one C-C bond is broken due to the dislocation of a C located in a distance of ~ 1.8Å from the ET H site, this C-C broken bond is relaxed by ~ 48%. The difference between the final configurations of these samples is the final location of the H, in the first sample, the H site is on
Figure 4.10: Initial configuration of a semi-frozen sample used. The blue bonds represent frozen bonds, the yellow, semi-frozen and the gray, free-to-move bonds.

the boundary between the frozen and unfrozen lattices, whereas in the second sample, the H moved to an ET site. The structural deformations are similar in both cases.

In the second type of sample, the H initially implanted at the $T_d$ site quickly diffused to the surface of the diamond lattice, near the vacuum region, causing the complete dislocation of the outer-most carbon atom, forming a C atom vacancy. The H then diffuses to this vacancy, bonding to the inner C atom, with a bond length of $\sim 1.08\,\text{Å}$. When a second H is implanted at the $T_d$ site, it diffuses to the vacancy already created, forming a C-H bond of $\sim 1.08\,\text{Å}$ to a second carbon in the vacancy, the distances between the hydrogens was calculated to be $\sim 1.3\,\text{Å}$ (there is no formation of an $H_2$ bond). The two $H$ are located in the $<\overline{1}10>$ direction in the diamond lattice. When a third H is introduced to the sample, again at the same $T_d$ site, it quickly diffuses out of the diamond lattice. In figure 4.12 one can easily
see the carbon vacancy in the diamond lattice and the two H atoms in its position
with the third H atom diffused out of the lattice. The electronic density of states of
the surfaced hydrogen of chapter 4.1 (figure 4.7), and of this sample is almost iden-
tical (see figure 4.13), revealing close relationships between computational methods.
Again, new states formed in the bandgap above the Fermi level.

Figure 4.11: Deformation of the unfrozen diamond lattice. Purple carbon atoms and
the green C-C bonds are marked for clarity

4.3 Hydrogen Molecule Diffusion

4.3.1 Sample Preparations

As for the single hydrogen atom, the samples for the hydrogen molecule \((H_2)\) were
arranged as perfect diamond crystals of 64 carbon atoms, as in section 5.1. The hy-
drogen molecule was initially placed with one atom at the \(T_d\) site and the other at
the distance of the hydrogen bond, i.e. 0.7Å, and in a second case at slightly smaller
Figure 4.12: H atoms (numbered 1 and 2) in a carbon vacancy, one H (numbered 3) diffuses out of the diamond lattice. Blue, yellow and gray bond are frozen, semi-frozen and free C-C bonds.

distance of 0.6Å (as suggested by [41]), to examine differences. Simulations were performed when the \( H_2 \) was oriented in the \( x-y \) plane, \( y-z \) plane and \( x-z \) plane. The results of all these simulations were approximately the same, hence, the orientation of the molecule did not have an effect on the final result.

The samples were simulated at 500°K and 1200°K for a period of 20ps. Additional H and \( H_2 \) were added to the samples at various distances from the previously above mentioned insertion sites and were also simulated at 500°K for a period of 20ps. The structural property of the simulated samples were studied.
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Figure 4.13: DOS of diamond with 2 H at the surface (black, Type 2 - see text) and a diamond with H without periodic boundaries (red - see section 4.1)

4.3.2 Final Configurations

At 500°K, the system rapidly enters a configuration where the $H_2$ bond is perpendicular to the $<110>$ direction of the diamond lattice. When the sample is heated to $\sim 1200°K$, the H atoms drift apart to a distance of $\sim 1 Å$ and they are found in two of the six ET sites around the same C-C bond, as happened with a single H atom.

The H-H bond length was calculated throughout the 500°K simulation and was found to be $\sim 0.72 Å$. The $H_2$ molecule was found to be in perfect symmetry with the diamond matrix (figure 4.14), the distance between the center of the H-H to the first three nearest carbon atoms was calculated to be 1.47 Å, for the next three carbon atoms the distance was 2.30 Å. Also, each of the H atoms was in perfect symmetry.
with the diamond matrix, and the distances to the first three nearest carbons was 1.47Å and 1.57Å for the next three carbons, for each of the H atoms. As described previously, the diamond matrix has two sets of hexagonal planes, which create an angle with the H-H bond vector. The center of the H-H bond is located in plane $< \bar{2}21 >$ creating an angle of 70.3°, the angle to the second adjacent plane $< 2\bar{2}1 >$, was calculated to 27.8°. This geometry result agrees with ab-initio calculations made by Estreicher et al. [41].

When a third H atom is added, at an adjacent non-occupied site, to a sample with $H_2$ already positioned as mentioned previously (in section 5.3.1), that is with two H atoms forming an $H_2$ molecule, the H-H bond length is 0.7Å, and the third atom is 1Å and 1.5Å away from the $H_2$ atoms. For a 20ps simulation at 500°K the $H_2$ occupies the same sites, as described earlier, preserving the H-H bond with a bond length of 0.7Å positioned with perfect symmetry with respect to the diamond lattice, while the third H occupies an ET site at 1.29Å and 1.41Å from the $H_2$ atoms, and 1.08Å to the nearest carbon atom (as for a single H), (see figure 4.16 and table 4.3). As before, at the higher temperature of 800°K the $H_2$ molecule jumps between equivalent ET sites, preserving the H-H bond, and the single, unbonded H jumps between its equivalent ET sites. Additional insight can be obtained when the single unbonded hydrogen atom is placed farther from the $H_2$, initially at a $T_d$ interstitial site, distanced 3.32Å and 2.98Å from H atoms. In this configuration, for a 20ps simulation, the $H_2$ resumes the same positions in the lattice space as before, and the unbonded, single H resumes its nearest ET site, as expected, since the H is distanced enough from the $H_2$, lacking any effective interaction. When the boundary conditions are removed, for
Figure 4.14: $H_2$ symmetry in a diamond sample, distance to nearest neighbors is blue line, second nearest is green line

Figure 4.15: $H_2$ vector angles with carbon diamond planes
a 7.5ps simulation, the $H_2$ rapidly moves to the surface of the sample, and then diffuses out of the diamond, while the single H atom remains within the diamond sample.

![Diagram of C-H distances](image)

**Figure 4.16: C-H distances for an unbonded H at 500°K. Refer to table 4.3**

<table>
<thead>
<tr>
<th>Distance [Å]</th>
<th>Bond Color</th>
</tr>
</thead>
<tbody>
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<td>Black</td>
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<td>1.80</td>
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</tr>
<tr>
<td>1.94</td>
<td>Blue</td>
</tr>
</tbody>
</table>

**Table 4.3: C-H Distances for an unbonded H at 500°K. Refer to figure 4.16**

A different approach was taken when two hydrogen atoms were placed apart, at a distance of $\sim 1.54\text{Å}$ away, at two separate $T_d$ interstitial sites, for a period of 20ps. The two H formed an H-H bond of length $0.73\text{Å}$, this $H_2$ found the same location as the $H_2$ described above, with perfect symmetry with respect to the diamond lattice.

Another sample was created with 2 $H_2$ molecules displaced initially by a distance of $3.06\text{Å}$ measured between the H-H bond centers. After a 20ps simulation, the molecules
were rearranged so that the bond vectors were perpendicular one to another, despite the 3.32Å between them (see figure 4.17). Each $H_2$ has preserved its H-H bond of $\sim 0.7Å$.

Figure 4.17: Two $H_2$ displaced 3.32Å apart. $<\bar{1}10>$ view (left) and $<\bar{1}\bar{1}0>$ view (right)

4.4 Hydrogen in Diamond/Amorphous Carbon Composite

4.4.1 Computational Details

Amorphous carbon/diamond composite samples were achieved by several computational steps (as suggested by [43]). At first, a pure $3 \times 3 \times 3$ unit cell of diamond (216 atoms), was constructed with a small region of 12 atoms, located at the center, frozen, i.e. the motion of these atoms was forbidden throughout the simulations (see
The density of the initial sample was $\rho = 3.55\text{gr/cc}$. The samples were heated to a temperature of 25000$^\circ$K. The frozen core tried to return the atoms in its vicinity to their initial ground state positions, therefore these atoms could not move as quickly as the atoms farther away from the core (see fig. 4.19). In this way a temperature gradient from the core to the outside was created. After liquidizing the diamond the samples were cooled to room temperature of 300$^\circ$ by the means of simulated quenching (see fig. 4.20).

Hydrogen atoms were then introduced to the boundary between the diamond core and the amorphous carbon regime in the sample, while later, H(s) were also implanted in the amorphous regime. First, one hydrogen atom was implanted, for 10ps at 300$^\circ$K, then a second hydrogen was added to the same site as before and the simulation continued for additional 10ps, then a third H and so on until local saturation of H was achieved. Once local saturation achieved, the H site was changed and the sequence restarted. Up to 26 hydrogen atoms were implanted to the sample at 5 different interstitial sites.

### 4.4.2 Final Configuration

Several physical properties were examined. First, the final positions of the hydrogen atoms were examined. We found for each simulation (each times, with an increasing number of hydrogen atoms in the sample), that the hydrogen diffused quickly out from the diamond core to the amorphous carbon regime (see fig. 4.21). This was further explored when the $sp^2$- and $sp^3$-bonded atoms were marked. We found that the hydrogen diffused to a region of the sample which was low in $sp^3$-bonds, hence, the
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hydrogen preferred the graphite-like amorphous carbon rather than the diamond-like. We also find, the hydrogen sites surrounded the diamond core with no specific spatial preference. As the hydrogen content increased, hydrogen molecules (H₂) formed.

Second, the ratio of \( sp^2 \) to \( sp^3 \) bonds was examined after each simulation. We found that as we increase the number of hydrogen atoms in the sample we got an increasing numbers of \( sp^3 \) bonds and decreasing numbers of \( sp^2 \) bonds (see table 4.4), till saturation of H in the interstitial region is achieved and a decrease in the \( sp^3 \) content begins (at 1.3%, 3.7%, 5% and 8.7% hydrogen content in graph 4.22). Once the sample has reached local saturation the H interstitial site is replaced, and the situation repeats itself, i.e, the \( sp^3 \) increases till saturation then a decrease and a new interstitial site is introduced. Finally, as the whole sample reaches its optimum H content, the decrease in \( sp^3 \) is low. When visualized (movie of 12% H content on the attached CD-ROM), one can see that the \( sp^3 \)-bonds form in the region near previously formed \( sp^3 \) bonds, this can suggest growth of the diamond cluster in the amorphous regime.

Radial Distribution Functions (RDF) were plotted in addition to the above mentioned calculations, and confirms the suspected result of the growth of the diamond cluster. The features of an amorphous carbon sample are seen in figure 4.23, which shows the RDF of the sample after the annealing process, which consists of broad peak around 1.5Å, an increment around 2Å and a peak around 2.5Å [44]. The features of \( sp^3 \)-coordinated carbon materials are seen at fig. 4.24, which shows the sample with 26 (12% hydrogen content) hydrogen atoms implanted, which include peaks at 1.6Å and 2.6Å associated with the first and second nearest neighbors. Furthermore, when
local density of states (LDOS) for atoms in the sp\(^3\)-rich regime is plotted, characteristics of a bulk diamond density of states reveals (see figure 4.25). This correlates to our previous assumptions of nanodiamond growth.

<table>
<thead>
<tr>
<th>H atoms</th>
<th>H to C content</th>
<th>sp(^3) content</th>
<th>H atoms</th>
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Table 4.4: sp\(^3\) bonds for different Hydrogen contents in the samples

כשת תומך חומיק ממול חומא sp\(^3\)
Figure 4.18: A pure $3 \times 3 \times 3$ unit cells diamond, with a frozen core (blue bonds), the semi-frozen bonds are represented by the yellow bonds.

Figure 4.19: Sample after heating to $25000^\circ K$. Blue bonds represent frozen core, yellow bonds represent semi-frozen bonds.
Figure 4.20: Sample after annealing to 300°K. Blue bonds represent frozen core, yellow bonds represent semi-frozen bonds.

Figure 4.21: The a:C-H/Diamond composite with 26 (12%) hydrogen atoms. Gray bonds represent $sp^3$ bonds, blue and yellow bonds represent frozen and semi-frozen bonds, respectively, red bond represent H-H bond.
Chapter 4. Results

Figure 4.22: $sp^3$ content as a function of total H content in a:C-H sample (1 H atom=$\approx 0.4\%$)

Figure 4.23: Radial Distribution Function of the amorphous carbon/Diamond composite after annealing

"לעומת חומרים מוסנים" $sp^3$

"פעקות החוטפתות הגרעיות לדרומתי יולום/חומרי אמוריים" annealing
Figure 4.24: Radial Distribution Function of the a:C-H sample, arrows are pointing to the diamond-characteristic 1<sup>st</sup> and 2<sup>nd</sup> nearest neighbors

Figure 4.25: Local Density of States (LDOS) of a:C:H sample in the sp<sup>3</sup>-rich regime
Chapter 5

Discussion and Summary

We applied the Molecular Dynamics scheme with Tight-Binding potentials to samples with different geometries and conditions to explain the phenomena of diffusion of hydrogen in diamond. The contribution of the hydrogen to the growth of the diamond phase in a:C structures was of special concern. In this chapter we summarize and discuss the main results and outcome of our research.

We have simulated single hydrogen atom diffusions in numerous configurations with periodic boundary conditions (samples 1-4 in table 4.1, section 4.1). We found that the hydrogen atom has a unique, six-folded energetically equivalent site, known as the ET site. This result is identical to the results already published by Saada et al [1] and is associated with experimentally found anomalous muonium, Mu*, in diamond.[24]. In detail, we found that the H formed a C-H bond with one of the C resulting in the stretching of the other C-C bonds. The resultant bond structure can be correlated with a $sp^3$ hybridized C-H bond. Albeit the different chemical structure, adsorption of H atoms on SWNTs (single walled nanotube) at the exterior and/or
interior of the walls were seen, by other groups[2], to expand the diameter of the nano-
tube hence, the C-C bond length enlarged in the vicinity of the C-H bond created, as it was in our case, enhancing the \( sp^3 \) rehybridization. In MWNTs (multi-walled nanotube), the H adsorption at the exterior (or interior) of the walls also expanded the MWNTs diameter, due to reduction (or increment) of repulsion forces, and the C-C bond expanded until saturation of the H on the walls was achieved[2].

We found by two different methods, that hydrogen has a tendency to diffuse to the surface layer of the diamond sample (samples 2 and 5 in table 4.1, sections 4.1 and 4.2, respectively), for example as seen in SIMS studies [11]. In addition to this experimental evidence, this result can also be correlated to a half coverage exohydro-
genated (8,0) SWNT. Calculations[3] reveal a deformation of the cylindrical nanotube to become a rectangular with a diamond-like carbon atom at each corner. The hy-
drogens were found to contribute new energy states at the Fermi level of the density of states resulting in a DOS plot very similar (almost identical) to our calculation of the hydrogen on the surface of diamond(see figure 4.7).

The sites of Hydrogen dimers were shown to have complete symmetry with the diamond lattice (sample 6-8 and 9 in table 4.1, section 4.3), which is consistent with previous ab-initio calculations [41]. With two Hydrogen dimers, it was found to form orientational order similar to the ground state (lowest energy) of molecular solid H\(_2\). This phenomena, usually observed in a low-temperature high-pressure environment, occurs when the molecular orbitals (or the axes of quantization of the molecular angular momenta) orient along the body diagonals. This structure can be decomposed into four interpenetrating simple cubic structures such that on any given sublattice
the axes of the individual molecular orbitals are all parallel[45]. Due to the $J = 1$
of the hydrogen dimers, this can also be applicable to magnetic frustration, where
magnetic ions are located on lattices of site-sharing frustrated units[46]. Geometric
frustration[47] arises when the arrangement of spins on a lattice precludes satisfying
all interactions at the same time. For example, a group of three antiferromagnetically
coupled spins: once two spins point in opposite directions, the third one cannot be
antiparallel to both of them. Therefore, our results suggests that with a third hydro-
gen dimer implanted the situation described above can arise.

We also studied samples of a:C/diamond composites (sample 9 in table 4.1, sec-
tion 4.4). We found that as we increased the number of hydrogen atoms the ratio of
the number of $sp^3$ carbon bonds increased until hydrogen saturation was achieved.
The saturation occurs both locally (in the vicinity of the initial H interstitial site, the
maxima in graph 4.22) and globally (throughout the simulated sample, for $> 10\%$ H
content in graph 4.22). The new $sp^3$ bonds formed due to the diffusion of the hydro-
gen atoms to the a:C phase of the sample, creating the needed stress for the carbon
atoms to create $sp^3$ bonds. The maximum ratio of $sp^3$ bonds achieved was when the
new formed $sp^3$ bonds crossed over the sample, from top to bottom and from left to
right. This result is in accordance with experimental data showing an increase in $sp^3$
bonds with an increase in hydrogen content [17]. The difference between the exper-
imental value of $\sim 19\%$ H content in the diamond films and the simulated $\sim 12\%$ H
content (26 atoms) can be explained in several ways,

1. Despite usage of highly technological advanced techniques, the experimental
value of \(\sim 19\%\) H content in the a:C/diamond composites is *not* precise, therefore, the real H content could be very well correlated with the computational value.

2. Due to our relatively small-sized sample, there cannot be more than one diamond nucleation site in the sample, hence the H content is limited.

3. The temperature simulated (\(\sim 500^\circ\)K) is not an accurate physical, but rather gives a scale of temperatures (i.e., high vs. low), while experimentally, the temperature was found to be an important factor in the growth of nanodiamonds (at temperatures deviating from 880°C the diamond content was low).

4. Due to our relatively small finite sample size, some physical phenomena maybe hidden if they have an origin in a long range interaction, as well as phenomena that require correlations over a large scale.

Further work should be directed to create a large scale a:C/diamond composite (such as \(4 \times 4 \times 4\) or even larger samples) hence, reducing boundary problems we have encountered and increasing the total hydrogen content. According to [48, 49] nanodiamonds have a “window” of stability in the range of \(\sim 1.9 - 5.2\)nm, this can be further verified with a large a:C/diamond composite samples suggested and in addition, the effect of hydrogens on this “window” could be examined.
Appendix A

Experimental Techniques

NEXAFS  Near Edge X-ray Absorption Fine Structure, spectroscopy refers to the absorption fine structure close to an absorption edge, about the first 30eV above the actual edge. The x-ray energy is scanned and the absorbed x-ray intensity is measured.

HR SEM  High Resolution Scanning Electron Microscopy, is a microscope that uses electrons rather than light to form an image. The image is formed by scanning an electron beam across a sample and collecting some signal from the beam-sample interaction, which is used to control the intensity of the spot.

AFM    Atomic Force Microscope, operates by measuring attractive or repulsive forces between a tip and the sample. In its repulsive "contact" mode, the instrument lightly touches a tip at the end of a leaf spring or "cantilever" to the sample. As a raster-scan drags the tip over the sample, some sort of detection apparatus measures the vertical deflection of the cantilever, which indicates the local sample height. Thus, in contact mode the AFM measures hard-sphere repulsion forces between the tip and sample. In noncontact mode, the AFM derives topographic images from measurements of attractive forces; the tip does not touch the sample.
HR TEM  High Resolution Transmission Electron Microscope, a thin specimen is irradiated with an electron beam of uniform current density. Electrons are emitted from the electron gun and illuminate the specimen through a two or three stage condenser lens system. Objective lens provides the formation of either image or diffraction pattern of the specimen. The electron intensity distribution behind the specimen is magnified with a three or four stage lens system and viewed on a fluorescent screen.

XRD  X-Ray Diffraction, X-rays are radiated and interact with a crystalline substance, giving a diffraction pattern. Every substance has its own unique diffraction pattern, hence the diffraction method is ideally suited for characterization and identification of polycrystalline phases.
Appendix B

Computer Program

This C code calculates the radial distribution function (RDF) for a given sample. The radial distribution function is basically a histogram for the atomic distance. This program uses as input coordinates of atoms which can be taken from an OXON output and is based on a xyz file type. It calculates the histogram for a user input of cut-off distance. The output of the sample is saved to a file which then can be used to plot the RDF.
// THIS WILL OPEN XYZ FILE AND COMPUTE R.D.F. (HISTOGRAM OF DISTANCES)
#include <stdio.h>
#include <math.h>
#include "DynamicArray.h"
int main(int argc, char **argv)
{
    FILE *in;
    if ((in=fopen(argv[1],"r")) == NULL)
    {
        printf("\nError opening file \%s\n",argv[1]);
        return(0);
    }
    int tot_atoms;
    char dummy[255];
    fscanf(in,"\%d\n",&tot_atoms);
    fscanf(in,"\%s\n",&dummy);
    char atom;
    float x,y,z;
    float r;
    float rcut;
    CDynamicArray<float> Cx,Cy,Cz;
    CDynamicArray<float> R;
    printf("total atoms \%d\n",tot_atoms);
    printf("enter r-cut:");
    scanf("\%f",&rcut);
while (!feof(in))
{
    fscanf(in,"%c %f %f %f\n",&atom,&x,&y,&z);
    if (atom=='C')
    {
        Cx.Add(x);
        Cy.Add(y);
        Cz.Add(z);
    }
}
fclose(in);
printf("computing rdf.\n");
for (int i=0;i<Cx.Count();i++)
    for (int j=0;j<Cx.Count();j++)
        if (i!=j)
        {
            r=sqrt(pow(Cx[i]-Cx[j],2)+pow(Cy[i]-Cy[j],2)+pow(Cz[i]-Cz[j],2));
            if (r<r_cut)
                R.Add(r);
        }
float rmin=1000;
float rmax=-1;
for (int i=0;i<R.Count();i++)
    if (rmin>R[i])
        rmin=R[i];
printf("Rij min is:%f",rmin);
for (int i=0;i<R.Count();i++)
    if (rmax<R[i])
        rmax=R[i];
printf("\tRij max is:%f\n",rmax);
int tot_bin;
printf("enter number of bins:");
scanf("%d",&tot_bin);
CDynamicArray<int> bins;
float stepsize=(rmax-rmin)/tot_bin;
float cbin=0;
int binumber=0;
while (cbin<rmax+stepsize)
{
    bins.Add(0);
    printf("bin #%d computing for %f<R<%f\n",binumber,cbin,cbin+stepsize);
    for (int i=0;i<R.Count();i++)
    {
        if ((R[i]>cbin) && (R[i]<(cbin+stepsize)))
        {
            int lastbin=bins.Count()-1;
            bins[lastbin]=bins[lastbin]+1;
        }
    }
    binumber++;
}
APPENDIX B. COMPUTER PROGRAM

```c
    cbin+=stepsize;
    }
    printf("total bins:%d\n",bins.Count());
    printf("tot atoms:%d\n",tot_atoms);
    int totatoms=0;
    FILE *out=fopen("rdf.data","w");
    cbin=0;
    for (int i=0;i<bins.Count();i++)
    {
        printf("Bin %d == %d  avg.%f\n",i,bins[i],float(bins[i]/tot_atoms));
        fprintf(out,"%f  %d\n",cbin,bins[i]);
        totatoms+=bins[i];
        cbin+=stepsize;
    }
    // printf("total distances under %f=%d\n",rcut,totatoms);
    fclose(out);
    }
```
References


REFERENCES


[45] Isaac F. Silvera, Rev. Mod. Phys. 52 393 (1980)


חקר היישובי של מים ביהלים בתחופות

فهمו - אמורפי רחב-ההלים

אורן הרשקוביץ
חקר חיים של ממין ביהלום ותרכובת פחמם-אמורפי נגור-הולד

חינר על מחקר

ليس מיילו חלק של הדרישות לقبول תואר
מגייסר lemידע
פיסיקה

אורז הרשקוביץ

המשכת הען הAGAIN — מרכז טכנולוגי לישראל
המצע עתיד"ד
חיפה
נובמבר 2004
הכרת תודה

ברצוני להודותلد"ר יוהנה א德尔 פורופ'آلף הופמן על הניחות והציות.

והמשיכו במחלקה מחקר לת"ד' מרימ לקרני על העצמות הפורות.
אניצי מדיה חצרינ', ניר שרייבר, אסといった סריס וסילבה סורקן על עורתם.
במחלקהニックפסמחקרה.
אניצי מדיה תודה לרין' אסא ואלי וינטעל הניחות והצירות.

אניצי מדיה להאקטיבי על הניחות הכספית הגדולה בחשלותינו.


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מ
תקציר

הفهم נרחב ומאורע בстраוטואנטילופים, זכרים, נקבות, בגרות מatures והאיסטמטופורת של רוב
הפריטים. עד פגי דקר האריך, מאפרים כי הפחמם הנקבה יוסד בהנחייה של הזרע המיחרי
이는 הפחמם מופעי ברעיות."רצות" הפרטים: גמוס, גרפייטי והלולמי. לכל פרט מאפרים
פגש קולימיוים שווים סמארה, בלשון, הרגים, אטום ומקלחש בנגזר.htm
שחי שחיים מסור vüc. קשקיו המבודד השמתלד, השוני בך הפרות ואת הפגים
ליס מהותי ומעניין.

בחללים, כל אנוס פחמם קושר ערביה פ램נטה גוספימ בינטר קישה ,ับבנה
טוטואנטילופים קשים. המנגה ייציב-תרמודימיט בנתיאס רגיל ולש טטרופורת הלוחים
גרפים, אשר חמודים מחוסים של טוטואם פחמם הקשה או בלולים של איסטמטופורת של
קשוי,בקשוי אלקטרוני מתחים של קושר הזרע המיחרי בלולים השמתלד,_lb. לג
הקשוי (sp2) ומקסימי במעdın רבד והschemas האלקטרונים הפיסיקליות של גור.
אות אלה של פחמם מוחוים ביעית מפותחה הבנה המשמעות של הולולום במנון
המגן הולולום של פחמם. העברה ח ברור ארבעה עץ-חרון הופי-בישיית המשמעות במובעדת
CVD, נמצאת תמדה מאורע במעיים. ברעיות שוניה בעלים מ蠊ים ביבשת מדרידה רבל
על ממת למדורן אצ ח묻ית ביוולום, אוכל קביעה את נסיעות של הזרע לש תמיין
הלולום מדורור לאל פורת. מחקרים מייגים כי אצרי חמידה המעיד על אטום מים

ס
הכתר

בנובלים וחולי המאמרים, (Bond Centered) BC את החידהдумать, את ET (Equilateral Triangle) ET שב הארצות נמסח יורה מוכריי
התרחיז האתרים האפשריים. אטומים המים באצרה זו יוצר קושיショפ סיבוב אטום פח-
מן סמר, וביחדעם פיצופי המשבים האלקטרוניםין. רמות הראויהו Mỹ利亚ן יד מרכז פער
הארמוניה בידולים. אטומים המים של לקפתי', ב' ארכיי
אקולייטיסים יהל מטוספורטור
של . 500K

במעבדה רבוד בועלמ. נעזר מחקר רחב הוק על גיווי יהלימיות. גדולים בנ-הלימיות\\nוזה בגע חっていました תכונות במוחו הסובע והארסאן עקוב האטמיוו המוחיות שלמה הימלד
האפריקסביט הנחשבים ריבי קוניפיס קוגるように לסערת מקוואלקטרומינוית
(MEMS). האלקטרודון אלקטרוכימיות הלא΄ דלק. המשמשים פלט-אלקטרונים המכסים
שטחית. סאמר, גידוי נ-גנ-ב出して פְּחֶרִים בול אפיי יהלמיות נודרBush ה-CBS.
יבת פלטמה. מחקריו פְּצִיב ביע על קשר הידע ביב טמפרטורות הים, והדרים הפְּלְשָמawe
לכמות הוזדד ג'ני יוני-יהלמ היצר. במעובה, נמצאו גם הגידול ה المواרי והנ יטב-\nפרטוד של מalent 880°C ממך 9% מצרת ו-91% ממך. ריכוזים ש JSGlobal שא הים אט טמפרטוד.
וזה שנות היבים לירידה במכאות הגונים-הלימיות. אך, הגואל הים בג הים בין
את במחות סאמר, שן החכבה ייידה במכאות הגונים-הלימיות. מידייתודן, לדגו שפמהת
בנתנאות האפריקסית, משביעות על כל שכיים 19% ממך ב400nm-הארסנון של לדג
כאמורなどが יוניו יד. יש ליצין כי לומדות שלישום בא ситעין הסרוים ביתר, מידייתודן
וזה חונה במעיים את אלו מדיקות, לפלכ COVERLESS השאלות מהש רמה המימיغني יוניו
הלים עם היריכו האפריקסית של המימי בגביש.

כימיים מולדים ריב המאמרים את האנטארקזקטי בים אטומיים והנהוגים הדינומית
שלום, התל ממודד, "כבי" חישובים המפוסל לבצע חישובים עבורה מسفر
הוק על אטומיים בצמ' אוניג, וوذ פְּונְצָליאלים אפגנירים קאלרסים שאנני מדיקיניה אולס
כדי ermögוץ את התחום של מחקר ופיתוח המים בבניית יולים בקונפוגורציות שוניות, מתאימה שפה מחוותיה והתקבלי כuster התודריה המושפעת או אתר ה-ET. לאפשר זו מייתדות הקיביעה הגינטיה של מולקולות אנרגיה, בילוס.

הוושרג הנמר בקמץ הפיכת נגזרת PKK ו-E3 לאפילים חכם יביתי. מטרות המבנה המ伸び פיתוח, נגזרת לארץ תופעת דוגמה ב-Carbon nanotubes - SWNT מימן על זרימת ממציתו של חקירה הפוסטר וגדלה קוטר היצורים.

כפי שכרמא עליי -SWNTs, בימסי פלועד הגינטיה וחינה הלבנה הקבעה לממש שקיימיות ב-SIMS, מייסר מיומן מסתפת על tube, שהוא ציר רמות ארגון זה הדור מת-DO, שזר אחר בישראל, כפי שחרש וב-DO

ובמקורות הוזה.
مولקולות manten החקблок עם סיטוארייה שלמה עצシリーズ הידלום והשקפת שילית

 abol-itio

עלו השירג עקוב יציבת האגרונまって וטורידים. חישוב זה עקבי עם חישוב

מפורים סופים קדומים. עלול, נמצאים 2 מולקולות סופים ציר הדר אוריינטיות של מכל הידלום

(בעל האגרונヷ הוזנכת ביווי) של שירג מוכנות אומה מוקד. חיתון זו הצפה בצבב של טמע

נמוכה, כושר איזר יסודות מוכנות (או ציר הקדונית בש.DoesNotExist החוזה המחלקה)

מותרמעים לאזור מג־אלכסוני. ענק 1 = 1 של מוכנות המוקד. נית ליוושה תופעה 2 מ baseman של מנוכ, שטש ינגו מנוכים הונכים על שריית הדר סיסול יאפורולר棕色-

מסודר הפסיפיס על השירג עקוב ניוגר לקיים את כל האטרטיבל السلط פּפּיִּפּ-פּירבּ-ומא

ניט ביב כל השיכות הקורבּים. בל, ההוחתה שעיצ Truyềnות כי כארש מוכנות 미ום גוספת

הוחזר לגיבוש החולשה והנדفئة והל לו חופי

נכתבו הרכבות על הילוך הפחתה אפורים עם מספר גודל של אטרופי מים. הוחכבוד

השנה על ידי תותב של הילוך צואר זיקור במחזורות חנק שפורartial- קפוא. אטרופייה הממחירו לפסיבי לנצל הידלום, העייר بكשיה, sp 3

 livro התוספות הממקומיות של חנק בסאיור הידלום מרפק אפרים הרחב, האפרים- ל

הילום. коллектив הפסיפיס מבוגר דגל, ע yab תחרות משנים חישוב, קפריר sp 2

טרנספורמציה לקפוא sp 3 בזאור הלאור הידלום דע קבלת סופריציית שלה מיום מביכוב.

מימסして ייבוב את הגוררים הידלום וגרם ל⋄יל הידלום הביתוב

تراثת על Malkolmas ומשהרות ואודרכיסות והעטאות ניסיוניים כשדים שפורסמות

ויתוכנות במק. מחקרים אחרים גורשים על מגע הפלסליות את התוספות היכלות שפרנספתה

בחמקון, מחקרים אחרים מתאימים "חלל" יציבת של המילון בדר של 1.9

לב, יש לווה את המחקר לדיין סימוליציות מבגיים ו يولיהם יזרע על מעבר למאער

בעילות שפה שלדוק השפעת הפֶּניִּימִּּי על "חלל" זה.