CLASSICAL AND QUANTUM SIMULATIONS OF NOVEL FUNCTIONAL MATERIALS

By

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I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/diploma at this or any other Institution/University.

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Part I

Background

1

Introduction

1.1 Overview

Materials have played a key role in the progress of human civilization. Since the ancient times when the most sophisticated materials were stones, our steady growth has been through the ways paved by materials science. The quest for new materials continues even today, in an attempt to meet the never-ending demand for smaller, cheaper and faster devices. Functional materials have enjoyed substantial scientific attention in recent years (1), as key components in the so called "smart systems" that can intelligently adapt to changing environmental conditions (2).

Novel functional materials are those with useful properties (electrical, magnetic or mechanical), that can be tuned as a function of external parameters such as temperature, stress, electromagnetic fields etc. Many materials fall into this category; including ferroelectrics, ferromagnets, piezoelectrics and superconductors, but to be technologically useful, they need to exhibit strong responses to the external parameters. In most cases such strong responses originate from the presence of a phase transitions in the system: metal-insulator transitions, structural transitions, the onset of ferroelectricity, ferromagnetism or superconductivity. In addition to the fundamental physics interest in the microscopic interactions that lead to the observed behavior, study of factors that affect the phase transitions in functional materials is important in efficient utilization of these materials in technological applications. For example, better understanding of the myriad of phase transitions exhibited by solids can lead to the design of better materials that can withstand extreme conditions.

1. INTRODUCTION

Although rare, a material can exhibit multifunctionality, where more than one functional property is realized simultaneously, opening up several exciting possibilities. Spintronic materials where magnetic and optoelectronic properties exist at the same time are examples of this type. In magnetic shape memory alloys, the order parameters strain and magnetization are coupled which makes it possible to control shape by magnetic field or magnetization by pressure.

The technological progress, propelled by the discovery of advanced materials, has led to powerful research tools which in return have accelerated the search for new materials. Computational materials science (CMS) has come into prominence in recent years due to the development of fast computers (thanks to semiconductors) and efficient algorithms. *Ab-initio* electronic structure and atomistic simulation techniques can now do "virtual experiments" and link experimental observations directly to the microscopic scale. They can also work as a testing ground for theoretical models helping us to better understand the fundamental laws that prevail at these scales. The greatest lure for industry is probably that simulations make it possible to carry out difficult or repetitive experiments on a computer before they are actually carried out in laboratories, saving money and time. CMS has now reached a stage, where they are accurate enough to be trusted with the study of materials in extreme thermodynamic conditions that are inaccessible to experiments or where efficient theoretical models do not exist.

Although presently available high performance parallel computers have made it possible to do simulations on a scale and accuracy unthinkable a few decades ago, computational power still remains limited and computer time expensive, so algorithms must rely on careful approximations depending on the available computational time and the accuracy desired from calculations. To this end, different methods have been developed and can be classified based on the length- and time-scales in which they are applicable as shown in Fig. 1.1. However, with the growing computational power and improving approximations, the regime of applicability of each method increases with time.

Atoms and the interactions between them give rise to all the properties observed in materials. Hence, the first step towards reasonably accurate simulation of condensed matter systems is to treat atoms explicitly. Now, depending on how the interaction is handled, the methods can be classified as classical or quantum mechanical.



Figure 1.1: A multiscale modeling approach to materials simulations. Regions marked in color are the ones used in the work presented in this thesis

The interaction between the atoms can be handled by efficient models derived from experimental or theoretical data (3), when such information exist. Classical equations of motion can be used to solve the system, which provides a good description in the nanometer-nanosecond range marked by *classical methods* in Fig. 1.1. Although, the applicability of classical methods are limited by the availability of good models representative of the physical systems, they can simulate thousands of atoms for several nanoseconds.

A more accurate way to handle interactions is to treat electrons explicitly. Electrons are the "quantum glue" that keep atoms together in materials. Solutions to the electronic wave equation will provide all the interactions, removing the necessity to use models. However, quantum methods are computationally expensive due to the overhead of solving Schrödinger equations (4). Quantum chemistry techniques are most expensive and are limited to systems with a few atoms like molecules, clusters etc. But they provide most accurate description of materials as they employ least approximations. For bulk systems, by far the best strategy is provided by density functional theory (DFT) proposed by Hohenberg and Kohn (5), which makes it possible to handle several hundreds of atoms providing a satisfactory description of extended systems.

1. INTRODUCTION

At longer length- and time-scales reaching the micro regime, the atomistic picture has to be abandoned for computational efficiency. For example, in coarse-grained methods, suitable for bio-systems and large molecules, atom groups or molecular fragments are approximated by a single coarse-grained particle. In continuum mechanics, discreteness of matter is altogether ignored and is treated as a continuous mass rather than as separate particles. At macroscopic scales, finite element methods offer a general framework for solving partial differential equations representing the approximate state of the system.

Even though this classification works in most cases, sometimes a single method alone cannot handle the whole system. A multiscale approach is then followed: different scales in the same problem are handled by different methods. For example, data generated by classical and quantum methods can be combined with model calculations to arrive at qualitative predictions. In Quantum Mechanics/Molecular Mechanics (QM/MM) simulations (6), both methods are combined on the fly; a region of the system is treated quantum mechanically while rest of the system is treated classically.

1.2 Functional Materials

In this section the materials that were investigated as part of the doctoral research work are summarized along with the methods that were used to study them.

1.2.1 Multiferroics

Multiferroics are multi-functional materials that exhibit coexistence and coupling of magnetism and ferroelectricity (and optionally ferro-elasticity) in the same phase (7). In these materials, applied electric fields can control magnetism and magnetic fields can control electric polarization. The realization that these materials have great potential for practical applications has lead to an extremely rapid development of the field of multiferroics. Applications include the ability to address magnetic memory electrically, the creation of new types of 4-state logic (i.e., with both up and down polarization and up and down magnetization) and magnetoelectric sensors.

 $MnWO_4$ is a type-II multiferroic in which an inversion symmetry breaking spiral magnetic structure induces ferro-electricity (8). Since the electric polarization originates as a consequence of the unique magnetic structure, the two order parameters are

strongly coupled. We investigated the origin and nature of ferro-electricity in the spiral magnetic state of $MnWO_4$ in detail (9). Since magnetism is essentially a quantum mechanical phenomena arising from interaction between spins of unpaired electrons, first principles electronic structure calculations was employed to study this system.

1.2.2 Nanomaterials

As size is reduced from bulk, several unexpected properties emerge in materials, like, the color of gold nanoparticles turning red below 100 nm (10). Nanomaterials find application in a wide range of fields, including chemical and biological sensors, energy and material storage devices etc. and come in many shapes: small clusters (quantum dot), balls (fullerene), tubes (SWCNT), rods (Si nanowire), sheets (graphene) etc. Much of their unique properties are a consequence of electronic wave functions starting to feel the effect of boundary conditions, the so called quantum confinement effect. Sheets, tubes and dots confine electrons in one two and three directions respectively. We have studied two types of systems: nanodots and nanotubes.

The exotic physical and chemical properties of nanodots are quite distinct from both bulk materials and single atoms, owing to the large surface to volume ratio which makes them often metastable and highly reactive. For instance, extensive studies revealed that optical properties of CdS quantum dots depend critically on their size and shape which led to their wide adoption in various industrial applications like biological imaging, solar cells and lasers (11). During synthesis, modification of chemistry in terms of monomer and ligand concentrations enabled the synthesis of nanocrystals in more exotic shapes, such as rods and multipods which further helped in tuning their properties. Naturally, it is vital to have a precise control over the factors that affect the size, shape and structure of these particles during their growth process (12). With this goal, we investigated the effect of organic capping molecules on the crystal structure of CdS nanoparticles (13).

Another interesting system is nanoparticles of silicon. As a consequence of a modified band structure, it has improved light absorption efficiency and luminance properties, with applications in solar cells and biological markers. The surface tension was found to affect the regime of stability of it's ordered phases at nanoscale, resulting in unique order-disorder transitions under pressure (14). To gain microscopic understanding of the observations, we studied the effect of pressure on an isolated nanocrystal of silicon.

1. INTRODUCTION

Nanotubes of carbon have been the center of intense research since their discovery (15). They exhibit extraordinary strength and unique electrical and thermal properties. These tubes form bundles in which cylindrical tubes are arranged lengthwise on a hexagonal lattice. This allows dense packing of tubes leading to a collective enhancement of individual tube properties. Since the mechanical stability of these tubes are vital to their applications, we studied the effect of increasing fluid densities on submerged single walled nanotubes (16).

Accuracy and speed requirements of different problems are clearly illustrated in these cases. Since calculation of organic molecule binding on a CdS nanoparticle require interactions to be treated explicitly, we used the electronic structure method based on DFT. On the other hand, behavior of several nanotubes immersed in a fluid demand large systems and long simulation times. Since, explicit treatment of electrons was not practical in this case, we substituted interactions by models and used classical MD. Both these requirements were simultaneously present in the case structural transitions in silicon nanoparticles: study of stability regime of crystalline phase require the interactions within the particle calculated accurately, while the application of pressure require submersion in a liquid necessitating a large simulation cell. We used QM/MM calculations in which the Si particle was treated quantum mechanically and the surrounding liquid was treated classically.

1.2.3 Molecular solids

Under suitable temperature and pressure, molecules can condense to form soft solids and careful organization of functional molecules in to 2D (thin films) and 3D (crystals) structures can effectively enhance their properties. In some cases, higher functionalities emerge as a consequence of this organization. Molecular electronics (molectronics, in which molecules replace the active and passive components of electronic circuits), molecular magnets, conductive polymers, organic LEDs etc. are few of the potential applications of molecular materials (17).

Silane (SiH₄, inorganic methane analogue) and H_2 , both of which are explosive gases under normal conditions form a stoichiometric molecular solid with many novel properties under pressure (18). Hydrogen was predicted to be "chemically precompressed" by the presence of the heavy element and to exhibit metalization and high temperature superconductivity at high pressures. Clearly, the interaction between silane and hydrogen molecules in this compound is unusually strong and responsible for it's properties. We studied the effect of structure and dynamics of the H_2 molecule in this system (19).

As the goal was to understand the novel interactions between two molecular species we had to use a method that derives it from first principles. Further, as dynamical simulations are necessary to incorporate the effect of finite temperature, quantum molecular dynamics (QMD) was employed.

1.2.4 Transition metal oxides

Out of all the functional responses observed in condensed matter systems, structural changes in crystals under pressure are probably the most dramatic. The stable configuration of a material corresponds to the lowest energy structure, however, the energy landscape changes when subjected to compression and it can transform from one structure to another.

Several ABO₄-type minerals that share the structure of zircon (which is an important constituent of rocks in earth's crust) also exhibit the characteristic first order phase transition from zircon to sheelite. Models developed through extensive studies predicted the transformation to proceed through an intermediate structure argued by various authors to be orthorhombic, monoclinic or triclinic. For the first time, in nanocrystalline YCrO₄, scientists were able observe an intermediate monoclinic phase using x-ray and Raman scattering measurements (20).

Lanthanum Hafnate ($La_2Hf_2O_7$) is a pyrochlore (major component of earth's mantle) with many potential applications, one of which is as a structural material in the encapsulation of actinide rich radio active nuclear waste. Since these structures need to withstand unknown pressure temperature conditions for several decades, stability of these materials against dissociation is an important criteria for their use (21).

Across a phase transition, electronic rearrangements take place, changing the very nature of bonding. As a consequence classical interaction models are often unsuitable to simulate these systems. Furthermore, the stability of different crystalline phases are dictated by delicate changes in free energy, necessitating accurate first principles calculations to study them.

1. INTRODUCTION

1.2.5 Amorphous solids

Although materials prefer structures of lowest free energy, they can become kinetically trapped in disordered metastable states called amorphous. One way to generate these structures is to rapidly cool (quench) a liquid before it has time to crystallize. Amorphous structures retain short range order, and as a consequence, more or less the functional properties of their crystalline counterparts. In many cases, it is easier to use amorphous structures in applications because they have lower working temperatures during manufacture, are more flexible or have desirable properties.

Amorphous silicon (a-Si) is used widely in electronic circuits because it can be deposited over large areas at relatively lower temperatures and is used to make thin film transistors for large LCD screens and solar cells. When heated, it crystallizes by random nucleation and growth (RNG) resulting in a polycrystalline structure, however, when a crystalline substrate is available, the growth proceeds through layer-by-layer conversion of amorphous to crystalline phase, a process known as solid phase epitaxial growth (SPEG). Many factors are known to affect the process: higher annealing temperatures, external force fields, presence of impurities, ion beam irradiation and applied stresses, but a clear microscopic understanding of the process is lacking (22, 23).

Crystallization of a-Si presented a challenging system to study using computational tools. Simulation of SPEG requires large supercells containing thousands of atoms and long simulation times spanning several nanoseconds to faithfully represent the structure of the amorphous phase and its crystallization respectively, touching the limits of classical MD simulations. But the second part – study of RNG – goes beyond the limit, as the formation of nuclei in the amorphous matrix is a thermally activated stochastic process. Hence we followed a new approach in which classical, quantum and model calculations were combined to draw useful conclusions.

1.3 Roadmap

Based on the methodology used to study the materials, the thesis is organized in four parts. The first part consists of two chapters that develop the background for the work carried out. The first chapter, which is this one, provides an overview to the various types of technologically relevant functional materials studied during the doctoral work, depicting their significance, motivation for study and various computational methods used to study them. A brief introduction to multiscale modeling is provided highlighting various challenges.

In chapter 2, the detailed theory of the computational methods used are explained. Depending on the length and time scale the simulation methods fall into two categories: (a) classical methods, in which the system is treated classically and the interaction is provided by a suitable model and (b) quantum methods, in which electrons are treated explicitly and wave equations are solved to obtain the interaction. Derivation of these methods from fundamental principles and various approximations involved in the simulation are discussed.

Second part consists of two chapters discussing studies that employed classical simulation methods. In chapter 3, we present the results on the effect of liquid argon on the collapse of carbon nanotubes. To resolve the controversy regarding the disappearance of Raman and X-ray intensity of carbon nanotubes under pressure which was attributed to the loss of hexagonal symmetry, we studied bundles of nanotubes immersed in a fluid, acting as pressure transmitting medium (16). Classical MD simulations showed that upon increasing density, the transition pressure (P_T) initially decreases and then begins to increase. The minimum in P_T was found to be a consequence of shifting argon-carbon potential energy minimum with density. Calculated x-ray diffraction patterns and vibrational density of states agreed well with experimental observations, confirming that our microscopic observations were consistent.

In chapter 4, crystallization of a-Si through SPE growth under various thermodynamic conditions using the bond order potentials by Tersoff are detailed (22). Crystallization is a complex process in which an ordered phase emerges from a disordered one through the movement of a crystalline amorphous (c/a) interface. Formation and growth of this interface costs energy while amorphous to crystal transformation lowers energy. A competition between the two factors determines the growth velocities in SPEG, which were found to increase with temperature and pressure. The activation free energy was found to decrease under pressure till it reached a minimum close to 10 GPa, when the densities of amorphous and crystalline phases became equal.

Part 3 consists of three chapters on the quantum simulations of condensed systems. Chapter 5 is devoted to the stability of crystalline structures. We present results of studies on the formation of metastable zinc-blend CdS nanoparticle, phase transition in YCrO₄ and dissociation of crystalline $La_2Hf_2O_7$ using first principles simulations.

1. INTRODUCTION

During the growth of CdS nanoparticles, organic molecules that act as capping agents were found to play a vital role in deciding the final crystal structure (12). Exact nature of these interactions were investigated using QMD (13). The capping molecules trioctylphosphine (TOP) and cis-oleic acid (cis-OA) were found to favor surfaces of zinc-blend and wurtzite respectively. Stability of the intermediate monoclinic phase observed in x-ray diffraction experiments on YCrO₄ was investigated by careful comparison of total energies of different crystallographic phases as a function of pressure (20). The energy differences between different phases showed the monoclinic structure to be stable over a small pressure range, in agreement with experiments. In this chapter, we also discuss the pressure induced dissociation of La₂Hf₂O₇ into it's constituent oxides which was shown to be feasible due to the large free volumes released during the transition (21).

In chapter 6, origin of ferro-electricity in the multiferroic material MnWO₄ is discussed (9). It has a complex spiral magnetic structure, which is also ferroelectric. The magnetic ion is in Mn^{2+} state and as a consequence is expected to have nominal orbital moment. However, Berry phase calculations showed the origin of ferroelectric polarization to be entirely electronic, necessitating the existence of spin orbit coupling in this system. Subsequent experiments confirmed small orbital moment arising as a consequence of mixing of Mn d states with oxygen p states.

In chapter 7, quantum MD simulations of the molecular solid $SiH_4(H_2)_2$ are presented. In this system, pressure was found to elongate the H₂ covalent bond leading to metalization and superconductivity (18). The calculated H₂ bond length and bond order confirmed this observation. Further, simulations revealed that a transfer of charge from bonding to anti bonding states was responsible for the observed elongation of the bonds (19). The hydrogen exchange observed in experiments was found to be a consequence of this bond weakening and to proceed in three stages.

Finally, in part 4, we discuss the use of hybrid methods in materials simulations and it has one chapter. Many systems require a "multiscale" approach combining both the atomistic and electronic structure methods. In the case of crystallization of amorphous silicon through random nucleation and growth, melting curves from classical MD, total energies from first principles and nucleation work from classical nucleation theory provided the complete picture (22). The melting curves showed that for the semi conducting state in ordered (diamond) and disordered (low density amorphous) forms, the melting temperature decreases, where as for the metallic phases (β -Sn and high density amorphous) it increases. Crystallization temperatures and nucleation work were also found to follow the same trend. In the case of high coordinated nano-silicon, QM/MM calculations confirmed that pressure induces disorder within the particle.

Due to the high computational demand of the problems undertaken, all calculations were carried out on parallel computing clusters. A parallel computer is a collection of high performance servers, connected together by a fast network. Various software and hardware considerations that went into the design of the cluster PLUTO are explained in Appendix A. The cluster, located in Purnima Labs, Bhabha Atomic Research Centre, is based on Intel Xeon dual processor quad core servers connected via fast Infiniband network to deliver an average performance of 1 TFLOPS.

1. INTRODUCTION
Methodology

 $\mathbf{2}$

2.1 Basic Equations

The starting point for a theoretical description of condensed matter systems from fundamental principles, is the Hamiltonian for a collection of electrons and nuclei. Consider, a system of N nuclei described by coordinates \mathbf{R} and N_e electrons described by coordinates \mathbf{r} and spin σ , the Hamiltonian of the system is given by (4),

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} - \sum_{I} \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$
(2.1)

where m_e is the mass of the electron, M_I is the mass and $Z_I e$ is the charge of the I^{th} nucleus. The time independent Schrödinger equation can be used to find the eigenvalues and eigenfunctions of this system,

$$[T_{\rm e} + V_{\rm ee}(\mathbf{r}) + V_{\rm eN}(\mathbf{r}, \mathbf{R}) + T_{\rm N} + V_{\rm NN}(\mathbf{R})]\Psi(\mathbf{r}, \sigma, \mathbf{R}) = E\Psi(\mathbf{r}, \sigma, \mathbf{R})$$
(2.2)

where, $T_{\rm e}$ and $T_{\rm N}$ are the electronic and nuclear kinetic energy operators and $V_{\rm ee}(\mathbf{r})$, $V_{\rm eN}(\mathbf{R})$, $V_{\rm NN}(\mathbf{r}, \mathbf{R})$ are electron-electron, electron-nuclear and nuclear-nuclear interaction potential operators, respectively. Unfortunately, Eq. 2.2 cannot be solved exactly for systems with three particles or more. However, using several intuitive approxima-

tions and fast computers, it can be solved numerically and can still provide many useful information, as discussed below.

The immediate simplification that can be made is the Born-Oppenheimer approximation (24), which allows separation of electronic and ionic wave functions. It relies on the fact that, since electrons are at least three orders of magnitude lighter than the nuclei, they move that much faster. As a consequence, looking from nuclear time scales, electrons appear to be always in their ground state. The wave function for the electron-nuclear system can be separated to,

$$\Psi(\mathbf{r},\sigma,\mathbf{R}) = \phi(\mathbf{r},\sigma,\mathbf{R})\chi(\mathbf{R})$$
(2.3)

where $\phi(\mathbf{r}, \sigma, \mathbf{R})$ is the electronic part and $\chi(\mathbf{R})$ is the ionic part of the wave functions. Applying this to Eq. 2.2 and using the approximation that $\nabla_I \chi(R) \gg \nabla_i \phi(\mathbf{r}, \sigma, \mathbf{R})$, the electronic and ionic degrees can be decoupled.

$$[T_{\rm e} + V_{\rm ee}(\mathbf{r}) + V_{\rm eN}(\mathbf{r}, \mathbf{R})]\phi(\mathbf{r}, \sigma, \mathbf{R}) = \varepsilon(\mathbf{R})\phi(\mathbf{r}, \sigma, \mathbf{R})$$
(2.4)

is an electronic eigenvalue equation which will yield a set of eigenfunctions, $\phi_n(\mathbf{r}, \sigma, \mathbf{R})$ and eigenvalues, $\varepsilon_n(\mathbf{R})$, for a particular nuclear position, **R**. For each electronic solution, there will be a nuclear eigenvalue equation:

$$[T_{\rm N} + V_{\rm NN}(\mathbf{R}) + \epsilon_n(\mathbf{R})]\chi(\mathbf{R}) = E\chi(\mathbf{R})$$
(2.5)

These equations characterize the energy states of the system, from which all static properties can be deduced. Information about the dynamics, however, requires the solution of time-dependent Schrödinger equation. In this thesis, since we are interested only in the ground state properties, dynamics of the electrons are ignored. We can think of the electronic eigenvalues, $\varepsilon_n(\mathbf{R})$ giving rise to an electronic energy surface on which the nuclear dynamics described by the time-dependent nuclear wave function $X(\mathbf{R}, t)$ takes place,

$$[T_{\rm N} + V_{\rm NN}(\mathbf{R}) + \epsilon_n(\mathbf{R})]\chi(\mathbf{R}, t) = i\hbar\frac{\partial}{\partial t}\chi(\mathbf{R}, t)$$
(2.6)

Now, since the nuclei are heavy, their quantum effects are often negligible. We can

arrive at the classical nuclear evolution by assuming $\chi(\mathbf{R}, t)$ is of the form,

$$\chi(\mathbf{R},t) = A(\mathbf{R},t)e^{iS(\mathbf{R},t)/\hbar}$$
(2.7)

substituting this to Eq. 2.6 and neglecting all terms involving \hbar , we get an approximate equation for $S(\mathbf{R}, t)$:

$$H_N^{(n)}(\nabla_1 S_1, ..., \nabla_N S_N, \mathbf{R}_1, ... \mathbf{R}_N) + \frac{\partial S}{\partial t} = 0$$
(2.8)

which is just the classical Hamilton-Jacobi equation (25) with

$$H_N^{(n)}(P_1, ..., P_N, \mathbf{R}_1, ..., \mathbf{R}_N) = \sum_{I=1}^N \frac{P_I^2}{2M_I} + V_{\rm NN}(\mathbf{R}) + \epsilon_n(\mathbf{R})$$
(2.9)

denoting the classical nuclear Hamiltonian. The Hamilton-Jacobi equation is equivalent to classical motion on the ground-state surface, $U(R) = \varepsilon_0(\mathbf{R}) + V_{NN}(\mathbf{R})$ given by,

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I U(\mathbf{R}) \tag{2.10}$$

the force on nuclei, $\nabla_I U(\mathbf{R})$, contains a term from the nuclear-nuclear repulsion and a term from the derivative of the electronic eigenvalue, $\varepsilon_0(\mathbf{R})$. Because of Hellman-Feynman theorem (26), this term is equivalent to:

$$\nabla_I \varepsilon_0(\mathbf{R}) = \langle \phi_0(\mathbf{R}) | \nabla_I H_e(\mathbf{R}) | \phi_i(\mathbf{R}) \rangle \tag{2.11}$$

where H_e is the electronic Hamiltonian of Eq. 2.5.

We now have two important equations: Eq. 2.4 which gives the electronic structure of materials for a given arrangement of nuclei, and Eq. 2.10 which defines the dynamics of the nuclei under a potential that is a consequence of the electronic structure. If we are interested only in the dynamics of nuclei and not the detailed energy structure due to electrons, we can make a giant leap by replacing the exact calculation of the potential energy $U(\mathbf{R})$ by functions derived from empirical models. This removes all quantum mechanics from the calculation, simplifying computations considerably. This method forms the basis of the atomistic simulation techniques discussed in the next section. Ways to solve the electronic structure from Eq. 2.4 are presented in section 2.3.

2.2 Classical Methods

Once the electrons are ignored, we have a system of N atoms (or nuclei) interacting under the influence of a global potential energy function $U(\mathbf{R})$. Since the interactions are discrete, this function can be divided into terms containing interactions between self, pairs, triplets etc. (3) as given below,

$$U(R) = \sum_{i}^{N} u^{(1)}(R_i) + \sum_{i,j}^{N} u^{(2)}(R_i, R_j) + \sum_{i,j,k}^{N} u^{(3)}(R_i, R_j, R_k) + \dots$$
(2.12)

The \sum_{ij} indicates a summation over all distinct pairs *i* and *j* without counting any pair twice; the same care must be taken for triplets etc. The first term in $u^{(1)}$ is a self interaction term, which can be set to zero in the absence of any external fields. The remaining terms represent particle interactions. The pairwise interaction $u^{(2)}$ is the dominant term, in most cases sufficient to capture the essential features of interaction in solids. The $u^{(3)}$ term, involving triplets of atoms, represents angle potentials and is sometimes necessary to correctly produce the structures of liquids and glasses (27). Four body term $u^{(4)}$, which takes care of dihedrals and torsions, is used rarely in simulations and all higher order terms can be safely neglected.

Construction of a model for the interaction is more like an art. It starts off by identifying the system constituents: atoms, molecules, surfaces etc. Next step is to choose suitable functional forms with empirical parameters for various terms in the expansion 2.12. This is by far the most difficult step, because detailed knowledge about various interactions in the system is necessary. Finally, the parameters in the functions are fit sot that they can correctly reproduce observables taken either from theoretical considerations or experimental data.

Depending on the distance over which the interaction potential is active, it can be classified as short ranged and long ranged as explained below.

2.2.1 Short range interactions

In solids, the dominant interaction is the bonding between the immediate neighbors, which is pairwise and short-ranged. In such cases, interaction of an atom need not be calculated with all possible pairs in the box; after some distance the potentials will become negligibly small. Hence, a cutoff radius can be introduced beyond which mutual interaction between the particles can be ignored. Thus, a short range potential may be written as,

$$u^{(2)} = \sum_{i < j}^{N} u(R_{ij} | R_{ij} < R_c) + U_{lrc}$$
(2.13)

where, U_{lrc} is the long range correction to the potential in order to compensate for the neglect of explicit calculations.

$$U_{lrc} = 2\pi N \rho_0 \int_{R_c}^{\infty} dR R^2 g(R) u(R)$$
(2.14)

where ρ_0 is the number density of the particles in the system and $g(R) = \rho(R)/\rho_0$ is the radial distribution function. For computational reasons, g(R) is most often only calculated up to R_c , so that in practice it is assumed that g(R) = 1 for $r > R_c$, which makes it possible for many types of potentials to calculate U_{lrc} analytically.



Figure 2.1: Schematic representation of various types of interparticle interactions in solids, indicating the independent variables.

Typical short ranged interactions used in MD are defined in Fig. 2.1 and a few examples of the commonly used functional forms are given below. One of the simplest interaction model for a solid is a harmonic bond of the form.

$$U(R_{ij}) = \frac{1}{2}k(R_{ij} - R_0)^2$$
(2.15)

where k and R_0 are parameters which can be fitted later using empirical data. Often, the parameters have physical meaning attached to them, for example, in the above potential, R_0 fixes the average bond length and k is the vibrational frequency of the bond.



Figure 2.2: Harmonic and Lennard-Jones potential functions for arbitrary parameter values. Minima of the potentials are made to coincide by setting $R_0 = 2^{1/6} \sigma$.

Another important short range pairwise interaction is van der Waals, which acts between non bonded atoms and molecules. For neutral particles these are the London forces arising from the induced dipole moments. Fluctuations of the electron distribution of a particle give rise to fluctuating dipole moments, which on average compensate to zero. But these instantaneous dipoles attract each other with a force $\propto R^{-7}$. One of the popular forms of the resulting interactions are the Lennard-Jones potential (28)

$$u_{LJ}^{(2)}(R_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{R_{ij}}\right)^{12} - \left(\frac{\sigma}{R_{ij}}\right)^6 \right]$$
(2.16)

where, again, ϵ and σ are system dependent parameters. Variation of the harmonic and LJ potentials for arbitrary choices of parameters are given in Fig 2.2. The potential energy becomes a minimum for a distance which corresponds to the ground state configuration.

Three body potentials, as shown in Fig 2.1, defines bond angles. A typical example

is a truncated harmonic form

$$u^{(3)}(\theta_{ijk}) = \frac{k}{2}(\theta_{ijk} - \theta_0)^2 \exp[-(R_{ij}/\rho_1 + R_{ik}/\rho_2)]$$
(2.17)

Dihedrals and inversions are examples of four body interaction forms (Fig. 2.1). Note that, calculations of many body terms are computationally expensive due to the difficulty in identifying connected atoms in the simulation box and are rarely used. Several more examples for possible functional forms exist and are discussed, for example in Ref (29).

$$u^{(4)}(\phi_{ijkn}) = A[1 + \cos(m\phi_{ijkn} - \delta)]$$
(2.18)

$$u^{(4)}(\zeta_{ijkn}) = \frac{1}{2}k(\zeta_{ijkn} - \zeta_0)^2$$
(2.19)

2.2.2 Long range interactions

In the case of Coulomb potential, which decays very slowly, interactions between all particles in the system must be taken into account, if treated without any approximation. For systems with open boundary conditions (like liquid droplets), this method is straightforwardly implemented and reduces to a double sum over all pairs of particles. However, simulations of bulk systems necessitate the use of periodic boundary conditions (PBCs) to overcome the spurious boundary effects. When PBCs are applied, not only the interactions with particles in *central cell* but also with all periodic images must be taken into account and formally a lattice sum has to be evaluated.

$$U = \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mathbf{n}} \frac{q_i q_j}{|R_{ij} - \mathbf{n}L|}$$
(2.20)

where **n** is a lattice vector and \sum_{n}' means that for $\mathbf{n} = 0$ it is $i \neq j$. It is, however, a well known problem that this type of lattice sum is conditionally convergent, i.e. the result depends on the sequence of evaluating the sum (30). A method to overcome this limitation was invented by Ewald (31). The idea is to introduce a convergence factor into the sum of Eq. 2.20 which depends on a parameter s, evaluate the sum and put $s \to 0$ in the end. A form which leads to the Ewald sum is an exponential e^{-sn^2} ,

transforming Eq. 2.20 into (32)

$$U = \underbrace{\frac{1}{2} \sum_{i,j=1}^{N} \sum_{n} \frac{q_{i}q_{j} \operatorname{erfc}(\alpha | R_{ij} - \mathbf{n}L|/L)}{|R_{ij} - \mathbf{n}L|}}_{U_{real}} + \underbrace{\frac{1}{2} \frac{4\pi q_{i}q_{j}}{L^{3}} \sum_{\mathbf{k}} \frac{1}{k^{2}} e^{i\mathbf{k}R_{ij}} e^{-k^{2}/4\alpha^{2}}}_{U_{reciprocal}}}_{U_{reciprocal}} + \underbrace{\frac{1}{2L} \left[\sum_{\mathbf{n}\neq 0} \frac{\operatorname{erfc}(\alpha \mathbf{n})}{|\mathbf{n}|} + \frac{e^{-\pi^{2}\mathbf{n}^{2}}/\alpha^{2}}{\pi \mathbf{n}^{2}} - \frac{2\alpha}{\sqrt{\pi}} \right] \sum_{i=1}^{N} q_{i}^{2} + \underbrace{\frac{2\pi}{L^{3}} |\sum_{i=1}^{N} q_{i}|^{2}}_{U_{surface}}}_{U_{surface}}$$
(2.21)

The evaluation of the potential thus splits into four different terms, where the so called *self* and *surface* terms are constant and may be calculated in the beginning of the simulation. The first two sums, however, depend on the inter-particle separations R_{ij} and need to be evaluated in each time step. It is seen that the lattice sum is essentially split into a sum which is evaluated in real space and a sum over reciprocal space-vectors $\mathbf{k} = 2\pi \mathbf{n}/L$. The parameter α appears formally in the derivation as a result of an integral splitting but it has a very intuitive physical meaning. The first sum gives the potential of a set of point charges which are screened by an opposite charge of the same magnitude but with a Gaussian form factor where the width of the Gaussian is given by α . The second sum subtracts this screening charge, but the sum is evaluated in reciprocal space. Since the error function $\operatorname{erfc}(x) = 1 - \operatorname{erfc}(x)$ decays as e^{-x^2} for large x, the first sum contains mainly short range contributions. On the other side, the second sum decays strongly for large k-vectors and thus contains mainly long range contributions. All three parameters α , R_c , \mathbf{k}_{max} may be chosen in an optimal way to balance the truncation error in each sum and the number of operations (33). Thus, the present form of the Ewald sum gives an exact representation of the potential energy of point like charges in a system with periodic boundary conditions.

2.3 Quantum Methods

A major limitation of atomistic methods, discussed in the previous section, is the empirical nature of the potentials, which can be overcome by solving Eq. 2.4 explicitly. It will yield an exact form for $U(\mathbf{R})$, making empirical functions unnecessary. However, to solve Eq. 2.4, we need (a) an iterative scheme that enable numerical solution on a

computer and (b) a way to convert the formidable many body problem to tractable multiple single-body problems.

The first of the requirements is achieved by density functional theory (DFT) formulated by Hohenberg and Kohn in 1964 (5, 34). As such, DFT has become the primary tool for calculation of electronic structure in condensed matter, and is becoming increasingly important for quantitative studies of molecules and other finite systems. The fundamental tenet of DFT is that *any* property of a system of many interacting particles can be viewed as a *functional* of the ground state density $n_0(\mathbf{r})$; that is, one scalar function of position, in principle, determines all the information in the many-body wave functions for the ground state. However, no guidance whatsoever for constructing the functionals are provided, and no exact functionals are known for any system of more than one electron. DFT would remain a minor curiosity today if it were not for the *ansatz* made by Kohn and Sham (35), which by allowing the electrons to be treated independently, provided a way to make useful, approximate ground state functionals for real systems of many electrons, thus satisfying the second requirement as well.

2.3.1 The Hohenberg-Kohn theorems

The formulation applies to any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, including any problem of electrons and fixed nuclei, where the Hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_i^2 + \sum_{i} V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
(2.22)

which is same as the Hamiltonian in Eq. 2.4, except that electron-nucleus potential $V_{\rm eN}$ has been replaced by $V_{\rm ext}$. Indeed, from electronic point of view, nuclei present a static external potential. The density of particles $n(\mathbf{r})$ which plays a central role in electronic structure theory, is given by the expectation value of density operator $\hat{n}(\mathbf{r}) = \sum_{i=1,N} \delta(\mathbf{r} - \mathbf{r}_i)$

$$n(\mathbf{r}) = \frac{\langle \phi | \hat{n}(\mathbf{r}) | \phi \rangle}{\langle \phi | \phi \rangle} \tag{2.23}$$

Density functional theory is based upon two theorems first proved by Hohenberg and Kohn (5).

- Theorem I: For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.
- Theorem II: A universal functional for the energy E[n] in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

In essence, DFT states that a total energy functional E[n] exists and minimizing it with respect to $n(\mathbf{r})$, one can find the ground state of the system.

$$E_{\rm HK}[n] = T[n] + E_{\rm int}[n] + \int d^3 r V_{\rm ext}(\mathbf{r}) n(\mathbf{r}) \qquad (2.24)$$

Unfortunately, Eq. 2.22 still remains unsolvable, because of it's many body nature. The most crucial step which made DFT the most widely used method today for electronic structure calculations is the Kohn-Sham *ansatz*.

2.3.2 Kohn-Sham ansatz

Kohn and Sham replaced (35) the difficult interacting many-body problem by an auxiliary independent particle problem based on two assumptions:

- 1. The exact ground state density can be represented by the ground state density of an auxiliary system of non-interacting particles.
- 2. The auxiliary Hamiltonian is chosen to have the usual kinetic operator and an effective potential $V_{eff}^{\sigma}(\mathbf{r})$ acting on an electron of spin σ at point \mathbf{r} .

Now, instead of one equation for the entire system having N_e electrons, we have N_e wave equations for each electronic state given as,

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + V_{\rm KS}^{\sigma}(\mathbf{r}) - \varepsilon_i^{\sigma}\right]\psi_i^{\sigma}(\mathbf{r}) = 0$$
(2.25)

where $V_{\text{KS}}^{\sigma}(\mathbf{r})$ is the Kohn-Sham potential acting on an electron, which takes into account the effect of all other electrons and nuclei. The density $n(\mathbf{r})$ can be redefined in

terms of one-electron wave functions $\psi_i^{\sigma}(\mathbf{r})$ as

$$n(\mathbf{r}) = \sum_{\sigma} n(\mathbf{r}, \sigma) = \sum_{\sigma} \sum_{i=1}^{N^{\sigma}} |\psi_i^{\sigma}(\mathbf{r})|^2$$
(2.26)

and Kohn-Sham potential $V_{\rm KS}^{\sigma}(\mathbf{r})$ is

$$V_{\rm KS}^{\sigma}(\mathbf{r}) = V_{\rm int}(\mathbf{r}) + V_{\rm ext}(\mathbf{r}) = V_{\rm H}(\mathbf{r}) + V_{\rm ext}(\mathbf{r}) + V_{\rm xc}^{\sigma}(\mathbf{r})$$
(2.27)

where we have split the electron-electron interaction to a pure Coulomb (Hartree) term, $V_{\rm H}$, and an exchange correlation term, which contains all other interactions not accounted by $V_{\rm H}$. The potentials are related to their corresponding energy functionals through the functional derivatives with respect to density (36, 37), for example,

$$V_{\rm H}(\mathbf{r}) = \frac{\delta E_{\rm H}[n]}{\delta n(\mathbf{r},\sigma)} \tag{2.28}$$

where, the Hartree energy is

$$E_{\rm H}[n] = \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|}$$
(2.29)

By explicitly separating out external potential and the long-range Hartree terms, the remaining exchange-correlation functional $E_{xc}[n]$ can reasonably be approximated as a local or nearly local functional of density.

2.3.3 Exchange & Correlation

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, great progress has been made with remarkably simple approximations. In their original work, Kohn and Sham pointed out (35) that since solids can be considered close to the limit of the homogeneous electron gas, the effects of exchange and correlation are local in character. This form of $E_{xc}[n]$ is called local density approximation (LSDA when spin polarization is considered), in which the exchange-correlation energy is simply an integral over all space with the exchange-correlation energy density at each point assumed to be the same as in a homogeneous electron gas with that density. Despite this simple minded approach, LDA works remarkably well and has been used extensively. Within LDA,

exchange-correlation energy functional and corresponding potential is given by

$$E_{\rm xc}^{\rm LSDA}[n^{\uparrow}, n^{\downarrow}] = \int d^3 r \ n(\mathbf{r}) \epsilon_{\rm xc}^{\rm hom}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r}))$$
(2.30)

$$V_{\rm xc}^{\sigma}(\mathbf{r}) = \left[\epsilon_{\rm xc}^{\rm hom} + n \frac{\partial \epsilon_{\rm xc}^{\rm hom}}{\partial n^{\sigma}}\right]_{\mathbf{r},\sigma}$$
(2.31)

The first step beyond the local approximation is a functional which depends on both the values of $n(\mathbf{r})$ and its gradient $|\nabla n^{\sigma}|$ at each point. Such a "gradient expansion approximation" (GEA) was suggested in the original paper of Kohn and Sham; however, the GEA does not lead to consistent improvement over LDA as it violates the sum rules and other relevant conditions (38). The term *generalized*-gradient expansion (GGA) denotes a variety of ways proposed for functions that modify the behavior at large gradients in such a way as to preserve desired properties (39). The EC functional for a spin polarized system in the generalized form,

$$E_{xc}^{\text{GGA}}[n^{\uparrow}, n^{\downarrow}] = \int d^3r \ n(\mathbf{r}) \epsilon_x^{\text{hom}}(n) F_{xc}(n^{\uparrow}, n^{\downarrow}, |\nabla n^{\uparrow}|, |\nabla n^{\downarrow}|, ...)$$
(2.32)

$$V_{\rm xc}^{\sigma}(\mathbf{r}) = \left[\epsilon_{\rm xc} + n\frac{\partial\epsilon_{\rm xc}}{\partial n^{\sigma}} - \nabla\left(n\frac{\partial\epsilon_{\rm xc}}{\partial\nabla n^{\sigma}}\right)\right]_{\mathbf{r},\sigma}$$
(2.33)

where F_{xc} is dimensionless and $\epsilon_x^{\text{hom}}(n)$ is the exchange energy of the unpolarized gas.

The most enduring problem with the Kohn-Sham approach is that no systematic way has been developed to improve the functionals for exchange and correlation. The problems are most severe in materials in which the electrons tend to be localized and strongly interacting, such as transition metal oxides and rare earth elements and compounds (40). One way to approach such problems is "LDA+U", which stands for methods that involve LDA- or GGA-type calculations coupled with an additional orbitaldependant interaction (41, 42). The additional interaction is usually considered only for highly localized atomic-like orbitals on the same site, i.e. of the same form as the "U" interaction in Hubbard models (43, 44). The effect of the added term is to shift the localized orbitals relative to the other orbitals, which attempts to correct errors known to be large in the usual LDA or GGA calculations.

2.4 Wavefunctions

We need to choose a proper set of functions that constitute a complete basis, in order to expand the KS wave functions. In a solid (or any state of condensed matter) it is convenient to require the states to be normalized and obey periodic boundary conditions in a large volume Ω that is allowed to go to infinity, because the orbitals, { $\psi_i(\mathbf{r})$ } then become Bloch functions (45), { $\psi_{i\mathbf{k}}(\mathbf{r})$ }, where **k** samples the first Brioullin zone (46).

2.4.1 Plane wave basis

The Bloch functions, $\{\psi_i(\mathbf{r})\}$, can be expanded in a plane wave basis. However, note that choice of plane waves as basis, although natural, is not unique. Several sets of functions satisfying completeness and orthonormality criteria will work.

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{g}} c_{\mathbf{g}}^{i\mathbf{k}} e^{i\mathbf{g}\cdot\mathbf{r}}$$
(2.34)

where $c_{\mathbf{g}}^{i\mathbf{k}}$ is a set of expansion coefficients, Ω is the system volume, $\mathbf{g} = 2\pi h^{-1}\hat{\mathbf{g}}$ is a reciprocal lattice vector, h is the cell matrix whose columns are the cell vectors, and $\hat{\mathbf{g}}$ is a vector of integers. An advantage of plane waves is that the sums needed to go back and forth between reciprocal space and real space can be performed efficiently using fast Fourier transforms (FFTs). The density $n(\mathbf{r})$ given by Eq. 2.23 can also be expanded in a plane wave basis:

$$n(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{g}} n_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{r}}$$
(2.35)

Since it is not practical to use infinite number of plane waves in simulations, the sum over $|\mathbf{g}|$ is terminated after $\hbar^2 |\mathbf{g}|^2 / 2m_e < E_{\text{cut}}$ in Eq. 2.34. However, since $n(\mathbf{r})$ is obtained as a square of the KS orbitals, the cutoff needed for density expansion is $4E_{\text{cut}}$ for consistency with the orbital expansion. Similarly, integrals in \mathbf{k} space are replaced by sum over a grid of suitable size N_k . Both E_{cut} and N_k limit the accuracy of the calculations and are chosen carefully.

Using these expressions and the orthogonality of the plane waves, it is straightforward to compute the various energy terms. For example, the kinetic, Hartree and

exchange-correlation energies can be shown to be,

$$\varepsilon_{\rm KE} = -\frac{1}{2} \sum_{i} \int d\mathbf{r} \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) = \frac{1}{2} \sum_{i} \sum_{\mathbf{g}} g^2 |c_{\mathbf{g}}^i|^2 \tag{2.36}$$

$$\varepsilon_{\rm H} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\Omega} \sum_{\mathbf{g}}' \frac{4\pi}{g^2} |n_{\mathbf{g}}|^2$$
(2.37)

$$\varepsilon_{\rm xc} = \sum_{\mathbf{g}} \epsilon_{xc}(\mathbf{g}) n(\mathbf{g}) \tag{2.38}$$

where $g = |\mathbf{g}|^2$ and the sum in Eq. 2.37 excludes the $\mathbf{g} = (0, 0, 0)$ term.

The external energy term corresponding to $V_{\text{ext}}(\mathbf{r})$ of Eq. 2.27 is made somewhat complicated by the fact that, in a plane wave basis, very large number of waves are needed to treat the rapid spatial fluctuations of core electrons (47). A solution to this problem is offered by pseudopotentials.

2.4.2 Pseudopotentials

Only electrons in the outer-most shells of atoms (valence electrons) participate in determining the properties of materials, while core electrons just screen the charge of the nucleus. Hence, we can introduce a "pseudopotential" (48, 49), which replaces strong Coulomb potential of the nucleus and the effects of the tightly bound core electrons by an effective ionic potential acting on the valence electrons.¹ In order to make this approximation, the valence orbitals, which, in principle must be orthogonal to the core orbitals, must see a different pseudopotential for each angular momentum component in the core, which means that the pseudopotential must be nonlocal. To see how this comes about, we consider a potential operator of the form (25)

$$\hat{V}_{ps} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} v_l(r) |lm\rangle \langle lm|$$
(2.39)

 $^{^{1}}$ This should not be confused with "interaction potentials" in classical methods: they are empirical forms that define the interaction between atoms, while a pseudopotential defines interaction of valence electrons with core region

where r is the distance from the ion, and $|lm\rangle\langle lm|$ is a projection operator onto each angular momentum component. It can be shown that (25), the complete pseudopotential operator for all atoms in the system will be

$$\hat{V}_{ps}(r, \mathbf{R}_1, ..., \mathbf{R}_N) = \sum_{I=1}^N \left[v_{loc}(|\mathbf{r} - \mathbf{R}_I|) + \sum_{l=0}^{\bar{l}-1} \sum_{m=-l}^l \Delta v_l(|\mathbf{r} - \mathbf{R}_I|) |lm\rangle \langle lm| \right]$$
(2.40)

where $v_{loc}(r) \equiv v_{\bar{l}}(r)$ is known as the local part of the pseudopotential (having no projection operator attached to it) (50). Now, the external energy corresponding to Eq. 2.27, being derived from the ground state expectation value of a one-body operator, is given by

$$\varepsilon_{\text{ext}} = \sum_{i} \langle \psi_i | \hat{V}_{ps} | \psi_i \rangle = \varepsilon_{\text{loc}} + \varepsilon_{\text{NL}}$$
(2.41)

The first (local) term gives simply a local energy of the form

$$\varepsilon_{\rm loc} = \sum_{I=1}^{N} \int d\mathbf{r} n(\mathbf{r}) v_{loc}(|\mathbf{r} - \mathbf{R}_{I}|) = \frac{1}{\Omega} \sum_{I=1}^{N} \sum_{\mathbf{g}} n_{\mathbf{g}}^{*}(\mathbf{r}) \tilde{v}_{loc}(\mathbf{g}) e^{-i\mathbf{g} \cdot \mathbf{R}_{I}}$$
(2.42)

where $v_{\text{loc}}(\mathbf{g})$ is the Fourier transform of the local potential. For the nonlocal contribution, an expansion of the plane waves in terms of spherical Bessel functions and spherical harmonics is made, and after some algebra, one obtains

$$\epsilon_{\rm NL} = \sum_{i=1}^{N_e} \sum_{I=1}^{N} \sum_{l=0}^{\bar{l}-1} \sum_{m=-l}^{l} Z_{iIlm}^* Z_{iIlm}$$
(2.43)

where

$$Z_{iIlm} = \sum_{\mathbf{g}} c^{i}_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{R}_{I}} \tilde{F}_{lm}(\mathbf{g})$$
(2.44)

and

$$\tilde{F}_{lm}(\mathbf{g}) = 4\pi N_{lm}^{-1/2} \int dr r^2 j_l(gr) \Delta v_l(ur) \phi_l(r) Y_{lm}(\theta_{\mathbf{g}}, \phi_{\mathbf{g}})$$
(2.45)

To generate a pseudopotential for an atom, first an all-electron wave equation is solved for a given atomic reference configuration and energy eigenvalues and eigenfunctions are calculated with a proper choice of the exchange-correlation functional. Then, the core region is replaced by an angular momentum dependent scattering potential, and is optimized till the conditions below are met (51):

- All electron and pseudo valence wavefunctions agree beyond a cut-off radius r_c .
- Logarithmic derivatives of the all electron and pseudo wavefunctions agree at r_c .
- Integrated charge inside r_c for all electron and pseudo wavefunctions agree.
- First energy derivative of the logarithmic derivatives of the all electron and pseudo wavefunctions agree at r_c .

The third condition (norm conservation), in particular, makes sure that the pseudo wavefunctions satisfy the orthonormality conditions and that the Kohn-Sham equations are unmodified. However, if one forgoes the norm-conservation condition, the pseudo wavefunctions can be made "smoother" inside the core region, substantially improving computational efficiency. This is the spirit of "ultrasoft" method (49), which however, comes at a cost of increased complexity in equations.

A more efficient approach is provided by projector augmented wave (PAW) method, which introduces projectors and auxiliary localized functions similar to "ultrasoft" method (52, 53). However, the difference is that the PAW approach keeps the full all-electron wavefunctions; since the full wavefunction varies rapidly near the nucleus, all integrals are evaluated as a combination of integrals of smooth functions extending throughout space plus localized contributions evaluated by radial integration over spheres around each atom.

2.4.3 PAW method

For the set of all-electron valence functions $\psi_i(\mathbf{r})$, one can define (54, 55) a smooth part of the wavefunction $\tilde{\psi}_i(\mathbf{r})$ and a linear transformation $\psi_i(\mathbf{r}) = \Im \tilde{\psi}_i(\mathbf{r})$ that relates the set $\psi_i(\mathbf{r})$ to the smooth functions $\tilde{\psi}_i(\mathbf{r})$. The transformation is assumed to be unity except within a sphere centered on the nucleus: $\Im = \mathbf{1} + \Im_0$. The expansion of each smooth function $|\tilde{\psi}\rangle$ in partial waves m within each sphere can be written,

$$|\tilde{\psi}\rangle = \sum_{m} c_{m} |\tilde{\psi}_{m}\rangle \tag{2.46}$$

with the corresponding all-electron function,

$$|\psi\rangle = \Im|\tilde{\psi}\rangle = \sum_{m} c_{m}|\psi_{m}\rangle \tag{2.47}$$

Hence the full wavefunction in all space can be written

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_{m} \{c_m\{|\psi\rangle - |\tilde{\psi}_m\rangle\}$$
(2.48)

If the transformation \mathcal{T} is required to be linear, then the coefficients must be given by a projection in each sphere $c_m = \langle \tilde{p}_m | \tilde{\psi} \rangle$, for some set of projection operators \tilde{p} .

The resemblance of the projection operators to the separable form of pseudopotential operators is apparent. Just as for pseudopotentials, there are many possible choices for the projectors of smooth functions for $\tilde{p}(\mathbf{r})$ closely related to pseudopotential projection operators. The difference from pseudopotentials, however, is that the transformation \mathcal{T} still involves the full all-electron wavefunction

$$\mathcal{T} = \mathbf{1} + \sum_{m} \{ |\psi_m\rangle - |\tilde{\psi}_m\rangle \} \langle \tilde{p}_m |$$
(2.49)

The expression for physical quantities in the PAW approach follow from Eq. 2.49. For example, the density is given by,

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + n^{1}(\mathbf{r}) - \tilde{n}^{1}(\mathbf{r})$$
(2.50)

which can be written in terms of eigenstates labeled i with occupations f_i as

$$\tilde{n}(\mathbf{r}) = \sum_{i} f_{i} |\tilde{\psi}_{i}(\mathbf{r})|^{2}$$
(2.51)

$$n^{1}(\mathbf{r}) = \sum_{i} f_{i} \sum_{mm'} \langle \tilde{\psi}_{i} | \tilde{\psi}_{m} \rangle \psi_{m}^{*}(\mathbf{r}) \psi_{m'}(\mathbf{r}) \langle \tilde{\psi}_{m'} | \tilde{\psi}_{i} \rangle$$
(2.52)

$$\tilde{n}^{1}(\mathbf{r}) = \sum_{i} f_{i} \sum_{mm'} \langle \tilde{\psi}_{i} | \tilde{\psi}_{m} \rangle \tilde{\psi}_{m}^{*}(\mathbf{r}) \tilde{\psi}_{m'}(\mathbf{r}) \langle \tilde{\psi}_{m'} | \tilde{\psi}_{i} \rangle$$
(2.53)

The last two terms are localized around each atom and the integrals can be done in spherical coordinates with no problems from the string variations near the nucleus, as in augmented methods.

2.5 Self consistent scheme

The Kohn-Sham equations provide a framework for finding the *exact* density and energy of the ground state of a many-body electron problem using standard independentparticle methods. The procedure followed in solving these equations in DFT is given in Flow diagram 2.3. The basic strategy is to start with an initial guess for the system wavefunction, which is generally taken to be a linear combination of atomic wavefunctions. Density and subsequently Kohn-Sham potential can be calculated from these wavefunctions. Using this initial guess for V_{KS}^{σ} , the KS equations are solved to get a set of KS energies ε_i^{σ} and corresponding wavefunctions $\psi_i^{\sigma}(\mathbf{r})$. A new density is calculated from these wavefunctions, which would be different from the previous value, because the initial guess did not correspond to the ground state of the system. An appropriate optimization algorithm can be used to correct the density so as to reduce the error and the cycle is repeated. The procedure is followed till the differences in energies, wavefunctions or densities fall below a specified convergence criteria. After the electronic ground state is determined, Eq. 2.11 can be used to calculate the interaction between the ions.

2.6 Molecular dynamics

Once the interaction between atoms are known, the Newton's equations of motion contained in Eq. 2.10 can be integrated to move particles to new positions and to get new velocities at these new positions using molecular dynamics (MD) simulations. Ingredients for an MD simulations are threefold: (i) **Interaction** between system constituents. This can either come from electronic structure methods (Quantum MD) or from a model potential (Classical MD), as explained in the previous sections. (ii) An **integrator**, which propagates particle positions and velocities from time t to $t + \delta t$. The time step δt has to be properly chosen to guarantee stability of the integrator, i.e. there should be no drift in system's energy. (iii) Appropriate **statistical ensemble**, which controls thermodynamic quantities like pressure, temperature or the particle number. The natural choice of an ensemble in MD simulations is the microcanonical ensemble (NVE), since the system's Hamiltonian without external potentials is a conserved quantity. Nevertheless, there are extensions to the Hamiltonian which also allow to simulate different statistical ensembles.



Figure 2.3: Schematic representation of the self-consistent loop for solution of Kohn-Sham equations. In general, one must iterate two such loops simultaneously for the two spins, with the potential for each spin a functional of the density of both spins

2.6.1 Integrators

A finite difference integrator is an approximation for a system developing continuously in time. An integrator breaks time into discrete steps of width δt and the system degrees of freedom (positions and momenta) are propagated from one step to the next. A good integrator should be accurate (so that the system always remains close to its true trajectory), stable (so that small perturbations do not lead to instabilities) and robust (so that it allows efficient simulation with large time steps and minimum CPU and memory requirements).

The simplest and most straight forward way to construct an integrator is by expanding the positions and velocities in a Taylor series. The integrators obtained this way are called Verlet-Stömer integrators (56, 57). For a small enough time step δt the expansion gives,

$$\mathbf{R}(t+\delta t) = \mathbf{R}(t) + \mathbf{v}(t)\delta t + \frac{1}{2}\mathbf{a}(t)\delta t^2 + \frac{1}{6}\mathbf{b}(t)\delta t^3 + \dots$$
(2.54)

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \mathbf{a}(t)\delta t + \frac{1}{2}\mathbf{b}(t)\delta t^2 + \frac{1}{6}\mathbf{c}(t)\delta t^3 + \dots$$
(2.55)

where **a**, **b**, **c** are the 2nd, 3rd, 4th time derivative of the coordinates. Performing a similar expansion for $\delta t \rightarrow -\delta t$, which will give $\mathbf{R}(t - \delta t)$ and $\mathbf{v}(t - \delta t)$ and subtracting the resultant equations from Eq. 2.54 we get,

$$\mathbf{R}(t+\delta t) = 2\mathbf{R}(t) - \mathbf{r}(t-\delta t)\delta t + \mathbf{a}(t)\delta t^{2} + \mathcal{O}(\delta t^{4})$$
(2.56)

$$\mathbf{v}(t+\delta t) = 2\mathbf{v}(t) - \mathbf{v}(t-\delta t)\delta t + \mathbf{b}(t)\delta t^2 + \mathcal{O}(\delta t^4)$$
(2.57)

Above equations are accurate up to 3^{rd} order in δt , however, it requires the 3^{rd} derivative of the coordinates which is not routinely calculated in MD simulations and thus introduces some additional computational and storage overhead. An equivalent algorithm, which stores only information from one time step is the so called *velocity Verlet* algorithm, which reads

$$\mathbf{R}(t+\delta t) = \mathbf{R}(t) + \mathbf{v}(t)\delta t + \frac{1}{2}\mathbf{a}(t)\delta t^2$$
(2.58)

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{1}{2}(\mathbf{a}(t) + \mathbf{a}(t+\delta t))\delta t$$
(2.59)

This scheme, however, requires the knowledge of the accelerations at time step $t+\delta t$. One may therefore decompose velocities in two steps. First calculate

$$\mathbf{v}(t+\delta t/2) = \mathbf{v}(t) + \frac{1}{2}\mathbf{a}(t)\delta t$$
(2.60)

Then compute the actual forces on the particles at time $t + \delta t$ and finish the velocity calculation with

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t+\delta t/2) + \frac{1}{2}\mathbf{a}(t+\delta t)\delta t$$
(2.61)

At this point the kinetic energy may be calculated without a time delay of δt . There are several other schemes, such as leap-frog (58) or Beeman's (59), but they all have the same accuracy and should produce identical trajectories in coordinate space. We have used velocity Verlet algorithm in the calculations presented in this thesis.

2.6.2 Statistical ensembles

Choice of a proper ensemble in molecular dynamics is crucial to obtain well averaged physical quantities. The microcanonical ensemble (NVE) may be considered as the *natural* ensemble for molecular dynamics, since, the system's Hamiltonian is constant in the absence of any time dependent external forces, implying that the dynamics evolves on a constant energy surface. However, real systems are often canonical in nature, they can exchange energy with the environment (NVT) or change volume to match external pressure (NPT). The two popular schemes to simulate statistical ensembles are, The Berendsen's scheme in which the variables are corrected at each step through a coupling constant towards the prescribed value (*proportional control*) and the Nosé-Hooever scheme in which the system Hamiltonian is extended so that the desired variables become automatically conserved (*integral control*).

2.6.2.1 Thermostats

Temperature and energy are canonical variables which means only one can be controlled at a time. Temperature is the measure of average kinetic energy of the system, given by equipartition theorem as,

$$\left\langle \frac{1}{2}m\mathbf{v}^2 \right\rangle = \frac{N_{\rm f}}{2}k_{\rm B}T \tag{2.62}$$

 $N_{\rm f}$ is the number of degrees of freedom in the system and $k_{\rm B}$ is the Boltzmann constant. The simplest way to keep the temperature of a system constant is to scale velocities (60) such that $\mathbf{v}_i(t) \rightarrow \sqrt{T_0/T(t)}\mathbf{v}_i(t)$, where T_0 is the reference temperature and T(t) is the actual instantaneous temperature. This method, however, leads to discontinuities in momentum part of the phase space trajectories and is undesirable. A better way is to use a scaling factor $\lambda(t)$ that allows a weak coupling of system temperature to an external bath, $\mathbf{v}_i(t) \rightarrow \lambda(t)\mathbf{v}_i(t)$, where

$$\lambda(t) = \left[1 + \frac{\delta t}{\tau_T} \left(\frac{T_0}{T(t)} - 1\right)\right]^{\frac{1}{2}}$$
(2.63)

The constant τ_T , is the relaxation time constant which determines the time scale on which the desired temperature is reached – allowing a way to control the properties of the thermostat (61, 62). Although efficient, the method cannot be mapped onto a specific thermodynamic ensemble. In computer simulations where average quantities only at the end of the simulation are of significance, this is not a problem. Still, a more physically intuitive approach is to use the integral thermostat, proposed by Nosé (63, 64), which adds an additional degree of freedom to the system which effectively introduces a "friction" in the momentum space, whenever the system tries deviate from the reference temperature. The modified equations of motion read:

$$\frac{d\mathbf{R}_i(t)}{dt} = \mathbf{v}_i(t) \tag{2.64}$$

$$\frac{d\mathbf{v}_i(t)}{dt} = \frac{f_i(t)}{m_i} - \chi(t)\mathbf{v}_i(t)$$
(2.65)

where f(t) is the force acting on the particle of mass m_i . The friction coefficient, χ , is controlled by the first order differential equation,

$$\frac{d\chi(t)}{dt} = \frac{N_f k_B}{Q} (T(t) - T_0)$$
(2.66)

where $Q = N_f k_B T_0 \tau_T^2$ is the 'effective mass' of the thermostat and τ_T is the time constant.

2.6.2.2 Barostats

It is sometimes useful to keep the pressure constant in simulations and allow volume to vary. Particularly, in first order transitions in solids, cell volume and shape can change abruptly when a new structure forms. A constant volume simulation will not be able to observe such transitions. For an infinite system generated by periodic boundary conditions, the pressure on the walls of the simulation cell is defined by the equation,

$$PV = N_f k_B T + \frac{1}{3} \sum_{i=1}^{N} \mathbf{R}_i \cdot f_i(t)$$
 (2.67)

where V is the volume and $f_i(t)$ is the force acting on the particle *i* due to all other particles. The second term is called the system virial. Controlling pressure is less straight forward and a simple scaling method will not work (65). The Berendsen barostat (61) works by making the system obey the equation

$$\frac{dP}{dt} = (P_0 - P)/\tau_P \tag{2.68}$$

where τ_P is a relaxation time associated with the barostat. When simulation cell size and shape are allowed to vary, the cell vectors are scaled by a factor $\bar{\eta}$, which is a 3×3 tensor given by

$$\bar{\bar{\eta}} = \bar{\bar{1}} - \frac{\beta \delta t}{\tau_P} (\bar{\bar{1}}P_0 - \bar{\bar{\sigma}})$$
(2.69)

where $\bar{\sigma}$ is the internal stress tensor and P_0 is a scalar variable representing hydrostatic pressure; when non-hydrostatic conditions are simulated we can replace it with a tensor $\bar{\sigma}_0$. The equations for integral barostat (66) are more complex as given below.

$$\frac{d\mathbf{R}_i(t)}{dt} = \mathbf{v}_i(t) + \eta(t)(\mathbf{R}(t) - R_0)$$
(2.70)

$$\frac{d\mathbf{v}_i(t)}{dt} = \frac{\mathbf{f}_i(t)}{m_i} - [\chi(t) + \eta(t)]\mathbf{v}_i(t)$$
(2.71)

$$\frac{d\chi(t)}{dt} = \frac{N_f k_B}{Q} (T(t) - T_0) + \frac{1}{Q} (W\eta(t)^2 - k_B T_0)$$
(2.72)

$$\frac{d\eta(t)}{dt} = \frac{3}{W}V(t)(P(t) - P_0) - \chi(t)\eta(t)$$
(2.73)

$$\frac{dV(t)}{dt} = 3\eta(t)V(t) \tag{2.74}$$

Above equations represent the case of isotropic cell variations. For anisotropic changes, one has to replace the factor η by a tensor $\overline{\eta}$ like before.

2.6.3 Car-Parrinello MD

Ordinarily, quantum MD (also called Born-Oppenheimer MD) simulations are carried out in two steps. First, the ground state electronic wave functions and energy eigenvalues are found following the recipe of Sec 2.3. In the next step, forces on ions are calculated and the system is propagated in time using the MD algorithms discussed above.

An alternate way to carry out quantum MD simulations was suggested by Car and Parrinello (67) which has proven very successful. The special feature of the CP algorithm is that it solves the quantum electronic problem also using MD. This is accomplished by adding a *fictitious* kinetic energy for the electronic states, which leads to a fictitious Lagrangian for both nuclei and electrons.

$$\mathcal{L} = \sum_{i=1}^{N} \frac{1}{2} (2\mu) \int d\mathbf{r} |\dot{\psi}_i(\mathbf{r})|^2 + \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - E[\psi_i, \mathbf{R}_I] + \sum_{ij} \Lambda_{ij} \left[\int d\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) - \delta_{ij} \right]$$
(2.75)

The final term is essential for orthonormality of the electronic states. This Lagrangian leads to MD equations for *both* classical ionic degrees of freedom \mathbf{R}_I and electronic degrees of freedom, expressed as independent-particle Kohn-Sham orbitals $\psi_i(\mathbf{r})$. The resulting equations of motion are

$$\mu \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E}{\delta \psi_i^*(\mathbf{r})} + \sum_k \Lambda_{ik} \psi_k(\mathbf{r}, t)$$
$$= -H \psi_i(\mathbf{r}, t) + \sum_k \Lambda_{ik} \psi_k(\mathbf{r}, t)$$
(2.76)

$$M_I \ddot{R}_I = \mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} \tag{2.77}$$

The equations of motion are just Newtonian equations for acceleration in terms of forces, subject to the constraint of orthogonality in the case of electrons.

2.7 Parallel computing

A parallel computer is a collection of independent processing units (nodes) interconnected through a fast network so that the processors share load and data. The success of parallel computing strongly depends both on the underlying problem to be solved and the optimization of the computer program. The former point is manifested in the so called Amdahl's law (68). If a problem has inherently certain parts which can be solved only in serial, this will give an upper limit for the parallelization which is possible. The speedup σ , which is a measure for the gain of using multiple processors with respect to a single one, is therefore bound

$$\sigma = \frac{N_p}{w_p + N_p w_s} \tag{2.78}$$

Here, N_p is the number of processors, w_p and w_s is the amount of work, which can be executed in parallel and in serial, i.e. $w_p + w_s = 1$. From above equation, it is obvious that the maximum efficiency is obtained when the problem is completely parallelizable, i.e. $w_p = 1$ which gives an N_p times faster execution of the program. In the other extreme, when $w_s = 1$ there is no gain in program execution at all and $\sigma = 1$, independent of N_p . Once the parallelizable regions of the problem are identified, it is important to implement it efficiently into a computational program. A problem which is inherently 100% parallel will not be solved with maximum speed if the program is not

100% mapped onto this problem. Hardware aspects also affect the speedup. Although, theoretical speedup is expected to increase continuously when number of processors are increased, in practice, it saturates because of the communication latency. Most parallel problems need to communicate data between nodes in order to take into account data dependencies and as shown in Appendix A, real life networks have finite bandwidth and the latency in communication will increase with increasing N_p , bringing down the speedup.

2.7.1 Classical methods

The replicated data strategy (69) is one of several ways to achieve parallelization in MD. Its name derives from the replication of the configuration data on each node of a parallel computer (i.e. the arrays defining the atomic coordinates \mathbf{R}_i , velocities \mathbf{v}_i and forces f_i , for all N atoms in the simulated system, are reproduced on every processing node). In this strategy, each node calculates forces and integrates equations of motion only for a fraction of the total atoms (N/N_p) . The method is relatively simple to program and is reasonably efficient. Moreover, it can be collapsed to run on a single processor very easily. However the strategy can be expensive in memory and have high communication overheads, but overall it has proven to be successful over a wide range of applications.

2.7.2 Quantum methods

Replicated strategy is unsuitable in electronic structure methods, because they use a lot more memory to store large matrices corresponding to wavefunctions. However, there are several alternative ways to achieve parallelization. One way is to solve Kohn-Sham equations only for a fraction of bands on each node. It requires the whole Hamiltonian to be stored on all nodes, but only a part of the the memory intense wavefunctions needs to be stored on each node. Another way is to split the plane wave expansion across the nodes. Parts of KS equations are solved separately and the results are combined. For cases where reciprocal integration over multiple \mathbf{k} points are carried out, the calculation can be separated to different nodes as the calculations are mostly independent.

2.8 Simulation codes

The major programs used to carry out simulation presented in this thesis are listed below. Several smaller programs were developed to prepare inputs and analyze results for different problems, details of which are given in respective chapters.

2.8.1 DL_POLY 2.19

DL_POLY version 2 (29) is a parallel molecular dynamics simulation package developed at Daresbury Laboratory by W. Smith and T.R. Forester under the auspices of the Engineering and Physical Sciences Research Council (EPSRC) at Daresbury Laboratory. The package is the property of the Science Facilities Research Council (STFC) of the United Kingdom. DL_POLY 2 is issued free under license to academic institutions pursuing scientific research of a non-commercial nature. DL_POLY can simulate a wide range of systems from simple atomic materials to complex macromolecules and biological systems. Several popular force-field types discussed in Section 2.2 are implemented by default and it is easy to add user defined functional forms. Several variations of boundary conditions, popular integrators and ensemble methods are also implemented. The easy-to-understand subroutine structure makes it amenable to implement new features. We have employed DL_POLY for the classical simulations presented in this work.

2.8.2 VASP 4.6

Vienna *ab-initio* simulation package (VASP) (70, 71) is a software package for performing ab-initio electronic structure calculations and quantum-mechanical molecular dynamics (MD) simulations using pseudo-potentials or projector-augmented waves and a plane wave basis set. The approach implemented in VASP for the MD simulations is based on the (finite-temperature) local-density approximation with energy as variational quantity and an exact evaluation of the instantaneous electronic ground state at each MD time step. VASP uses efficient matrix diagonalisation schemes and an efficient Pulay/Broyden charge density mixing. The interaction between ions and electrons is described by ultra-soft Vanderbilt pseudopotentials (US-PP) or by the projector-augmented wave (PAW) method. US-PP and the PAW method allow for a considerable reduction of the number of plane-waves per atom for transition metals and

first row elements. Forces and the full stress tensor can be calculated with VASP and used to relax atoms into their instantaneous ground-state. VASP offers parallelization over bands and parallelization over plane wave coefficients. It is a commercial code and requires a license to use it.

2.8.3 CPMD 3.13

The Car-Parrinello molecular dynamics (CPMD) (72) code is a plane wave and pseudopotential implementation of Density Functional Theory, particularly designed for abinitio molecular dynamics using the Car-Parrinello method (67). It is distributed free of charge to non-profit organizations. Its first version was developed by Jurg Hutter at IBM Zurich Research Laboratory starting from the original Car-Parrinello codes. CPMD can be used to carry out quantum mechanics/molecular mechanics (QM/MM) simulations as it offers internal routines to simulate a part of the system classically using interaction potentials while a specifically chosen region can be treated quantummechanically.

In the following chapters we shall address the specific problems related to functional materials using the methods explained here.

Part II

Classical Methods

Argon filled carbon nanotubes

Carbon nanotubes are well known for their mechanical strength. Under relatively low pressures, some high pressure experiments observed disappearance of Raman modes, which was taken to be indicative of collapse of cylindrical tubes. However, subsequent experiments found the necessary pressure to be much higher. To resolve this apparent contradiction, we carried out classical molecular dynamics simulations of bundles of single walled carbon nanotubes (SWCNTs). When tubes were empty, the applied pressure caused them to collapse from the cylindrical structure to a ribbon-like one close to 2 GPa, in agreement with the initial experiments. When tubes were immersed in argon, the behavior was found to be substantially different. The collapse pressure shifted to higher values when the number of argon atoms was increased beyond a critical value. Computed x-ray diffraction patterns of argon-filled nanotubes confirmed that seemingly varied experimental observations in the high-pressure phase transitions of carbon nanotubes is due to the pressure transmitting medium used in high pressure experiments.

3.1 Background

Due to many extraordinary properties arising from the unique one-dimensional structure, carbon nanotubes have been the subject of intense theoretical and experimental investigations since their discovery (15). Early theoretical studies had indicated that isolated tubes may be able to withstand large deformations without much irreversible structural modifications (73). Later experiments based on Raman, (74, 75, 76) x-ray

3. ARGON FILLED CARBON NANOTUBES

diffraction (77, 78) and neutron diffraction (79) measurements provided evidence for a pressure-induced structural phase transition at low pressures. In particular, the highpressure Raman spectroscopic investigations carried out on bundles of single-walled carbon nanotubes (SWCNTs) showed that the peak position of the tangential mode shifts linearly to higher frequencies, with a change in the slope at 2 GPa. A number of studies also reported the disappearance of the radial breathing mode (RBM) from the spectrum above that critical pressure (80). X-ray diffraction studies (77, 78) showed that at 1.5 GPa, the (100) diffraction peak associated with the two-dimensional lattice of the SWCNTs bundles to disappear reversibly, if pressure was kept less than 4 GPa. Subsequent computer simulations, using classical molecular dynamics, found that the carbon nanotubes collapse to a ribbon-like structure at low pressures (81, 82) and that the collapse pressure decreases with the increase in the tube diameter, apparently supporting the experimental observations. It was also shown that the tubes having diameter larger than a critical value would spontaneously collapse at atmospheric pressure. Studies on double-walled carbon nanotubes reported similar results but with higher collapse pressures, as the two tubes support each other (83, 84). First-principles studies, however, found the behavior of SWCNTs under uniaxial stress (perpendicular to the tube axis) to be non monotonous as a function of the tube diameter. (85)

However, these results were not found to be consistent with the observations of a number of other experimental studies (86, 87, 88, 89). In situ x-ray diffraction investigations (90) on SWCNTs under quasi hydrostatic pressures found that the 2D lattice continues to persist up to 10 GPa, in contrast to the earlier results. Kawasaki *et al.* (91) compared the effect of the solid and liquid pressure transmitting medium (PTM) on the high-pressure x-ray diffraction patterns and concluded that the penetration of liquid PTM could explain the observed differences in results. Raman spectroscopic studies (92, 93) of open-ended SWCNTs using different PTM (paraffin oil, argon, methanol ethanol, etc.) could not observe signatures of any phase transition at low pressures. Instead, they found that the pressure-induced changes in Raman spectra depend significantly on the PTM. Similar PTM dependence was observed for double-walled tubes as well. (86)

From these results appeared that for open-ended tubes, the pressure transmitter used in the hydrostatic experiments might enter tubes and affect their high-pressure behavior. Indeed, Rols *et al.* (94) demonstrated that the substantial argon adsorption takes place at the inner walls of SWCNTs. Hence, to understand the diverse experimental reports, we have simulated SWCNTs immersed in fluid argon using the classical MD method.

3.2 Methods

Simulations were carried out on (10, 10) arm-chair SWCNTs of diameter 13.59 Å generated using the TUBEGEN (95) code. Macrocell used in the simulations consisted of these SWCNTs arranged in a 4×4 two-dimensional hexagonal lattice that were ten graphene unit cells long (24.6 Å) in the z direction. Periodic boundary conditions were applied in all the three directions. For our simulations, we have used DL_POLY code (29) with the NPT statistical ensemble with variable cell method. The equations of motion were integrated using standard Verlet algorithm with a time step of 1 fs. The temperature (300 K) and the hydrostatic pressure were maintained using the Berendsen thermostat and barostat. The bundles were initially equilibrated at 0 GPa and subsequently the pressure was raised in steps, allowing the cell volume to equilibrate for at least 10 ps after each increase. To remove any memory of starting structures, the system was equilibrated for a long time under ambient conditions.

3.2.1 DREIDING force field

The covalent interactions between carbon atoms were modeled by the standard generic macro molecular force field DREIDING (96) which has been successfully used in many earlier studies (81, 82). The functional forms for the different terms in the potential and the parameters used in this simulation are listed in Table 3.1. As shown in Fig. 2.1, E_{bond} is a two body term representing pairwise interactions, E_{angle} and E_{tors} are three body terms representing bond angle and torsion and E_{inv} is the four body term representing inversion symmetry of the system. Inter-tube C-C as well as C-Ar and Ar-Ar short-range interactions were of the Lennard-Jones functional form $U(r_{ij}) = 4\epsilon [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ with a 12 Å cutoff. Parameters of L-J potentials are listed in Table 3.2 (96, 97).

Table 3.1: Parameters for the C_R atom type $(sp^2$ hybridized carbon atom involved in resonance), in DREIDING, a standard generic macromolecular force field used in all our molecular dynamics simulations.

Functional form	Parameters					
$E_{bond} = \frac{1}{2}K_b(R - R_0)^2$	R_0	1.39 Å	K_b	1050 kcal/mol/Å ²		
$E_{angle} = \frac{1}{2} K_{\theta} (\cos\theta - \cos\theta_0)^2$	$ heta_0$	120°	K_{θ}	$100 \text{ kcal/mol/rad}^2$		
$E_{tors} = \frac{1}{2}V\{1 - \cos[n(\phi - phi_0)]\}$	ϕ_0	180°	V	25 kcal/mol	n	2
$E_{inv} = \frac{1}{2} \frac{K_i}{(sin\Psi_0)^2} (cos\Psi - cos\Psi_0)^2$	Ψ_0	0°	K_i	$40 \text{ kcal/mol/rad}^2$		

 Table 3.2: Parameters for the short range LJ interatomic potential between the elements used in the simulations

Atoms	$\epsilon~(\rm kcal/mol)$	σ (Å)
C-C	0.0951	3.473
Ar-Ar	0.2862	3.350
C-Ar	0.2827	3.573

3.2.2 Adsorption sites for argon

Rols *et al.* (94) studied argon adsorption on open-ended SWCNTs through thermodynamics and neutron diffraction experiments and proposed the following adsorption scenario. The inner walls of the nanotubes (INT-T) and the groove sites (G) on the outer surface of the bundle are populated first followed by the filling of the axial sites inside the tubes (INT-t) and remainder of the outer bundle surface as shown in Fig 3.1. Although direct evidence was limited, a few intertubular sites (IC) seemed to be progressively populated as a function of the Ar chemical potential (94). Interestingly, subsequent studies on rubidium-intercalated SWCNTs showed that Rb ions prefer IC sites at very low stoichiometry. At higher Rb levels, IC sites (see Fig. 3.1) become unfavorable and INT and bundle surface sites begin to get occupied (98). Based on these propositions, we have carried out two sets of simulations. In the first set, presented Sec 3.3.2, IC sites were neglected and argon was restricted to INT sites. The second set of simulations, in which both INT and IC sites were populated, are presented in Sec 3.3.3. Note that due to the requirement of an infinite periodic system, we have ignored the outer surfaces of the bundle altogether, but those sites are unlikely to affect the high-pressure behavior of the bundle.



Figure 3.1: Schematic section of a nanotube bundle indicating the probable adsorption sites proposed by Rols *et al.* from neutron scattering experiments in Ref (94)

3.2.3 Vibrational DOS

The autocorrelation function of velocity (VAF) can be used to calculate vibrational density of states (vDOS). If the velocity vector for a system of atoms is $\mathbf{v}(t)$, then the velocity autocorrelation Z(t) can be written as

$$Z(t) = \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle}$$
(3.1)

The vibrational spectrum of the system can be calculated by taking the Fourier transform of the VAF:

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt e^{i\omega t} Z(t)$$
(3.2)

The vibrational density of states (vDOS) is then $\Phi(\omega) = F^2(\omega)$.

Since molecular dynamics provides a discrete sampling of position and velocity along a time vector, the continuous VAF is replaced with an appropriate discrete estimator of the function, \hat{Z} . For a simulation with N time-steps, the n^{th} element of the VAF estimator \hat{Z}_n can be computed as,

$$\hat{Z}_n = \frac{1}{N-n} \sum_{i=0}^{N-n-1} \frac{\langle \mathbf{v}(t_{i+n}) \cdot \mathbf{v}(t_i) \rangle}{\langle \mathbf{v}(t_0) \cdot \mathbf{v}(0) \rangle}$$
(3.3)

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The summation is used so that \hat{Z}_n is an average of all possible VAF that can be constructed from the discretely sampled velocity data by shifting the time origin by nsteps. Finally, the Fourier transform in Eq. 3.12 can be calculated using FFT routines. To avoid spurious truncation effects, the VAF data is multiplied with a smoothing function. An example of a smoothing function is a Gaussian of the form,

$$\phi(n) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(n-\mu)^2}{2\sigma^2}\right]$$
(3.4)

where μ shifts the peak along n and σ defines the breadth of the peak. As the Gaussian should approach zero as n approaches N, $\sigma = M/2.5$ and $\mu = 0$.

3.2.4 X-ray diffraction pattern

To make a contact between our microscopic observations and experimental predictions, we also calculated powder x-ray diffraction intensities, I_{hkl} , as $I_{hkl} = F_{hkl}^2$, where the structure factor, F_{hkl} , is defined by

$$F_{hkl} = \sum_{j}^{cell} f_j \exp\left[2\pi i \left(hx_j + ky_j + lz_j\right)\right] \exp\left(-B_j \frac{\sin^2 \theta}{\lambda^2}\right)$$
(3.5)

where f is the atomic form factor of atom j at sites (x_j, y_j, z_j) and B_j is the Debye-Waller factor. The structure factor is generally plotted as a function of wave vector $\mathbf{q} = 2\pi(h, k, l)$. The form factors are approximated by the analytical function

$$f(\sin\theta/\lambda) = \sum_{i=1}^{4} a_i \exp\left(-\frac{b_i \sin^2\theta}{\lambda^2}\right) + c \qquad (3.6)$$

The coefficients a_i , b_i and c are taken from x-ray data in International Tables (99) automatically by the program.

3.3 Results

3.3.1 Empty SWCNTs

Although different computer simulations agreed on the existence of a transition to a collapsed phase, the exact structure of the daughter phase was not settled unambiguously (100, 101). Computations using DREIDING potentials on single and double-
walled carbon nanotubes (83, 101) observed a herringbone structure whereas studies using Tersoff-Brenner potential (82) found a linear arrangement of similarly deformed tubes at comparable pressures. Energy considerations seemed to favor the linear structure, (100) but the energy differences between the two structures were found to be less than the thermal energy ($k_{\beta}T$) at the temperature of the simulations. It was argued that the precise arrangement of the collapsed nanotubes within a bundle might vary depending on the size of the macrocell, local environment, and compression rate (101). Later, first-principles studies of structural, electronic, and optical properties of collapsed SWCNTs bundles found an in-between configuration which was distinct from both the linear and herringbone structures found previously (102).



Figure 3.2: (a) Simulated structure of SWCNTs at 0 GPa and 300 K as viewed along z axis. Structures (b)–(f) represent snapshots of the collapsed phases at 3 GPa. (b) The linear-o and (c) herringbone structures are the result of fine and coarse pressure steps, respectively. (d) Linear-n, (e) basket-weave, and (f) disordered structures are new arrangements observed in our simulations.

Since, the pressure step used to compress the system is known to affect transitions under pressure, we carried out a series of simulations to investigate its effect on the behavior of nanotubes. The initial state generated through equilibration of (10, 10) carbon nanotubes at 300 K remained nearly circular as shown in Fig. 3.2(a). When very

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fine steps close to 0.1 GPa were used to compress this system, an abrupt volume drop of about 33% was observed at 2.4 GPa, resulting in a new phase with ribbon-like tubes shown in Fig. 3.2(b) which is similar to the linear structure of Ref. (100). When we used larger compression rates in the range of 1-2 GPa, the herringbone structure [Fig. 3.2(c)] was obtained, also observed in the earlier studies using DREIDING potentials. Careful inspection of trajectories during the transition to herringbone structure revealed that the deformation of the tubes passed through a transient linear structure in which the tubes were arranged along the [110] direction. At the very final stage of the evolution, the zigzag ordering characteristic of the herringbone set in. To test whether the thermal fluctuations at 300 K were responsible for stabilizing the herringbone structure, we repeated these simulations at very low temperatures (≈ 2 K). To our surprise, we found that a new linear structure with a different cell shape and tube arrangement is stable. To differentiate the two linear structures, hereafter we refer the structure of Fig. 3.2(b)as linear-o and that of Fig. 3.2(d) as linear-n. Upon increasing the temperature of linear-n slowly to 300 K, the tubes retained the arrangement. Interestingly, still higherpressure steps (3 GPa) at room temperature resulted in a new phase that had a basketweave-like ordering with tubes arranged in parallel pairs, almost perpendicular to one another [Fig. 3.2(e)]. The transition in empty SWCNTs was also found to depend on thermostat and barostat relaxation times used in the simulations. Tubes became disordered [Fig. 3.2(f)] when relaxation times of 10 ps each were used. Simulations on a smaller $3 \times 3 \times 10$ macro-cell also yielded the disordered structure similar to Fig. 3.2(f). In all the cases, the transition is completely reversible; structures return to the ambient phase with cylindrical tubes upon the release of pressure. In agreement with the elastic ring model by Liew et.al. (103), the structures of collapsed tubes show a peanut-shaped deformation under hydrostatic pressure.

Table 3.3 summarizes the relative energies, enthalpies, and volumes per atom for the cases discussed above. We found that the linear-n structure has the lowest energy and although the energy of the linear-o structure is lower than that of the herringbone, the energy difference between these two is within the thermal fluctuations at room temperature. Calculation of volume occupied by the collapsed tubes in different cases indicated that while the tube volume is roughly equal, the interstitial volume increases systematically from linear-n to disordered phases resulting in less compact structures with higher energies, in agreement with the conclusions of Ref. (101). The lower volume

 $V/atom (Å^3)$ Structure E/atom (eV)H/atom (eV)Linear-n 7.627.799.21Linear-o 7.68(0.06)7.86(0.07)9.29(0.08)Herringbone 7.70(0.08)7.88(0.09)9.50(0.29)Basket-weave 7.75(0.13)7.93(0.14)9.55(0.34)Disordered 7.77(0.15)7.95(0.16)9.59(0.38)

Table 3.3: Total energies, enthalpies and volumes of different high-pressure phases given in Fig. 3.2 at 3 GPa (300 K). Values in parenthesis correspond to differences from the linear-n structure

(hence, lower energy) of linear-n as compared to the linear-o was probably because of the arrangement of tubes rather than their direction. In the first case, the tubes were arranged such that the tubes point to the empty spaces between the neighbors (along [110] direction), whereas for linear-o the collapsed tubes were arranged end to end.

We carried out simulated annealing on the herringbone structure up to 1000 K, but it did not transform to the lower energy structures in Fig. 3.2, indicating that such reconstructions are kinetically hindered up to this temperature. Although our simulations demonstrated the existence of a variety of structures in the high-pressure phase, we feel that Fig. 3.2 may not represent a complete set of all possible arrangements of the collapsed tubes under pressure. For example, inclusion of non hydrostatic stresses may lead to still newer structures.

3.3.2 SWCNTs with argon at INT sites

To study the effect of PTM on the high-pressure behavior of carbon nanotubes, we simulated argon-filled nanotubes at different argon densities. Choice of argon was partly due to the simplicity of its interatomic interactions (being an inert element, argon interacts with environment through simple van der Waals forces, which can be easily modeled through the Lennard-Jones type of pair potentials) and partly as an effort to understand the recent experiments which used argon as PTM. The results would be qualitatively similar for any other PTMs which do not chemically react with the carbon atoms of the tubes. However, an important limitation of the simulations was that the interaction potentials and periodic boundary conditions did not allow the expulsion of argon atoms from within the carbon nanotubes, whereas in experiments this might occur due to defects in the tube walls or the absence of end caps.

3. ARGON FILLED CARBON NANOTUBES

In a typical high-pressure experiment, the pressure cell containing the sample is kept immersed in a bath to fill the sample region with PTM. Since computer representation of such a scenario was not practical in a periodic cell, we carried out several simulations at different densities to explore the effect of PTM on the behavior of nanotubes.



Figure 3.3: Variation in the energy with the number of argon atoms at INT sites fitted with a fourth-order polynomial (solid line). The inset shows the derivative of total energy with respect to the argon number density.

Fig. 3.3 shows the computed variation in energy/atom with the argon number density. It decreases linearly for low argon densities to become minimum close to 60, which correspond to optimum filling under ambient conditions (the negative value of the chemical potential at lower densities indicate that these tubes are under filled). Although in experiments under ambient conditions, tubes would be filled to an optimal value, one can certainly generate the under or over filled tubes by varying equilibration time and density of argon atoms in the bath (94).

SWCNTs with argon densities varying from 0 to 70 atoms/tube were subjected to increasing pressures in steps of 1 GPa (or 0.1 GPa close to phase transitions) up to 10 GPa. Pressure was then released back to zero in similar steps. As can be seen from the few representative cases given in Fig. 3.4, depending on the degree of filling of the tubes, the volume decreased discontinuously at some pressure, marking a



Figure 3.4: Pressure-volume behavior for single-walled carbon nanotubes at different argon densities. Closed and open symbols represent compression and decompression, respectively.

structural phase transition of the first order. For a particular case of 40 atoms/tube, however, we observed multiple volume drops at 2.5, 5.4, and 8.5 GPa. Inspection of the intermediate structures revealed that argon undergoes structural modifications of different compactness, forcing the enveloping nanotubes to collapse in stages. Multiple phase transitions similar to this case was also observed in experiments (87), when nanotubes filled with fullerenes were subjected to high pressures. Another important observation is that as the density increases, the change in volume at the transition becomes smaller. Hence, at higher argon densities the transformation might appear gradual, which would explain the resonant Raman spectroscopic studies (92) on openended nanotubes using argon PTM that found the structural changes to be progressive rather than abrupt.

Computed variation in the transition pressure (P_T) in Fig. 3.5 shows that when the number of argon atoms per nanotubes is increased beyond a critical value (≈ 40 argon atoms/tube), the P_T increases almost quadratically and at the optimum density (60 atoms/tube), it is close to 7 GPa. During the release of pressure, a similar curve is followed; although with lower values of P_T , representing the well-known hysteresis in



Figure 3.5: Variation in the transition pressure with the number of argon atoms per nanotube. Closed and open symbols represent the results during compression and decompression, respectively. Solid and dotted lines indicate a quadratic fit to the transition pressure.

the first-order phase transitions. The lowering of the transformation pressure below 40 atoms/tube is puzzling because intuitively one would expect that when an empty tube is filled with some fluid, it will become less compressible and thus withstand higher stresses before collapse. This seemingly unusual result can be rationalized as follows:

As the tubes are quite incompressible along the axial direction, the effect of the applied stress is felt primarily in the radial direction. When it is filled with argon, due to van der Waals interaction between the argon and carbon atoms, the tubes will experience an additional force which – due to the cylindrical symmetry – will also be directed along the radius of the tubes. Van der Waals interaction is repulsive at short distances (below a radius r_{\min})¹ but is weakly attractive above it. As a result, when too few argon atoms are inside the tubes, the average distances between argon atoms and tube walls are greater than the r_{\min} and the average interaction is attractive. This effective attractive force adds to the external pressure and increases the inward stress on the tube, collapsing it at a lower pressure. But when the argon density inside the tubes becomes large enough to have the average argon-carbon distance less than r_{\min} ,

 $^{^{1}}r_{\rm min}$ corresponds to the distance, where force becomes zero. It is related to σ as $r_{\rm min} = 2^{1/6}\sigma$. From Table 3.2, $\sigma=3.573$ Å for C-Ar and hence $r_{\rm min} = 4.01$ Å.



Figure 3.6: Computed Ar-C pair-correlation functions for different argon atomic densities. The vertical line corresponds to r_{min} (see text) of the Lennard-Jones potential used in our simulations.

the interactions become repulsive, which, in turn helps the tubes withstand higher pressures. Thus the collapse pressure increases. Fig. 3.6 shows that for 20 atoms/tube, the Ar-C pair distribution function, g(r) peaks above r_{\min} and for higher Ar densities, the maximum shifts toward lower r values accompanied by an increase in the transition pressure. It would be interesting to test these results by carrying out experiments with carbon nanotubes filled with pressure transmitter at lower densities.



Figure 3.7: Snapshots of the simulation cell containing single-walled carbon nanotubes filled with (a) 40 and (b) 60 argon atoms/tube at INT sites at 0 GPa showing argon forming cylindrical structures inside the tubes.

Interestingly, the zero pressure structures of SWCNTs with INT argon (Fig. 3.7

resemble multiwalled nanotubes, although argon atoms are quite disordered. Similar local partial ordering and shell formation of the pressure medium around the nanotubes is supported by ab initio studies, which also find it to have a strong impact on pressure transmission. (86) Similar to our results beyond the critical argon density, computer simulations on double-walled tubes (83) had found transition pressures to be higher as the two walls support each other. To compare, the P_T for a double-walled nanotube of type (5,5)@(10,10) is 18 GPa (Ref. (83)) whereas for optimally filled SWCNTs it is 7 GPa.



Figure 3.8: High-pressure phases of nanotubes at 10 GPa with (a) 40, (b) 50, (c) 60, and (d) 70 argon atoms per tube. Side view argon atoms inside a single nanotube for 60 atoms/tube is shown at (e) 0 GPa and (f) 10 GPa.

High-pressure structures of argon-filled nanotubes were also quite varied (Fig. 3.8). Up to 40 atoms/tube, the collapsed tubes adopted linear arrangements similar to those of empty tubes and argon atoms formed a linear array parallel to the walls of the tubes. The intermediate densities shown in Figs. 3.8(b) and 3.8(c) represent a transitional regime in which faceting emerges along with the limited collapse of the tubes. All these structures preferred an arrangement similar to Fig. 3.2(d). At densities over 70 atoms/tube, the forces favored faceting and nanotubes become "polygonized". It is interesting to note that in many early studies, authors had argued in favor of polygo-

nization over collapse and our simulations show that indeed both regimes exist when a PTM is present in the system. Figs 3.8(e) and 3.8(f) demonstrate the ordering of argon along z direction inside a single nanotube across the phase transition.

3.3.3 SWCNTs with argon at INT and IC sites



Figure 3.9: Variation in the total energy with the number of argon atoms in the intertubular region. Argon inside the tubes is kept fixed at 50 atoms/tube. The chemical potential in the inset shows essentially linear behavior.

To calculate the minimum energy configuration, we fixed the INT argon at 50 atoms/tube and varied the IC site density. A value lower than the optimum INT density was chosen because the additional stress due to the presence of argon at IC sites would increase the chemical potential at INT sites and would lower the optimum value.¹ Minimum energy was found to occur when alternate IC sites are filled with about 7 atoms per tube (Fig. 3.9). As argon atoms at IC sites were arranged as a one-dimensional chain along z axis, for more than 7 atoms/tube, Ar-Ar distances became less than r_{min} (≈ 3.76 Å), making the interaction repulsive.

As we can see from pressure-volume curves given in Fig. 3.10, argon atoms present outside the tubes further affect the behavior of the tubes. A significant observation is

 $^{^1\}mathrm{Equilibration}$ of a 60+7 bundle at ambient pressure resulted in an increase in volume justifying this argument



Figure 3.10: (a) P-V behavior of argon-filled carbon nanotubes with 50 atoms inside (INT sites) and 7 atoms in the interstitial (IC sites). Similar curves are plotted for (b) 40 INT+7 IC and (c) 35 INT+7 IC cases. (d) Variation in the transition pressure with the total number of argon atoms.

that in all cases studied, the transition pressures are higher. We feel that the reduced intertubular space diminishes fluctuations that lead to the collapse of nanotubes and hence increases the transition pressure. The transition is abrupt for the case of 50+7 (INT+IC) atoms/tube, whereas for 35+7 it is spread over a wider range of pressures. Similar to the case without IC atoms, there are multiple transitions for 40+7, though the largest drop is found at 5.3 GPa instead of 2.5 GPa.

The structures of collapsed tubes were also different when argon is present at IC sites. At ambient pressures, IC argon atoms formed a triangular lattice [Fig. 3.11(a)]. At 10 GPa, the collapsed tubes were arranged in layers and tubes in the neighboring layers form an angle of $\sim 70^{\circ}$ with each other and argon atoms, which were initially arranged on an approximate equilateral triangular lattice of side 17 Å, now formed bilateral triangles with two sides of 17 Å and one of 13 Å.



Figure 3.11: Snapshots of simulation containing SWCNTs and argon at INT+IC sites. (a) 50+7 argon atoms/tube at 0 GPa, (b) 50+7 atoms/tube at 10 GPa, and (c) 40+7 atoms/tube at 10 GPa.

3.3.4 Vibrational DOS

To understand the effect of argon fluid on the vibrational properties of nanotubes, we calculated vibrational density of states by Fourier transforming velocity auto-correlation function. Fig. 3.12 shows vDOS at 0 GPa for empty tubes (bottom) and tubes with 50 INT+7 IC argon atoms per tube. These results can be compared with inelastic neutron scattering experiments (104) that observed peaks around 60, 75, 100, and 175 meV in both SWCNT and graphite.



Figure 3.12: Calculated phonon density of states. From bottom to top: empty SWCNT bundle, SWCNT+Ar system with 50 INT+7 IC Ar atoms per tube

In the case of empty tubes we can find generally good agreement between experiment and calculations shown in Fig. 3.12. In particular, the positions of features in the experimental spectrum (104) are well reproduced. However, the relative intensities of the high energy bands (175 meV) are not well reproduced, and the peak at 155 meV which is predicted by Fig. 3.12 is not observed in experiments. These discrepancies in intensities might be due to multiphonon scattering and/or anharmonicity, both of which become important at high energy. From the figure we can also see that effect of argon is to broaden the low energy bands; the peaks close to 60, 75 and 100 meV. The peaks at 75 and 100 meV merged to become a broad peak centered around 85 meV. So far no experimental data is available to compare argon filled results.

3.3.5 Powder x-ray patterns

X-ray diffraction patterns (105) for the simulated structures were calculated using Eq. 3.5. Under ambient conditions, the observed diffraction patterns showed (100) as the dominant peak. The next most intense peak (at $\mathbf{q} \sim 1.0 \text{ Å}^{-1}$ for our system) was found to be almost one order of magnitude weaker. In a diamond-anvil cell, only the first diffraction peak was observed even in synchrotron-based experiments, which was attributed to the 2D hexagonal order of the tubes in the bundles. This peak disappears at the transition, which was interpreted as the loss of the translational order. The calculated diffraction profile in Fig. 3.13 for the equilibrated ambient nanotubes bundle shows features which are in a very good agreement with that of experimental patterns (106). The diffraction pattern of herringbone structure of empty SWCNTs [Fig. 3.13(b)] shows loss of intensity of (100) peak by several orders of magnitude consistent with the observations in the high-pressure experiments. Other structures of the linearized tubes shown in Fig. 3.2 also have equally weak-computed intensities, making them indistinguishable with reference to presently published x-ray results. However, as is evident from Fig. 3.2, the translation order is not completely lost in these structures and in fact, calculated patterns show subtle differences. So, in principle, more sensitive experiments might be able to identify the physically realized structure.

The loss of the diffracted intensity of the first peak with argon at INT sites¹ was not as dramatic as empty SWCNTs [Fig. 3.13(c)]. The remnant order after collapse is still

 $^{^1\}mathrm{Note}$ that diffraction pattern is from carbon alone: effect of argon is removed by setting argon form factors to zero



Figure 3.13: Calculated x-ray diffraction patterns of SWCNTs (a) empty cylindrical tubes at 0 GPa. Collapsed tubes at 10 GPa for (b) empty herringbone, (c) with INT Ar and (d) with INT+IC Ar.

appreciable to produce intense peaks. However, when argon was present at INT as well as IC sites the diffraction signal reduced substantially. Since the transition pressure in this case was higher, the inferred loss of 2D order in the filled SWCNTs would take place at higher pressures when compared to that for the empty tubes. These results provide a rational understanding of the results of Ref. (84) as those tubes were prepared by arc-discharge method and hence might have missing end caps and could be filled in a manner representative of the previous section.

We may also add that though for the present comparison, the form factors of Ar were set to zero, the inclusion of scattering from Ar shows the emergence of ordered structures of Ar in SWCNTs. Therefore, it may be interesting to carry out such experiments to determine the ordering of Ar atoms in SWCNTs under high pressures.

3.4 Summary

Our classical MD simulations showed that for SWCNTs at high pressures several competing kinetically separated arrangements of the collapsed tubes are possible. We also showed that compared to the empty tubes, nanotubes bundles filled with argon atoms behave quite differently under pressure. As the density of argon atoms at INT sites was increased beyond the critical value of 40 atoms/tube, the pressure of transformation increased. At the critical density, multiple volume changes were observed as argon atoms underwent ordering in stages. Interestingly, at low argon concentrations, the nanotubes were found to adopt a collapsed structure whereas at high concentrations they became faceted. Calculated diffraction patterns implied that for empty SWC-NTs the diffraction experiments would show loss of the first diffraction peak across the phase transition ≈ 2.4 GPa. In contrast, for Ar-filled SWCNTs, the pressure of transformation, as determined through the loss of diffraction signal, would be much higher. Calculated vibrational spectra showed good agreement with experimental data for empty tubes and, for argon filled tubes, broad peaks at lower energies. Ar atoms showed the emergence of order at high pressures and these results should encourage further experimental investigations.

Although we assumed the fluid particles to interact with nanotubes only through weak van der Waal's forces in our calculations, in practice, they can make chemical bonds with carbon and affect the properties of the tubes more dramatically. In fact, experiments observed subtle changes in Raman spectra when different pressure transmitting fluids were used. Hence it will be interesting to carry out electronic structure calculations to study the detailed interaction of PTM with nanotubes.

4

Crystallization of amorphous silicon

Crystallization of an amorphous phase is one of the most fundamental non-equilibrium phenomena universal to a variety of materials. It represents an important area of research not only because of its significance in understanding the underlying microscopic mechanisms that govern the process, but also for its practical importance in synthesizing advanced materials with novel properties. We studied the crystallization kinetics of amorphous silicon using classical molecular dynamics. Empirical potentials that take into account bond order effects without complex many body terms were used to model the system. Calculated activation energies for solid phase epitaxial growth (SPEG) of the cubic diamond phase exhibit a minimum at the pressure where densities of the amorphous and crystalline phases become equal. Calculations also suggested the growth rates of metallic β -Sn phase to be higher under pressure.

4.1 Background

Amorphous materials are non-crystalline solids, that lack the characteristic long-range order of crystals. It defines a broad class of disordered systems which may include gels, thin films and nanostructured materials. Glasses are special type of amorphous materials, which transform to a liquid upon heating through a characteristic glass transition temperature. They are thermodynamically metastable and will be crystallized into one or more metastable or stable polycrystalline phases upon thermal annealing or mechanical activation.

Factors that affect the process are studied intensively, because many technologically relevant materials like silicates, chalcogenides, elemental semiconductors etc. are good glass formers by virtue of their strongly directional covalent bonds. Silicon, which is used in a very broad spectrum of electronic applications, is a prototypical example of such a network forming covalent solid. When heated, amorphous silicon (a-Si) crystallizes by random nucleation and growth (RNG) resulting in a polycrystalline diamond-like structure with small grains of randomly oriented crystals that finds usage in making MOSFETS. However, when a crystalline substrate is available, the growth proceeds through layer-by-layer conversion of amorphous to crystalline phase, a process known as solid phase epitaxial growth (SPEG), which is widely used in industry to produce high quality semiconducting thin films for integrated circuits. In the present chapter, results of studies on crystallization process through SPEG is discussed. Our studies on RNG process shall be discussed in Chapter 8.

According to classical nucleation and growth theory (107, 108, 109) the emergence of ordered phase from a disordered phase is controlled by the competition between the free energy gain due to the transformation and the free energy loss associated with the formation of a crystal amorphous (c/a) interface. Many external and internal parameters affect the process, although their effect is often system dependant. In a-Si, extensive studies have shown that higher annealing temperatures (110), external force fields (111), presence of impurities (112, 113), ion beam irradiation (114) and applied stresses (115, 116) all enhance the process. Among these, pressure is an important thermodynamic parameter, the impact of which on the crystallization are not clearly understood.

Normally, crystallization is a prohibitively slow process at room temperatures as the necessary structural relaxation is inhibited by the high viscosity in the amorphous phase. Since external pressure increases density, one would intuitively expect the process to be further suppressed under pressure. Surprisingly, however, pressure above 15 GPa has been shown to induce crystallization at room temperature in amorphous silicon, although some disagreement about the resulting crystalline structure exists: earlier studies had reported the structure to be an octahedrally connected β -Sn phase (117, 118), while recently (14) it has been shown to be an eight coordinated primitive hexagonal (ph) structure (119). Pressure induces other structural changes within the amorphous phase: similar to glassy water (120), a-Si undergoes a pseudo-first-order polymorphous transition from a low density amorphous (LDA) phase to a high density amorphous (HDA) phase close to 14 GPa (121), which has been rationalized as the non-ergodic manifestation of a first-order transition between two liquid phases as in the supercooled regime of water (122, 123, 124).

A large body of literature exists for the crystallization of a-Si at ambient pressures. Many experiments (110) on SPEG of thin films of Si found the interface velocity (growth rate) to exhibit Arrhenius behavior with an activation energy of $E_a \approx 2.7$ eV. RNG process for silicon was found to have activation energies higher by about 1.3 eV and, as a consequence, to compete with SPEG above 1000 K. Theoretically, structure and growth of c/a interface was studied using tight binding (125) and several molecular dynamics (MD) simulations (126, 127). Simulations found the growth velocities to be similar along [100] and [110], but up to five times lower along the [111] direction (128). Two distinct temperature regions with different activation energies (129) were also found to exist.

In the only experimental study on crystallization of a-Si under pressure, using *insitu* time resolved visible interferometry Lu *et al.* measured the effect of hydrostatic pressure up to 5 GPa on the growth velocity of (100) planes of doped and undoped silicon and found it to increase exponentially with pressure (115). It was explained on the basis of migration of dangling bonds generated at the interface, reconstructing the random network into a crystalline network and was verified by subsequent computer simulations (130). However, the microscopic parameters that result in the enhanced crystallization of silicon under pressure were not clearly understood. Also, the effect of structural transition from a covalent to a metallic system on the crystallization phenomena was not studied.

4.2 Methods

Large simulation boxes containing thousands of atoms would be required for simulations containing amorphous structures, to faithfully represent the disordered nature of the phase and to avoid spurious boundary effects. Also, since SPEG is a slow process, long simulation times spanning several nanoseconds would be necessary. Classical molecular dynamics with empirical interaction potentials were ideally suited for this purpose and we carried out extensive simulations using the DL_POLY code (29). Velocity Verlet algorithm was employed to integrate the equations of motion with Berendsen thermostat and barostat keeping temperature and pressure constant. The system was equilibrated for several nanoseconds at each temperature/pressure using a fine timestep of 1 fs.

In simulations, the amorphous phase was generated by first melting the cd structure and quenching the liquid from 3500 K at a rate 1 K/ps and subsequently annealing at 1000 K for several million steps. LDA with a coordination defect density less than 5% was thus obtained. Following a similar procedure, when β -Sn was melted and quenched, it transformed to a high density amorphous (HDA), that has a higher coordination of ≈ 5.5 .

To simulate SPEG, an interface containing a-Si/(001)Si system had to be generated. For this, a well equilibrated crystalline phase (cd or β -Sn) consisting of about 1000 atoms and an amorphous phase consisting of about 983 atoms were joined together along *c*-axis. A lower number of atoms in the amorphous phase is due to the density difference between amorphous and crystalline silicon and the requirement of single cell dimension for both structures. At the boundary between the structures the atomic distances were fixed to be compatible with the average bond length of silicon in bulk. Periodic boundary conditions are employed in all three directions. Extensive annealing at 1000 K ensured that bonds are rebuilt and the interface is relax to a reasonable structure of low energy.

4.2.1 Tersoff potential

Interatomic potentials by Tersoff (131, 132) that incorporate bond order without complex many body terms are employed in the simulations. It is a special example of a density dependent potential, which has been designed to reproduce the properties of covalent bonding in systems containing carbon, silicon, germanium etc and alloys of these elements. A special feature of the potential is that it allows bond breaking and associated changes in hybridization. The energy is modeled in a pairwise form, where the attractive part depends on the local environment giving a many-body potential.

$$u_{ij} = f_C(R_{ij})[f_R(R_{ij}) - \gamma_{ij}f_A(R_{ij})]$$
(4.1)

with

$$f_R(R_{ij}) = A_{ij} \exp(-\lambda_{ij} R_{ij})$$

$$f_A(R_{ij}) = -B_{ij} \exp(-\mu_{ij} R_{ij})$$

$$f_C(R_{ij}) = \begin{cases} 1 & R_{ij} < R_{ij}^c \\ \frac{1}{2} + \frac{1}{2} \cos[\pi (R_{ij} - R_{ij}^c / S_{ij}^c - R_{ij}^c)] & R_{ij}^c < R_{ij} < S_{ij}^c \\ 0 & R_{ij} > S_{ij}^c \end{cases}$$

$$(4.2)$$

and

$$\gamma_{ij} = \chi_{ij} (1 + \beta_i^{n_i} \zeta_{ij}^{n_i})^{1/2n_i}$$

$$\zeta_{ij} = \sum_{k \neq i} f_C(R_{ij}) \omega_{ik} g(\theta_{ijk})$$

$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{[d_i^2 + (h_i - \cos \theta_{ijk})^2]}$$
(4.3)

Here *i*, *j* and *k* label the atoms in the system, R_{ij} is the length of the *ij* bond, and θ_{ijk} is the bond angle between the bonds *ij* and *ik*. Single subscripted parameters, such as λ_i and ζ_i , depend only on the type of atom. In the potential, γ_{ij} is the multi-body parameter for bond-formation energy and is affected by local atomic arrangement, especially, by the presence of other neighboring atoms (atom k), ζ is the effective coordination number and the function of the angle between R_{ij} and R_{ik} , $g(\theta_{ijk})$, is fitted to stabilize the tetrahedral structure. The potential parameters for the potential model for silicon are given in Table 4.1. They have been shown to reproduce the structure of low pressure crystalline and amorphous silicon as well as recrystallization process in a-Si quite well (126), although melting points are somewhat overestimated. We also found that Tersoff potentials were unable to stabilize the primitive hexagonal phase; probably because the potentials were parametrized for structures at low pressures (132). Hence,

in the following sections, we concentrate only on the two low pressure structures shown in Fig. 4.1

Table 4.1: Parameters for silicon to be used in Tersoff potential

	Si
A (eV)	$1.8308{ imes}10^3$
$B~(\mathrm{eV})$	4.7118×10^{2}
$\lambda (\text{\AA}^{-1})$	2.4799
μ (Å ⁻¹)	1.7322
$\beta ~(\mathrm{eV})$	1.5724×10^{-7}
n	7.8734×10^{-1}
c	1.0039×10^{5}
d	1.6217×10^{1}
h	-5.9825×10^{-1}
R^c (Å)	2.7
S^c (Å)	3.0

4.2.2 Structures of silicon

Crystalline silicon can exist in several structural polymorphs as summarized in Table 4.2. The well known semi-conducting form of silicon has cubic diamond (cd) structure with four coordinated silicon atoms. As the density increases under pressure, the coordination of the Si atoms also increases and becomes six in β -Sn structure. Pressure reduces the band gap in silicon and beyond β -Sn the structures are metallic. Single units cells of cd and β -Sn are shown in Fig 4.1

4.2.3 Thermodynamic analysis

Growth of the crystalline phase during SPEG, proceeds through the movement of c/a interface across the amorphous region. The velocity v(T, P) of growth has been shown to obey the Arrhenius behavior (116),

$$v(T,P) = v_0(P) \times \exp\left(-\frac{Q_n(P)}{k_{\rm B}T}\right)$$
(4.4)

where $v_0(P)$ is a temperature independent velocity prefactor, $Q_n(P) = E + PV$ is the activation free energy for the transport of an atom across the c/a interface and k_B is the Boltzmann constant.

Si-	Structure	Pressure (GPa)			Symmetry	Volume/atom
Ι	cubic diamond	0	-	12	Fd3m	20.02
II	β -Sn	11	-	14	$I4_1/amd$	13.93
XI	orthorhombic	13	-	16	Imma	13.6
V	primitive hexagonal	16	-	38	P6/mmm	12.0
VI	orthorhombic	38	-	45	Cmca	11.31
VII	hexagonal	42	-	78	$P6_3/mmc$	10.17
Х	cubic		>	79	Fm3m	9.32
III	cubic	0	-	9	Ia3	18.26
XII	rhombohedral	2	-	9	$R\bar{3}$	16.61
IV	wurtzite			0	$P6_3/mmc$	19.63

Table 4.2: Stable and metastable structures of silicon



Figure 4.1: Crystal structures of (a) cubic diamond and (b) β -Sn crystalline phases of silicon studied in this chapter. In cd phase, silicon forms a tetrahedral network while in β -Sn it forms an octahedral one

4.2.4 Radial distribution function

The radial distribution function $g_{\alpha\beta}(R)$, between two types of atoms α and β gives a measure of probability of finding an atom β at a distance of R from an atom α and is calculated by considering spherical shells of thickness ΔR around the atom α and then counting the number of atoms of type β in the shell. The corresponding probability is given by the relation (133),

$$\langle n_{\alpha}(R)n_{\beta}(R+\Delta R)\rangle = \rho_{\beta}4\pi R^2 g_{\alpha\beta}(R)\Delta R \tag{4.5}$$

where ρ_{β} is the density of species β and n_{β} is the probability amplitude. Experimental techniques using x-ray and neutron measure the structure factors that are calculated

by Fourier transforming the corresponding radial distribution function, as

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + 4\pi\rho (c_{\alpha}c_{\beta})^{1/2} \int_{0}^{R_{c}} dR R^{2} [g_{\alpha\beta}(R) - 1] \frac{\sin(kR)}{kR} W(R)$$
(4.6)

where $c_{\alpha} = N_{\alpha}/N$ is the concentration of α species. The window function $W(R) = \sin(\pi R/R_c)/(\pi R/R_c)$ is used to reduce termination effects and R_c is the cut-off radius generally chosen to be about half of the simulation cell. In the case of silicon, as it has a single species, $\alpha = \beta$.

4.3 Results

Since the results obtained from classical simulations depend crucially on the quality of potentials used, it is important to test them against known results. Hence, to check the validity of Tersoff potentials, we subjected various structures of silicon listed in Table 4.2 to increasing pressures using classical MD.



Figure 4.2: Equation of state for phases of silicon from classical MD. Arrows indicate phase transitions.

Results for structures that were stable under the potentials are summarized in Fig 4.2. It shows that PV behavior of the various polymorphs are reproduced well in simulations. For example, the densities of cd, β -Sn, *Imma*, LDA and HDA phases are

calculated correctly. At ambient pressure amorphous phase had lower density (LDA) than the crystalline phase; but also had a higher compressibility. As a consequence, density of LDA became equal to that of diamond close to 10 GPa (Fig. 4.2), which, as shown later has important effect on SPEG.

However, not all the structural transitions are reproduced. While we were able to observe the LDA-HDA transition above 15 GPa and β -Sn to *Imma* transition close to 17 GPa; cd to β -Sn transition was not observed. This indicates that an energy barrier exists between cd and β -Sn phases. It is well known that in the case of structures separated by an energy barrier, computer simulations may not be able to achieve fluctuations necessary to cause the transitions due to small simulation times.



Figure 4.3: Pair correlation functions and structure factors for low density (LDA) and high density (HDA) amorphous forms of silicon.

The disordered LDA phase forms a continuous random network of fourfold silicon atoms. The radial distribution functions in Fig 4.3 show that in the case of HDA, the second neighbor peak moves to lower distances making the structure more compact. Structure factors have lesser features at larger wavelengths, indicating that the structure at lower distances is more distorted.

Next, following the procedure elucidated in the previous section we prepared an a-Si/diamond structure at 0 GPa and a-Si/ β -Sn at 15 GPa. These were then equilibrated



Figure 4.4: Snapshots of the simulation cell containing c/a interface during SPEG. Each row shows the beginning (left), intermediate (middle) and final (right) stages of simulation. Structures of the top two rows (P=0 and P=10 GPa) represent crystallization to diamond while the bottom row (P=15 GPa) represent crystallization to β -Sn.

for about 1 ns at different pressures and were subjected to increasing temperatures allowing up to 5 ns at each temperature. The procedure of Mattoni and Colombo based on the calculation of a one dimensional structure factor (134) was used to get the position of the c/a interface during the transition (128). Structure of the simulation cell at various temperatures and pressures are given in Fig 4.4 which shows the amorphous, crystalline and the interface region clearly.

4.3.1 SPEG of cubic diamond phase

To understand the effect of pressure on the growth process better, we define a crystallization temperature (T_c^*) at which the simulation cell is completely transformed to a crystalline phase at the end of a 5 ns simulation or in other words, which corresponds to a growth velocity of 0.25 m/s.¹ Normalized T_c^* for crystallization to cd phase is plotted in Fig 4.5.



Figure 4.5: Normalized crystallization temperature T_c^* (at which growth velocity is 0.25 m/s) as a function of external pressure for SPEG of cd phase. Solid line is quadratic fit to simulation data.

Under pressure, T_c^* decreases rapidly indicating that pressure enhances SPEG of cd-Si in agreement with earlier studies (115, 130). Interestingly, close to 10 GPa, where

¹SPEG takes place at all temperatures, so the absolute value of T_c^* is not important.

amorphous and crystalline densities become equal, T_c^* reaches a minimum. The curve terminates close to a critical pressure $P_c = 15$ GPa, above which the crystalline cd phase does not grow. This pressure, in fact, marks significant phase changes in silicon. At this pressure, a-Si transforms from LDA to HDA with substantial volume change, as mentioned earlier. Also, from Table 4.2 cd is expected to transform to β -Sn close to this pressure, which means that cd is metastable above 15 GPa and its growth is not possible.



Figure 4.6: Arrhenius plots of the regrowth velocity as a function of temperature at various pressures for crystallization to cd structure. Symbols correspond to simulation data and the straight lines are fit to the data

The activation energies of growth, $Q_n(P)$, can be estimated by measuring the growth velocities v(T, P) at various temperatures and pressures and then fitting Eq. 4.4 to them. In Fig. 4.6 the logarithm of v(T, P) as a function of inverse of temperature has been plotted for the crystallization to cd phase. The straight lines fit using Eq 4.4 can be seen to exhibit the expected Arrhenius behavior. The values calculated from the slope, $Q_n(P)$, and intercept (velocity prefactor v_0) are given in Table 4.3. Calculated $Q_n(P)$ at ambient pressure is close to the experimentally reported value of 2.7 eV (110). While v_0 increases monotonously under pressure, $Q_n(P)$ exhibits a minimum at 10 GPa similar to T_c^* .

Pressure (GPa)	$Q_n \ (eV)$	$v_0 \ ({\rm m/s} \ {\times} 10^5)$
0	2.33	4.88
5	1.80	7.01
10	1.61	10.24
13	1.72	18.67

Table 4.3: Activation free energy and velocity prefactor at different pressures calculatedfrom Arrhenius fit to simulation data



Figure 4.7: Atomic volumes distribution (symbols) in a simulation cell containing c/a interface at 0 GPa. Solid lines are Gaussian fit corresponding to crystalline and amorphous phases

To understand the structural changes that led to the observed variation in activation energies, we looked at the atomic volume distribution in a cell containing both crystalline and amorphous phases during SPE growth. Atomic volumes are calculated by estimating the Voronoi polyhedra from nearest neighbor distances. The distribution can be seen to be (Fig 4.7) made up of a convolution of two peaks, where the narrower peak corresponds to the ordered cd phase and the broader peak corresponds to the disordered LDA. Width of the distribution, known as the regularity factor (135), is a measure of the distortion in the structure. Figure also shows that the peak position indicating the average atomic volume shifts to higher values in amorphous silicon, in agreement with predictions.

The variation of atomic volumes and coordination along the length of the simulation

cell at different pressures are shown in Fig 4.8. Under ambient conditions, in the amorphous region, the atomic volumes are more spread out and their average higher than the crystalline region (center of simulation box) owing to the lower density and higher distortion in a-Si. The thickness of the c/a interface at 0 GPa is close to 6Å, as can be seen in Fig 4.8, in good agreement with earlier estimates (125). At 10 GPa, although amorphous and crystalline parts have similar density ($\Delta V = 0$), the former has a higher coordination of 4.3. The distribution of atomic volumes at this pressure is somewhat narrower, pointing to an increased regularity factor which is a consequence of collapse of voids that result in better packing.



Figure 4.8: Voronoi volumes and coordination of silicon at 0 GPa and 10 GPa with amorphous-diamond interface (note that simulation box has been shifted to center the crystalline region). Red lines are the average of atomic volumes and the lower panel represent Si coordination across the unit cell length.

As LDA has a lower density, the transformation causes a negative volume change $(\Delta V = V^c - V^a)$ during the amorphous to crystalline transition, which favors crystallization under pressure. On the other hand, as pressure is raised, the coordination of silicon in the amorphous region increases (Fig 4.8) and the difference in coordination $(\Delta C = C^c - C^a)$ across the interface hinders growth. Our simulations suggest that at lower pressures, crystallization is dominated by ΔV while at higher pressures ΔC dominates and the competition results in the minimum. Interestingly, an analogous behavior has been observed in the melting curve of ice II (among many other systems) which exhibits maximum under pressure (136). Water has lower density and higher compressibility than ice II at lower pressures and at the melting maximum, density of the two phases become equal. Thus we find a common feature in two apparently distinct phenomena: at crystallization minimum as well as melting maximum, the densities of participating phases become equal.

4.3.2 SPEG of β -Sn phase



Figure 4.9: Crystallization temperature (normalized by T_c^* of cd phase at 0 GPa) as a function of external pressure for SPEG of β -Sn silicon. Solid line is quadratic fit to simulation data.

 T_c^* of β -Sn structured silicon, normalized with that of cd phase at P = 0 is shown in Fig 4.9. Comparing with Fig 4.5, we can see that T_c^* exhibits a qualitatively similar behavior as that of cd phase, with the minimum close to 25 GPa. The important feature of Fig 4.9 is the lower transition temperatures of β -Sn which indicates lower activation energies in this phase. Growth of crystalline phase during SPEG requires substantial rearrangement of bonds in the amorphous structure. The covalent bonds in LDA are strong and highly directional and their dissociations cost energy. On the other hand, the metallic bonds in HDA are malleable and can be rearranged easily. Hence, in the transition from semiconducting LDA to metallic HDA, the lost directionality of silicon bonds facilitate growth of the crystalline phase. In fact, in the case of hydrogenated silicon, it has been observed that presence of interstitial hydrogen weakens Si bonds which substantially lowers crystallization temperature (113).

At 15 GPa, the crystalline phase is six coordinated and the amorphous phase is 5.5 coordinated (Fig. 4.10). The amorphous side boundary is less discernible at this pressure, with the interface gradually changing to HDA. Despite large difference in volume and coordination between the crystalline and amorphous structures, the activation energy is much smaller due to the metallic nature of the two structures.



Figure 4.10: Voronoi volumes and coordination of silicon at 15 GPa with a morphous β -Sn interface.

4.4 Summary

Our classical calculations of crystallization process in amorphous silicon predicted many interesting features. For the growth of cd phase, activation energy for growth (and hence respective crystallization temperatures) was shown to exhibit a minimum close to 10 GPa at which densities of amorphous and crystalline phases also become equal. Crystallization temperature for β -Sn phase was found to be much lower than that of diamond phase under pressure, explained to be a consequence of loss of directionality of covalent bonds upon the phase transition.

Calculations presented in this chapter were concerned with the growth of crystalline silicon phase through SPEG. The second mechanism of growth, namely, random nucleation and growth (RNG) is important when a crystalline substrate is not available. Study of RNG can provide valuable insight into many experimental observations, including the pressure induced crystallization (23) observed in nano and bulk amorphous silicon. However, since the formation of nuclei in the amorphous matrix is a thermally activated stochastic process, achieving RNG in computer simulations would be a formidable task, requiring impractically long simulation times. Therefore, we adopted a hybrid approach to RNG in silicon; combining classical, first principles and model calculations, results of which are presented in Chapter 8.

4. CRYSTALLIZATION OF AMORPHOUS SILICON

Part III

Quantum Methods

$\mathbf{5}$

Polymorphism in crystalline structures

Packing polymorphism is the ability of materials have an ability to exist in more than one ordered form with the same composition. Reversible structural transitions can be observed when free energies of the various polymorphs cross each other before the melting point of the solid. Electronic structure calculations, because they can estimate accurate energies, are ideally suited to study these transitions. Studies on three typical cases are presented in this chapter: formation (zinc-blende CdS), structural phase transition $(YCrO_4)$ and dissociation $(La_2Hf_2O_7)$ of crystalline solids. In the case of CdS nanoparticles, it was found that by carefully choosing the capping molecules used during the growth process, the otherwise metastable zinc-blende structured nano particles could be synthesized. Detailed investigation of the binding process of the organic molecules (cis-oleic acid and trioctylphosphine) on various surfaces of CdS nanocrystals revealed that adsorption energies play a crucial role in determining the crystal structure. In YCrO₄, calculations established the existence of an intermediate monoclinic phase during the zircon \rightarrow scheelite transition, showing that it is not a one step process as thought before. The pyrochlore structured $La_2Hf_2O_7$ was found to undergo dissociation under pressure to its constituent oxides, facilitated by a large volume change during the transition.

5.1 Background

Crystals are ordered structures, in which a basic building unit (can be an atom, molecule or polyhedral unit) is repeated in all directions to generate a periodic structure. A particular structure or polymorph can be thought of as forming a lower energy pocket on free energy hypersurface in the configurational space of the material. Many such pockets may exist and the stable structure of a material will correspond to the lowest energy one. To change from one structure to another, the system needs to overcome an energy barrier equal to the height of the pocket where it is currently residing. Since the Gibb's free energy (G = U + PV - TS) is a function of pressure P and temperature T, under changing external parameters, the energy landscape will also change, bringing the barriers within thermal energy and resulting in structural transformations.

5.1.1 Formation of zinc-blende CdS

As a crystal grows from a liquid phase, it explores the configuration space to find the lowest energy structure. However, in many cases, chemical and physical environment can be tweaked to generate a particular structure, shape or size. For example, in colloidal chemistry techniques, which is used to grow inorganic nanocrystals in solution, by suitably controlling the growth environments, one can synthesize high quality semiconducting nanocrystals (quantum dots) in controlled shapes and sizes. Nanocrystals are usually prepared in the presence of suitable organic molecules acting as capping agents, which typically consist of a polar headgroup and of one or more hydrocarbon chains, the latter forming the hydrophobic part. During nanocrystal synthesis the headgroup can adsorb to favorable surfaces on the nanocrystal and thus affect the growth process. Extensive studies revealed that optical properties of these dots depended critically on their size and shape which led to their wide adoption in various industrial applications like, biological imaging (11), solar cells (137) and lasers (138). Modification of chemistry in terms of monomer and ligand concentrations (139, 140) led to the synthesis of nanocrystals in more exotic shapes, such as rods and multipods which further helped in tuning their properties.

It has been shown that in addition to size and shape, the structure of the nano particles also critically affects their properties (141, 142). In fact, CdS can exist either in wurtzite (W) or zinc-blende (ZB) structures in both bulk and nano crystalline
form (143, 144) and it was found that band gap and impurity doping levels crucially depended on the particular crystal structure of the host. However, the dependence of nanomaterial properties on crystal structure was relatively less explored and their applicability was restricted, mainly because of the inability in controlling the crystal structure during synthesis until recently.

In the past, various authors had suggested different parameters to decide the crystal structure of nano-crystalline CdS and its close neighbor CdSe. For example, some considered lower reaction temperatures (below 240° C) to be the primary cause for stabilizing the metastable ZB structure (145, 146). Gautham *et al* (147) suggested that ZB nano-crystals of CdS may be realized only under high pressure. Another suggestion was that small particle sizes (≈ 4.5 nm) favor ZB structure (148). The solvent used in the growth process was also suspected to play a crucial role (149); where the non-coordinating solvents believed to favor ZB structure.

Density functional theory based calculations were successfully used to study the effect of organic ligand binding on the shape of wurtzite CdSe nanoparticles (150) and it was found from the calculated relative binding strengths of ligands to different facets control the relative growth rates of different facets. Calculations were also used to study the relaxations and reconstructions (151) of several wurtzite CdSe surfaces and subsequent organic ligand binding on these surfaces (152). Molecular dynamics simulations on wurtzite and zinc-blende CdS nanoparticles found that small upcapped particles are not nanocrystalline, but are amorphous with ordered surfaces (153).

Recently, through careful experiments Nag *et al.* found that in contrast to the earlier reports, both crystallographic phases of CdS can be stabilized in the nanometer size regime by a proper choice of the capping ligand (12). The key to their success was the choice of the anionic reaction mixture: when sulphur was dissolved in 1-octadecene (ODE) and allowed to react with Cd solution in cis-oleic acid (cis-OA), CdS particles in the usual W structure were formed (method I). However, when sulphur dissolved in organic precursor trioctylphosphine (TOP) was used instead (method II), it lead to the ZB structured CdS particles beyond a critical concentration (12). To understand how different capping molecules affect the crystal structure of the CdS nanoparticles, we carried out first principles total energy calculations.

5.1.2 Phase transition in YCrO₄

Structural phase transitions in crystals can be either *displacive* or reconstructive depending on how the transformation is brought about. In the former case, the initial structure transforms to the final structure by a correlated motion of the atoms and, in latter, a new structure grows out of the initial one through substantial rearrangement of atoms. Displacive transformation is the dominant mechanism under pressure, because it involves relatively less bond breaking and atomic displacements.

Zircon (ZrSiO₄) is an important mineral found in the earth's crust, mainly in igneous rocks and sediments (154). It is known to undergo a first order crystalline phase transition from the zircon (space group $I4_1/amd$) to the scheelite (space group $I4_1/a$) form at ~ 23 GPa. Several iso-structural ABO₄ type compounds, such as the vanadates, chromates, germanates, also undergo the same high pressure phase transition, displaying a typical density increase of ~ 10% (155, 156, 157). Static as well as shock experiments on ZrSiO₄ support the displacive nature of this phase transformation (158).

Several attempts were made to explain the nature of this phase transformation. Kusaba *et al.* suggested that zircon to scheelite transformation might be brought about by shear deformations (159). However, based on the observations of abrupt changes in frequencies of the internal Raman modes across this transition, others (156) argued that the transformation path involve substantial rearrangement of the cations and the anions, both in length and angle. Subsequent theoretical *ab-initio* and shell model calculations on $ZrSiO_4$ showed absence of any dynamical structural instability upto ~ 70 GPa from which they concluded that hydrostatic compression alone could not be responsible for this phase transition (160). Energy barrier heights obtained through first principles calculations by Florez *et al.*, indicated that transient states between zircon and scheelite phases were likely monoclinic structures (161).

In high pressure x-ray diffraction and Raman spectroscopic measurements, Mishra *et al.* observed that nano-crystalline YCrO₄ transformed from zircon to scheelite structure close to 7 GPa (20). More interestingly, some of the diffraction peaks just before the transformation exhibited an anomalous increase in full width half maximum (FWHM), which was indicative of a new structure; possibly as a result of a slight distortion of the parent phase. To understand the nature of the transformation better, first principles calculations were carried out.

5.1.3 Decomposition of La₂Hf₂O₇

Beyond the stability regime of a polymorph, if the energy barriers are too high or if transformation paths to stable phases do not exist, crystalline structures may undergo amorphization or dissociation (162). Solid state decomposition of crystalline structures into dense-packed daughter phases is common at high temperatures. However, pressure induced dissociation is unusual, as the large atomic diffusion necessary for growth of daughter phases are hindered under pressure. Consequently, at ambient temperature, these compounds invariably exhibit pressure-induced-amorphization (PIA) when decomposition is kinetically hindered but energetically favored (163).

 $A_2B_2O_7$ compounds having pyrochlore structure, due to the structural compatibility with several radionuclides, were perceived as materials for encapsulation of actinide rich nuclear waste (164, 165). The pyrochlore structure belongs to $Fd\bar{3}m$ space group (fcc) with A^{3+} cations occupying the 16d, B^{4+} atoms at 16c and oxygen occupying 48f and 8b positions respectively. The structure can be viewed as made of eightfold and sixfold coordination polyhedra of oxygen atoms around A and B cations and these polyhedra change shape under pressure by changing the only free parameter, which is x coordinate of 48f oxygen atoms.

It was observed that substitution of the B cation with a larger ion progressively increases disorder (166). It is well known that in many compounds, particularly having polyhedral network structures, amorphization can also be induced by subjecting the compounds to high pressure. The onset pressure is determined by the limiting distances of non-bonded atoms (167). In some such cases, the inaccessible high pressure equilibrium phases could be the products of dissociation (162).

X-ray diffraction experiments by Garg *et al.* showed that close to 18 GPa, several new peaks appeared, which could not be assigned to possible structure of $La_2Hf_2O_7$ obtained through subgroup analysis of the parent phase (21). Their studies seemed to indicate that the diffraction pattern could be due to a mixture of oxides. To test this prediction, energies of $La_2Hf_2O_7$, La_2O_3 and HfO_2 were calculated as a function of pressure using first principles methods.

5.2 Methods

All first-principles calculations were performed with the DFT code Vienna Ab-initio Simulation Package (70, 71), employing PAW method to describe atomic core electrons and a plane wave basis set with a kinetic energy cutoff of 500 eV to expand the Kohn-Sham electronic states. We applied the generalized gradient approximation to the exchange correlation functional with Perdue–Burke–Ernzerhof parametrization (168, 169). Sampling of the reciprocal space was done using Monkhorst-Pack mesh. Since finer grids were required for systems that have smaller unit cells in direct space, we employed Γ -point only sampling for nanoparticles, a grid of $4 \times 4 \times 1$ for surfaces and a fine mesh of $5 \times 5 \times 5$ for crystalline structures. The valence electrons explicitly treated in the PAW potentials are; Cd: $5s^24d^{10}$, S: $3s^23p^4$, Y: $4s^24p^65s^24d^1$, Cr: $3p^63d^54s^1$, O: $2s^22p^4$, La: $5s^25p^65d^16s^2$ and Hf: $5p^65d^26s^2$.

5.2.1 Adsorption energy of molecules on CdS surfaces

The binding energy calculations were done in two steps. First we estimated the probable binding sites of the molecules by equilibrating a system in which molecules were attached to infinite surfaces. The surfaces were described by periodically repeated slabs perpendicular to z-axis: continuous along x & y directions and separated by a vacuum layer along the z-direction as shown in Fig. 5.1. Symmetric surfaces with five or more bulk layers of Cd or S were constructed by slicing the fully relaxed bulk unit cell in appropriate directions. The slabs were then reoriented to be perpendicular to the z-axis and a vacuum layer of 11 Å or more was added to avoid interaction of adjacent slabs.

To verify that the neighboring slabs were sufficiently isolated, we increased vacuum thickness, surface size and number of bilayers in all the cases and the change in total energy was less than 0.01 eV. The top surface layers were allowed to fully relax while two bottom layers were constrained to be fixed to their bulk positions. In addition to relaxation, some of the surfaces were allowed to reconstruct; by generating surface adatom or vacancy which further reduces the energies. The reconstruction energies were calculated as:

$$\Delta E_{rec} = E_{rec}^{slab} - E_{rel}^{slab} \pm E_{Cd,S} \tag{5.1}$$



Figure 5.1: (a) Zinc-blende unit cell marking the (111) plane (b) smallest surface unit cell preserving the symmetry of the structure is cut with three CdS layers (c) the structure after reorientation to z-axis and a vacuum layer is added to remove interaction with periodic images.

where E_{rec}^{slab} is the energy of the slab after reconstruction through suitable addition or subtraction of elements, E_{rel}^{slab} is the energy of a well relaxed slab before reconstruction and $E_{Cd,S}$ is the energy of a Cd or S atom in vacuum and positive or negative sign means vacancy or adatom reconstruction respectively. Larger supercells were constructed, where necessary, to accommodate the capping molecules. Starting configurations were selected by attaching the molecules to all the probable adsorption sites. The system was then annealed using molecular dynamics for about 200 fs with a time step of 0.5 fs to allow the system to reach the lowest energy configurations.

Next, we studied adsorption of molecules on nanoparticles of CdS. For this, roughly spherical nanoparticles of ~ 15 Å size were constructed from bulk W and ZB structures of CdS taking care to minimize the dangling bonds. The nano-particles had composition Cd₄₂S₄₅ for W structure and Cd₄₃S₄₄ for ZB structure. Periodic supercells were chosen with at least 10 Å between replicas to reduce spurious image interactions.

The binding energies (BE) of the adsorbate (capping ligands) on various surfaces are calculated by subtracting the energy of the combined surface+molecule system (E^{surf+A}) from the sum of energies of the adsorbate (E^A) and surface (E^{surf}) system defined as

$$BE = E^{surf} + E^A - E^{surf+A}$$

$$(5.2)$$

5.2.2 Equation of state

For the crystalline phases YCrO₄ and La₂Hf₂O₇, the lattice constants and fractional coordinates as determined from the Rietveld analysis of experimental data were used as the starting structures for the simulations. Structural optimizations were continued until the forces on the atoms had converged to less than 1 meV/Å and the pressure on the cell had minimized within the constraint of constant volume. Our calculated lattice constants for YCrO₄ and La₂Hf₂O₇ are 7.20 Å and 10.69 Å, which are close to the experimental values of 7.07 Å and 10.78 Å respectively. For analysis, the computed energy volume data was fitted using Murnaghan equation of state (170),

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1},$$
(5.3)

where E_0 is the energy at the minimum volume V_0 when external pressure on the system is zero. B_0 and B'_0 are the bulk modulus and pressure derivative of bulk modulus respectively.

5.3 Results

5.3.1 Formation of zinc-blende CdS

The lattice parameter for the wurtzite (zinc-blende) structure of CdS was calculated to be 4.20 Å (5.81 Å) which is within 2.2% (1.5%) of the experimental value. Our calculations on bulk CdS, summarised in Table 5.1 show that after complete ionic relaxation the difference in total energy/atom between W and ZB structures of bulk CdS is small (-3.07 meV) which is in agreement with earlier calculations.

 Table 5.1: Total Energies and volumes of bulk CdS structures

	W	ZB	Difference
Total E (eV/atom)	-6.3195	$-6.3164 \\ 52.45$	-0.003
Volume ($Å^3$ /atom)	52.43		-0.02

The various surfaces of W and ZB CdS considered in our calculations are given in Table 5.2 along with corresponding relaxation and reconstruction energies. Surfaces with Miller Bravais indices (0001) for W and (111) for ZB are asymmetric and after each

Ţ	Wurtzite		Zi	nc-blend	e
Surface	ΔE_{rel}	ΔE_{rec}	Surface	ΔE_{rel}	ΔE_{rec}
$11\overline{2}0$	-3.191	-	001	-0.171	-
$10\overline{1}0$	-3.338	-	110	-2.379	-
0001A	-0.886	0.084	111A	-0.259	-0.491
0001B	-0.089	-0.194	111B	-0.176	-2.326
$000\bar{1}A$	-1.642	0.475	$\bar{1}\bar{1}\bar{1}A$	-1.373	0.1564
$000\bar{1}B$	-0.079	2.976	$\bar{1}\bar{1}\bar{1}B$	-0.097	3.0145

Table 5.2: Relaxation and reconstruction energies for surfaces of W and ZB structures.

monolayer of growth they are either Cd terminated (represented by A in the surface name) or S terminated (represented by B). Large values of relaxation energies for some cases in Table 5.2 means that the bulk terminated surfaces were highly strained and rearranged their atoms to reduce strain. For excess Cd or S surfaces, further reduction in energies can be achieved by either losing a surface atom (vacancy) or allowing an excess atom (addatom); a process known as reconstruction. We considered vacancy reconstructions for W(0001) and ZB(111) surfaces and found that vacancies help reduce energies of ZB(111)A,B and W(0001)A,B surfaces.¹ These results are consistent with earlier calculations (151) for CdSe on W surfaces that found (1010) to be most stable surface and reconstructions on (0001) surfaces to be less favorable.



Figure 5.2: Structures of the truncated molecules, (a) cis-oleic acid (cis-OA) and (b) trioctylphosphine (TOP). Small white spheres are hydrogens, reds are oxygens, pink is phosphorus and the rest are carbon

¹The small positive value of ΔE_{rec} for W(0001)A surface is because during relaxation the surface automatically ejected a Cd atom and as a consequence the relaxation energy already contain the effect of reconstruction

5. POLYMORPHISM IN CRYSTALLINE STRUCTURES

Next, we considered the interaction of the capping molecule with the various surface terminations. As we discussed earlier, TOP molecules present in method II for the synthesis and cis-OA molecules present in the Cd^{2+} precursor solution in both methods act as effective capping agents.¹ We have calculated the binding energy of both these ligands with the various surface terminations. In the case of TOP, the phosphorous with lone pair of electrons is the "functional group" and can interact with the electron deficient sites on the surface. Similarly, the -COO group of cis-OA molecule after removal of a hydrogen can bind with electron rich sites. To reduce the computational cost of calculating the ligand binding energies, in our simulations we modeled the molecules by retaining the functional group and truncating the length of the alkene chains by an ethyl group (-CH₂-CH₃), resulting in (CH₃-CH₂)₃P for TOP and (CH₃-CH₂)COO for cis-OA (see Fig. 5.2), which are found sufficient to grasp the essential features of adsorption. Several possible binding sites of the two model ligands on the relaxed and reconstructed surfaces of CdS are considered, however only the most energetically stable configurations are explored in detail.



Figure 5.3: Reconstructed surfaces of (a) zinc-blende and (b) wurtzite viewed along *a*direction. Large red spheres represent Cd atoms while smaller green are S atoms. Filled and empty arrows show the site at which TOP and cis-OA adsorb respectively. Coordination numbers of the surface atoms are marked in the figure.

Fig. 5.3 shows some of the reconstructed ZB and W surfaces as well as the lowest energy binding sites for the TOP and cis-OA molecules.² In bulk zinc-blende and wurtzite structure Cd and S are tetrahedrally co-ordinated as a result Cd (S) has four

¹Note that ODE, which is a noncoordinating solvent does not interfere with the growth process.

²Upon molecular binding the surface relaxes further, which is not shown here

S (Cd) atoms as neighbors. On the surface, due to the broken periodicity the coordination number of Cd and S are reduced from the ideal bulk structure giving rise to unsaturated dangling bonds $(4 - z_i)$ where z_i is the local co-ordination of either Cd or S as shown in Fig. 5.3. The TOP molecule with P as the functional group binds with the unsaturated S sites while the oxygen atoms in the cis-OA molecules are attracted to the electron rich Cd sites on the surface. Calculated binding energies with the various surface terminations as displayed in Table 5.3 show that among all the surfaces studied, the molecules bind strongly to (0001) and (1010) surfaces of W and (001) and (111) surfaces of ZB.

Table 5.3: Binding energy (in eV) for the molecules TOP and cis-OA on various surfaces of CdS in ZB and W structures

	Surface	TOP	cis-OA
	001	3.71	0.13
7D	111A	0.48	1.53
D	111B	1.32	3.15
	110	0.19	0.24
	$10\bar{1}0$	0.44	2.66
117	$11\overline{2}0$	0.47	0.71
vv	0001A	0.48	0.48
	0001B	3.13	3.73

In order to explore the adsorption process in more detail, we constructed nanoparticles of CdS as shown in Fig. 5.4. These particles had a diameter of approximately 1.5 nm and were relaxed from bulk geometry. As expected (171), these surface relaxations lead to a large intrinsic band gap in these particles.

In Fig. 5.5 we show the binding of the molecules on the (0001) (1010) and (001)and (111) facets of W and ZB nanoparticles. As can be seen from the figure, both oxygen atoms in the cis-OA molecule interact with the Cd sites on the surface while TOP interacts strongly with S on the surface. In Fig. 5.6 we have shown the binding energies of the cis-OA and TOP molecules for these surfaces. Our calculations clearly reveal that TOP prefers ZB crystal structure. The binding of TOP is most favorable for the (001) facets of the ZB CdS NCs. On the other hand, cis-OA favor (1010) surface of W structure. From Fig. 5.6 we gather that since the binding energy of cis-OA, which is present in both the methods, is higher on W surfaces, it favors W structure. However



Figure 5.4: Ideal and relaxed structures of wurtzite and zinc-blende nanoparticles of CdS. Large red spheres are Cd and small green ones are S.

the binding energy of the TOP molecule is found to be strongest for the ZB surface. As the total energy of a nanoparticle is the sum of energy of its core plus the surface energy, ZB particle capped with TOP can have overall energy lower than that of a W particle. As a consequence when TOP is used as a capping agent in the synthesis of method II, it can stabilize the otherwise metastable zinc-blende phase.



Figure 5.5: Calculated structures of organic ligand binding on (0001), $(10\overline{1}0)$, (001) and (111) facets of CdS nanoparticles.

The binding is more effective and therefore energetically more favorable if the capping ligands are able to saturate the dangling bonds of the exposed surface facets of the CdS nanocluster. In order to understand this mechanism in detail, we have shown



Figure 5.6: Binding energies of cis-OA and TOP on various nanocrystal surfaces of ZB and W CdS. Cis-OA prefer the stable W structure whereas TOP prefer the metastable ZB surface.

the charge density plots in Fig. 5.7. When the TOP molecule interacts with the (0001) facet of CdS nanocrystals it cannot saturate all the three S dangling bonds. Further, the topology of the TOP molecule only allows it to bind the W surface from directly above it and the P-S-Cd bond angle (175°) is large in comparison to Cd-S-Cd bond angle (109°) in bulk CdS thereby adding to the weakening of the binding of the ligand. However TOP molecule on the (001) ZB surface is able to saturate both the S dangling bonds and interestingly P-S-Cd bond angle (124°) is very close to that of bulk CdS. A similar mechanism also holds good of cis-OA.

Thus, our calculations clearly demonstrated the important role of the ligands in stabilizing a particular crystal structure of CdS nano-particles.

5.3.2 Phase transitions in YCrO₄

Although experiments were carried out on nanocrystalline $YCrO_4$, the observed phase transition may not be unique to the nano structure. Hence, as a first step, we computed total energies of bulk $YCrO_4$. Complete ionic relaxation was carried out on zircon and monoclinic structures at various volumes in anti-ferromagnetic spin arrangement (i.e., the magnetic moments of two chromium atoms in the primitive cell point in opposite directions) to find the lowest energy configuration. For this, symmetry and



Figure 5.7: Charge density plots for the adsorption of cis-OA and TOP on the surfaces wurtzite and zinc-blende nanoparticles.

volume of the simulation box was fixed and the ionic degrees of freedom were allowed to relax to the minimum energy configurations. To determine the relative stability of the monoclinic phase compared to the zircon phase these calculations were repeated at different volumes.

The bulk modulus of zircon structured YCrO₄ determined from these calculations was found to be 121 GPa, in agreement with the earlier published results (172) and close to the experimentally determined value of 103 GPa.¹ The computed total energies in Fig 5.8 show that the monoclinic phase is very close in energy to the zircon phase. In fact, our calculations showed that the monoclinic phase was consequence of very small distortion of the zircon phase: the angle γ changes from 90° to 90.4°. To see the energy variation clearly, we have plotted the difference in energies $E_z - E_m$ and $E_z - E_s$ (where E_z , E_m and E_s are energies of zircon, monoclinic and scheelite phases respectively) in Fig. 5.9. We can see that energy of the monoclinic phase, which is initially (at lower pressures and higher volumes) higher, becomes lower than that of

¹The difference in bulk modulus could be because the experimental bulk modulus was determined for nano $YCrO_4$ whereas the theoretical bulk modulus was determined for bulk $YCrO_4$.



Figure 5.8: Variation in computed total energy per formula unit (f.u.) with volume/f.u. for zircon, scheelite, and monoclinic phases of yttrium chromate.

zircon below 78 Å³. The dotted line corresponding to the energy of scheelite phase soon takes over; marking a small stability region for monoclinic phase between 75–78 Å³. Thus, our theoretical studies confirmed that the zircon to scheelite phase transition in these compounds might not be a one step process. Rather, we showed it to proceed via a symmetry descent and then a symmetry ascent, with a small window of stability for the intermediate phase.

5.3.3 Decomposition of $La_2Hf_2O_7$

To understand the experimentally observed high pressure changes in La₂Hf₂O₇, the total energy E(V) was calculated as a function of the volume, for the parent monoclinic (La₂Hf₂O₇) and daughter (La₂O₃ and HfO₂) phases. At each volume, the positional coordinates were optimized by structure relaxation and the structure with the lowest energy was obtained. At nonzero temperatures the stable structure corresponds to a minimum in Gibbs free energy G = E + PV - TS. However, since these calculations were carried out at T = 0 K the structural stability is related to enthalpy. For comparison with total energy of La₂Hf₂O₇, the total energy and volume of the mixture of products of dissociation (i.e., La₂O₃+HfO₂) is calculated as $A_t = 2 \times A(HfO_2) + A(La_2O_3)$ where A is energy E or volume V.



Figure 5.9: Energy difference $(E_z - E_m)$ and $E_z - E_s)$ per f.u. versus volume/f.u. Crystal structures of zircon and sheelite phases are shown in the inset



Figure 5.10: Calculated total energy versus volume per f.u. for lanthanum hafnate and its disassociation products. The structures are shown in the inset

Fig. 5.10 shows the total energy E_t as a function of volume (per formula unit of lanthanum hafnate) in the composite and disassociated phases. The solid and dashed lines are fits of the computed data of parent and daughter states using Eq. 5.3. The fit gives $B_0 = 165$ GPa, which is reasonably close to the experimental value of 147 GPa. The sum of total energies of the disassociated products at zero pressure is higher than that of lanthanum hafnate by 175 meV. However, below a volume of 137Å³ the total energy of the disassociated phase is always lower than that of the parent phase.



Figure 5.11: Calculated enthalpy versus pressure for lanthanum hafnate and its disassociation products.

The calculated enthalpy as a function of pressure is given in Fig. 5.11 which shows that beyond ~ 20 GPa the disassociation products are more stable than lanthanum hafnate. Thus the results of our first principles calculations strongly support the conclusions deduced from our experimental measurements.

5.4 Summary

Our detailed theoretical calculations revealed that, in the case of CdS, suitable choice of the ligands was important in thermodynamically stabilizing the rare zinc-blende form, confirming experimental observations. The adsorption energies were found to play the key role in stabilizing the unusual ZB phase. Hence, a suitably chosen surface capping molecules can act as a control parameter for crystal structure engineering of nanoparticles.

In the case of YCrO₄, the monoclinic phase has been shown to be a lower energy intermediate phase. Our calculations suggested that the observation of monoclinic phase in nano-crystalline samples may purely be incidental, as bulk YCrO₄ is also predicted to exhibit a similar behavior. Hence these results should encourage more careful experiments on bulk and nano iso-structural compounds to ascertain (a) if nano size plays a role in the observability of the monoclinic phase (b) if this path is specific to chromates.

Our first principles calculations showed that lanthanum hafnate disassociates into a mixture of HfO_2 and La_2O_3 beyond 20 GPa. The results were interesting in the sense that this was the first time that a pyrochlore had been shown to decompose under high pressures. Since lanthanum hafnate is one of potential compounds for use in the nuclear waste disposal, (due to the presence of Hf as a neutron absorber), the results might have implications on its utility in this context.

Even though our calculations showed that energetics drive the crystalline transformations in solids, dynamics may also play an important role. For example, in the case of CdS nanoparticles, dynamics in the growth environment may also affect the structure. As shown in chapter 8, QM/MM calculations can include the effect of solvent on the binding process of the organic ligand on the nanoparticle and provide the complete picture. An important limitation of the electronic structure calculations presented in this chapter is that they rely on experimental knowledge of the structures involved. Genetic algorithm based structure predicting tools (173), can start from just the composition and approximate volumes to find the lowest energy structures. They can provide a complete understanding of the phase diagram of crystals with least prior knowledge.

Origin of ferroelectric polarization in $MnWO_4$

Multifunctional materials have gained substantial attention in recent years due to the simultaneous existence and strong interaction between multiple functional properties. Multiferroics, where spontaneous magnetic and dipolar orders coexist, combine rich and fascinating physics with novel technological applications. In manganese tungstate (MnWO₄), ferroelectricity arises as a secondary effect and is coupled with magnetic ordering. We studied the origin of magnetism and ferroelectricity in MnWO₄ using *ab-initio* electronic structure calculations. Our calculations correctly reproduced the magnetic ground state and the calculated ferroelectric polarization was in good agreement with experiments. Our results revealed that spin-orbit interaction is necessary and sufficient to explain the observed ferroelectric polarization, establishing an entirely electronic origin of ferroelectricity in MnWO₄. The origin of spin-orbit interaction in this compound with a nominally $d^5 L=0$ orbitally quenched state was shown to be possible due to the mixing of ligand p states with Mn d states. The origin of the non-collinear magnetic state in MnWO₄ was analyzed in detail by calculating spin exchange parameters for the isostructural tungstate family (MWO₄, where M=Mn, Fe, Ni)

6.1 Background

6

Multiferroics are materials that have simultaneous ferromagnetic, ferroelectric and/or ferroelastic ordering. In addition to several new properties that emerge (7, 174, 175),

the coupling between magnetic and electric degrees of freedom can lead to magneto electric (ME) effects (176, 177) where one can control magnetization with applied electric fields and vice versa. Such a coupling would open up entirely new possibilities in data storage technologies, such as ferroelectric memory elements that could be read out nondestructively via the accompanying magnetization.

Although a large number of ferroelectric and ferromagnetic materials exist, there are relatively few multiferroics (177). The reason lies in the microscopic origin of ferroelectricity and magnetism. Most ferroelectrics are transition metal oxides, in which transition ions have empty d shells. These positively charged ions like to form 'molecules' with one (or several) of the neighboring negative oxygen ions. This collective shift of cations and anions inside a periodic crystal induces bulk electric polarization. The mechanism of the covalent bonding (electronic pairing) in such molecules is the virtual hopping of electrons from the filled oxygen shell to the empty d shell of a transition metal ion. Magnetism, on the contrary, requires transition metal ions with partially filled d shells, as the spins of electrons occupying completely filled shells add to zero and do not participate in magnetic ordering.

Depending on the origin of ferroelectricity, there are two groups of multiferroics. The first group, called type-I multiferroics, contains those materials in which ferroelectricity and magnetism have different sources and appear largely independently of one another, though there is some coupling between them. In these materials, ferroelectricity typically appears at higher temperatures than magnetism, and the spontaneous polarization **P** is often rather large (of order $10 - 100\mu$ C/cm²). An example is BiFeO₃ (178), in which magnetism is due to unpaired electrons in Fe³⁺ ion and ferroelectricity is caused by the 6s lone pair in Bi ion. Ferroelectricity can also be 'improper', in the sense that it appears as an accidental by-product of some other ordering. Examples are geometric ferroelectrics, RMnO₃ in which nonpolar lattice distortion causes dipole moment (179) and electronic ferroelectrics, LuFe₂O₄ where a non-centrosymmetric charge distribution leads to net electric polarization (180).

The second group, the type-II multiferroics, is the relatively recently discovered materials (7, 181), in which magnetism causes ferroelectricity, implying a strong coupling between the two. However, the polarization in these materials is usually much smaller ($\sim 10^{-2} \mu C/cm^2$). In collinear spin systems this can happen via symmetric exchange striction effects as observed in YMn₂O₅ (182), Ca₃CoMnO₆ (183), *etc.* Ferroelectricity can appear in the cycloidal-spiral spin phase without centrosymmetry (184, 185), in which the spin rotation axis is not parallel to the magnetic modulation vector \mathbf{Q} as shown in Fig. 6.1. This correlation between the FE polarization and the cycloidal-spiral spin structure is suggested to be associated with the antisymmetric part of exchange coupling, which is the so-called Dzyaloshinskii-Moriya (DM) interaction (186, 187, 188). The microscopic model proposed by H. Katsura *et al.* (186) describes the relationship between an electric dipole moment, \mathbf{P} , and canted spin moments, S_i and S_j , on the neighboring two sites (*i* and *j*) as follows

$$\mathbf{P} = \gamma \hat{e}_{ij} \times (S_i \times S_j) \tag{6.1}$$

Here, \hat{e}_{ij} denotes the unit vector connecting the two sites. The coefficient γ is a constant which depends on the strength of spin-orbit interaction and the superexchange interaction. This mechanism is often referred to as inverse DM interaction (187). As a result, spin-orbit interaction is indispensable in generating electric dipole moments. In fact, several materials, e.g. in TbMnO₃, Ni₃V₂O₈, CoCr₂O₄ and MnWO₄ (7, 8, 189, 190) exhibit this type of behavior.



Figure 6.1: Different types of spin structures relevant for type-II multiferroics. (a) Sinusoidal spin density wave, in which spins point along one direction but vary in magnitude. This structure is centrosymmetic and consequently not ferroelectric. (b) The cycloidal spiral with the wave vector $\mathbf{Q} = \mathbf{Q}_x$ and spins rotating in the (x, z)-plane. It is in this case where one finds nonzero polarization, $\mathbf{P}_z \neq 0$. (c) In a so-called "proper screw" the spins rotate in a plane perpendicular to \mathbf{Q} . Here the inversion symmetry is broken, but most often it does not produce polarization (191)

Model Hamiltonian studies of spin-spiral multiferroic compounds have provided two different pictures. The first is a purely electronic mechanisms based on the KatsuraNagaosa-Balatsky (KNB) model (186), promoted by the spin-orbit interaction (SOI) that modifies the hybridization of the electronic orbitals in such a way as to shift the center of charge even if the ions are not displaced from their centro-symmetric positions (192). The second one relies on *lattice mechanism* where DMI not only stabilizes helical magnetic structures (188), but also induces ferroelectric lattice displacements of oxygen ions. Recent *ab-initio* calculations have provided evidence for both the mechanisms (180, 193, 194) in spin spiral systems.

Among cycloidal spiral magnets, the origin of ferroelectric polarization in the compound MnWO₄ (8, 195, 196, 197) was particularly intriguing, since the role of SOI was not clear. The system was believed to be in Mn²⁺ ($3d^5$) O²⁻ ($2p^6$) configuration which would be expected to have quenched orbital moment, similar to the spin spiral multiferroic FeVO₄ (198). Model Hamiltonian calculations suggested that either mixing of ligand p orbitals with d orbitals or t_{2g} - e_g orbital mixing by SOI could lead to electric polarization in systems with non-zero spin (S) with an arbitrary d^n configuration (192). In this chapter, we present results of first principles electronic structure calculations to understand the electronic structure and the origin of ferroelectric polarization in the multiferroic MnWO₄.

6.2 Methods

First-principles density functional theory calculations were performed using the Vienna ab initio simulation package (70, 71), within the projector augmented wave method by explicitly treating 7 valence electrons for Mn $(3d^54s^2)$, 6 for W $(5d^46s^2)$ and 6 for O $(2s^22p^4)$. We used local spin density approximation with on-site coulomb interactions, U = 4 eV applied to the *d* states of Mn using an approach described by Dudarev *et al.* (199). We approximated the incommensurate wave vector $\mathbf{q} \simeq (-0.214, 1/2, 0.457)$ by a commensurate one *viz.* $\mathbf{q} = (-1/4, 1/2, 1/2)$, and used a super cell which is $(4 \times 2 \times 2)$ times the original crystallographic unit cell with 192 atoms. A plane wave energy cut-off of 500 eV and k-space sampling on a $1 \times 2 \times 2$ Monkhorst-Pack grid were employed. Brillouin zone integrations were performed with a Gaussian broadening of 0.1 eV. We have checked our calculations on a finer k-mesh $1 \times 4 \times 4$ and the results hardly changed indicating the chosen k-mesh to be adequate. All structural relaxations are carried out till Hellman-Feynman forces became less than 0.01 eV/Å.

6.2.1 Crystal and magnetic structure

MnWO₄ crystallizes in a monoclinic wolframite structure (200) with a space group P2/c, as shown in Fig. 6.2. The values of lattice constants a, b, c, and β are 4.82 Å, 5.75 Å, 4.99 Å, and 91.075°, respectively. Each unit cell includes two Mn²⁺ ions at $\mathbf{r}_1 = (\frac{1}{2}, y, \frac{1}{4})$ and $\mathbf{r}_2 = (\frac{1}{2}, 1 - y, \frac{3}{4})$ with y = 0.685; the ions are interconnected via the common edges of distorted MnO₆ octahedra and form zigzag chains along the c axis. MnWO₄ with magnetic Mn²⁺ is known to be a moderately frustrated antiferromagnetic (AF) system. A relatively weak nearest-neighbor superexchange via the bending of Mn–O–Mn bonds competes with other Mn–O–O–Mn superexchange interactions, inducing successive magnetic phase transitions at 13.5 K (T_{N3}), 12.7 K (T_{N2}), and 7.6 K (T_{N1}) (200, 201). In all the magnetic structures the moments of Mn²⁺ align along the easy axis that lies in the ac plane forming an angle of $\alpha = 34^{\circ}$ with the a axis, as shown in Fig. 6.2(b). There are three magnetic ordered phases; AF1 ($T \leq T_{N1}$), AF2 ($T_{N1} \leq T \leq T_{N2}$), and AF3 ($T_{N2} \leq T \leq T_{N3}$) phases.



Figure 6.2: (a) Crystal structure of MnWO₄ showing MnO₆ octahedra, (b) The basal plane of the spiral spin structure in the ferroelectric phase. The easy spin direction forms angle $\alpha = 34^{\circ}$ with the *a* axis. The direction of the magnetic wave vector **k** is also indicated

In the AF1 phase below T_{N1} , the magnetic structure is commensurate with a propagation vector $\mathbf{k}_{AF1} = (\pm \frac{1}{4}, \frac{1}{2}, \frac{1}{2})$. The magnetic structure of the AF1 phase is characterized by the up-up-down-down ($\uparrow\uparrow\downarrow\downarrow\downarrow$) spin configuration along the *a* and the *c* axes,



Figure 6.3: Elliptical spiral spin structure in AF2 phase of $MnWO_4$. The arrows represent the spins and the ellipses indicate their plane of rotation

which is often realized in the ground state of the system with competing magnetic interactions. In the AF2 and AF3 phases, the propagation vector becomes incommensurate with $\mathbf{k}_{AF2} = (-0.214, \frac{1}{2}, 0.457)$. At the transition between the AF2 and AF3 phases, the incommensurate propagation vector does not change. The difference between the two phases is the existence of a component of the magnetic moments along the b(||y)axis in the AF2 phase, which does not exist in the AF3 phase. In more detail, the magnetic structure in the AF2 phase shows an elliptically modulated noncollinear spiral spin structure, in which the basal pane of the elliptical spiral contains the easy axis of magnetization and the y axis. The AF3 phase is a collinear sinusoidal magnetic structure with the magnetic moments lying along the easy axis. The magnetic structure of the AF2 can be categorized in a cycloidal spiral as in Fig 6.3.

In contrast, the isostructural tungstates FeWO₄ and NiWO₄ exhibit only one ordered magnetic phase, which is collinear with antiferromagnetic ordering along *a*-axis and ferromagnetic along other two directions making a magnetic cell $2a \times b \times c$ times the conventional cell (202). Apparently, the magnetic instability leading to the spiral structure in MnWO₄ does not exist in other tungstates.

6.2.2 Exchange interactions

The origin of the complex magnetic structure was studied by mapping the system onto a localized Heisenberg model (203). Ehrenberg *et al.* experimentally analyzed the spin wave dispersion curves of the magnetic state AF1 of MnWO₄, determined from inelastic neutron scattering measurements, in terms of nine spin-exchange parameters (201). For comparison, we used the same definition of interaction paths. Fig. 6.4 shows the position of Mn^{2+} ions in $MnWO_4$ structure indicating the exchange paths. Out of the nine relevant parameters, the exchanges J_1 and J_2 are in the zigzag chains of Mn^{2+} ions along the *c* direction, the exchanges J_3 and J_4 are between adjacent ||c chains of Mn^{2+} ions in each ||bc layer of Mn^{2+} ions, and the exchanges $J_5 - J_9$ between the adjacent ||bc layers of Mn^{2+} ions along the *a* direction.



Figure 6.4: Position of Mn ions (circles) in MnWO₄ structure viewed along the *a* axis. Colored lines represent exchange interaction paths. (a) Four spin exchange paths $J_1 - J_4$ in MnWO₄ within each ||bc| layer of Mn²⁺ ions. (b) Five spin exchange paths $J_5 - J_9$ between adjacent ||bc| layers. The numbers 1 - 9 refer to the spin exchange paths $J_1 - J_9$, respectively.

To evaluate $J_1 - J_9$, we examined the 10 ordered spin states defined in Ref. (203). For the calculation of the various exchange interactions we performed total energy calculations in the framework of GGA+U method for these 10 ordered spin states using a supercell of $4 \times 2 \times 2$. Finally, the various exchange interactions were extracted by mapping the relative energies of these ordered spin states determined from the GGA+U calculations onto the corresponding energies obtained from the total spin exchange energies of the Heisenberg spin Hamiltonian defined as,

$$\hat{H} = -\sum_{i < j} J_{ij}(\hat{S}_i \cdot \hat{S}_j) \tag{6.2}$$

where J_{ij} is the spin exchange parameter for the interaction between the spin sites *i* and *j*, while \hat{S} is the spin angular momentum operators. All the spin interaction paths in the cell were counted and by applying the energy expression Eq. 6.2 obtained for spin dimers with N unpaired spins per spin site, the total spin exchange energies of

the 10 ordered spin states (per two formula units) can be written as a 9×10 matrix equation,

N is the number of unpaired spins and is 5 for Mn, 4 for Fe, and 2 for Ni. Thus, by calculating the relative energies $E_1 - E_9$ with respect to $E_{\rm fm}$ and inverting the above equation, we could estimate the exchange parameters $J_1 - J_9$.

6.2.3 Berry phase method

In a finite system, the average value of electric polarization \mathbf{P} can be easily defined as,

$$\mathbf{P} = \frac{\mathbf{d}}{\Omega} = \frac{1}{\Omega} \int d\mathbf{r} \ n(\mathbf{r})\mathbf{r}$$
(6.4)

where **d** is the total dipole moment, Ω is the system volume and $n(\mathbf{r})$ is the density. The integral leads to a finite number, since $\mathbf{P}(\mathbf{r}) = 0$ outside the body. However, for an infinite system with periodic boundary conditions, the integral is conditionally convergent and cannot be used to evaluate **P**.

We calculated the electronic contribution to the polarization as a Berry phase using the method first developed by King-Smith and Vanderbilt (204, 205), the so called modern theory of polarization. In this approach, the change in polarization can be found when a parameter of the Hamiltonian, λ , is changed adiabatically (e.g. when atoms are displaced which leads to a Kohn-Sham potential $V_{\rm KS}^{\lambda}$),

$$\Delta \mathbf{P} = \int_0^1 \mathrm{d}\lambda \; \frac{\partial \mathbf{P}}{\partial \lambda} \tag{6.5}$$

where, one of the end points $\lambda = 0$ can be taken to be a centrosymmetric structure

where macroscopic polarization is zero and the other point $\lambda = 1$ to be the structure of interest. $\Delta \mathbf{P}$ can determined by evaluating the phase of the product of overlaps between cell-periodic Bloch functions, $u_{\mathbf{k}i}^{\lambda}$, along a densely sampled string of neighboring points in \mathbf{k} space. For a particular cell direction α , it can be written as,

$$\Delta \mathbf{P}_{\alpha} = i \frac{-|e|}{(2\pi)^3} \int_{\mathrm{BZ}} \mathrm{d}\mathbf{k} \sum_{i}^{\mathrm{occ}} [\langle u_{\mathbf{k}i}^{\lambda=1} | \partial_{k\alpha} u_{\mathbf{k}i}^{\lambda=1} \rangle - \langle u_{\mathbf{k}i}^{\lambda=0} | \partial_{k\alpha} u_{\mathbf{k}i}^{\lambda=0} \rangle] + n \times \frac{-|e|}{A}$$
(6.6)

where, n is an integer and A is the cell volume divided by the length of the unit cell in the direction α , i.e. the area of a cell perpendicular to α . The above expression can be cast in terms of functions involving the centers of Wannier functions (206), as

$$\Delta \mathbf{P}_{\alpha} = \frac{-|e|}{\Omega} \sum_{i}^{\text{occ}} [\langle 0i | \hat{\mathbf{r}} | 0i \rangle^{\lambda=1} - \langle 0i | \hat{\mathbf{r}} | 0i \rangle^{\lambda=0}]$$
(6.7)

which has the simple interpretation that the change in polarization is the same as if the electrons were localized at points corresponding to the centers of the Wannier functions.

The total polarization $\Delta \mathbf{P}$ for a given crystalline geometry can be calculated as the sum of ionic and electronic contributions. The ionic contribution is obtained by summing the product of the position of each ion in the unit cell (with a given choice of basis vectors) with the nominal charge of its rigid core. Here, we used four symmetrized strings consisting of 15 k-points to obtain the electronic contribution to the polarization, which was calculated separately for each spin channel.

6.3 Results

6.3.1 Magnetism

Total energy calculations were carried out for the ferromagnetic, $\mathbf{q}=(0,0,0)$, anti-ferro magnetic, $\mathbf{q}=(\frac{1}{2},0,0)$, AF1 and AF2 with $\mathbf{q}=(\frac{1}{4},\frac{1}{2},\frac{1}{2})$ states of MnWO₄. Our results (shown in Table 6.1) both within LDA and LDA+U reveal that the antiferromagnetic state AF1 has the lowest energy, in agreement with experiment. The energy difference ΔE between AF1 and the FM, AFM, AF2 was found to be 0.17, 0.16, 0.01 eV/f.u., respectively, with U = 4 eV. In the AF2 phase, the computed magnetic moment is 4.57 μ B with same U and rotate in a plane as described earlier. Calculations with different U parameters gave average Mn magnetic moments of 4.30 μ_B (U=0 eV) and 4.67 μ_B (U=6 eV), suggesting a rather weak dependence of magnetic moment on U. All magnetic states were found to be insulating both in the LDA and LDA+U method. The band gap in the AF1 state was calculated to be 1.19 eV with LDA and 2.16 eV with LDA+U which is comparable to the experimentally reported band gap of 3 eV from photoelectron measurements (207).

Table 6.1: Total energy difference ΔE (in eV/f.u.) and calculated magnetic moments m (in μB) of each of the atom in FM, AFM, AF1 and AF2 structures of MnWO₄

	LDA			LDA+U				
	FM	AFM	AF1	AF2	\mathbf{FM}	AFM	AF1	AF2
ΔE	0.19	0.16	0.00	0.01	0.17	0.16	0.00	0.01
Mn	4.32	4.28	4.28	4.30	4.58	4.56	4.57	4.57
W	0.20	0.06	0.00	0.05	0.12	0.04	0.00	0.03
01	0.04	0.02	0.02	0.02	0.02	0.01	0.01	0.01
O2	0.05	0.01	0.00	0.02	0.02	0.00	0.01	0.01

6.3.2 Density of states

To gain insight into the electronic structure of $MnWO_4$, the total and site projected DOS for $MnWO_4$ in the AF1 phase was calculated within LDA+U. Results are displayed in Fig 6.5. From the figure we gather that, the spin up Mn *d* states are completely occupied while the spin down states are completely empty, consistent with the Mn^{2+} valence of Mn with a nominal $3d^5$ configuration. Similarly, O-*p* states are completely occupied while the W states are completely empty, indicating the valence of W to be W^{6+} , consistent with experimental results.

In Fig. 6.5 we can clearly see the effect of crystal field on Mn d states. In the octahedral crystal field provided by the MnO₆ octahedra the Mn d-states split into triply degenerate t_{2g} states and doubly degenerate e_g states with the latter higher in energy. However the exchange splitting (due to the repulsion of electrons in the same orbital) dominates over the crystal field and therefore Mn²⁺ in high spin d^5 configuration is realized. This is reflected in Fig. 6.5 as completely filled up spin channel and completely empty down spin channel for the Mn-d states. Also, the d^5 electronic configuration of Mn favors the anti ferromagnetic configuration in the AF1 phase as found in our total energy calculations.



Figure 6.5: Calculated total and partial density of states within LDA+U for MnWO₄ in the AF1 phase. All energies are measured with respect to the Fermi level. Spin-up and spin-down states are plotted on the positive and negative axes respectively

6.3.3 Electric polarization

We then calculated the polarization using the Berry Phase method (204) as implemented in VASP. Our results for various cases are summarized in Table 6.2. Electric polarization in the AF2 phase with centrosymmetric crystal (wolframite) structure in the absence of SOI was found to be zero, as expected. This provided a clear evidence that symmetric exchange striction effects did not offer an explanation for the origin of ferroelectric polarization in MnWO₄. Since, SOI is what connects spin structure to the lattice, when SOI is turned on, one would expect the broken inversion symmetry in the spin sector to be communicated to the spatial (charge) degrees of freedom, and indeed our calculations confirmed this. In the experimental structure with SOI the computed electric polarization was $\mathbf{P} = 42.02 \mu C/m^2$ along the *b* direction. Both the magnitude and the direction of the polarization is in excellent agreement with the experimental value of $50-60\mu C/m^2$ (8, 195). We also found zero polarization in the collinear AF1 phase even in the presence of SOI suggesting that the spiral magnetic order is crucial for the realization of this finite (and large) electric polarization. Earlier studies (193) had shown that the relaxation of the ionic coordinates improved calculated polarization. Upon relaxation without imposing any symmetry constraints in the AF2 phase, we found **P** in the resulting structure in absence of SOI to be (-5.78, 4.99, 18.22) μ C/m² with a magnitude of 19.75 μ C/m². This was much smaller than the experimental value and it was also inconsistent in direction (not along *b*-axis).

Structure	Polarization ($\mu C/m^2$)
Exp. AF2 without SOI Exp. AF2 with SOI Exp. AF1 with SOI Relx. AF2 without SOI Relx. AF2 with SOI	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$

Table 6.2: Calculated electric polarization various magnetic structures of MnWO₄

However, when SOI was included in the Berry phase calculations, an additional polarization of 123.8 μ C/m² developed along *b* direction. In the relaxed structure, the average deviation from the centrosymmetric position is found to be ~ 2.7×10^{-6} Å for Mn, while for W and O they are ~ 2.5×10^{-6} Å and ~ 3.7×10^{-7} Å, respectively. We also carried out constrained ionic relaxation calculations in which Mn and W special

positions (x and z coordinates) were kept fixed. In this case, polarization without SOI remained zero, while it was (0,121.9,0) μ C/m² in presence of SOI. The largest deviation from centrosymmetric positions was less than ~ 2 × 10⁻⁶ Å. Such tiny displacements in both the cases (unconstrained and constrained ionic relaxations) would be hardly detectable in any experiment and possibly their effects would be swamped by zero point vibrational effects (193).

From the above discussion we conclude that our *ab-initio* calculations offer clear evidence that spin-orbit interaction alone can account for the origin of polarization in MnWO₄ without involving any structural effects, establishing an electronic mechanism as the origin of ferroelectricity in this compound. Since Mn^{2+} in the high spin state $(d^5, S=5/2)$ has L=0 in the free ion state, where the orbital moment is expected to be quenched, an induced mechanism either due to mixing of the ligand p-orbitals or $t_{2a}-e_a$ orbitals is possibly operative on this system. Indeed, band structure results provided evidence for substantial oxygen p- Mn d-mixing (Fig. 6.5) as well as finite t_{2g} - e_g mixing (not shown here) in partial densities of states. The orbital moment was found to be tiny (0.001 μ_B) but in the same direction as the spin moment indicating Mn 3d states were more than half filled (208). However, it was difficult to estimate quantitatively the extent of Mn 3d occupancy or its deviation from the ionic d^5 state in terms of such ab initio band structure calculations, since the association of the electronic charge with an atomic center within this approach is dependent on the somewhat arbitrary space partitioning and thus, lead to non-uniqueness. Within this approach, it is also not possible to estimate the expectation value of the angular momentum associated with the deviation of the Mn 3d occupancy from the half-filling. High energy electron spectroscopies like x-ray absorption spectroscopy, on the other hand, are particularly suited to provide a well-defined estimate of the 3d occupancy and also the expectation value of angular momentum when analyzed in conjunction with many-electron configuration interaction (CI) model (209, 210).

Following our predictions, XAS measurements and CI model calculations with full multiplet Coulomb interactions were carried out by Choudhury and Sarma (9). Their fit to the experimental data showed that the ground-state wave function for the true distorted structure with the optimal parameters to have an average 3*d* occupancy, n_{3d} , of 5.15, with 86.48% d^5 character, 12.99% $d^6\underline{L}^1$ character, and only 0.52% $d^7\underline{L}^2$ character. Similarly, the expectation value of the orbital angular momentum for the ground

	$MnWO_4$	FeWO_4	$NiWO_4$
A1	-22.63	-21.32	-13.50
A2	-19.72	-20.17	-12.57
A3	-6.87	-16.56	-19.17
A4	-20.99	-34.95	-31.51
A5	-10.21	-13.74	-11.56
A6	-4.58	-5.42	-3.51
A7	-4.38	-4.61	-2.46
A8	-4.24	-4.81	-2.89
A9	-4.45	-5.07	-3.40

Table 6.3: Relative energies (in meV/f.u.) of the ordered spin states of RWO_4

state was calculated to be 0.51. Thus, the experiments conclusively established a significant population of Mn 3*d* level and a consequent finite expectation value of angular momentum for the ground state (0.51), beyond the half-filling in MnWO₄, providing a way to understand the critical presence of SOI and consequent finite polarization in this compound.

6.3.4 Exchange interaction

In order to analyze the magnetic structure, we calculated the exchange parameters. The calculated relative energies $E_i - E_{\rm fm}$ of the magnetic structures considered (203) are given in Table 6.3. In the only experimental study of exchange interactions in MnWO₄ Ehrenberg *et al.* (201), estimated the nearest-neighbor intrachain exchange J_1 to be antiferromagnetic (AFM) and the next-nearest-neighbor intrachain exchange J_2 to be FM. The latter means that the spin exchanges within each ||c| chain are not spin frustrated, which is inconsistent with the occurrence of spiral-spin within each ||c| chain. However, our calculations for MnWO₄ listed in Table 6.4, in agreement with previous estimates (203), show that both J_1 and J_2 are AFM, and $J_2/J_1 \gg 0.25$, so that geometric spin frustration exists within each ||c| chain. This finding accounts for the occurrence, in each ||c| chain, of the spiral-spin order in the AF2 state and the $\uparrow\uparrow\downarrow\downarrow$ spin order in the AF1 state of MnWO₄, and may require further evaluation.

Our calculations also correctly reproduce the behavior of NiWO₄ for which J_1 is found to be FM and J_2 is AFM thus predicting no instability. However, calculations seem to suggest that for FeWO₄ also possess a magnetic instability similar to MnWO₄,

	$MnWO_4$	FeWO_4	NiWO_4
J_1	-3.04	-2.03	26.7
J_2	-3.89	-6.89	-16.8
J_3	-0.29	-15.8	27.57
J_4	-0.29	-14.1	-28.9
J_5	-2.57	3.94	2.05
J_6	-0.56	-2.16	-2.84
J_7	-2.04	-11.6	-51.4
J_8	-1.47	-6.25	-7.79
J_9	-3.09	-9.27	-31.3

Table 6.4: Spin exchange parameters $J_1 - J_9$ (in $k_B K$) for RWO₄

which is surprising considering that experiments does not support such an instability. Further calculations are necessary to identify the origin of the exchange parameters for $FeWO_4$.

6.4 Summary

In conclusion, our first principles electronic structure calculations not only correctly reproduced the electronic and magnetic ground state of MnWO₄, but also provided an accurate estimate of the value of the ferroelectric polarization. In addition, we found that the polarization develops only in the spin spiral AF2 state driven by the spin-orbit interaction. The spin exchange parameters revealed that the exchange interactions to be frustrated within each ||c| chain of Mn²⁺ ions and between such ||c| chains along the *a* direction.

The magnetic instability leading to a non-collinear structure can also be a consequence of nesting effects of paramagnetic Fermi surface. Calculation of nesting functions (211) can provide more insight in to the noncollinear structure of MnWO₄. It will also be interesting to investigate the effect of pressure on the magnetic structure and strength of electric polarization using electronic structure methods, in an attempt to find the factors that improve the value of electric polarization in this compound.

6. ORIGIN OF FERROELECTRIC POLARIZATION IN MNWO₄

Strength of H_2 bond in the molecular solid $SiH_4(H_2)_2$

Hydrogen might seem the simplest element in nature; however, it exhibits many puzzling and unusual properties which actually makes it quite complex. One of them is the predicted metallic phase under pressure, which has led to detailed investigations of hydrogen and hydrogen rich compounds under various thermodynamic conditions and chemical environments. To understand the recent experimental observations, we studied the effect of pressure on the strength of H₂ covalent bond in the molecular solid SiH₄(H₂)₂ using quantum molecular dynamics simulations and charge density analysis. Our calculations showed, in agreement with experimental predictions, that substantial elongation of H₂ bond could be achieved at lower pressures in this system, compared to pure H₂. Model calculations showed the redistribution of charge from bonding to antibonding states to be responsible for the behavior. The exchange of hydrogen speculated to be operative in SiH₄, D₂ mixture was confirmed by our calculations and was shown to be a three step process driven by thermal fluctuations alone.

7.1 Background

7

Hydrogen appears prominently at the top left corner of Mendeleev's imposing periodic table and it is the most abundant element in the universe (more than 90% by number). It is widely accepted that hydrogen is present in the interiors of Saturn and Jupiter where it is both liquid and metallic (212), and the origin of their magnetospheres. In

7. STRENGTH OF H_2 BOND IN THE MOLECULAR SOLID $SIH_4(H_2)_2$

1935 Wigner and Huntington predicted that hydrogen would undergo a molecular to atomic transition to a metallic phase as the density is increased and estimated that this transition would occur above pressures of 0.25 Mbar (213). Since then, hydrogen had been the center of immense scientific research. The metallic phase was expected to display novel behavior, such as superconductivity, superfluidity and a quantum liquid state (214, 215, 216). In fact, based on the simple BCS theory of superconductivity, one could understand why metallic hydrogen would be a good superconductor: this system has very high phonon frequencies due to the light H mass, and it has a possibly strong electron-phonon interaction related to the lack of core electrons and to the quite strong covalent bonding (214).

The metallic phase (217), however, has eluded experimental realization under static pressures till now. Most recent estimate was that it requires pressures above 400 GPa (218, 219), which lie just outside the experimental capabilities. However, hydrogen dominant solids, i.e., those containing small amount of non-hydrogen atoms embedded in a network of hydrogen stabilized by intermolecular and intramolecular interactions, had been proposed as analog materials which might mimic the behavior of solid hydrogen at relatively lower pressures (220). In such systems, such as group IV hydrides, presence of heavier elements were expected to "chemically pre-compress" hydrogen. In fact, in the case of silane (SiH₄), several theoretical (221, 222, 223) and experimental (224, 225) studies showed metalization pressures to be substantially lower than that of pure hydrogen.

Remarkably, these hydrogen rich full-shell IV hydrides could absorb additional hydrogen at high pressures and form stoichiometric van der Waals compounds such as $CH_4(H_2)_2$, $SiH_4(H_2)_2$ etc. (226, 227). X-ray diffraction experiments by Strobel *et al.* on $SiH_4(H_2)_2$ showed that it formed a highly symmetrical, well ordered structure above 7 GPa (18). Their Raman and IR measurements under pressure showed anti-correlated pressure frequency dependence, implying H_2 bond weakening at unusually low pressures. They also observed a darkening of the sample at a pressure around 35 GPa, which could eventually be associated with a insulator-metal transition. Studies on the isostructural compound $SiH_4(D_2)_2$ revealed a time evolution of Raman spectra, which was interpreted as an exchange of H and D ions by the two molecules (18). This indicates high proton mobility in this system which was speculated to be related to pressure induced quantum lattice melting. A flurry of theoretical studies followed, which predicted that the structure might deviate from the ideal fcc lattice and form a tetragonal structure with a slightly elongated *c*-axis (228). Total energy calculations combined with genetic algorithms confirmed the structural transformation to a metallic orthorhombic state, albeit at much higher pressures of 248 GPa which was also predicted to have interesting superconducting properties (229). Apparently, theoretical calculations employing different computational methods disagreed on the exact transformation pressure: some calculations predicted the metalization pressure to be 164 GPa (230) and 200 GPa (231), although they all support the prediction of substantial overlap between silane and hydrogen charge densities (232). Also, calculations observed only a marginal increase (< 0.01Å) in the H₂ bond length up to 35 GPa, which was surprising considering the experimental predictions. More recent calculations predicted the experimental observed frequency pressure anticorrelation to be a consequence of donor-acceptor interactions between the two molecules (233).

Although the electronic structure and the energy volume characteristics of this compound were thoroughly investigated, several questions remained. The calculations did not explain the experimentally observed darkening of the sample close to 35 GPa. Large spread in the metalization pressures predicted by different theoretical calculations was unclear. Factors that lead to the exchange of hydrogen between the molecules were not addressed. We believed that dynamics play an important role in the observed properties and a quantum mechanical molecular dynamics simulation could shed more light onto the observations.

7.2 Methods

First-principles calculations were performed using the Vienna *ab initio* simulation package (70, 71) with the ion-electron interaction described by the projector augmented wave method (52). The energy cutoff for the plane-wave expansion of eigenfunctions was set to 700 eV. We used the local density approximation for the exchange-correlation functional. For properties at low pressures, we also checked higher plane wave cut-offs and found them to be nearly unchanged. Optimization of structural parameters was achieved by minimizing forces below 0.01 eV/Å. Highly converged results were obtained utilizing a dense $4 \times 4 \times 4$ k-point grid for the Brillouin-zone integration. To calculate the amount of electronic charge, we used the code for Bader charge analysis (234) including both valence and core charges. Simulations employed a time step of 0.5 fs to integrate the equations of motion under constant volume and Nosé-Hoover thermostat to keep temperature constant. Equilibration runs were typically done for 0.5 ps and average quantities were calculated over another 0.5 ps.

7.2.1 Structure of $SiH_4(H_2)_2$

Experiments had proposed a face-centered cubic (fcc) $F\bar{4}3m$ space group with as the structure of silane hydrogen molecular solid under pressure (18). The tetrahedral SiH₄ unit occupies the fcc lattice sites. The positions of eight H₂ pairs are at two nonequivalent sites. Four equivalent pairs are at the middle of each axis of the cubic structure and in the center of the cube. The other four pairs of H₂ are at the 1/4 or 3/4 position of the four-body diagonal lines forming a tetrahedron. The latter four are the nearest neighbors of a SiH₄ molecule. The optimized structure at 9.3 GPa is shown in Fig. 7.1



Figure 7.1: Snapshot of the simulation cell at 9.3 GPa. Large pink spheres are silicon atoms while small green spheres are hydrogen. The unit cell has FCC structure with SiH_4 molecules at corners and face centers.

7.2.2 Bond lengths

Generally, average bond lengths at the end of the simulation are calculated by averaging over the distances up to the first minima in the pair correlation function between bonded
atoms. However, this procedure does not take into account the "baseline" caused by nearby molecules and unbound atoms. To avoid this overestimation of bond lengths, we fitted each of the H-H pair correlation functions to the functional form:

$$g(r) = \lambda g_f(r; c_f, \sigma_f) + (1 - \lambda)g_s(r; c_s, \sigma_s)$$
(7.1)

where g_f and g_s are Gaussians for the first and second neighbor peaks and c and σ are fitting parameters corresponding to center and width of the Gaussian respectively. The bond order parameter λ determines the fraction of protons that are bound into a molecule.

7.3 Results



Figure 7.2: Variation of enthalpy as a function of pressure for a simulation cell containing pure hydrogen. Snapshots of the simulation cell are shown in the inset.

7.3.1 Hydrogen under pressure

First, to understand how well our calculations reproduce the behavior of hydrogen under pressure, we subjected hydrogen in molecular phase in hcp crystal phase, both containing 128 hydrogen atoms, to gradual compression using QMD. As shown in Fig. 7.2, we found that at lower pressures molecular hydrogen was of lower energy and hence was the stable phase. In fact, the atomic crystalline phase was unstable at lower pressures and transformed spontaneously to a disordered molecular structure. Close to 150 GPa, the H_2 bondlengths elongated abruptly and the atomic phase became stable. Not surprisingly, the energy of the ordered hcp phase became lower above this pressure (Fig. 7.2). These results are in agreement with earlier first principles simulations (235), that predicted a liquid-liquid phase transition close to this value. Our calculations showed that, there is also an underlying liquid-solid transition at this pressure.



Figure 7.3: H-H radial distribution function at a few representative pressures of (a) pure hydrogen and (b) $SiH_4(H_2)_2$

We examined pair distributions functions for the molecular fluid phase as a function of pressure and is given in Fig 7.3(a). Initially, the bonded nearest neighbor peak, located close to 0.76 Å is very sharp and was well separated from the next nearest neighbor peak around 2 Å. Upon increasing pressure, the second peak corresponding to intermolecular correlations moved to lower distances and finally merged with the first peak indicating a weakening of H-H bond length.

7.3.2 H_2 bond in SiH₄(H₂)₂

A unit cell containing four silane and 8 hydrogen molecules as shown in Fig. 7.1 was used as the starting configuration. Upon structural relaxation at constant volume, this cell was found to have a pressure of 9.3 GPa, which was within the predictive capabilities of DFT-LDA based calculations when compared to experiments (18). We also found that H_2 and SiH₄ molecules are free to rotate in the structure, confirming earlier observations (233).



Figure 7.4: Variation of H-H bond length and bond order as a function of pressure for silane-H₂ solid. Abrupt changes are observed close to 40 GPa.

Volume of a well equilibrated simulation cell containing $SiH_4(H_2)_2$ was reduced gradually, allowing the system several thousand steps at each volume. The H-H radial distribution functions (RDF) averaged over 100 configurations and at various pressures are given in Fig. 7.3. It shows that, the first peak corresponding to bonded hydrogen atoms move to higher values at higher pressures. The figure also shows that the second peak, corresponding to inter-molecular H-H distance approaches the first peak and merges with it at some pressure. In the case of the system containing only H₂ this happened between 113 GPa and 169 GPa, while in the case of $SiH_4(H_2)_2$ this happened above 46 GPa.

The average bond length (c_f) and bond order (λ) of Eq. 7.1 are plotted as a function of pressure in Fig. 7.4. As we can see the H₂ covalent bond length and bond order exhibit a change in behavior close to 40 GPa. Bond order remains 1 up to 40 GPa, drops abruptly and continues to decrease, indicating that H₂ molecule is becoming progressively weaker beyond this pressure. In the case of pure hydrogen, a similar decrease in bond order was observed in the range of 150-200 GPa in earlier studies (236). This behavior of bond length seems to suggest two regimes (below 40 GPa with almost zero variation and above 60 GPa with constant elongation rate) connected by an abrupt increase. It is to be noted that the sudden change close to 40 GPa does not lead to metalization as predicted by experiments (18).

7.3.3 Charge transfer



Figure 7.5: Variation of bond length of H_2 molecule (H1-H2) as a function of intermolecular H-H distance (H2-H3). Arrangement of molecules for the calculation is shown in the inset.

To understand why silane molecules are more effective in weakening H_2 bond

strength, we considered a simple one dimensional model in which only the nearest neighbor interactions along the axis of the molecule are allowed. For this, two H_2 molecules are placed end-on along z-axis as shown in the inset of Fig. 7.5. We then varied H_2 non bonded distance (d_{nbo} between H3-H2) by constraining the positions of adjacent hydrogen atoms and monitored the H_2 bond length (d_{bnd} between H1-H2). The farther atoms (H4 and H1 in the figure) were allowed to relax along the z-axis. The calculations were then repeated by replacing one of the molecules (H4-H2) by XH_4 , the other known hydrides of IV group elements, forming CH₄, SiH₄, GeH₄ and SnH₄ with one of the hydrogen atom pointing along the axis as shown in figures. Although we have approximated the complex three dimensional interactions with multiple neighbors to a single interaction in 1D, we believe this model to be a reasonable representation of the real system for providing essential insights. In fact, this simple model does predict SiH_4 to have a higher effect than H_2 as expected (Fig. 7.5). The model also predicts that GeH_4 causes similar elongation and that SnH_4 would be more effective in bringing about metalization in hydrogen. Curiously, CH_4 causes less elongation of d_{bnd} than H_2 above $d_{nbo} = 0.9$ Å.



Figure 7.6: Isosurfaces for the difference in charge densities between isolated hydrogen molecule (on the far side) and one with adjacent H₂ or XH₄ (where X is C, Si, Ge, Sn) molecules (shown inside the isosurface). Blue and red surfaces correspond to isovalues of $(1 \times 10^{-6} \text{ and } -1 \times 10^{-6} / \text{Å}^3)$ respectively. Note that large blue surfaces represent unsubtracted charge cloud of the molecule and only features on the left side are significant. Nonbonded H-H distance is fixed at 1 Å and all other distances are allowed to relax.

In the case of H_2 in the interstitials of GaAs crystals, it was found that the lattice induced charge transfer from bonding to anti-bonding states which caused elongation of bond length and downward shift of vibrational frequencies. The charge density differences plotted in Fig. 7.6 between an isolated hydrogen molecule and one with a neighboring molecule shows that a similar effect is produced in the present case as well.¹

¹The asymmetry in charge density difference the case of two H_2 can be removed if we consider an

Moreover, we find that, the redistribution of charge from bonding to anti-bonding states is higher when the neighboring molecule is XH_4 , instead of H_2 . The plots also show substantial overlap between H_2 and neighboring molecule in agreement with Ref (232).



Figure 7.7: One dimensional charge density differences induced on a hydrogen molecule by an adjacent molecule. Filled circles represent hydrogen atoms.

To have a better look at the exact charge reordering, we integrated the charge densities perpendicular to z-axis (around ϕ) utilizing the cylindrical symmetry of the hydrogen molecule. Results presented in Fig. 7.7 show that the charge redistribution affects the bond length in two ways: removal of charge from the bonding region reduces the attraction between the bonded nuclei and addition of charge in the antibonding region increases the repulsion; both of which cause the bond to elongate. At the same time, antibonding charge also helps to reduce the repulsion between nonbonded nuclei. The figure shows that CH₄ results in lowest reduction in bonding charge density (lower than H₂), while SnH₄ results in the maximum reduction and interestingly, the bond elongation also follows the same order (Fig. 7.5). In the case of SiH₄ and GeH₄, according to Fig. 7.5 both exhibit similar elongation behavior although Ge clearly has

infinite chain instead of two isolated molecules. Such a calculation, however, would not change the main conclusions of this section

a larger effect on bonding density. But SiH_4 has a larger effect on antibonding density which we believe compensates for the reduced effect on bonding density resulting in similar effect for both molecules. Our Bader charge analysis shows that hydrogen atoms bonded to Si, Ge and Sn have charges higher than isolated hydrogen atom (1.6e, 1.2e and 1.25e respectively); while hydrogen connected to C has less (0.95e) which may also explain the observed behaviors.

7.3.4 Hydrogen exchange

The dynamical simulations showed that at 300 K, hydrogen exchange between silane and hydrogen molecules takes place only above 90 GPa. At lower pressures the process requires elevated temperatures, indicating the presence of a kinetics barrier which reduces under pressure and disappears above 90 GPa. Hydrogen exchange was found to take place in three steps: (1) a transition state forms by the transfer of hydrogen between two adjacent SiH₄ molecules forming a SiH₃ and SiH₅, (2) H₂ molecule dissociates and one of the hydrogen atoms moves to the SiH₃, and (3) SiH₅ gives up a hydrogen atom, which combines with the single hydrogen to form H₂. The three distinct stages in the process are depicted pictorially in Fig. 7.8



Figure 7.8: Hydrogen exchange mechanism (explained in the text) in silane hydrogen mixture. Note that only hydrogen atoms participating in the event are shown. The back face of the cell is marked by a cross and the arrows represent the movement of atoms. A & B, and numbers 1, 2, 3 & 4 represent two silicon and four hydrogen atoms that participate in the event.

Fig. 7.9 shows the temporal evolution or the dynamics of the process. We have plotted the relevant bond lengths between four hydrogen and two silicon atoms that took part in the process. The three steps mentioned earlier are marked by arrows in the plot. We see that the process initiates when H^4 leaves Si^A around 50 fs after the beginning of the simulations, marked by the first arrow. Beyond the second arrow (75 fs) it is attached to the second silicon Si^{B} . At this moment Si^{A} is hydrogen deficient and Si^{B} is hydrogen rich. As one would expect, immediately after H⁴ attaches to Si^{B} , one of its bonds (H³) starts weakening. Around 125 fs, marked by the third arrow, the hydrogen molecule donates a hydrogen to the deficient silane Si^{A} and H³ detaches completely from Si^{B} to form H₂ molecule back.

In short, the exchange was initiated by transfer of hydrogen between two silane molecules. At 90 GPa distance between Si atoms on adjacent face centers (A and B) was 3.3 Å, which was small enough (Si-H distance at this pressure was 1.6 Å) to allow hydrogen transfer between them without thermal activation. Hence, according to our simulations, the hydrogen exchange is a classical process, expedited by elongation of bond lengths and reduction in volume. However, in experiments, H-D exchange was observed at a pressure as low as 10 GPa which might be due to large experimental time scales or catalysis by gasket as speculated by the authors of Ref (18). We believe quantum lattice melting may not be operative in the present case.



Figure 7.9: Evolution of bond distances as a function time in the hydrogen exchange process at 90 GPa and 300 K. Bond breaking/formation is marked by arrows. The exchange process starts around 50 fs and is completed before 125 fs and the system equilibrates beyond it.

7.3.5 Summary

Our ab-initio calculations on $SiH_4(H_2)_2$ crystallized in FCC lattice with orientationally disordered hydrogen showed that pressure caused substantial elongation of H_2 bond length above 40 GPa. Transfer of charge from bonding to antibonding states was responsible for the elongation and our studies indicated that $SnH_4(H_2)_2$ might be more effective in bringing about this transition. H-D exchange was confirmed as the reason for observed variation of Raman spectra and dynamics of the process indicated it to be a three step process. An activation barrier prevents the exchange from taking place at room temperatures in simulations below 90 GPa.

Even though our calculations showed substantial elongation of H_2 bond length under pressure, they did not support the experimentally observed darkening of sample close to 35 GPa. Similar to the case of pure silane, the darkening may be a consequence of dissociation of the solid itself, aided by the metallic gasket acting as a catalyst. In this context, it will be interesting to investigate the effect of gasket materials on the high pressure behavior of SiH₄(H₂)₂ using computer simulations.

7. STRENGTH OF H_2 BOND IN THE MOLECULAR SOLID $SIH_4(H_2)_2$

Part IV

Hybrid Methods

8

Order-disorder transitions in Si under pressure

In this chapter, we present studies on crystallization and amorphization of silicon, in which a combination of classical, quantum and model calculations were used. Recent experiments had found that nano amorphous silicon undergoes crystallization to an eight coordinated primitive hexagonal (ph) phase under pressure, which returns to the amorphous phase upon pressure release. Our first principles total energy calculations on bulk and nano silicon showed that at nanoscale the amorphous is not a metastable phase and quantum mechanics/molecular mechanics (QM/MM) simulations confirmed the progressive disordering of nano-ph phase. The crystallization kinetics in amorphous silicon was studied using classical nucleation theory with data derived from first principles calculations, which showed the nucleation work to decrease with pressure. Crystallization temperatures of cubic diamond (cd) and β -Sn structures were estimated using empirical relations derived by Okui and melting data calculated from classical molecular dynamics. They were found to decrease with pressure.

8.1 Background

The two computational methods used so far in this thesis mainly differed in their speed and accuracy. DFT based electronic structure methods provide very accurate description of materials, but are computationally expensive and, as a consequence, can handle only small systems under reasonable simulation times. Atomistic methods, even though less accurate, are fast and can handle very large simulations. So far, the compromise on a particular method had been based on whether the properties of interest demanded larger speed or higher accuracy. Often, there are situations when a satisfactory description of the system cannot be reached with either of the methods alone. One such case is presented in this final chapter.

As shown in Table 4.2, several structural polymorphs with different density and coordination exist for bulk silicon. However, at nanoscale, the behavior was found to be different: cubic diamond phase of nano-crystalline Si (~ 50 nm) transforms directly to the primitive hexagonal (ph) form at 22 GPa, by-passing all other intermediate structures (237). Increased stability regime of the diamond phase due to surface tension effects was attributed to the non-realization of the intermediate phases. Surprisingly, for nano-crystallites embedded in porous Si (π -Si), the initial cubic phase was claimed to undergo pressure induced amorphization (PIA) close 14 GPa (238), explained in terms of pressure induced pseudo-melting. Like water, liquid Si has a higher density than its solid phase and, hence, has a negative Claperyon slope (i.e., it melts at lower temperatures at higher pressures) for the liquid crystal coexistence curve. Thus, in the absence of any other phase transition, amorphous phase could melt at room temperature at sufficiently high pressure.

However, in subsequent high pressure experiments on nano π -Si and bulk a-Si using x-ray diffraction and Raman techniques, Garg *et al* made several new and interesting observations (14). In disagreement with earlier reported PIA, that the cubic nano Si was found to undergo a phase transition to a crystalline ph phase at ~ 20 GPa. When they released pressure on the newly formed nano-ph phase, it underwent amorphization. The bulk ph phase was also found to exhibit a similar behavior, but only upon abrupt pressure release; slower releases resulted in a new crystalline phase called *R*8 (23). Finally, the nano-amorphous phase obtained on pressure release was found to transform reversibly back to the ph phase under subsequent compression. Although, formation of crystalline ph upon compression of a-Si is also observed in bulk (23), a reversible amorphous-crystalline transformation in an elemental solid was surprising and led to the speculation that the nano a-Si might be favorably predisposed towards transformation to a particular crystalline phase.

Two important order-disorder transitions in silicon are outlined in the above experimental results: amorphization and crystallization. As explained in Chapter 4, amorphous is a metastable, kinetically trapped phase. It can be generated through abrupt cooling from a liquid or abrupt decompression from a crystal; a process known as quenching. Hence, realization of bulk amorphous phase during abrupt release of pressure is not surprising. However, the fact that the nano-ph phase amorphizes irrespective of rate of decompression points to a novel mechanism or a novel amorphous phase that is not metastable.

Also interesting is the reversible recrystallization of the nano-LDA back to the ph phase upon compression. In fact, similar "memory glass" behavior was reported in the case of berlinite $AlPO_4$ at high temperatures (239), where the amorphous phase "remembers" the orientation of the original crystalline phase. Subsequent studies, however, found the amorphous phase to be a poorly resolved crystalline phase (240). Reversibility in crystal-to-crystal transformation is understandable as collective reordering of atoms from one structure to another and is possible due to the long range order in crystals. In the case of an amorphous phase, which is disordered, it is difficult to imagine a simple transformation path that would take it reversibly to a crystalline structure. However, if the energy barriers for crystallization in this system is such that all other structures are forbidden, the observations can be explained.

It is reasonable to assume that crystallization in the above experiments proceeds through random nucleation and growth (RNG) discussed in Chapter 4. Thermal fluctuations induce formation of many tiny crystalline nuclei in the amorphous matrix, a process which may be enhanced by presence of impurities or defects. The nuclei is comprised of a crystalline core and a low density crystal-amorphous (c/a) interface layer which forms due to the difference in the structure between the crystalline and amorphous phases. Classical nucleation theory predicts that, as the diameter of the nucleus increases, the energy of the nucleus increases, passes through a maximum and then decreases. Thus, beyond a critical size, a crystalline nucleus will grow spontaneously, as it will lower energy. The energy necessary to form a crystalline nucleus of critical diameter is called the nucleation work (ΔG^*) and it acts as a barrier preventing crystallization at low temperatures. However, since pressure affects relative energies in the system, it changes the required nucleation work as well (241).

However, the effect of pressure on the nucleation work is not straight forward. For example, in many systems pressure is known to lower ΔG^* (242, 243), while it also raises ΔG^* in many others (244, 245). A notable example is the elemental solid, amorphous selenium, (which undergoes polymorphous crystallization similar to a-Si) in which pressure significantly elevates crystallization temperature (246). The behavior was later explained to be because of the increase in nucleation work with pressure (241). In the amorphous alloy $Al_{89}La_6Ni_5$, applied pressure resulted in the increase of T_c after an initial reduction (247) which was explained as a result of competition between the reduction in thermodynamic potential barrier and the diffusion activation energy under pressure.

From a microscopic point of view, pressure has multiple effects on crystallization. Pressure is an obstacle to the formation of c/a interface, which has a lower density and coordination than the surrounding crystalline and amorphous regions. Pressure also inhibits atomic diffusion as a consequence of reduced free volumes and inversely affects the movement of the interface. On the other hand, there occurs a negative volume change ($\Delta V < 0$) during amorphous to crystal transition, due to the lower density of the amorphous phase, which would favor crystallization under pressures. Such a density driven crystallization was first reported in case of water (248). Finally, pressure induces several structural transitions (Table 4.2) which causes abrupt changes in free energy. Their effects on nucleation work cannot be easily predicted.

To understand the order-disorder transitions in Si, we carried out following simulations. First, the amorphization of ph phase was studied using total energies (firstprinciples) for different silicon clusters which showed that amorphous state has a lower energy compared to the, otherwise stable, cd phase. We subjected bulk (first-principles) and nano-ph (QM/MM) structures of silicon to abrupt and slow release of pressure and found that in the case nano, the structure becomes disordered, in agreement with experimental observations. Crystallization of a-Si was studied by calculating nucleation work (first-principles and model) and crystallization temperatures from melting curves (classical MD and model).

8.2 Methods

8.2.1 Classical MD

Classical MD simulations were carried out using the DL_POLY code (29) and interatomic potentials by Tersoff (131, 132). Velocity Verlet algorithm was employed to integrate the equations of motion with Berendsen thermostat and barostat keeping temperature and pressure constant. The system was equilibrated for several nanoseconds at each temperature/pressure using a fine timestep of 1 fs. The amorphous phase was generated by quenching liquid silicon from 3500 K at a rate 1 K/ps and annealing at 1000 K for several million steps. Melting curve for a-Si was estimated by subjecting the amorphous structure to increasing temperatures and changes in diffusion constant and volume were monitored to identify the melting point. To obtain the crystalline melting curves, a cell containing the crystal-liquid interface was heated and the melting point was identified as the temperature at which the interface moves towards the crystalline region.¹

8.2.2 First-principles calculations

Density functional theory based calculations were used to optimize ionic positions of small silicon clusters of approximately ~ 110 atoms and diameter ~ 1.4 nm. Structural relaxations were performed within generalized gradient approximation (168) using projector augmented wave (52) method as implemented in Vienna *ab-initio* simulation package (70, 71) starting from roughly spherical clusters. An energy cutoff of 400 eV with Γ point sampling was used to find the lowest energy configurations of clusters in a 20 Å supercell. The amorphous structure was generated by heating cubic silicon cluster to 1500 K and quenching it. Molecular Dynamics simulations were then carried out for 0.3 ps at 300 K to equilibrate the cluster and was then subsequently optimized at 0 K. The resultant cluster had almost the same volume as the diamond structure. The energy volume characteristics of amorphous were calculated using a supercell containing 216 atoms and Γ centered k-point sampling. Each structure was equilibrated for 0.5 ps at 500 K and subsequently fully relaxed.

8.2.3 QM/MM simulations

The simulation box consisted of a cluster of silicon treated quantum mechanically submerged in a liquid which was treated classically as shown in Fig. 8.1. Since the main role of the liquid was to transmit the hydrostatic pressure, it was actually not necessary to model the specific properties of a real liquid in the simulations. It is known that basic properties of a real simple liquid are captured by a classical short-range repulsive

 $^{^{1}}$ The crystal-liquid interface was constructed by heating a crystal-amorphous cell shown in Fig. 4.4 of Chapter 4 above the glass melting temperature.

8. ORDER-DISORDER TRANSITIONS IN SI UNDER PRESSURE

pair potential (249). Thus we chose the liquid-liquid and cluster-liquid interactions to be pairwise additive potentials, $V_{\rm L-L}(r)$ and $V_{\rm C-L}(r)$, respectively. Adding both interactions as well as the kinetic energy of the liquid particles to the Car-Parrinello Lagrangian of Eq. 2.75, we obtain a new Lagrangian for the extended system, consisting of electrons and ions of the cluster and the liquid particles,

$$L = \frac{1}{2} \sum_{i} \mu \int d\mathbf{r} |\dot{\psi}_{i}(\mathbf{r})|^{2} + \frac{1}{2} \sum_{I} M_{I} \dot{\mathbf{R}}_{I}^{2} - E[\{\psi_{i}\}, \{\mathbf{R}_{I}\}]$$

$$+ \sum_{ij} \Lambda_{ij} (\langle\psi_{i}|\psi_{j}\rangle - \delta_{ij} + \frac{1}{2} \sum_{I} m_{I} \dot{\mathbf{X}}_{I}^{2}$$

$$- \sum_{IJ} V_{\mathrm{C}-\mathrm{L}} (|\mathbf{R}_{I} - \mathbf{X}_{J}|) - \sum_{I < J} V_{\mathrm{L}-\mathrm{L}} (|\mathbf{X}_{I} - \mathbf{X}_{j}|)$$

$$(8.1)$$

Here, \mathbf{X}_I and m_I are the coordinates and masses of the liquid particles, \mathbf{R}_I and M_I those of the cluster atoms and ψ_i and μ the electronic wave functions and the associated electronic fictitious mass. From this Lagrangian, equations of motion corresponding to the coupled Car-Parrinello/classical MD can be derived (250).

Since the pressure might induce a macroscopic shape change in the cluster, the liquid should be able to flow fast enough to accommodate such a change, without developing appreciable pressure gradients or shear components which might hinder the transformation. Also, under high pressure the liquid may crystallize or undergo glass transition, marked by a dramatic slowing down of the liquid dynamics. To avoid these effects, we have used a repulsive soft-sphere potential with carefully chosen parameters of the form,

$$V_{\rm L-L}(r) = \epsilon (\sigma_{\rm L-L}/r)^{12} \tag{8.2}$$

A similar form is chosen for the cluster-liquid interaction $\sigma_{\rm C-L}$ as well. We set $\epsilon = 1$ a.u.; the potential is then fully specified by the single parameter $\sigma_{\rm L-L}$. The parameters used for the potentials are $\sigma_{\rm L-L} = 1.05$ Å, $\sigma_{\rm C-L} = 3.30$ Å. Other constants of simulation are mass of the liquid particles m = 20 a.u., fictitious electron mass $\mu = 400$ a.u. and a time step of $\Delta t \approx 0.1$ fs.



Figure 8.1: Snapshot of the simulation cell containing the silicon cluster (114 atoms) and surrounding liquid (~ 28000 atoms)

8.2.4 Model calculations

The energy required to form a nucleus of critical size (nucleation work ΔG^*) is related to the growth rate I at a temperature T according to crystallization kinetics theory (241),

$$I = I_0 \exp\left(\frac{\Delta G^* + Q_n}{k_{\rm B}T}\right) \times \exp\left[-\frac{KT_m^2}{k_{\rm B}T(T_m - T)}\right]$$
(8.3)

where I_0 is a constant, Q_n is the activation energy for the transport of an atom across the c/a interface, K is nucleation parameter, T_m is the melting temperatuer of the crystalline phase and $k_{\rm B}$ is the Boltzmann constant. For homogeneous nucleation, forming a spherical crystalline nucleus with a diameter d from an amorphous matrix with an interface between them, Gibb's free energy change (243) can be expressed as a sum of a volume term corresponding to the energy of the crystalline core $(\frac{1}{6}\pi d^3)$ and a surface term (πd^2) corresponding to the interface energy,

$$\Delta G^n(T,P) = \frac{\pi d^3}{6V^c} (\Delta G^{a \to c} + E) + \pi d^2 \sigma \tag{8.4}$$

where, $G^{a\to c}$ is the molar free energy change for the transformation from amorphous to crystalline phase, σ is the free energy increase for forming the unit area c/a interface, i.e., the interfacial energy, V^c is the molar volume of crystalline phase and E is the elastic energy induced by the volume change during the phase transformation in the solid state. The nucleation work ΔG^* and critical nucleus diameter d^* for the crystallization under pressure can be calculated when $\partial G^n/\partial d = 0$.

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G^{a\to c}/V^c)^2} \tag{8.5}$$

where the elastic energy, E, has been omitted since its effect on the free energy change has been shown to be minor (243).

Turnbull (251) showed that for most metals the ratio of liquid solid interface energy, σ , to the enthalpy of fusion, ΔH_f , is approximately 0.45 at ambient pressure. However, ΔH_f is generally expressed in kJ/mol while σ is expressed in J/m². To find the ratio, we need to convert the interface energy to a molar quantity σ_m , which may be defined as the free energy of an interface containing Avogadro number, N, of atoms. If the area of such an interface is A, and thickness is one atom; then $A = N^{1/2}V^{2/3}$ and the interface energy can be written as,

$$\sigma_m = N^{\frac{1}{2}} V^{\frac{2}{3}} \sigma \tag{8.6}$$

where N is the Avogadro number and V is the volume per atom at the surface.

The second term in Eq. 8.3 incorporates the effect of melting at high enough temperatures. Thus crystallization temperature increases with temperature and reaches a maximum at T_c^{max} above the glass transition temperature T_g and below the melting point of the crystalline phase T_m (252). It has been shown that the ratios of temperatures T_c^{max} , T_g and T_m are related by a constant at ambient pressure (253, 254). Okui derived expressions for these ratios in terms of activation energy of migration through the nucleus-melt interface and a nucleation parameter associated with the mean surface energy and the heat of fusion (255). Using them, one can arrive at the following relation for T_c^{max} :

$$T_c^{\max} = \frac{T_m}{2} \left(1 + \frac{T_g}{T_m} \right) \tag{8.7}$$

8.3 Results

8.3.1 Amorphization

The structures of the different phases of silicon, obtained after structural optimization, are shown in Fig. 8.2. According to our calculations on small clusters, amorphous phase has lower energy than the cubic diamond structure (energy difference, $E_{cd} - E_{am}$, is 67.9 meV). The β -Sn structure did not stabilize at the end of structural optimization, but transformed to a four coordinated disordered structure. Hence, in case of nanoclusters, the cubic diamond phase is actually a metastable state, in contrast to the situation in bulk. This means that emergence of LDA on release of pressure is basically kinetics independent. These calculations also explain the non-observability of the β -Sn phase during the compression of nano π -Si (14). A similar size dependent structural transformation has been observed recently in silver (256).



Figure 8.2: Clusters of different structures of silicon at the end of first principles ionic relaxation. (a) cubic diamond (b) β -Sn, which becomes disordered upon relaxation, and (c) the amorphous phases.

High pressure experiments submerge the nanoparticles in a fluid which acts as a pressure transmitting medium (PTM). A quantum mechanical simulation of the particle plus the pressure-transmitting liquid is beyond the limit of what could be handled computationally. Hence we employed the method implemented by Martoňák *et al.* where only the cluster is treated quantum mechanically while the surrounding liquid is treated classically (250).

To prepare an initial configuration for the QM/MM simulations, we first equilibrated



Figure 8.3: Final configurations of the cluster at different pressures. The surrounding liquid is not shown for clarity. Decompression induces progressive disorder.

the liquid at ~ 600 K and 25 GPa with about $N_{\rm L} = 31^3 = 29791$ in a simulation cell of ~ $(68 \text{ Å})^3$. A spherical ph-cluster made up of 114 silicon atoms was made from bulk ph phase equilibrated at ~ 25 GPa. The cluster was immersed in the liquid and those liquid particles which were closer than 2.5 Å to any Si atom were removed. The liquid was then equilibrated for about 2 ps while the cluster was kept frozen.

The conventional way to change the pressure on this system would be to change the volume of the classical cell. A more efficient way is to change the liquid repulsion parameter, σ_{L-L} . Decreasing the repulsion between the liquid particles will increase free volumes in the liquid and will reduce the pressure on the surface of the cluster. This method of controlling pressure has the advantage that, the volume of the simulation box can be kept fixed. We found that varying $\sigma_{L-L} = 1.05 \rightarrow 0.05$ resulted in decrease of pressure $35 \rightarrow 0.3$ GPa. Thus, changing pressure of the simulation cell involved two steps. First, the parameter σ_{L-L} is changed, and only the liquid is equilibrated keeping the cluster atoms fixed. In the second step, once the required pressure is reached, the cluster is also allowed to relax.

Fig. 8.3 shows snapshots of the cluster at different pressures. We can see that, reducing pressure introduces disorder in the cluster. Initially, the surface atoms begins to get disordered which soon spreads to the core, causing the entire cluster to amorphize. This is evidenced by the distribution of first neighbor distances plotted in the Fig. 8.4, which shows that as the pressure decreases the peak moves to slightly higher values and becomes broad.



Figure 8.4: Bond length distribution for silicon ph cluster under decompression. Broader distribution indicate disorder.

These calculations show that even under slow release of pressure, the ph cluster transforms to amorphous structure. Our first principles MD calculations on bulk ph showed that it does not become amorphous upon gradual reduction in pressure, in agreement with experimental observations (23).

8.3.2 Crystallization through RNG

To understand the nature of crystallization via random nucleation in silicon, we have calculated nucleation work using Eq. 8.5. For this, the free energy change $\Delta G^{a\to c}$ and V^c were calculated using first principles methods. Since change in entropy $\Delta S^{a\to c}$ is three orders of magnitude smaller (246) than change in enthalpy $\Delta H^{a\to c}$, we have used $\Delta H^{a\to c}$ in our calculations. The energy volume characteristics under pressure estimated from simulations are depicted in Fig. 8.5.

The results are in good agreement with earlier reports (257). Volume of a-Si which is initially higher than that of the diamond phase by about 3% and decreases faster and crosses the cd curve ~ 10 GPa, which is also similar to the observations in classical MD simulations discussed in Chapter 4. Also similar is the first order phase transition from LDA to HDA, which is accompanied by a large volume drop of ~ 16%. The kink



Figure 8.5: Variation of volume and energy as a function of pressure, obtained from first principles simulations. Red dotted line represents extension of the HDA enthalpy to the metastability region of LDA

in the LDA-HDA enthalpy due to the first order nature of the transition is removed by extending the HDA enthalpy to lower pressures (red dotted line).

Using the melting enthalpy of 40.06 kJ/mol calculated from a classical simulation (Fig. 8.7) and the ratio $\Delta H_f/\sigma = 0.45$, we estimate the c/a interface energy to be 0.41 J/m² which is close to the value 0.49 J/m² determined by Bernstein *et al.* from tight binding calculations (125). We used this value for σ for both diamond and β -Sn interfaces while calculating nucleation work using Eq. 8.5 and is given in Fig. 8.6.

Consistent with our simulations on SPEG presented in Chapter 4, we observe a minimum in the nucleation work close to 10 GPa. This shows that underlying microscopic parameters affecting both processes are similar. We also see that ΔG^* for β -Sn is lower than that for diamond, as observed earlier (Fig. 4.9). The discontinuity in ΔG^* close to 8 GPa is because the denser HDA phase is energetically favorable above this pressure (even though the first order LDA-HDA transition is not observed till 15 GPa). Calculations also showed that for β -Sn nucleation work decreases as pressure is increased beyond 15 GPa. We should note that, though we have used same value for σ , in principle it can be pressure dependent and different for two structures. Care-



Figure 8.6: Variation of nucleation work with the applied pressure for crystallization of a-Si to diamond and β -Sn structures

ful first principles calculations are necessary to identify such differences, if any. We have also calculated nucleation work for the ph phase (23) and found that it is lower than that of β -Sn, which may explain the pressure induced crystallization observed in experiments (14).

8.3.3 Melting behavior

Finally, to check the relationship between crystallization and melting temperatures under pressure, we simulated the melting process in amorphous and crystalline silicon.

Fig. 8.7 shows the results of this simulation which agree well with available experimental data. The melting curves for amorphous and crystalline phase of silicon display negative Clayperon slope and remain almost parallel as a function of pressure. Melting temperatures at ambient pressure obtained from our calculations were 2000 K for amorphous-Si and 2600 K for d-Si, in agreement with earlier calculations carried out using the same interaction potentials (131). Since experimental estimates are 1420 K for amorphous and 1685 K for crystalline silicon (258) our calculations showed that Tersoff potentials overestimate the melting temperatures by 40-50% as predicted.

8. ORDER-DISORDER TRANSITIONS IN SI UNDER PRESSURE

At ambient pressure the ratio of calculated melting temperatures $T_g/T_m = 2/2.6$, which is close to the experimental value of 2/3 (59, 259, 260). The negative slope of the melting curve under pressure suggests increased self-diffusion (261), which is a common characteristic of negative Clapeyron slope materials where the liquid phase is denser than the solid phase, as in water (261). This increased diffusion with pressure also results in reduction of the crystallization temperature observed in Si. Close to 15 GPa, melting curves exhibit minima, as a result of structural transition from a "strong" to a "fragile" system in both crystalline and amorphous phases.



Figure 8.7: Melting curves for amorphous and crystalline silicon under pressure. Solid black lines are quadratic fit to simulation data. The red lines represent calculated crystal-lization curves using Eq. 8.7.

The red lines in Fig. 8.7 represent T_c^{max} calculated using Eq. 8.7 (a continuous fit to amorphous data is used for this case) which agrees qualitatively with earlier calculations of T_c^* (Fig. 4.5, Fig. 4.9) and ΔG^* (Fig. 8.6). T_c^{max} for diamond shows a 50% decrease up to 10 GPa similar to T_c^* .

8.4 Summary

Experiments observed that in nano silicon, an amorphous phase is stable under ambient pressure, which arises only upon abrupt pressure release in the bulk. This amorphous phase was found to undergo pressure induced crystallization at room temperature. Our classical and quantum calculations provided a qualitative understanding of these experimental results. Total energy calculations confirmed that increased surface to volume ratio stabilizes the amorphous structure at the nanoscale. Using QM/MM simulations, we were able to observe amorphization of nano-ph upon slow pressure release. Model calculations based on classical nucleation theory and melting behavior indicated that crystallization of amorphous silicon is enhanced under pressure and showed that high pressure phases of silicon have lower crystallization temperatures, explaining the pressure induced crystallization observed in this system.

A way to observe probability driven events like nuceation in simulations is to use faster configuration space sampling tools like simulated annealing, parallel tempering etc. within the Monte Carlo method. It may be interesting to use these methods to study the effect of finite size on crystallization kinetics in nanoparticles of silicon.

8. ORDER-DISORDER TRANSITIONS IN SI UNDER PRESSURE

Appendix A

Parallel Cluster

By distributing a computational task across multiple processors, the work load can be shared and the required computational time can be reduced substantially. A larger parallel computer, in principle, makes it possible to handle larger problem sizes and longer simulation times. It also gives the program access to larger physical memory which can be utilized to divide the memory requirement of the problem across multiple processors. This allows execution of jobs which could otherwise not run on smaller systems due to memory limitations. The most important advantage of parallel computing is that it is much cheaper to built and maintain a parallel cluster compared to any other system with similar performance. Details of the PLUTO cluster setup during the course of the doctoral work is presented in this chapter.

A.1 Architecture

During the past decade, many different computer systems supporting high performance computing have emerged. Their taxonomy is based on how their processors, memory, and interconnect are laid out. The most common systems are: Massively Parallel Processors (MPP), Symmetric Multiprocessors (SMP), Cache-Coherent Nonuniform Memory Access (CC-NUMA), Distributed Systems and Clusters.

In the 1980s it was believed that computer performance was best improved by creating faster and more efficient processors. This idea was challenged by parallel processing, which in essence means linking together two or more computers to jointly solve some computational problem. Since the early 1990s there has been an increasing trend to move away from expensive and specialized proprietary parallel supercomputers towards networks of workstations. One of the driving forces that enabled this transition was the rapid improvement in the availability of commodity high performance components for workstations and networks.

A computer node can be a single or multiprocessor system (PCs, workstations, or SMPs) with memory, I/O facilities, and an operating system. A cluster generally refers to two or more computers (nodes) connected together. The nodes can exist in a single cabinet or be physically separated and connected via a local area network (LAN). An interconnected cluster of computers can appear as a single system to users and applications.



Figure A.1: Time taken by a sample VASP job on ANUPAM parallel computing cluster. Simulation over gigabit used MPICH while simulation over Infiniband used OPENMPI interface

As explained in Chapter 2, without efficient algorithms that parallelize problems, the strength of parallel computers cannot be exploited. A typical parallel program works in three steps. A master node initializes the input and output arrays and distributes data across all the compute nodes. The nodes then carries out operations on the data they each have independently and in parallel. Finally, the master node collects the results from compute nodes and combines them back. The process is repeated if necessary. Example of a real life first principles simulation using VASP is shown in Fig. A.1. It takes only 2.1 hours when run on 32 processors compared to 14.2 hours on 4 processors, which shows the significance of parallel computing. The figure also shows that the interconnecting network affects the scaling of the parallel jobs significantly. In the absence of network latency, the step involving transfer of data between the nodes would be instantaneous and program execution speed would increase indefinitely with number of processors. In practice, however, network has a finite response time and bandwidth. As the number of processors increase, higher network traffic will cause nodes to wait in idle processor cycles for the communication to finish, reducing the overall performance. In fact, as shown in Fig. A.1, after a particular size, the speedup will start to decrease due to the communication bottleneck. For this job, on Gigabit network based on 1 Gbps Ethernet connection, the limit is 24 processors while on Infiniband based on 8 Gbps connection the limit is reached at 64 processors. Note that, since the limit depends on the communication level and size of the problem, it is highly job dependent.

The prominent hardware and software components of a cluster computer are:

- Multiple high performance computers (PCs, workstations, SMPs)
- High performance network (Gigabit Ethernet, Infiniband)
- Operating system (Linux, Windows NT)
- Cluster middleware (Rocks, Oscar)
- Parallel programming environment (Compilers, MPI, PVM)
- Applications

A.2 Hardware considerations

One of the most fundamental design decisions of cluster building is the choice of the processor. As the price varies substantially across different processor speeds, it is often advisable to build a larger cluster with mid-range processors and a fast interconnect than a smaller cluster with top-range processors. The physical memory also affects the performance of the cluster. Higher clock speeds are desirable because it allows faster data transfer between CPU and RAM, but more important is the amount of RAM per processor, as the largest problem sizes the cluster can handle are decided by

A. PARALLEL CLUSTER

it. Another important design parameter is the network fabric. As shown in Fig. A.1, with a slow interconnect will actually slow down program execution beyond a limit. Since scalability depends crucially on the interconnect, it is advisable to use the fastest affordable network technology.

Finally, a factor that affects not the performance but the usability of the cluster is storage and backup solutions. Since computer simulations generate large amounts of data, a fast and reliable storage array is required. Typically, a file server with all the user directories sits in the private network of the cluster but is not used for computations. The files are made available to the compute nodes through a network file system (NFS). This arrangement ensures that the file server is available at all times and is not loaded by computational jobs. For reliability of the file system, a fault tolerant RAID5 array, which has on-line error checking and redundancy against disk failure can be used. A routine backup system can ensure additional data security.

Based on the above design criteria, a parallel computing cluster has been setup in Purnima Labs, BARC for condensed matter simulations. The cluster, named PLUTO, is based on dual processor quad-core Intel Xeon processors comprising of 16 individual servers of 1U form factor as shown in Fig. A.2. The final configuration of the PLUTO is given the Table A.1.

A.3 Software considerations

Individual nodes and the file server of the HPC require an operating system like any other computer to manage the local resources like CPU, RAM, storage etc. Any of the modern day operating systems like Linux, Unix, Windows etc. can be used in a cluster. If the nodes have local disks, the OS can be installed on each them allowing the nodes to boot independently of each other. Another approach is master-client architecture where only one master server holds the operating system and the compute nodes boot from it over the network. Even though the latter case is less difficult to set up and manage, the former puts less burden over the network.

In addition to the operating system, parallel computers require software libraries that allow communication between different nodes and utilities that manage the cluster. They make it possible for a program to distribute itself across the cluster and communicate with it's components on different nodes.

Item	Specification	Per Node	Total
Hardware			
Processor	Quad core Xeon @ 2.33 GHz	$2\mathrm{P}$	128
RAM	DDR2 667 MHz	8 GB	128 GB
Local storage	SATA2 7200 rpm	$160~\mathrm{GB}$	-
Network storage	$15 \mathrm{Krpm} \mathrm{SAS}$ in RAID5	-	2 TB
Gigabit NIC	Dual PXE 1000 Base T	1	16
Infiniband NIC	4X DDR Infiniband PCIe	1	16
Gigabit switch	48 RJ45 (1 Gbps)	-	1
Infiniband switch	24 CX4 (8 Gbps)	-	1
Backup	Ultrium 3 LTO 800 GB Tape	-	1
Management	16 port KVM	-	1
Software			
OS	Scientific Linux 5.2	1	-
Management	OSCAR 6.0.2	-	1
Resource	Torque 5.1	-	1
Scheduler	MAUI	-	1

 Table A.1: PLUTO hardware & software configuration

There are also few cluster specific operating systems which integrate several libraries and utilities into the operating system itself. Rocks Cluster Distribution developed by a group at University of California (UCSD), is such an operating system, with a modified Anaconda installer that simplifies mass installation onto many computers and pre-configured libraries and utilities to run and manage the cluster. Even though Rocks provides an integrated and streamlined cluster management option, it lacks the flexibility necessary for experimentation. After extensive testing, we opted for manual cluster setup using Scientific Linux as operating system and Open Source Cluster Application Resources (OSCAR) for cluster management. Scientific Linux produced by FNAL and CERN is based on the RedHat Enterprise Linux from which Rocks is also built.

OSCAR is a cluster software stack providing a complete infrastructure for cluster computing. The core components enable a user to construct a virtual image of the target machine using System Installation Suite (SIS). A master node keeps a single installation image for all the compute nodes. Node reinstallation involves pushing this image to the local disk of the node, ensuring fast installation. This method also makes sure that all nodes are identical. It include a parallel distributed "shell" tool set called C3 and an environment management facility called Env-Switcher. These components

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help in diagnosis and trouble-shooting. Cluster usage monitoring and statistics are handled by ANULIB routines developed by Computer Division, BARC.

Another component in the cluster setup is the Resource Management and Scheduling (RMS). Since multiple users are expected to use the cluster simultaneously, RMS ensures that user jobs are distributed over all available resources. It also enables the effective and efficient utilization of the resources available. The software that performs the RMS consists of two components: a resource manager and a resource scheduler. The resource manager component is concerned with problems, such as locating and allocating computational resources, authentication, as well as tasks such as process creation and migration. The resource scheduler component is concerned with tasks such as queuing applications, as well as resource location and assignment. RMS has come about for a number of reasons, including: load balancing, utilizing spare CPU cycles, providing fault tolerant systems, managed access to powerful systems, and so on. But the main reason for their existence is their ability to provide an increased, and reliable, throughput of user applications on the systems they manage. We have used MAUI resource manager and TORQUE scheduler to control user jobs.

The most vital software component that makes a collection of interconnected computers into a parallel cluster is the collection of libraries that allow a program to run in parallel. MPI libraries allow efficient parallel programs to be written for distributed memory systems. These libraries provide routines to initiate and configure the messaging environment as well as sending and receiving packets of data. The MPI standard is the amalgamation of what were considered the best aspects of the most popular message passing systems at the time of its conception. The goals of the MPI design were portability, efficiency and functionality. The standard only defines a message passing library and leaves, among other things, the initialization and control of processes to individual developers to define. Like PVM, MPI is available on a wide range of platforms from tightly coupled systems to metacomputers. MPI libraries are available for Fortran 77, Fortran 90, ANSI C and C++.

A.4 LINPACK Benchmark

LINPACK is a software library for performing numerical linear algebra on digital computers. It makes use of the BLAS (Basic Linear Algebra Subprograms) libraries for



Figure A.2: The parallel computing cluster PLUTO located in Purnima Labs, Bhabha Atomic Research Center

performing basic vector and matrix operations. The LINPACK Benchmarks are a measure of a system's floating point computing power. They measure how fast a computer solves a dense $N \times N$ system of linear equations Ax = b, which is a common task in computational science. The solution is obtained by Gaussian elimination with partial pivoting, with $2/3N^3 + 2N^2$ floating point operations. The result is reported in number of floating point operations per second (FLOPS). The Fig. A.3 shows the LINPACK score of PLUTO as a function of number of processors. Each computing server with 8 cores (2CPU×4Cores) scored an average of 73 GFlops. However, when benchmark is run on multiple servers, latency of the network comes into play and affects the overall score. The total LINPACK score for 16 servers is found to be 1.005 TFlops which is ~ 85% of the sum of individual scores. It is the expected latency from the Infiniband network.



Figure A.3: LINPACK score for PLUTO cluster using Infiniband network and OpenMPI libraries. With 128 nodes, the cluster scored just above 1 TFlops.
Appendix B

List of Publications

- N. GARG, K. K. PANDEY, K. V. SHANAVAS, C. A. BETTY, AND S. M. SHARMA. Memory effect in low-density amorphous silicon under pressure. *Phys. Rev. B*, 83(11):115202, March 2011.
- A. NAG, A. HAZARIKA, K. V. SHANAVAS, S. M. SHARMA, I. DASGUPTA, AND D. D. SARMA. Crystal Structure Engineering by Fine-Tuning the Surface Energy: The Case of CdE (E = S/Se) Nanocrystals. J. Chem. Phys. Lett., 2:706, February 2011
- K. V. SHANAVAS, D. CHAUDHURY, I. DASGUPTA, S. M. SHARMA, AND D. D. SARMA. Origin of ferroelectric polarization in spiral magnetic structure of MnWO₄. *Phys. Rev. B*, 81(21):212406, June 2010.
- A. K. MISHRA, N. GARG, K. K. PANDEY, K. V. SHANAVAS, A. K. TYAGI, AND S. M. SHARMA. Zircon-monoclinic-scheelite transformation in nanocrystalline chromates. *Phys. Rev. B*, 81(10):104109, March 2010.
- 5. K. V. SHANAVAS AND S. M. SHARMA. Molecular dynamics simulations of phase transitions in argon-filled single-walled carbon nanotube bundles under high pressure. *Phys. Rev. B*, **79**(15):155425, April 2009.
- N. GARG, K. K. PANDEY, C. MURLI, K. V. SHANAVAS, B. P. MANDAL, A. K. TYAGI, AND S. M. SHARMA. Decomposition of lanthanum hafnate at high pressures. *Phys. Rev. B*, 77(21):214105, June 2008.

- K. V. SHANAVAS, K. K. PANDEY, N. GARG, AND S. M. SHARMA. Computer simulations of the crystallization kinetics in amorphous silicon under pressure. Submitted to Phys. Rev. B, 2011.
- K. V. SHANAVAS, A. NAG, A. HAZARIKA, I. DASGUPTA, D. D. SARMA, AND S. M. SHARMA. First principles study of the effect of organic ligands in the crystal structure of CdS nanoparticles. Submitted to J. Phys. Chem. C, 2011.
- K. V. SHANAVAS, H. K. POSWAL, AND S. M. SHARMA. First principles studies on the high pressure behavior of SiH₄(H₂)₂. Submitted to J. Phys.:Condens. Matter, 2011.

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