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Timothy J. Campbell

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NANOSTRUCTURE MODELING IN OXIDE CERAMICS USING LARGE SCALE PARALLEL MOLECULAR-DYNAMICS SIMULATIONS

A Dissertation

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in

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by
Timothy J. Campbell
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ABSTRACT

The purpose of this dissertation is to investigate the properties and processes in nanostructured oxide ceramics using molecular-dynamics (MD) simulations. These simulations are based on realistic interatomic potentials and require scalable and portable multiresolution algorithms implemented on parallel computers.

The dynamics of oxidation of aluminum nanoclusters is studied with a MD scheme that can simultaneously treat metallic and oxide systems. Dynamic charge transfer between anions and cations which gives rise to a compute-intensive Coulomb interaction, is treated by the O(N) Fast Multipole Method. Structural and dynamical correlations and local stresses reveal significant charge transfer and stress variations which cause rapid diffusion of Al and O on the nanocluster surface. At a constant temperature, the formation of an amorphous surface-oxide layer is observed during the first 100 picoseconds. Subsequent sharp decrease in O diffusion normal to the cluster surface arrests the growth of the oxide layer with a saturation thickness of 4 nanometers; this is in excellent agreement with experiments. Analyses of the oxide scale reveal significant charge transfer and variations in local structure. When the heat is not extracted from the cluster, the oxidizing reaction becomes explosive.

Sintering, structural correlations, vibrational properties, and mechanical behavior of nanophase silica glasses are also studied using the MD approach based on an empirical interatomic potential that consists of both two and three-body interactions. Nanophase silica glasses with densities ranging from 76 to 93% of the bulk glass density are obtained using an isothermal-isobaric MD approach. During the sintering process, the pore sizes and distribution change without any discernable change in the pore morphology. The height and position of the first sharp diffraction peak (the signature of intermediate-range order) in the neutron static structure factor shows significant differences in the nanophase glasses relative to the bulk silica glass.
Enhancement of the low-energy vibrational modes is observed. The effect of densification on mechanical properties is also examined.
CHAPTER 1

INTRODUCTION

Advanced materials comprise the improvement of natural resources and traditional materials and the development of new materials and combinations thereof. These materials establish the foundation for industry and the present day living standards we enjoy [1]. Critical to continued developments of advanced materials is progress in our understanding of the underlying structures and properties, and the processes involved when these materials interact with their service environment.

Over the past decade, nanostructured materials containing ultrafine microstructures on the order of a few nanometers have spurred a great deal of interest in the materials science community. Of particular interest to this dissertation are cluster-assembled nanostructured materials. The possibility of tailoring physical properties by controlling the size and distribution of nanoclusters has far-reaching technological implications; in particular, it may be possible to synthesize materials with unique mechanical, electrical, magnetic, and optical properties [2-7]. Experiments have shown that nanostructured metals are much harder than conventional metals with coarse-grained microstructures [8]. Conventional coarse-grain ceramic materials are known to be very brittle. It is firmly established that nanostructured ceramics are much more ductile and have much lower sintering temperatures than their coarse-grained counterparts [9-11]. Lower sintering temperatures translate into considerable savings in production costs. Recently, nanostructured composites, consisting of nanometer size metallic clusters passivated with an oxide layer, have been synthesized [12-14]. These composites are found to be harder and have higher melting temperatures while still retaining important metallic properties. Understanding the behavior of such nanostructured materials requires extensive research into the role of atoms in the interface regions, which comprise a large portion of the
material [4,15,16]. To this end, numerous theoretical, experimental, and computational approaches are being utilized.

Computational modeling is making a significant impact in the area of materials science. Due to the advances in mathematical algorithms, numerical methods, and high performance computing technologies the computational prediction of material properties is becoming increasingly possible [17-20]. A broad range of industries, such as pharmaceutical, microelectronics, and transportation, are already experiencing the impact of computational modeling technologies. The complexity of material systems precludes the formulation of a single comprehensive theory capable of describing the extreme range of length and time scales involved in the behavior of a material. However, powerful techniques have been developed that adequately describe material properties and processes within certain regimes.

In the microscopic regime, the interactions among nuclei and electrons are computed directly from the fundamental quantum mechanical description. Several quantum mechanical approaches are employed: quantum chemical methods, density-functional theory (DFT) within the local-density approximation (LDA), etc. [21,22]. These approaches are very accurate. However, the computational demands are enormous for even small system sizes (10 to 100 atoms). A combined DFT-LDA and molecular-dynamics approach was proposed by Car and Parrinello [23]. In this approach, the motion of atomic nuclei is computed using molecular dynamics while the electronic degrees of freedom are considered in the framework of DFT. The Car-Parrinello approach, which requires the orthogonalization of single-particle wavefunctions, is limited to systems containing $10^2$ to $10^3$ atoms. The desire to simulate larger system sizes, while still including quantum mechanical effects, has led to the development of the tight-binding molecular-dynamics (TBMD) approach [24,25]. In this method, a limited basis for localized interactions is used to describe an effective Hamiltonian for the electronic degrees of freedom. Direct implementation involves diagonalization and thus
scales as $N^3$. Recently $O(N)$ TBMD algorithms have been proposed, thus making it possible to simulate large systems ($10^3$ atoms on serial processors) [26-29].

In order to simulate larger system sizes, it is necessary to utilize a different description; the next step being to model only the interactions between atoms with an empirical potential. In this approach, known as molecular-dynamics (MD), each atom is treated as a point mass and the resulting Newton's equations of motion are integrated to obtain the phase-space trajectories. Empirical potentials to describe realistic physical systems may be formulated from more fundamental microscopic theories and usually have complicated functional forms. Parameters are fitted to experimental data and results of \textit{ab initio} calculations. Usually MD simulation is performed in the microcanonical ensemble. Advances have been made to extend MD simulations to different ensembles, such as constant temperature and/or constant pressure [30,31]. With these extensions it is possible to study phenomena such as sintering and pressure induced structural phase transformations.

The relatively short characteristic length and time scales of atomic motion limit the regime of MD simulations. Typically, time steps must be limited to the femtosecond scale in order to maintain numerical stability; thus thousands of timesteps are required to simulate even picoseconds of real time. Greater difficulty arises in ionic systems where long-range Coulombic forces are prevalent. Direct calculation of Coulomb energy in a system of $N$ atoms requires $O(N^2)$ operations. Significant gains can be made through the application of multiresolution techniques, such as reversible multiple-time step integrators [32], in conjunction with fast algorithms like the $O(N)$ Fast Multipole Method [33] for long-range interactions.

On serial processors, it is possible to simulate systems involving around $10^4$ to $10^5$ atoms using the MD technique. For the purposes of studying realistic systems (such as nanophase and nanocomposite materials) and complicated phenomena (such as oxidation, dynamic fracture, and nano-indentation), it is necessary to simulate much
larger systems for long time periods. Domain decomposition schemes can be applied to efficiently implement MD on parallel computers [34]. Powerful new parallel architectures have now made it possible to perform MD simulations on systems with $10^6$ to $10^8$ atoms [35-38].

Future approaches to simulating realistic systems will require combining multiple approaches to bridge the length and time scales. Consider, for example, the fracture of a material. Accurate description of the bond-breaking process near the crack tip requires a microscopic view of the material. However, away from the crack tip it becomes unnecessary to treat each and every atomic degree of freedom. Due to the long-range behavior of the stress fields around the crack, large system sizes and proper treatment of boundary conditions are necessary. Away from the singular region of the crack tip, the behavior of the material can be accurately described by continuum elasticity theory. Understanding how the processes near the crack tip lead to the observed macroscopic failure of the material requires the combination of quantum mechanical, atomistic, and continuum approaches. Progress in this area is being made [39-41], but realistic applications are still in the future. Bridging the time scales is a much more difficult problem; MD in the microsecond regime is still a goal to be attained. Recent work by Voter [42] has made significant progress in accelerating MD simulations of infrequent processes in solids based on transition state theory [43].

The theme of this dissertation is the modeling of nanostructured oxide ceramics using MD simulations on parallel computers. The focus is two-fold: (i) the oxidation of aluminum nanoclusters is investigated with a MD approach based on dynamic charge transfer among atoms; and (ii) sintering, structural correlations, vibrational properties, and mechanical behavior are investigated in nanophase silica glasses.

Silicon and aluminum, together with oxygen, account for 90% of the elements found in the earth's crust [44]. The importance of these elements and the subsequent oxides that are formed in electronic, optical, chemical, and structural applications is well
established [45-47]. Like most metals, aluminum is known to react with oxygen. Understanding the oxidation process and its effects on the properties of the oxidized material is a long-standing problem and the focus of numerous research efforts [48]. The pioneering works of Mott [49] and Cabrera and Mott [50] on the oxidation of metals provide a general theoretical framework in which much of the complicated phenomena can be understood for an infinite flat surface. Only recently, with the advent of nanophase materials, has there been experimental research into understanding the oxidation behavior of small metallic clusters [51]. The presence of a passivating oxide layer can greatly affect the adhesive properties of the metal. Prior to the work presented in this dissertation, no known MD simulations of the oxidation of aluminum nanoclusters had been performed. Among the unique features of these MD simulations is the incorporation of dynamic charge transfer between anions and cations. In this manner the important atomic scale dynamics near the metal-oxide interface can be simulated. These simulations provide a framework for future MD studies of oxidation and also set the stage for continued simulations of nanocomposite materials.

Nanophase materials are known to have unique thermo-mechanical properties in comparison to conventional crystalline or amorphous materials. Much of the research in nanophase materials has focused on what is known as “nanocrystalline” materials synthesized from nanometer sized crystalline clusters. It is also of interest to consider the production of unique non-crystalline materials by assembling nanometer sized amorphous clusters. It is observed that the structure and mechanical behavior of these nanophase amorphous materials is quite different from that of bulk amorphous solids [52-54]. In order to investigate these differences we perform million atom MD simulations on the most widely studied amorphous material – silica. Nanometer size clusters contain ~10^4 atoms; with ~10^2 clusters a reasonable model of nanophase material can be constructed.

The outline of this dissertation is as follows: Chapter 2 is a description of the MD scheme and its connection to physical properties; Chapter 3 discusses the multiresolution
MD algorithms used; Chapter 4 describes an implementation of MD simulations on parallel computers; in Chapter 5 the simulations of the oxidation of aluminum nanoclusters are reported; the MD simulations of nanophase silica are presented in Chapter 6; and Chapter 7 is conclusions and a discussion of future directions.
CHAPTER 2

MOLECULAR-DYNAMICS SIMULATIONS

In the molecular-dynamics (MD) simulation technique the dynamical history of an ensemble of atoms is computed from the Newton's equations of motion. Hence, we are able to observe the time evolution of microscopic phenomena. Additionally, macroscopic physical properties can be obtained from this detailed information using statistical mechanics. The connection between MD simulation and statistical mechanics will be discussed more fully in section 2.4. In section 2.1 the formulation of molecular dynamics will be described for several statistical ensembles. Sections 2.2 and 2.3 will then discuss in general the interatomic potentials used in MD simulations and how the initialization and boundary conditions in MD are handled.

2.1 Formulation of molecular-dynamics approach

Each statistical ensemble is characterized by a set of conserved thermodynamic quantities such as volume \( V \), energy \( E \), temperature \( T \), and pressure \( P \). The microcanonical ensemble \((NVE)\) is the most commonly used statistical ensemble in MD simulations. Here the system of \( N \) atoms is considered to be completely isolated from the surrounding environment. In order to simulate other statistical ensembles, additional variables are introduced into the Lagrangian to represent the coupling of the system with external sources. In the canonical ensemble \((NVT)\), the system is thermally coupled with a heat reservoir. In addition to the heat reservoir, a mechanical coupling can also be introduced to represent the isothermal-isobaric ensemble \((NPT)\). In this section, the basic formalisms of MD simulations for each of these ensembles will be discussed.

We consider a system of \( N \) atoms with coordinates \( \{ r_i : i = 1, \ldots, N \} \) and momenta \( \{ p_i : i = 1, \ldots, N \} \) within a fixed volume \( V \). The atoms are assumed to interact with a potential \( V = V(\{r_i\}) \). Treating the atoms as classical point-like objects the Hamiltonian of the system is written as,
\[ \mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \mathcal{V}(\{r_i\}) , \tag{2.1} \]

where \( m_i \) are the masses of atoms in the system. Classical treatment corresponds to the criterion that the interatomic spacing be much larger than the thermal wavelength \( h/(2\pi \hbar k_B T)^{1/2} \) associated with the atoms. Substituting (2.1) into the Hamilton equations of motion,

\[ r_i = \frac{\partial \mathcal{H}}{\partial p_i} , \quad p_i = -\frac{\partial \mathcal{H}}{\partial r_i} , \tag{2.2} \]

we obtain the Newton equations of motion

\[ m_i \ddot{r}_i = -\nabla r_i \mathcal{V} = f_i , \quad i = 1, \ldots, N , \tag{2.3} \]

where \( f_i \) is the force on atom \( i \). We now have a set of \( 3N \) coupled second-order differential equations which can be numerically integrated in time to generate the dynamical history of the system. The Hamiltonian is a constant of the motion when the forces among atoms are conservative. In the case of the microcanonical ensemble, the total energy is conserved, and is therefore equal to the Hamiltonian.

The canonical ensemble was first introduced in MD simulations by Nosé [30,55]. Starting with the extended Hamiltonian,

\[ \mathcal{H}_{\text{Nosé}} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i s^2} + \mathcal{V}(\{r_i\}) + \frac{p_i^2}{2Q} + (3N + 1)k_B T \ln s , \tag{2.4} \]

where \( Q \) is the "mass" associated with the variable \( s \), Nosé showed that microcanonical distribution for the extended system is equivalent to the canonical distribution of the set of variables \( \{r_i,p_i/s\} \). The variable \( s \) is interpreted as a time scaling factor, where the time in the canonical distribution is related to the real time as \( t' = t/s \). A slightly different representation that is free of the time scaling was later developed by Hoover [56] who showed that the equations of motion of Nosé are in fact unique and therefore the two representations are equivalent. Martyna, et al. [57] extended the Nosé-Hoover dynamics to employ a chain of thermostats by proposing the following equations of motion:
\[ \dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}, \]
\[ \dot{\mathbf{p}}_i = f_i - \mathbf{p}_i \frac{p_{\xi_j}}{Q_i}, \]
\[ \dot{\mathbf{p}}_{\xi_j} = \frac{p_{\xi_j}}{Q_i}, \]
\[ \dot{p}_{\xi_{i}} = \left[ \sum_{i=1}^{N} \frac{P_{i}^{2}}{m_{i}} - 3Nk_{B}T \right] - p_{\xi_{i}} \frac{p_{\xi_{i}}}{Q_{2}}, \]
\[ \dot{p}_{\xi_{j}} = \left[ \frac{p_{\xi_{j+1}}^{2}}{Q_{j-1}} - k_{B}T \right] - p_{\xi_{j}} \frac{p_{\xi_{j}}}{Q_{j-1}}, \]
\[ \dot{p}_{\xi_{M}} = \left[ \frac{p_{\xi_{M+1}}^{2}}{Q_{M-1}} - k_{B}T \right]. \]

where \( M \) is the number of thermostats \( \xi_{j} \), and \( Q_{j} \) and \( p_{\xi_{j}} \) are respectively the mass and momenta of thermostat \( \xi_{j} \). The conserved quantity for this system is,

\[ \mathcal{H} = \sum_{i=1}^{N} \frac{P_{i}^{2}}{2m_{i}} + \sum_{i=1}^{M} \frac{p_{\xi_{i}}^{2}}{2Q_{i}} + V(\{r_{i}\}) + 3Nk_{B}T\sum_{i=2}^{M} p_{\xi_{i}} + k_{B}T\sum_{i=2}^{M} \xi_{i}. \]  

(2.6)

In MD simulations of nanophase materials, it is necessary to consider the conditions of constant temperature and pressure to study the sintering process. Several techniques have been introduced to accomplish this [30,58,59]. In these extended system techniques, both the size and the shape of the MD cell are allowed to vary with time. The varying MD cell is incorporated by defining a transformation matrix \( \mathbf{H} = \{\mathbf{h}_{1}, \mathbf{h}_{2}, \mathbf{h}_{3}\} \) (typically referred to as the \( h \)-matrix) whose columns are the three vectors \( \mathbf{h}_{a} \) representing the sides of the MD cell, as illustrated in Fig. 2.1. The volume of the MD cell is given by,

\[ V = \det[\mathbf{H}] = \mathbf{h}_{1} \cdot \mathbf{h}_{2} \times \mathbf{h}_{3}. \]  

(2.7)

Scaled coordinates are introduced through the transformation,

\[ \mathbf{r} = \mathbf{Hs}, \]  

(2.8)

where \( s_{ia} \in [0,1] \).
Following the approach of Martyna et al. [60] the equations of motion necessary to produce the isothermal-isobaric ensemble are,

\[
\begin{align*}
\dot{r}_i &= \frac{p_i}{m_i} + \frac{P_{x}}{W_g} r_i, \\
\dot{p}_i &= f_i - \frac{P_x}{W_g} p_i - \left( \frac{1}{3N} \text{Tr}[P_x] \right) \frac{P_x}{Q} p_i, \\
\dot{H} &= \frac{P H}{W_g}, \\
\dot{P}_x &= V(P_{int} - IP_{ext}) + \left[ \frac{1}{3N} \sum_{i=1}^{N} \frac{p_i^2}{m_i} \right] I - \frac{P_x}{Q} P_x, \\
\dot{\xi} &= \frac{P_x}{Q}, \\
\dot{\mu} &= \sum_{i=1}^{N} \frac{p_i^2}{m_i} + \frac{1}{W_g} \text{Tr}[\dot{P}_x P_x] - (3N+9)kT.
\end{align*}
\]

(2.9)

where $I$ is the identity matrix and $P_x$ is the so called cell variable momentum matrix. The atoms and the cell variables have been coupled to a single thermostat. The pressure tensor is defined as,

\[
(P_{int})_{\alpha\beta} = \frac{1}{V} \left[ \sum_{i=1}^{N} \left( \frac{p_{i\alpha} p_{i\beta}}{m_i} + f_{i\alpha} r_{i\beta} \right) - \left( \Phi H \right)_{\alpha\beta} \right], \quad \phi_{\alpha\beta} = \frac{\partial \nu\{\{r_i, H\}}{\partial h_{\alpha\beta}}.
\]

(2.10)
The possibility for explicit dependence of the potential on $H$ is included. This is necessary whenever long-range interactions, such as the Coulomb potential, are present. The conserved quantity for the equations of motion (2.9) is,

$$
\mathcal{H} = \sum_{i=1}^{n} \frac{p_i^2}{2m_i} + \frac{1}{2W} \text{tr} [\hat{p}^2 \hat{p}^2] + \frac{p_x^2}{2Q} + \mathcal{V}\{\{\textbf{r}_i\},\textbf{H}\}.
$$

(2.11)

Because the equations of motion (2.9) use the full matrix of Cartesian cell parameters $H$, the cell can, in general, rotate in space. This motion can make data analysis difficult. Elimination of the cell rotations can be accomplished by working with a symmetrized tensor $P_{\alpha\beta} = \frac{1}{2} (P_{\alpha\beta} + P_{\beta\alpha})$. In this manner, if the initial total angular momentum of the cell is zero, the cell will not rotate. This approach is implemented by constraining $\text{G} = \tilde{\text{G}}$, where $P = W \text{G}$ [60,61].

2.2 Interatomic potentials for molecular-dynamics simulations

The underpinning of MD simulations is the interatomic potential. The quality of the simulation results are determined by the accuracy of the potential, and the amount of compute time is determined by its functional complexity. In principle, the potential energy may be written as a sum of one-body, two-body, and higher order interactions:

$$
\mathcal{V} = \sum_i \nu^{(1)}(\textbf{r}_i) + \sum_{j \neq i} \nu^{(2)}(\textbf{r}_i, \textbf{r}_j) + \sum_{k > j > i} \nu^{(3)}(\textbf{r}_i, \textbf{r}_j, \textbf{r}_k) + \ldots
$$

(2.12)

The one-body contribution depends on the absolute atomic positions and represents the effects of an external field. The two-body interaction potentials are among the simplest approaches and have been successful in approximating the interaction between atoms. A typical example of a two-body potential is the Lennard-Jones potential,

$$
\nu(r_{ij}) = 4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right],
$$

(2.13)

where $r_{ij}$ is the separation between atoms $i$ and $j$, $\varepsilon$ represents the potential well depth, and $\sigma$ is the characteristic length in the potential. The scale of the atomic sizes is described by the repulsive part (first term) of (2.13). Depending on the material properties, the
potential also has a cutoff at \( r_{ij} = r_c \). This potential has been used successfully to give reasonable model for solids and liquids composed of inert gas atoms. In order to approximate molecular systems involving covalent bonding, it is necessary to also consider the interactions among triplets of atoms. A potential form commonly used for covalent materials is the Stillinger-Weber potential [62] in which the three-body contribution is given by

\[
\nu^{(3)}(r_{ij}, r_{ik}) = \exp \left[ \xi (r_{ij} - a)^{-1} + \xi (r_{ik} - a)^{-1} \right] \left( \cos \theta_{ijk} - \cos \bar{\theta}_{ijk} \right)^2, \tag{2.14}
\]

where

\[
\cos \theta_{ijk} = \frac{\vec{r}_{ij} \cdot \vec{r}_{ik}}{r_{ij} r_{ik}}. \tag{2.15}
\]

The first term in the three-body interaction (2.14) incorporates the effects of bond stretching and the second term bond bending.

The bond-order formalism yields a different class of interatomic potentials that, unlike the three-body interaction (2.14), can effectively treat the dependence of the bond strength on coordination. These potentials were developed from ideas originally proposed by George Abell [63] based on the chemical pseudopotential theory. Abell derived the following expression for the binding energy \( E_i \) of each atom \( i \) as a function of the nearest-neighbor distance \( r_{ij} \):

\[
E_i = \frac{1}{2} \sum_{j=1}^{Z} \left[ q V_r (r_{ij}) + b V_a (r_{ij}) \right]. \tag{2.16}
\]

The quantity \( Z \) is the number of nearest neighbors, \( q \) is the number of valence electrons per atom, and \( b \) is the bond order. The functions \( V_r (r_{ij}) \) and \( V_a (r_{ij}) \) represent the interatomic repulsion and attraction, respectively. The bond order \( b \), which indicates the strength of a chemical bond, is derived from electronic-structure theory. Subsequently, Tersoff added additional features to Abell’s formalism that led to a set of classical potential functions for silicon [64], carbon [65], germanium, and silicon carbide [66]. Tersoff’s form of the bond order function \( b = b_{ij} \) was assumed to depend on the local
coordination and bond angles. The general behavior of the bond order is such that it decreases when the coordination of an atom increases, resulting in a decrease in the bond strength. This is the Pauling bond order/bond-length relationship [67] that is followed by most materials. Based on Abell’s bond-order ideas and Tersoff’s success in modeling covalent solids, Brenner et al. developed the Reactive Empirical Bond-Order (REBO) potentials for modeling hydrocarbons [68]. The uniqueness of the REBO model lies in its ability to describe with a single classical expression the bonding in molecular and solid-state structures.

The modeling of metallic systems has found the most success in a number of approaches introduced in the 1980's and collectively known as the embedded-atom methods (EAM) [69-71]. In these methods, the total energy is represented by an expression of the form

\[ E = \sum_i F_i \left( \sum_{j \neq i}^{} f_j(r_{ij}) \right) + \frac{1}{2} \sum_{i,j} \phi_{ij}(r_{ij}). \]  

(2.17)

In Eq. (2.17), \( r_{ij} \) is the separation between atoms \( i \) and \( j \), and \( F, f, \) and \( \phi \) depend on the species involved, as well as \( r_{ij} \). Interpretation of the terms in (2.17) can be made based on the idea of an embedding energy where the cohesive energy of an atom is largely determined by the local electron density into which the atom is placed [72,73]. The contribution to the electron density at a site \( i \) due to the neighboring atom \( j \) is given by \( f_j(r_{ij}) \). Thus, the sum over the \( f_j \) is a measure of the local electron density. The energy associated with placing atom \( i \) in that environment is given by the embedding energy \( F \). The pair-potential term \( \phi_{ij} \) incorporates residual pair interactions, including electrostatic contributions. Alternative interpretations based on various models, such as a tight-binding [70], exist to describe these parameters. However, these individual approaches all tend to give similar results [71].
2.3 Initial conditions and boundary conditions

Before starting an MD simulation, it is necessary to specify an initial configuration, the details of which will depend on the chosen integration algorithm. For the algorithm used in this work (Velocity-Verlet), it is necessary that the positions and velocities of all atoms and all extended variables be specified. Typically three initial configurations are possible: (i) the atoms are initially placed at their equilibrium lattice positions and random velocities are assigned; (ii) random atomic positions and velocities are assigned; and (iii) a previous phase-space configuration is chosen.

When specifying the initial velocities in MD simulations it is usual to choose random velocities, with magnitudes that corresponds to a Maxwell-Boltzmann distribution. The desired temperature is obtained by scaling the magnitudes of the initial velocities according to the equipartition theorem. The total linear and angular momentum are set to zero.

Computational resources limit the size of the system that can be studied in MD simulations. In order to circumvent these limitations and approximate the behavior of the infinite system, periodic boundary conditions (pbc) are typically used. Figure (2.2) illustrates how pbc is implemented in MD simulations. The simulation cell is repeated throughout space to form an infinite lattice. Each image cell contains \(N\) atoms with the same relative positions and corresponding velocities as the central cell. When an atom leaves a cell, an image of that atom enters the cell through the opposite face. In this manner there are no walls at the boundary of the central cell and the number of atoms in the entire system remains constant.

Typically the range of interaction in MD simulations is limited to a certain finite separation between atoms. If this range is smaller than half of the MD cell size, it is then only necessary to consider interactions with the closest image atoms (the “minimum image convention”). In the case of long-range interactions, it is necessary to take into account
interactions with all periodic images. Special algorithms to compute the infinite summations associated with long-range interactions are discussed in Chapter 3.

Figure 2.2 Periodic boundary conditions in MD. The simulation cell (shaded) is infinitely repeated in each direction. When atom B leaves the MD cell to the left, its periodic image enters from the right.

When simulating inhomogeneous systems such as a solid-gas interface, it may be necessary to apply a different kind of boundary condition. The gas atoms can be contained within the MD cell by making the walls of the cell perfectly reflecting with infinite mass. In other words, when an atom hits the wall with a momentum \( \mathbf{p} \) it is reflected back with a new momentum \( \mathbf{p}' = \mathbf{p} - 2(\mathbf{p} \cdot \mathbf{n})\mathbf{n} \), where \( \mathbf{n} \) is the inward normal vector for the wall of contact. In this manner, the magnitude of an atom's momentum and the total kinetic energy of the system are unchanged. In the oxidation simulations presented in Chapter 5 a spherical version of the reflecting wall boundary condition is used.

### 2.4 Evaluation of physical properties

Typically, only a few parameters define the thermodynamic state of a system. For example, the canonical ensemble is described by the number of atoms \( N \), the volume \( V \),
and the temperature $T$. Knowledge of the equations of state and thermodynamic equations may be used to derive other thermodynamic properties of the system. In other words, thermodynamic quantities are not determined by the instantaneous mechanical state, rather they are representative of an average behavior of the system. For a system of $N$ atoms without constraints, the phase space is a $6N$ dimensional hyperspace consisting of positions and momenta of all the atoms. A point in phase space $\Gamma$ represents an instantaneous state of the system. A microscopic property $A$ (such as pressure) may be calculated from the time average of the instantaneous value $A(\Gamma)$:

$$
A = \langle A \rangle_{\text{time}} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(\Gamma(t)) dt.
$$

(2.18)

where $\tau$ is the time over which we let the system evolve. In MD simulations, (2.18) is computed over successive time steps of size $\delta t$:

$$
A = \langle A \rangle_{\text{time}} = \frac{1}{N_{\text{step}}} \sum_{n=1}^{N_{\text{step}}} A(\Gamma_n).
$$

(2.19)

The conventional approach in statistical mechanics is to use the ensemble average to calculate thermodynamic properties. Here, an ensemble is a collection of points $\Gamma$ in the phase space that are distributed according to the probability density $\rho(\Gamma)$ which is defined by the chosen fixed thermodynamic parameters. The equivalence of the time average (2.18) and the ensemble average in statistical mechanics allows the calculation of physical quantities in MD simulations. This equivalence can only be made when the system is ergodic, i.e. given a sufficiently long time, a trajectory in phase space will eventually visit all state points.

**2.4.1 Thermodynamic properties**

The thermodynamic temperature can be calculated from the average kinetic energy using the equipartition principle:

$$
T = \frac{2\langle K \rangle}{3Nk_B}.
$$

(2.20)

The thermodynamic pressure may be calculated from the virial:
\[ PV = N k_b T + \left( \frac{1}{2} \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i \right). \] (2.21)

When \( pbc \) are employed it is essential to use
\[ PV = N k_b T + \left( \frac{1}{2} \sum_{i} \sum_{j \neq i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right), \] (2.22)

where \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \) and \( \mathbf{f}_{ij} \) is the force on atom \( i \) due to atom \( j \). Equation (2.22) is explicitly independent of the choice of origin.

Physical quantities may also be obtained from the root mean square (RMS) fluctuation of thermodynamic variables. A common example is the constant-volume heat capacity \( C_v = (\partial E/\partial T)_V \). In the microcanonical ensemble, \( C_v \) may be calculated from the RMS fluctuations of the potential or kinetic energies:
\[ \langle \delta V^2 \rangle = \langle \delta K^2 \rangle = \frac{1}{2} N k_b T^2 \left( 1 - \frac{3N k_b}{2C_v} \right). \] (2.23)

### 2.4.2 Structural correlations

One of the most convenient functions for examining two-body structural correlations is the pair-distribution function, \( g_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \), defined via
\[ \langle n_\alpha(\mathbf{r}_1) \rangle g_{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) \langle n_\beta(\mathbf{r}_2) \rangle = \left( \sum_{i \in [\alpha]} \sum_{j \in [\beta]} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \right). \] (2.24)

where \( n_\alpha(\mathbf{r}_1) \) is the number density of atoms of species \( \alpha \) at a position \( \mathbf{r}_1 \), and \( \langle ... \rangle \) denotes an ensemble average. When the system is translationally invariant, the pair-distribution function depends only on the relative separation \( \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \):
\[ \langle n_\alpha \rangle g_{\alpha\beta}(\mathbf{r}) \langle n_\beta \rangle = \frac{1}{V} \left( \sum_{i \in [\alpha]} \sum_{j \in [\beta]} \delta(\mathbf{r} - \mathbf{r}_j) \right). \] (2.25)

Furthermore, if the system is isotropic, Eq. (2.25) may be averaged over all directions of \( \mathbf{r} \). The result may be written as,
where \( \langle n_{\alpha\beta}(r) \rangle \Delta r \) denotes the average number of atoms of species \( \beta \) in a shell of width \( \Delta r \) at a radius \( r \) about an atom of species \( \alpha \).

We may obtain the coordination number of a species \( \alpha \) by integrating over (2.26):

\[
N_{\alpha\beta}(R) = 4\pi \langle n_{\beta} \rangle \int_0^R g_{\alpha\beta}(r)^2 dr.
\]

(2.27)

\( N_{\alpha\beta}(R) \) is the number of atoms of species \( \beta \) within a sphere of radius \( R \) surrounding an atom of species \( \alpha \). The total pair-distribution function \( g(r) \) is defined as

\[
g(r) = \sum_{\alpha, \beta} c_\alpha c_\beta g_{\alpha\beta}(r),
\]

(2.28)

where \( c_\alpha \) and \( c_\beta \) are the concentrations \( (N_\alpha/N \) and \( N_\beta/N \) of species \( \alpha \) and \( \beta \), respectively.

Partial static structure factors are calculated from the Fourier transforms of corresponding partial pair-distribution functions:

\[
S_{\alpha\beta}(q) = \delta_{\alpha\beta} + (c_\alpha c_\beta)^{1/2} \langle n \rangle \int g_{\alpha\beta}(r) e^{iq\cdot r} d^3 r.
\]

(2.29)

When the system is isotropic the angular dependence is integrated out and (2.29) simplifies to

\[
S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4\pi \langle n \rangle (c_\alpha c_\beta)^{1/2} \int_0^\infty \left[ g_{\alpha\beta}(r) - 1 \right] \frac{\sin(qr)}{qr} r^2 dr.
\]

(2.30)

The total static structure factor is given by

\[
S(q) = \sum_{\alpha, \beta} (c_\alpha c_\beta)^{1/2} S_{\alpha\beta}(q).
\]

(2.31)

By weighting the partial static structure factors with coherent neutron-scattering lengths, we may obtain the neutron-scattering static structure factor [74]:

\[
S_N(q) = \sum_{\alpha, \beta} b_\alpha b_\beta (c_\alpha c_\beta)^{1/2} \left[ \frac{S_{\alpha\beta}(q) - \delta_{\alpha\beta} + (c_\alpha c_\beta)^{1/2}}{\left( \sum_\alpha b_\alpha c_\alpha \right)^2} \right].
\]

(2.32)

where \( b_\alpha \) denotes the coherent neutron-scattering length of species \( \alpha \).
Orientational order can be investigated by analyzing bond-angle distributions. These represent important three-particle correlations. To calculate bond-angle distributions in MD simulations, it is necessary to consider a cutoff distance that defines the nearest-neighbor list of species $\beta$ for each atom of species $\alpha$. This cutoff is taken to be the first minimum in $g_{\alpha\beta}(r)$. In a two component system with species $A$ and $X$, the set of possible bond-angle distributions to consider is \{X-A-X, A-X-A, A-A-X, X-X-A, A-A-A, X-X-X\}. As an example calculation, consider the X-A-X bond-angle distribution. In this case a list of nearest-neighbor atoms of species $X$ around an atom of species $A$ is constructed using the defined cutoff. From this nearest-neighbor list for each $A$ atom, a histogram is constructed from all X-A-X angles.

2.4.3 Dynamic correlations

The dynamic correlation between two quantities $A$ and $B$ can be measured by calculating the correlation coefficient $c_{AB}$,

$$c_{AB} = \frac{(A - \langle A \rangle)(B - \langle B \rangle)}{\sqrt{\langle \delta A^2 \rangle \langle \delta B^2 \rangle}},$$

(2.33)

where $\langle \delta A^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$ is the fluctuation of $A$. A useful extension to (2.33) is to consider $A$ and $B$ at two different times, $t_A$ and $t_B$. Then $c_{AB}$ then becomes a time correlation function $c_{AB}(t)$ of the time difference $t = |t_B - t_A|$. The absolute value of $c_{AB}$ lies between 0 and 1, with values close to 1 indicating a high degree of correlation. The autocorrelation function, $c_{AA}(t)$, measures the correlation of a quantity with itself. Time correlations are useful in calculating macroscopic transport coefficients and their Fourier transforms may be related to experimental spectra.

One important time correlation function is the velocity autocorrelation function,

$$Z_v(t) = \frac{\langle v_i(0) \cdot v_i(t) \rangle}{\langle v_i^2(0) \rangle},$$

(2.34)

which is related to the constant of self-diffusion $D_v$ via,
\[ D_\alpha = \frac{k_b T}{m_\alpha} \int_0^\infty Z_\alpha(t) dt, \]  

(2.35)

where \( m_\alpha \) is the mass of species \( \alpha \). In the harmonic approximation, the partial phonon density-of-states (DOS) is proportional to the Fourier transform of the velocity autocorrelation function.

The constant of self-diffusion can also be calculated from mean-square displacements

\[ D_\alpha = \lim_{t \to +\infty} \left( \frac{\langle r^2 \rangle_\alpha}{6t} \right), \]  

(2.36)

where

\[ \langle r^2 \rangle_\alpha = \left( \frac{1}{N_\alpha} \sum_{i,j(\alpha)} [r_j(t+s) - r_j(s)]^2 \right), \]  

(2.37)

and \( N_\alpha \) is the number of atoms of species \( \alpha \).

2.4.3 Mechanical properties

The internal stress tensor may be calculated from the virial \([75]\):

\[ \sigma_{\alpha\beta} = \frac{1}{V} \left( \sum_i m_i v_i^\alpha v_i^\beta + \sum_{i,j(i)} r_{ij}^\alpha f_{ij}^\beta \right), \]  

(2.38)

where \( \alpha \) and \( \beta \) are Cartesian indices. When the forces are short-ranged the \( r_{ij} \) in (2.38) are minimum-image separations. Contributions to the stress tensor from long-range forces require special techniques that will be discussed in Chapter 3. In (2.38) it is assumed that the potential can be decomposed into a two-body form with \( f_{ij} = -f_{ji} \). Local stress distributions are conveniently calculated using (2.38) by restricting the summation over \( i \) to atoms within a small volume \( \Omega [76] \):

\[ \sigma_{\alpha\beta} = \frac{1}{\Omega} \left( \sum_{i,r,\in\Omega} m_i v_i^\alpha v_i^\beta + \sum_{i,r,\in\Omega} \sum_{j>i} r_{ij}^\alpha f_{ij}^\beta \right). \]  

(2.39)

Elastic constants describe the thermodynamic equilibrium response of the stress tensor to applied strain. The deformation of a three-dimensional solid may be determined
by specifying six independent strains \((u_x, u_y, u_z, u_{yz}, u_{zx}, u_{xy})\) and appropriately modifying the \(h\)-matrix. When a homogeneous deformation of the system occurs the \(h\)-matrix changes from \(\mathbf{H}_0\) to \(\mathbf{H}\), and \(\mathbf{H}\) can be calculated from

\[
\bar{\mathbf{H}} \mathbf{H} = \bar{\mathbf{H}}_0 (1 + 2\mathbf{U}) \mathbf{H}_0,
\]

(2.40)

where \(\mathbf{U}\) is the strain tensor [31]. For small deformations we write \(\mathbf{H} = \mathbf{H}_0 + \delta\mathbf{H}\). In this case (2.40) can be written as

\[
2\bar{\mathbf{H}}_0 \mathbf{U} \mathbf{H}_0 = \bar{\mathbf{H}}_0 \delta\mathbf{H} + \delta\mathbf{H} \mathbf{H}_0,
\]

(2.41)

where terms second order in \(\delta\mathbf{H}\) are neglected. Note that the LHS of (2.41) is symmetric, thus we can write \(\bar{\mathbf{H}}_0 \delta\mathbf{H}\) as the sum 1/2 times the LHS plus any antisymmetric matrix \(\mathbf{C}\). When this is done (2.41) becomes

\[
\delta\mathbf{H} = \mathbf{U} \mathbf{H}_0 + \bar{\mathbf{H}}_0^{-1} \mathbf{C}.
\]

(2.42)

Taking \(\mathbf{C}\) to be zero in (2.42) gives us a practical method for calculating elastic moduli in a MD simulation. First, the system is brought to the zero-force configuration using the steepest descent quench. Then the deformed \(h\)-matrix, \(\mathbf{H}\), that corresponds to the specified strain is computed from (2.42). Subsequently, the system is relaxed using the conjugate-gradient approach [77]. The elastic moduli, \(C_{\alpha\beta\gamma\delta}\) are calculated from Hooke’s law,

\[
\sigma_{\alpha\beta} = \sum_{\gamma,\delta} C_{\alpha\beta\gamma\delta} \epsilon_{\gamma\delta},
\]

(2.43)

where the stress, \(\sigma_{\alpha\beta}\) is computed using (2.38).
CHAPTER 3

MULTIRESOLUTION ALGORITHMS

Molecular-dynamics (MD) simulations for complex physical systems can be computationally very demanding: they may require large numbers of atoms, long simulation times, and computationally intensive interatomic interactions. For example, MD simulations of cluster-assembled nanophase materials can require $10^6$ to $10^7$ atoms, since each cluster consists of $10^3$ to $10^5$ atoms. Preparation of well-thermalized nanophase systems and calculation of mechanical and thermal properties can require $10^5$ to $10^7$ time steps. Clearly, it is necessary to employ algorithms that reduce the amount of required computation. In this chapter we present several "multiresolution" algorithms that are utilized in order to facilitate the MD simulations of multimillion atom systems. Multiresolution algorithms improve the performance of MD simulations by taking advantage of the multiple length and time scales that are inherent in many of the problems of interest.

3.1 Short-range interactions

3.1.1 Two-body vs. three-body potentials

Three-body force calculations can be a time consuming part of MD; direct calculation requires $O(N^3)$ operations. Speedup of the three-body force calculation has been accomplished by using a separable three-body force calculation [78,79]. In this approach, the three-body potential is rewritten by decomposing the inner product, $\mathbf{r}_i \cdot \mathbf{r}_k$.

$$\mathbf{r}_i \cdot \mathbf{r}_k = x_{ik}x_{ik} + y_{ik}y_{ik} + z_{ik}z_{ik}.$$  \hspace{1cm} (3.1)

The resulting expressions for the potential energy and forces become separable into two factors, each of which involves only pairwise interactions, thus reducing the computational complexity from $O(N^3)$ to $O(N^2)$.
Short-range two-body potentials may be modified with a cutoff radius $r_c$, beyond which the potential is zero. In order to circumvent truncation errors in the calculation of forces, the potential is modified in such a way that both the potential and the force vanish at $r_c$ [80]:

$$
\nu(r) = \begin{cases} 
\nu(r) - (r - r_c) \left( \frac{d\nu(r)}{dr} \right)_{r=r_c} , & r \leq r_c \\
0 , & r > r_c 
\end{cases}
$$

(3.2)

3.1.2 Link-cell and neighbor lists

Application of range reducing techniques, such as the shifted-force potential (3.2), allow the incorporation of additional strategies that reduce the time required for identifying pairs separated by less than $r_c$. Two such strategies are the neighbor list method and link-cell list method.

In the link-cell list method, shown in Fig. 3.1(a), the MD cell is subdivided into cells of equal volume and the atoms are sorted into a linked list associated with each cell. The cell size is chosen to be slightly larger than $r_c$, so that the link-cell list can be recomputed after several time steps. To calculate the forces on an atom $i$, we need only to consider the atoms within the same cell that $i$ resides in and those atoms within neighboring cells. Suppose the average number of neighbors with which an atom interacts is $N_b$, which is independent of $N$. Then the force computation in the link-cell list method scales as $N_bN$, which reduces the complexity from $O(N^2)$ to $O(N)$. Further reduction in the computation can be made by using Newton’s third law and performing the force computation over half of the neighboring cells, as illustrated in Fig. 3.1(b).

Additional reduction in computation can be achieved by using the link-cell lists to construct neighbor lists for each atom $i$. The neighbor list is an index table for all the neighbors of $i$ that lie within $r_c$ of $i$. Approximately $N_bN$ amount of storage is required for
the neighbor list, which makes this strategy memory intensive and therefore limited to potentials that are very short ranged, such as the three-body potential.

![Diagram of link-cell list method in 2-D](image)

Figure 3.1 The link-cell list method in 2-D. The link-cell size is slightly larger than the cutoff \(r_c\). (a) Only nearest-neighbor cells (lightly shaded cells) are necessary for force calculations in the dark cell. (b) Only half of the link-cells need to be considered when using Newton's third law.

### 3.2 Long-range interactions

Long-range interactions, such as the Coulomb interaction, present a major computational challenge in MD simulations. In the presence of periodic boundary conditions (\(pbc\)), the total Coulomb energy of a charge neutral system of \(N\) atoms is given by

\[
\mathcal{V} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\mathbf{n}} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{n}|},
\]

where \(q_i\) is the charge of atom \(i\). The simple cubic lattice translation vector is \(\mathbf{n} = (n_x L_x, n_y L_y, n_z L_z)\), where the \(L_a\) are the side lengths of the central MD cell. The prime on the sum over \(\mathbf{n}\) implies that terms with \(i = j\) are omitted when \(\mathbf{n} = 0\). The sum (3.3) is conditionally convergent, i.e. the result depends upon the order of summation [80]. Conventional approaches conceptually build the infinite periodic system in roughly spherical layers for proper convergence. Direct computation of (3.3) requires \(\mathcal{O}(N^3)\) operations, which is clearly intractable for the large \(N\) required for realistic simulations.
The popular approach to solving (3.3) is the Ewald summation technique which has been shown to scale as $N^{3/2}$. Recently, fast summation methods that can further reduce the computational complexity to $O(N)$ have been developed.

### 3.2.1 Ewald summation

Ewald summation is a popular approach to calculating the Coulomb interaction in MD and Monte Carlo simulations of bulk systems [80-82]. In this approach (3.3) is rewritten as a sum of two rapidly converging series in real and Fourier space plus a constant term:

$$V_{\text{Ewald}} = V_r + V_k + V_0,$$

where

$$V_r = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{n} q_i q_j \frac{\text{erfc}(\alpha |r_i - r_j - n|)}{|r_i - r_j - n|},$$

$$V_k = \frac{2\pi}{V} \sum_{k} \left( \frac{q_i - q_j}{k^2} \right) e^{-k^2/4\alpha^2} \left[ \sum_{i=1}^{N} q_i e^{ik \cdot r_i} \right]^2,$$

$$V_0 = \frac{-\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2.$$

$V$ is the volume of the MD cell, $k = \left( \frac{2\pi}{L_x}, \frac{2\pi}{L_y}, \frac{2\pi}{L_z} \right)$ is a reciprocal-space vector, and $n$ is as defined in (3.3). Here erfc$(x)$ is the complimentary error function, erfc$(x) = 1 - \text{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt$, which decreases monotonically as $x$ increases. In MD the force is needed to integrate the dynamics forward in time. Direct differentiation of (3.4) and (3.5) gives the force on an atom $i$:

$$f_i = \frac{4\pi}{V} \sum_{k} \left( \frac{q_i - q_j}{k^2} \right) e^{-k^2/4\alpha^2} \left( \sum_{j} q_j e^{ik \cdot r_j} \right)$$

$$+ \sum_{j \neq i} (\delta_{ij} - \delta_{ji}) q_i q_j \sum_{n} (r_{ij} - n) \left[ \frac{\text{erfc}(\alpha |r_{ij} - n|)}{|r_{ij} - n|^3} + \frac{2\alpha \exp(-\alpha^2 |r_{ij} - n|^2)}{\sqrt{\pi} |r_{ij} - n|^2} \right].$$

The force exerted on an atom is a sum of real-space and reciprocal-space contributions. The Ewald contribution to the stress tensor is computed from,
A physical interpretation of the decomposition (3.4) can be made by viewing each point-charge in the system as being surrounded by a Gaussian charge distribution of equal magnitude and opposite sign, with a charge density \[ \rho_i = \frac{q_i \alpha^3}{\pi^{3/2}} \exp\left(-\alpha^2 |\mathbf{r} - \mathbf{r}_i|^2\right), \] where \( \alpha \) is a positive parameter that determines the width of the charge distribution. This charge distribution screens the point-charge interaction, thus reducing it to short-range. The sum over all point-charges and their respective image distributions converges rapidly in real space. A second Gaussian charge distribution with the same sign and magnitude as the original point-charge distribution is also introduced to counteract the effect of the first distribution. The sum over the second distribution is performed in reciprocal space using Fourier transforms to solve the resulting Poisson’s equation. The constant term \( V_0 \) in (3.5), called the self interaction, is necessary to cancel the interaction of each of the introduced charge distributions with itself. The Gaussian charge distribution is not unique, other appropriate functional forms have been used [84].

The convergence of the sums in (3.5) is controlled by (i) the maximum number of image cells in the real space sum, (ii) the range of the sum in reciprocal space, and (iii) the Ewald convergence parameter \( \alpha \). If \( \alpha \) is chosen to be large enough only the \( n = 0 \) term will contribute to \( V_\kappa \), thus reducing the real space sum to the normal minimum image convention. This choice corresponds to making the width of the charge distribution very narrow, thus requiring an increased number of reciprocal-space vectors for \( V_\kappa \). An
O(N^{3/2}) algorithm for Ewald summation without using approximation techniques was first recognized by Perram et al. [85]. The approach involves dividing the MD cell into m cells in each direction. The real-space convergence parameter, α, is then chosen such that atom interactions beyond nearest-neighbor cells can be neglected based on a predetermined error. The range of the reciprocal-space sum is taken to be proportional to the number of cells. Minimization of the total execution time with respect to m results in a proper division of the real-space and reciprocal-space computations, leading to an Ewald sum that scales as N^{3/2}. Toukmaji et al. [86] give a useful discussion of various techniques used to optimize the Ewald summation procedure.

It has been pointed out by de Leeuw et al. [81] that the final result for the sum (3.3) is dependent upon the medium surrounding the system. When the system is surrounded by vacuum the contribution of a surface dipole layer must be included. The dipole term includes the effects of the total dipole moment in the MD cell and the shape of the macroscopic lattice. Systems surrounded by a conductor do not experience a surface dipole. The Ewald formulation given above corresponds to the system surrounded by a conducting medium; in this case the surface dipole is zero.

3.2.2 Fast multipole method

The Fast Multipole Method (FMM), originally developed by Greengard and Rokhlin [33,87], has been successfully used to rapidly accelerate the calculation of the long-range pairwise interactions in a large ensemble of sources in a single cell without pbc. In N particle simulations involving long-range interactions, such as Coulomb or gravitational interactions, the FMM reduces the number of computations required to evaluate all pairwise interactions from O(N^2) to O(N). The FMM algorithm has also been adapted to the solution of boundary integral equations (as in electromagnetic scattering) to accelerate iterative solution schemes like conjugate gradient or generalized minimum residual [88-90]. The basic theme of FMM is the reduction of computational costs through the encapsulation of far-field information in terms of the moments of a source.
distribution. The details of the algorithm will now be described. First the underlying multipole translation theory will be presented using the compact representation of Epton and Dembart [91]. Then the methodology of FMM will be described with analysis showing the reduction in the computational complexity. Issues related to parallel implementation of FMM will be covered in Chapter 4.

The motivation in multipole translation is to formulate a far-field representation for a collection of charges about some point in space and then to translate the result to a different point. We start with the translation theorem of classical potential theory. Given a unit charge at a point \( x' = (r', \theta', \phi') \), the potential induced by that charge at \( x = (r, \theta, \phi) \) is given by [92]

\[
\frac{1}{|x - x'|} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{r^{n}}{r'^{n+1}} Y_{n}^{-m}(\theta', \phi') Y_{n}^{m}(\theta, \phi),
\]

where \( r = \min(r, r') \), \( r' = \max(r, r') \), and the functions \( Y_{n}^{m} \) are the spherical harmonics. The \( Y_{n}^{m} \) used in this discussion are defined from the associated Legendre polynomials:

\[
Y_{n}^{m}(\theta, \phi) = \begin{cases} 
(-1)^{m}, & m \geq 0 \\
1, & m < 0 
\end{cases} \left( \frac{(n-m)!}{(n+m)!} \right) \left[ \frac{m!}{(n+m)!} \right] P_{n}^{m}(\cos \theta) e^{im\phi},
\]

\[
P_{n}^{m}(x) = \frac{1}{2^n n! (n-m)!} (1 - x^2)^{-m/2} \frac{d^{n-m}}{dx^{n-m}} (x^2 - 1)^n \quad (-n \leq m \leq n).
\]

The rapid decay of expansion (3.9) in each of the defined domains allows the calculation of the Coulomb potential with a specified level of precision.

Now consider a collection of point charges \( \{q_i, x_i = (r_i, \theta_i, \phi_i) : i = 1, \ldots, N \} \) that are lying within a sphere of radius \( R \) centered at the origin. The electrostatic potential at a point \( x = (r, \theta, \phi) \) lying outside the sphere may be expressed in the form of a multipole expansion

\[
V(x) = \sum_{i=1}^{N} \frac{q_i}{|x - x_i|} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left( \sum_{i=1}^{N} q_i r_i \right) Y_{n}^{-m}(\theta_i, \phi_i) \frac{Y_{n}^{m}(\theta, \phi)}{r^{n+1}}.
\]
The form (3.11), called the far-field representation, is characterized by the set of outer multipole coefficients $C_n^m$ defined by

$$C_n^m = \sum_{i=1}^{N} q_i r_i^n Y_n^m(\theta_i, \phi_i).$$

(3.12)

With the following definitions of outer functions $O_n^m$ and inner functions $I_n^m$,

$$O_n^m(x) = O_n^m(r, \theta, \phi) = \frac{(-1)^n i^{|m|} Y_n^m(\theta, \phi)}{A_n^m r^{n+1}},$$

(3.13)

$$I_n^m(x) = I_n^m(r, \theta, \phi) = i^{-|m|} A_n^m r^n Y_n^m(\theta, \phi),$$

(3.14)

where

$$A_n^m = A_n^{-m} = \frac{(-1)^n}{\sqrt{(n-m)!(n+m)!}},$$

(3.15)

the translation theorem (3.9) can be rewritten as (for $r > r^*$)

$$\frac{1}{|x - x'|} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} (-1)^n I_n^m(x') O_n^m(x).$$

(3.16)

In practice a finite limit in the sums over $n$ and $m$ must be taken. Let $p \geq 1$ be the maximum order of multipoles considered in (3.11), then the error bound in computing the far-field representation is given by [87,93]

$$\left| V(x) - \sum_{n=0}^{p} \sum_{m=-n}^{n} C_n^m Y_n^m(\theta, \phi) \right| \leq \sum_{i=1}^{N} \left| q_i \right| \left( \frac{R}{r} \right)^{p+1}.$$

(3.17)

We see that error bound is a function of $R/r$, this is an important factor in the design of the FMM algorithm. For a given multipole order $p$, a constant error bound can be achieved by fixing the ratio of the clustering size to the distance of the point of evaluation.

There are three basic transformation operations necessary to implement the FMM: the (i) outer-to-outer, (ii) outer-to-inner, and (iii) inner-to-inner transformation [91]. These operations will be defined and described in sequence; they are illustrated in Fig. 3.2. First we consider a set of point sources $\{q_i, x_i=(r_i, \theta, \phi) : i = 1, \ldots, N\}$, located within a sphere $S_0$ of radius $R_0$ centered at $x_0$ (i.e. $x_i \in \{x : |x - x_0| \leq R_0\}$). The objective is to obtain an inner expansion for the potential due to the charges in sphere $S_0$ that is
valid for points located in sphere $S_3$. The outer multipoles $C_n^m$ that characterize the far-field representation (3.11) for this set of charges can be computed from (3.12). Then the potential at a point $x$ outside the sphere $S_0$ is given by,

$$V(x) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} C_n^m O_n^{-m}(x - x_0), \quad x \notin \{x : |x - x_0| \leq R_0\}. \quad (3.18)$$

We now consider a sphere $S_1$ that completely contains $S_0$ and desire to obtain a far-field representation for $V(x)$ that is centered at $x_1$ and is valid for $x$ outside the sphere $S_1$. The outer-to-inner transformation that accomplishes this is given by

$$V(x) = \sum_{l=0}^{\infty} \sum_{j=-l}^{l} D_l^j O_l^{-j}(x - x_1), \quad (3.19)$$

where

$$D_l^j = \sum_{n=0}^{l} \sum_{m=-n}^{n} I_{l-n}^{-m}(x_1 - x_0) C_n^m. \quad (3.20)$$

Suppose that sphere $S_2$ lies completely outside sphere $S_1$. The outer-to-inner transformation that gives a representation for $V(x)$ valid for $x \in \{x : |x - x_2| \leq R_2\}$ is given by,

$$V(x) = \sum_{l=0}^{\infty} \sum_{j=-l}^{l} E_l^j I_l^j(x - x_2), \quad (3.21)$$

where the inner multipole coefficients are given by

$$E_l^j = \sum_{n=0}^{l} \sum_{m=-n}^{n} O_{l+n}^{-m-j}(x_2 - x_1) D_n^m. \quad (3.22)$$

The final transformation takes the inner expansion centered at $x_2$ and translates it to an inner expansion centered at $x_3$:

$$V(x) = \sum_{l=0}^{\infty} \sum_{j=-l}^{l} F_l^j I_l^j(x - x_3), \quad (3.23)$$

where

$$F_l^j = \sum_{n=0}^{l} \sum_{m=-n}^{n} I_{l-n}^{-m-j}(x_3 - x_2) E_n^m. \quad (3.24)$$
Equation (3.22) may now be used to compute the potential due to the charges in sphere $S_0$ at any point $\mathbf{x}$ that lies within the sphere $S_3$.

![Diagram showing multipole transformation operations used in FMM for well separated sets of charges.](image)

**Figure 3.2** Illustration of multipole transformation operations used in FMM for well separated sets of charges.

In FMM the Coulomb potential is computed in a hierarchical manner. The MD cell is recursively divided in half along each of the Cartesian axes to obtain multiple sets of cells. This recursive decomposition is illustrated for the two-dimensional case in Fig. 3.3. In three-dimensions the entire structure can be viewed as an oct-tree structure with the MD cell as the root of the tree, corresponding to level $l = 0$. At each level in the tree there are $8^l$ number of cells (each parent in level $l-1$ produces 8 children). The recursive decomposition continues to a level $L$ at which point further refinements would make the cell size smaller than the cutoff distance for the short-range potentials. In other words, at the highest level of refinement each cell corresponds to a link-cell in the link-cell list structure. Because the hierarchical decomposition in FMM is related to a tree structure, the cells at the highest level of refinement are often referred to as leaf-cells. The FMM algorithm decomposes into two main procedures: the *upward pass* and the *downward pass*.
The *upward pass* starts at the highest level of refinement $L$ by computing the outer multipoles $C^n_m$ for each leaf-cell (with respect to the center of the leaf-cell) using (3.12). Since information about each atom is used only once, the computational cost is $O(Np^2)$, where $p$ is the order of the multipole expansion. The outer multipoles $D^i_l$ for each cell $c$ in level $L-1$ are then computed from the outer multipoles $C^n_m$ of $c$'s children in level $L$ by using the outer-to-outer transformation (3.20) to translate each child's outer multipoles to the parent's center and then they are added together. This procedure is repeated for each of the successive levels in the tree until level 2 is reached. Since the maximum number of possible leaf-cells is $N$ and each translation involves $p^4$ operations the computational cost is $O(Np^4)$. At the end of the *upward pass* the outer multipoles for all cells at all levels are determined. For bulk systems with *pbc*, the coarsest level of refinement is $l=0$. The application of FMM in bulk systems will be discussed Sec. 3.2.3.

Before describing the *downward pass* it is necessary to make a few definitions [87] that are illustrated for two-dimensions in Fig. 3.4. At a level $l$ the *nearest neighbors* of a cell $c$ (dark cell in Fig. 3.4) are defined to be the set of 26 cells that share a boundary point with $c$ (hatched cells in Fig. 3.4). Two cells are said to be *well-separated* if they are separated by at least one cell. The *interaction set* for a cell $c$ is defined to be the set of cells at the same level as $c$ that are not *nearest neighbors* of $c$ and whose parent cells are
nearest neighbors of the parent of $c$ (shaded cells in Fig. 3.4). Note that at any level there are at most 189 entries in the interaction list of a cell.

![Figure 3.4](image.png)

Figure 3.4 Two-dimensional illustration of defined sets used in FMM. The hatched cells are the nearest neighbors of the dark cell. The interaction set for the dark cell is the set of shaded cells at the same level as the dark cell.

The downward pass operates by consistently computing interactions between cells at the coarsest level possible. This is accomplished for a given cell by computing interactions with those cells which are well-separated and whose interactions have not been accounted for at the parent’s level. The downward pass is initiated at the coarsest level by computing all the inner multipoles for each cell in the level. When free boundary conditions (no pbc) are used, the coarsest level that contains well-separated cells is $l = 2$. The inner multipoles for each cell $c$ in the coarsest level are computed by converting the outer expansion of each cell that is well-separated from $c$ to an inner expansion about the center of $c$ using the outer-to-inner translation (3.22), then adding them together. The downward pass then proceeds in a recursive manner, beginning at the next coarsest level, as follows: (i) for each cell $c$ in level $l$ convert the inner expansion belonging to $c$'s parent.
to an inner expansion about c's center using the inner-to-inner translation (3.24); (ii) for each cell c in level l convert the outer expansion of each cell in c’s interaction list to an inner expansion about c’s center using the outer-to-inner translation (3.22) and then add them together; (iii) repeat steps (i) and (ii) for level l+1 until they are completed for all levels including the leaf-level L. Once steps (i) and (ii) have been completed at the leaf-level, the inner expansion for each leaf-cell will contain the interactions with all other well-separated leaf-cells. The number of operations required for steps (i) and (ii) is \( \leq 190Np^4 \). Finally, the far field contribution to the potential at each atomic position is computed from the inner expansion (3.23). This step requires \( \leq Np^2 \) operations. Altogether, the computation for the downward pass scales as \( Np^4 \).

The nearest neighbor leaf-cell contributions are computed directly using the link-cell lists with the number of operations proportional to \( N/N_b \), where \( N_b = N/8^L \) the average number of atoms per link-cell. From the discussion of the upward pass, downward pass, and direct calculation it can be seen that the computational complexity of the FMM algorithm is \( O(N) \). For realistic system sizes serial implementation can still be impractical, thus motivating the need for parallel computation.

3.2.3 FMM in bulk systems

FMM has been extended to bulk systems. Schmidt and Lee [94] developed a method that combines the conventional FMM with Ewald summation to yield a technique that can effectively compute the Coulomb interaction with infinite \( pbc \) in three-dimensions. In their approach, the FMM is used to compute the outer and inner expansions for all cells at all levels (including \( l = 0, 1 \)). This is accomplished by including the additional interactions with cells that reside in the nearest-neighbor image MD cells. The outer expansion for all image cells is available since the outer expansion for an image cell with respect to its center is the same as the outer expansion for the MD cell. The interaction between the MD cell and all but twenty-six non-nearest neighbor image cells is computed using the Ewald sum formulation to express the outer-to-inner
translations. After accounting for the well-separated image cells, the downward pass proceeds in a similar fashion as the conventional FMM.

Another technique called the Reduced Cell Multipole Method (RCMM) [95,96] has also been proposed. The idea is similar to that of Schmidt and Lee except significant speedup is achieved in the Ewald summation by replacing each of the well-separated image cells with a reduced cell. The reduced cell contains only a small number of randomly placed point charges, such that the leading multipole moments of the MD cell are reproduced. A highly efficient multiresolution MD algorithm based on the RCMM has been developed by Nakano et al. [35].

An alternative to the Ewald based approaches described above is the Macroscopic Multipole Method (MMM) of Lambert and Board [97]. The MMM uses the fast multipole techniques to compute the Coulomb interactions in a finite system of periodic cells arranged in a lattice of $3^i \times 3^j \times 3^k$ cells. The method is based on the realization [94] that the multipole expansion of the MD cell is independent of the position of the cell. The FMM algorithm proceeds in the same manner as above, except that the contributions from well-separated image cells at the root level are computed using outer-to-inner translations on the multipole expansions for a finite number of image cells. The algorithm is efficient and can be adapted to study systems that are finite in one of three dimensions.

3.3 Reversible integration algorithms

Many numerical integration algorithms exist for Newton's equations of motion. Some common examples are Gear's predictor-corrector method, Beeman's methods, and Verlet's algorithms [80,98,99]. In choosing an integration technique several considerations must be made concerning the long-time stability and the short-time accuracy. Long-time stability of integration schemes is desirable and is attained for algorithms that are symplectic (or canonical) and time-reversible. Symplectic integration schemes are based upon canonical transformations of phase space and therefore preserve certain invariants of the Hamiltonian system (such as the volume of an arbitrary region in

35
phase-space) [100-103]. One should keep in mind that over a long time period an exact solution is not possible. This is due to the fact that after a sufficiently long time arbitrarily small differences in initial conditions will produce exponentially divergent phase-space trajectories. It is also desirable for the integration algorithm to provide a reasonably accurate approximation to the equations of motion over short time scales. Increased accuracy may be obtained by decreasing the size of the integration time step. However, this is counterproductive since the force calculation at each time step is computationally expensive.

3.3.1 Liouville operator formalism

Tuckerman and Berne [32] have recently proposed a strategy for generating reversible integrators for MD based on the Trotter factorization of the Liouville operator. The method has been used to derive what is known as reversible reference system propagator algorithms (RESPA) that can accelerate the simulation of systems with multiple length and time scales.

The Liouville operator for a Hamiltonian system of $N$ atoms is defined as,

$$iL = \sum_{j=1}^{N} \left[ \dot{x}_j \frac{\partial}{\partial x_j} + \dot{p}_j \frac{\partial}{\partial p_j} \right].$$

(3.25)

The classical propagator is

$$U(t) = e^{it\hat{H}},$$

(3.26)

and the state of the system, $\Gamma$, at time $t$ can be obtained from,

$$\Gamma(t) = U(t)\Gamma(0).$$

(3.27)

The propagation is reversible in time in the sense that $U(-t) = U^{-1}(t)$. If the Liouville operator is decomposed into two parts,

$$iL = iL_1 + iL_2,$$

(3.28)

then the application to the Trotter expansion for a small time interval $\Delta t$ yields,
\[ U(\Delta t) = e^{(L_1 + L_2)\Delta t} = e^{iL_1\Delta t/2} e^{iL_2\Delta t/2} + O(\Delta t^3) \]

\[ = U_1(\Delta t/2) U_2(\Delta t) U_1(\Delta t/2) + O(\Delta t^3). \] (3.29)

The above procedure can be used to derive the velocity-Verlet integrator. Consider the following decomposition:

\[ iL_1 = \sum_{j=1}^{N} p_j \frac{\partial}{\partial x_j}, \quad iL_2 = \sum_{j=1}^{N} p_j \frac{\partial}{\partial p_j}. \] (3.30)

Substitution of (3.30) into (3.29) yields

\[ U(\Delta t) = U_1(\Delta t/2) U_2(\Delta t) U_1(\Delta t/2) \]

\[ = \exp \left( \frac{\Delta t}{2} \sum_{j=1}^{N} p_j \frac{\partial}{\partial x_j} \right) \exp \left( \Delta t \sum_{j=1}^{N} p_j \frac{\partial}{\partial p_j} \right) \exp \left( \frac{\Delta t}{2} \sum_{j=1}^{N} p_j \frac{\partial}{\partial x_j} \right). \] (3.31)

Using the property \( e^{a\partial/\partial x} f(x) = f(x + a) \) and operating with this factorization on a state \( \Gamma(t) = \{x(t), p(t)\} \) gives the velocity-Verlet integrator:

\[ \dot{x}_i(t + \Delta t/2) = \ddot{x}_i(t) + \frac{\Delta t}{2m_i} f_i(t), \]

\[ x_i(t + \Delta t) = x_i(t) + \Delta t \dot{x}_i \left( t + \frac{\Delta t}{2} \right), \]

\[ \dot{x}_i(t + \Delta t) = \ddot{x}_i \left( t + \frac{\Delta t}{2} \right) + \frac{\Delta t}{2m_i} f_i \left( t + \frac{\Delta t}{2} \right), \] (3.32)

where \( f(t) \) is the force at time \( t \). Starting with the state \( \{x_i(t), p_i(t)\} \) the velocities at the half-step \( t + \Delta t/2 \) are computed from the positions and forces at time \( t \). Next the positions are advanced to time \( t + \Delta t \) from the previous positions and the half-step velocities. Finally, the velocities are also calculated at the full-step \( t + \Delta t \). Recursive application of the algorithm generates the phase-space trajectories of the MD system. The velocity-Verlet algorithm is symplectic [102,104] and reversible in time [32] and therefore insures long-time stability. The next section will discuss the application of the RESPA method to systems with short-range and long-range forces.
3.3.2 Short-range and long-range forces

Multiple time-step algorithms may also be derived using the decomposition (3.28) to separate the short-range \( f_s \) and long-range \( f_l \) force contributions:

\[
i_L = i_{Ls} + i_{Ll},
\]

\[
i_{Ls} = \sum_j \dot{x}_j \frac{\partial}{\partial x_j} + f'_j \frac{\partial}{\partial p_j},
\]

\[
i_{Ll} = \sum_j f'_j \frac{\partial}{\partial p_j}.
\]  

(3.33)

Using the Trotter expansion the propagator can be factorized as,

\[
U_{td}(\Delta t) = \exp \left( \frac{\Delta t}{2} \sum_j f'_j \frac{\partial}{\partial p_j} \right) \exp \left( i_{Ls} \Delta t \right) \exp \left( \frac{\Delta t}{2} \sum_j f'_j \frac{\partial}{\partial p_j} \right).
\]  

(3.34)

The middle propagator generates the motion due to short-range forces. By dividing the time step \( \Delta t \) into \( n \) subintervals \( \Delta t = \Delta t/n \) and applying the Trotter factorization to the middle propagator, we obtain:

\[
\exp(i_{Ls} \Delta t) \left[ \exp \left( \frac{\Delta t}{2} \sum_j f'_j \frac{\partial}{\partial p_j} \right) \exp \left( (\Delta t) \sum_j \dot{x}_j \frac{\partial}{\partial x_j} \right) \exp \left( \frac{\Delta t}{2} \sum_j f'_j \frac{\partial}{\partial p_j} \right) \right]^n.
\]  

(3.35)

The size of the smaller time step \( \Delta t \) is chosen to ensure stable dynamics. The middle propagator (3.35) is the velocity-Verlet integrator with a time step of \( \Delta t \). The overall algorithm works as follows. First, the long-range forces at time \( t \) are computed and used to increment the velocities. Subsequently, the positions and velocities are incremented over \( n \) small time steps using the velocity-Verlet algorithm with only the short-range force contributions. Finally, the velocities are incremented again using the long-range forces computed at the new atomic positions.

Implementation of the above algorithm is facilitated by defining a switching function [32]:

\[ \text{Implementation details...} \]
The switching function is used to divide the two-body potential into short-range and long-range parts:

\[
S(r) = \begin{cases} 
1, & r < r_s - w \\
1 + \frac{(r - r_s + w)^2}{2(r - r_s)w - w^2}, & r_s - w < r < r_s \\
0, & r > r_s 
\end{cases}
\]  
(3.36)

The values of the switching function parameters may be chosen such that the short-range interactions only involve atoms in the nearest-neighbor shell. This will minimize the problem of double-counting the force contributions.

Explicit reversible integrators have also been developed for extended systems yielding the canonical and isobaric-isothermal ensembles [57, 60, 105]. The integrators are derived using the formalism of the Liouville operator and the Trotter factorization. Full derivations and Fortran code implementing each algorithm are found in the work of Martyna et al. [105].
CHAPTER 4

IMPLEMENTATION OF MOLECULAR DYNAMICS ON PARALLEL COMPUTERS

In recent years, the computing power of conventional serial processors has increased dramatically. The high-end serial and vector computing is very expensive and is liable to saturate because of physical limitations. A viable alternative to the observed saturation in performance is to form an ensemble of processors that work concurrently (in parallel) on solving a problem. Many areas of computer application are now experiencing the benefits of parallel processing; examples include weather modeling, signal processing, discrete optimization, quantum chromodynamics, and materials modeling. In many areas, parallel processing has made it possible to address problems that were hitherto beyond the capability of serial processing techniques.

Numerous models of parallel computers exist [106]. For the purposes of this work, we will consider only what is known as the message-passing model (architecture) for parallel processing. A typical message-passing architecture is illustrated in Fig. 4.1. In the message-passing architecture (also called distributed-memory architecture), each

![Interconnection Network Diagram](image)
node consists of at least a processor and a local memory accessible only to the processor of the same node. Nodes communicate by message-passing through the interconnection network.

Numerous parallel implementations of molecular-dynamics (MD) approach can be found in the literature [34, 107-112]; some implementations are designed with a specific interconnection network in mind [107-110]. The parallel MD implementation described in this chapter is independent of the topology of the interconnection network.

4.1 Domain decomposition

We consider a system of $N$ atoms contained within a unit MD cell. The partitioning of work among $P$ processors (nodes) is accomplished via a divide-and-conquer strategy based on domain decomposition (see Fig. 4.2). The MD cell is subdivided into $P = P_x \times P_y \times P_z$ subsystems of equal volume. The nodes are logically arranged in an array such that a node $p$ ($0 \leq p \leq P-1$) corresponds to the subsystem indexed by three integers [34],

$$
p_x = \left\lfloor \frac{p}{P_z P_y} \right\rfloor, \quad p_y = \left\lfloor \frac{p}{P_z} \right\rfloor \mod P_y, \quad p_z = p \mod P_z,
$$

where $\left\lfloor x \right\rfloor$ denotes the greatest integer less than or equal to $x$. Figure 4.2 illustrates the domain decomposition for a two-dimensional system. All the attributes (coordinates, velocities, accelerations, species, etc) associated with atoms located within a particular subsystem are stored within the memory of the corresponding node. The mapping of an atom’s coordinates, $s_i$, to a sequential node ID, $p(s_i)$, is given by

$$
p(s_i) = p_x(s_i)P_y P_z + p_y(s_i)P_z + p_z(s_i),
$$

where

$$
p_x(s_i) = \left\lfloor s_{ix} P_x \right\rfloor, \quad (\alpha = x, y, z).
$$

When atoms move out of a subsystem into a neighboring subsystem, the corresponding attributes (positions, velocities, etc.) are transferred using standard message-passing library routines [113].
The calculation of short-range forces on atoms in a subsystem is done using the link-cell list scheme described in Chapter 2. To calculate the forces on atoms within a subsystem, the coordinates of all the boundary atoms that reside in the 26 nearest-neighbor subsystems are required. The coordinates of boundary atoms are exchanged between nearest-neighbor nodes using non-blocking send and blocking receive operations. Newly received boundary atom coordinates are stored in augmented link-cell lists. Boundary atom exchange between nearest-neighbor is accomplished through six message-passing steps: north, south, east, west, upper, and lower. Boundary atom coordinates that need to be exchanged with edge-sharing and corner-sharing neighbors are first passed to the appropriate face sharing neighbor and then forwarded to the appropriate destination node during the subsequent message-passing steps. Newton’s third law can be used to reduce the number of message-passing steps by a factor of two. In this case, it is necessary to send the forces computed for boundary atoms back to the source node.

When computing pair-distribution functions for distances smaller than the subsystem size, it is only necessary to communicate with nearest-neighbor nodes. However, in order to compute intermediate and long-range structural correlations, communication between all nodes may be necessary. This is accomplished by logically
arranging the nodes in a ring topology [111], as illustrated in Fig. 4.3 for 8 nodes. For \( P \) nodes, a sequence of \( \lfloor P/2 \rfloor \) message-passing steps is required, where \( \lfloor x \rfloor \) denotes the least integer greater than or equal to \( x \). In order to prevent a possible deadlock, each node is assigned a parity (\( e = \text{even}, o = \text{odd} \)) that depends upon the message-passing step. The message-passing during a step \( s \) consists of 2 cycles: (i) each even node \( p \) sends its data to node \( (p + s) \mod P \) (dark arrows in Fig. 4.3), while the odd nodes post receives; (ii) each odd node \( p \) sends its data to node \( (p + s) \mod P \) (light arrows in Fig. 4.3), while the even nodes post receives. With this strategy a full calculation of the pair-distribution functions scales with time as \( N^2/P \).

![Figure 4.3 Internode communication strategy for calculation of full pair-distribution functions on eight nodes [111]. Node parity is denoted by \( e \) (even) and \( o \) (odd). Arrows indicate message-passing directions.](image)

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4.2 Parallel fast multipole method

Several parallel implementations of the fast multipole method (FMM) for Coulombic systems have been reported [35,95,114-116]. The present parallel implementation of the FMM is similar to the work of Nakano et al. [35], except in [35] the multipole expansion is based on Cartesian rather than spherical coordinates.

Just as in the case of short-range forces, the unit MD cell is decomposed into $P = P_x \times P_y \times P_z$ subsystems with the requirement that each $P_a$ be a power of 2. We define a level $L_g = \log_2 \left[ \max(P_x, P_y, P_z) \right]$ in the FMM tree. In the lower levels of the hierarchy, $l \geq L_g$, each cell is uniquely assigned to a node. For upper levels, $l < L_g$, the number of cells becomes smaller than the number of nodes. In this case, assignment of each cell to a node results in processors becoming idle. An alternative approach is to duplicate the multipole computations in the upper levels by setting the cells to be global. Figure 4.4 illustrates this decomposition scheme for a two-dimensional system.

In the parallel FMM implementation, the upward pass and downward pass proceed in a similar manner as in the serial case. The calculation of multipole expansions for the leaf-cells according to Eq. (3.12) is local to each node. Because a parent cell and its children reside on the same node, the outer-to-outer translations of the upward pass and the inner-to-inner translations of the downward pass do not require any communication between nodes. To compute the outer-to-inner translations from a cell's interaction set, the outer multipoles of two boundary layer cells must be copied from the nearest-neighbor nodes, see Fig. 4.5. This is accomplished through message passing steps similar to that required for the short-range force calculations. The $8^l/P$ cells on a node are augmented with the copied outer multipoles to form an array consisting of the outer multipoles of $(2^l/P_x + 2)(2^l/P_y + 2)(2^l/P_z + 2)$ cells at each layer. The outer-to-inner translations at each of the lower levels ($l \geq L_g$) are computed using the augmented set of outer multipoles. For upper levels ($l < L_g$) the global set of outer multipoles is used. The
near-field calculation only requires nearest-neighbor leaf-cells and is carried out using the communication strategy described in Section 4.1.

Figure 4.4 Domain decomposition scheme for FMM in a two-dimensional system. In the lower levels, cells are local to a node. Cell information in the upper levels is made global to all nodes.

4.3 Dynamic load-balancing algorithm

Uniform spatial decomposition of a system containing an inhomogeneous distribution of atoms can result in unequal partition of workloads among nodes which degrades the efficiency of a parallel implementation. Global rearrangement of structures
during a simulation can also present a load-imbalance. Dynamic load-balancing schemes that adaptively repartition the workload are formulated to address these issues.

![Diagram of FMM cells at levels 2 and 3 in a two-dimensional system on 4 nodes. At each level in the FMM hierarchy the interaction set (shaded cells) for cells on a node consists of at most 2 boundary layer cells in neighboring nodes.](image)

We have designed an adaptive low overhead load-balancing scheme that minimizes the amount of communication and incorporates appropriate boundary conditions [117]. The main idea is to introduce an adaptive curvilinear-coordinate system, $\xi$, which is related to the dimensionless atomic coordinate, $s$, by a mapping, $\xi = s + u(s)$. We have implemented both plane wave and wavelet representations for the transformation:

$$u(s) = \sum_q a_q \exp(iq \cdot s),$$  \hspace{1cm} (4.4)$$

$$u(s) = \sum_{n,m} d_{n,m} \psi_{n,m}(s).$$ \hspace{1cm} (4.5)$$

We apply the uniform spatial decomposition in the curvilinear space, see Fig. 4.6(a). The coordinate transformation is then dynamically adapted to minimize the load-imbalance and communication costs using the simulated annealing technique. Such a uniform
decomposition in the curvilinear space generally results in curved partition boundaries in the Euclidean space, see Fig. 4.6(b). We find that a multiresolution analysis based on wavelets leads to a compact representation of \( u(s) \), and accordingly to fast convergence of the minimization procedure [118].

![Figure 4.6](image)

Figure 4.6 Decomposition of 2,964 atom system into \( 2 \times 2 \times 1 \) nodes using plane wave representation for curvilinear mapping [117]: (a) uniform spatial decomposition in curvilinear space; (b) curved partition boundaries in the Euclidean space. Circles are two dimensional projection of atoms, and solid curves represent a slice through the partition boundaries.

The load-balancer has been implemented on parallel computers and incorporated into existing MD codes. In benchmark tests on 32 nodes, the load-balancer reduced the time to compute forces by a factor of 4.2, while the overhead due to the load-balancer was only 3.2% of the total execution time of the MD program (repartitioning with 5 simulated annealing iterations every 60 MD steps) [117]. We also find that the load-balancer is highly scalable: for a \( 1.04 \times 10^9 \) atom MD simulation on 64 IBM SP2 nodes, the parallel efficiency is 92% (see Fig. 4.7) [118].
Figure 4.7 Performance of the adaptive curvilinear-coordinate load-balancer using a wavelet representation on the IBM SP2 [118]. Each node contains $16.25 \times 10^8$ atoms. The parallel efficiency for $1.04 \times 10^9$ atoms on 64 nodes is 92%.
CHAPTER 5

OXIDATION OF ALUMINUM NANOCLUSTERS

5.1 Background

In recent times a great deal of research has focused on understanding the role of ultrafine microstructures in the physical and chemical behavior of materials synthesized from nanometer size clusters [2-7]. These materials are called nanophase materials; their unique properties distinguish them from conventional crystalline and amorphous materials. In contrast to conventional polycrystalline solids, nanophase materials have a large fraction of atoms in the interfacial regions, which has a dramatic effect on the structure and physical properties of these materials [4,15,16]. The mechanical strength of nanophase metals is known to be higher than that of conventional polycrystalline metals of the same chemical composition [8]. It has been shown that nanophase ceramic materials are much more ductile and have lower sintering temperatures than conventional brittle ceramics [9-11].

A particularly interesting possibility in nanophase materials is the synthesis of nanocomposites consisting of metallic nanoclusters coated with a passivation layer. Upon compaction, the passivation layer forms a boundary layer between the isolated metallic grains. The presence of the passivating network is known to have a dramatic effect on the electrical, chemical, and mechanical behavior of the material. In a recent study by Sánchez-López et al. [12], Al/Al-oxide nanocomposites were found to have a metallic shine and an ohmic electrical resistivity that was dependent upon the compaction conditions. The nanocomposite consisted of 300 Å aluminum particles with an interconnected 40 Å oxide layer that prevented the material from falling apart when heated to temperatures above the melting point of aluminum. Other studies point out that the final properties of these nanocomposite materials are strongly dependent on the nature of the passivation layer [13,14,119,120].
A few experimental studies of the passivation behavior of ultrafine Al particles have been reported in recent years. Nuclear Magnetic Resonance (NMR) measurements and microscopic and spectroscopic studies reveal that 500 to 700 Å size Al particles form a 25 to 50 Å thick oxide scale when exposed to air. The oxide scale is observed to remain intact, even after compacting the Al nanopowders at high pressures. Thermogravimetric studies of small metallic particles show that a 200 Å Al cluster forms an oxide scale with a thickness of 30 to 40 Å [51]. Aumann et al. [120] have studied the oxidation of aluminum nanopowders with the intention of raising the ignition threshold of highly reactive ultrafine grain Al/MoO₃ powders. They observe that powders consisting of Al particles with diameters between 240 and 650 Å oxidize with a square-root time dependence similar to flat Al samples. Additionally, they find that the increased surface area of Al particles lowers the oxidizing activation energy relative to that of flat Al samples. More recent studies by Sánchez-López [13] on the passivation of Al nanoclusters show that for the range of particle sizes studied (120 – 410 Å) an oxide scale of 40 Å is formed which is independent of the route of oxygen dosage. Experimentally, the structure of the oxide scale on Al nanoclusters is considered to be amorphous. However, in all of the known literature there is no detailed structural analysis of the oxide scale on Al nanoclusters. Recent studies have pointed out that the local structure of the amorphous oxide scale for Al nanoclusters is different from the amorphous scale that forms on the bulk Al surface [13,120]. However, details of the differences between the two amorphous oxides is not given.

Experimentally, the growth of oxide scales on bulk metallic surfaces is known to exhibit several types of behavior. Most of the theoretical understanding of oxidation rate behavior of bulk metal surfaces is described in the pioneering works of Mott [49] and Cabrera and Mott [50]. The rate of oxidation depends on the temperature and access of oxygen to the metal atoms. A linear rate of oxidation occurs when the oxide is porous and the metal surface is continually exposed to oxygen. This behavior is typical of metals
like magnesium in which the oxide occupies a smaller volume than the metal from which it is formed. The resulting tensile stresses cause the oxide film to crack and become porous. Oxide growth that exhibits a square root time dependence occurs whenever the controlling factor is the diffusion of ions or electrons through a non-porous oxide layer. Some examples of metals that follow this behavior are Al, Cu, Fe, and Ti. Schematically, the oxidation reaction can be described as a two-step process. First a metal ion is formed at the metal-oxide interface, releasing electrons. Then oxygen ions are formed through the adsorption of released electrons. The oxidation reaction occurs at the metal-oxide interface whenever oxygen diffusion through the oxide is more rapid than the metal-ion diffusion. Otherwise, if the metal-ion diffusion is more rapid, oxidation will occur at the oxide-environment interface. Because the oxidation is controlled by diffusion processes, the oxidation rates follow an Arrhenius relationship, that is, the rate increases exponentially as the temperature is increased.

5.2 Interatomic potential for aluminum and aluminum-oxide

The MD simulations of oxidation of aluminum nanoclusters are based on a highly reliable interaction model developed by Streitz and Mintmire [121] that can successfully describe a wide range of physical properties of Al and Al\textsubscript{2}O\textsubscript{3}. This so-called electrostatic plus (ES+) model is capable of treating: i) both metallic and ceramic systems; ii) bond formation and bond breakage; and iii) changes in charge transfer as the atoms move and their local environments are constantly altered. In the ES+ model, the potential energy of the system is expressed as the sum of an electrostatic potential (ES) and an embedded-atom potential: $\mathcal{V} = \mathcal{V}_\text{EAM} + \mathcal{V}_\text{ES}$. 

The embedded-atom method (EAM) is a common technique for modeling metallic bonding. The potential in EAM is defined as

$$\mathcal{V}_\text{EAM} = \sum_i \mathcal{F}[\rho_i] + \sum_{i<j} \phi_{ij}(r_{ij}).$$  \hspace{1cm} (5.1)
where $\mathcal{F}_i[\rho_i]$ represents the energy required to embed atom $i$ in a local electron density $\rho_i$ and $\phi_q(r_q)$ is an additional pair-wise interaction, with $r_q$ the interatomic distance between atoms $i$ and $j$. In the ES+ model a Finnis-Sinclair [70] form is chosen for the embedding energy,

$$\mathcal{F}_i[\rho_i] = -A_i \sqrt{\rho_i/\xi_i},$$

(5.2)

where,

$$\rho_i(r) = \sum_j \xi_j \exp\left[\beta_j (r_{ij} - r_{ij}^*)\right].$$

(5.3)

In Eq. (5.3) the local atomic density $\rho_i$ is expressed as a linear superposition of atomic densities of all other atoms. The pair-wise potential is chosen to be

$$\phi_q(r) = 2\beta_q \exp\left[-\frac{\beta_q}{2} (r - r_q^*)\right] - C_q \left[1 + \alpha (r - r_q^*)\right] \exp\left[-\alpha (r - r_q^*)\right].$$

(5.4)

In order to determine the local atomic charge from the local environment of each atom, it is necessary to describe the total electrostatic energy of a system of atoms as a function of the atomic charges and positions:

$$V_{ES} = \sum_i v_i(q_i) + \frac{1}{2} \sum_{i \neq j} v_{ij}(r_{ij}; q_i, q_j),$$

(5.5)

$$v_i(q_i) = v_i(0) + \chi_i q_i + \frac{1}{2} J_i q_i^2,$$

$$v_{ij}(r_{ij}; q_i, q_j) = \int d^3 r_1 \int d^3 r_2 \rho_i(r_{ij}; q_i) \rho_j(r_{ij}; q_j) / r_{ij}.$$ 

The local atomic energy $v_i(q_i)$ in Eq. (5.5) is expressed as a second-order Taylor expansion in the partial charge $q_i$. The first derivative $\chi$ is the electronegativity [122] and the second derivative $J$ is associated with a self-Coulomb repulsion [123]. The Coulomb interaction $v_{ij}(r_{ij}; q_i, q_j)$ in Eq. (5.5) represents the electrostatic interaction energy between atoms $i$ and $j$. The function $\rho_i(r; q_i)$ represents the charge-density distribution about an atom $i$ (including the nuclear point charge) for a total charge $q_i$. It is possible to choose a realistic charge-density distribution function that would allow for directional dependence.
of bonds and local polarizability. This approach may prove to be useful in simulating less ionic materials. For mathematical convenience, Streitz and Mintmire chose a distribution that is an extended form of a Slater-type 1s orbital:

$$\rho_i(r, q_i) = Z_i \delta(r - r_i) + (q_i + Z'_i) \left( \frac{\zeta_i^2}{r} \right) \exp \left( -2\zeta_i |r - r_i| \right).$$  

(5.6)

where $\zeta_i$ is the decay length for atomic orbitals and $Z'_i$ is an effective core charge ($0 < Z'_i < Z_i$, with $Z_i$ the total nuclear charge of an atom). Applying equations (5.5) and (5.6) together with the two-center Coulomb integrals [124] yields an expression for the electrostatic energy:

$$\nu_{ES} = \sum_i q_i \left[ Z'_i + \sum_j Z_j \omega_j(r_j) - v_f(r_i) \right]$$

$$+ \frac{1}{2} \sum_i q_i^2 J_i^0 + \frac{1}{2} \sum_{j \neq i} q_i q_j \left( \frac{1}{r_{ij}} + v_f(r_{ij}) \right),$$

(5.7)

where the short-range Coulomb-interaction integral $v_f(r)$ is

$$v_f(r) = -\frac{(1 - \kappa)^2}{4r} \left( 2 + \kappa + \zeta_i r \right) \exp \left( -2\zeta_i r \right)$$

$$- \frac{(1 + \kappa)^2}{4r} \left( 2 - \kappa + \zeta_i r \right) \exp \left( -2\zeta_i r \right),$$

(5.8)

with $\kappa = (\zeta_i^2 + \zeta_j^2)/(\zeta_i^2 - \zeta_j^2)$, and the short-range nuclear-attraction integral $\omega_j(r)$ is

$$\omega_j(r) = -\frac{1 + \zeta_j r}{r} \exp \left( -2\zeta_j r \right).$$

(5.9)

The charge independent contributions (not shown) are implicitly included in the pair potentials of the EAM contribution described in the preceding paragraph. Note that the electrostatic energy Eq. (5.7) contains a long-range Coulomb term. Calculation of the Coulomb contribution to the energy and forces in large-scale MD simulations requires special techniques outlined in Chapter 3. For the oxidation simulations we use the O(2N) fast multipole method [87].

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Streitz and Mintmire chose the ES+ potential parameters to optimize the bulk properties of both fcc aluminum and α-alumina crystal structures. In addition, the potential yields reasonable surface energies and relaxations for several low-index surfaces of α-alumina. Table (5.1) lists the optimized ES+ potential parameters for aluminum and oxygen.

Table 5.1 Optimized interatomic potential parameters for the ES+ model [121].

<table>
<thead>
<tr>
<th>i</th>
<th>$\chi$ (eV)</th>
<th>$J$ (eV)</th>
<th>$\zeta$ (Å$^{-1}$)</th>
<th>$Z$</th>
<th>$A$ (eV)</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.00</td>
<td>10.328655</td>
<td>0.968438</td>
<td>0.746759</td>
<td>0.763905</td>
<td>0.147699</td>
</tr>
<tr>
<td>O</td>
<td>5.484763</td>
<td>14.035715</td>
<td>2.143957</td>
<td>0.00</td>
<td>2.116850</td>
<td>1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$i-j$</th>
<th>$r^*$ (Å)</th>
<th>$\alpha$ (Å$^{-1}$)</th>
<th>$\beta$ (Å$^{-1}$)</th>
<th>$B$ (eV)</th>
<th>$C$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Al</td>
<td>3.365875</td>
<td>1.767488</td>
<td>2.017519</td>
<td>0.075016</td>
<td>0.159472</td>
</tr>
<tr>
<td>Al-O</td>
<td>2.358570</td>
<td>4.233670</td>
<td>4.507976</td>
<td>0.154548</td>
<td>0.094594</td>
</tr>
<tr>
<td>O-O</td>
<td>2.005092</td>
<td>8.389842</td>
<td>6.871329</td>
<td>1.693145</td>
<td>1.865072</td>
</tr>
</tbody>
</table>

5.3 Dynamic charge transfer

The unique feature of the ES+ model potential is that it explicitly includes dynamic charge transfer between anions and cations. The method is based on a semiempirical approach in which atomic charges are determined according to the electronegativity equalization condition [123,125-127]. In other words, as atomic positions change dynamically charge is redistributed in such a way as to cause the chemical potential or electronegativity to be equal at every atomic site.

In MD simulations, the atomic charges, $q_i$, are determined at each time step by minimizing the electrostatic energy Eq. (5.7), subject to the charge-neutrality constraint, $\sum_i q_i = 0$. This constrained minimization is algebraically equivalent to the electronegativity equalization condition that the chemical potentials $\partial V_{ES} / \partial q_i$ be equal for all atoms. This leads to a set of linear equations.
where $M_{ij}$ is the Coulomb-interaction matrix and $\mu$ is a Lagrange multiplier used to determine the charge-neutrality constraint. In practice the solution to Eq. (5.10) involves concurrent solution of two sets of linear equations:

$$\sum_j M_{ij} q'_j = -\chi_i,$$  

$$\sum_j M_{ij} q''_j = -1.$$  

The solution to Eq. (5.10) is obtained as

$$q_i = q'_i - \mu q''_i,$$  

where the chemical potential, $\mu$, is calculated from

$$\mu = \frac{\sum_i q'_i}{\sum_i q''_i}.$$  

We use a conjugate gradient (CG) method [128] to solve the linear systems, Eqs. (5.11) and (5.12). A preconditioning scheme based on splitting the Coulomb-interaction matrix into short-range and long-range components has recently been proposed by Nakano [129]. The preconditioning scheme is found to substantially improve the convergence and parallel efficiency by increasing data locality.

An alternative approach to the above variable charge method is to treat the atomic charges as dynamic variables in an extended Lagrangian [127]. Charges are given fictitious masses and velocities and then propagated with the atomic degrees of freedom in Newton’s equations of motion. Typically, the timestep for the charge degree of freedom is much smaller than the time step for the atomic motion. Multiple time step integration schemes can be applied to speed up the computations [32].

5.4 Setup of oxidation simulations

The setup for the oxidation simulations is as follows (see Fig. 5.1). A fcc-crystalline Al-sphere (diameter = 200 Å) composed of 252,158 atoms and thermalized at 300 K is placed at the center of a cubic box of length 800 Å. A total of 530,720 oxygen
are distributed randomly outside the Al-sphere (radius 110 to 400 Å) either in the form of atomic (O₁) or molecular (O₂) oxygen at a temperature of 300 K. The oxygen density is 40 times that of the normal state (1 atm and 300 K). A spherical reflecting wall of radius 400 Å confines the entire system. The equations of motion are integrated with $\Delta t = 1$ fs for short-range forces and $\Delta t = 20$ fs for long-range forces. New atomic charges are determined every 100 time steps such that the electrostatic energy is minimized subject to the constraint that the total system remains neutral. Canonical MD simulation, in which the temperature of the whole system is fixed at 400 K using Nose-Hoover thermostat chain [105], is performed for the case of O₂. In addition, microcanonical MD simulations are performed for both O₁ and O₂.

Figure 5.1 Initial setup of oxidation simulation. This is an 8 Å thick slice through the middle of the system. The aluminum cluster is cyan and the surrounding oxygen are red. A spherical reflecting wall of radius 400 Å contains the oxygen atoms.
5.5 Oxidation simulations in the microcanonical ensemble

Microcanonical simulations have been performed for both the O$_1$ and O$_2$ cases. Figure 5.2 shows a plot of the time evolution of temperature and density profiles in the O$_2$ microcanonical simulation as a function of distance from the center of the cluster. We observe that the energy released from Al-O bond formation leads to a dramatic increase in temperature in the surface region. Thermal energy is rapidly transported through the Al cluster, resulting in an average temperature of 1000 K in the core of the Al cluster (the melting temperature of Al is 933 K) by 40 ps. Due to the increase in temperature, the density of aluminum atoms in the surface region drops and the cluster boundary increases to around 110 Å by 30 ps, see Fig. 5.2 (middle). Figure 5.2 (bottom) shows that oxygen atoms rapidly diffuse into the Al cluster, reaching a radius of 80 Å during the first 30 ps. The peak oxygen density increases rapidly during the first 30 ps and then saturates by 40 ps.

The rate of temperature increase at the nanocluster surface in the O$_1$ microcanonical simulation is 30% higher than that of O$_2$ case. This difference is attributed to the energy required to dissociate the O$_2$ molecules before Al-O bonding occurs. Correspondingly, we observe that the rate of increase of the oxide layer thickness for the O$_1$ simulation is 13% larger than that of the O$_2$ simulation. This can be seen in Fig. 5.3(a) in which the oxide thickness as a function of simulation time is plotted for both the O$_1$ and O$_2$ cases. In addition, the saturation density of oxygen in the nanocluster surface region for the O$_1$ simulation is 9% lower than that of the O$_2$ simulation, see Fig. 5.3(b).

Figure 5.4 shows snapshots of a small slice (150 Å × 150 Å × 8 Å) of the O$_2$ microcanonical system at various times during the simulation. The larger spheres correspond to oxygen and smaller spheres to aluminum. The color of each sphere represents the sign and magnitude of the charge on an atom. The charge transfer is localized to the surface region where the Al-O bonding occurs. Disordering of the Al crystal begins at the surface and moves rapidly inward as the temperature increases. By
40 ps the thickness of the oxide scale is 22 Å and the temperature in the oxide region is 2000 K. Subsequently, we observe the ejection of small fragments from the nanocluster surface.

Figure 5.2 Time evolution of temperature and density profiles as a function of distance from the center of the aluminum cluster for the O₂ microcanonical simulation.
We have analyzed the evolution of local stresses during the oxidation process. The local stresses were calculated by subdividing the system into cells of length 10 Å and averaging the virial stress (2.39) in each cell over 1 ps intervals. We observe large transient stress gradients followed by equilibration as the oxidation progresses. Figure 5.5 depicts the time evolution of local pressure in the nanocluster for the O₁ microcanonical simulation. Initially, the surface region is tensile, while the inner region of the cluster is at zero pressure. We attribute the tensile stress in the surface region to the strong Coulomb forces created by the charge transfer between the surface Al atoms and the incoming O atoms. Heat transfer from the surface to the inner region then causes the pressure in the inner region to become compressive. Subsequently, the pressure differences between the surface and interior regions equilibrate.

![Figure 5.3](image)

**Figure 5.3** (a) Thickness of oxide and (b) average density of oxygen in the oxide region as a function of simulation time in the O₁ and O₂ microcanonical simulations.
Figure 5.4 Snapshots of a small slice (150 Å x 150 Å x 8 Å) of the O\textsubscript{2} microcanonical system at various times during the simulation. The larger spheres correspond to oxygen and smaller spheres to aluminum; color represents the sign and magnitude of the charge on an atom.
Figure 5.5 Three-dimensional views of local pressures in the O₁ microcanonical simulation. The system is subdivided into 10 Å cells and the virial stress in each cell is averaged over 1 ps intervals.
5.6 Oxidation simulations in the canonical ensemble

In addition to the microcanonical simulations we have investigated the oxidation process in the canonical ensemble. Figure 5.6 shows the oxide thickness as a function of simulation time for the first 260 ps of the O$_2$ canonical simulation. For the first 50 ps, we observe that the oxide thickness increases linearly with time, subsequently the rate becomes smaller and the thickness saturates at 33 Å. The inset for Fig. 5.6 shows the inner and outer radial extent of the oxide. We observe that the oxide scale grows both inward and outward; the inner and outer radial extent saturate at 77 Å and 110 Å, respectively.

![Graph showing oxide thickness and radial extent](image)

Figure 5.6 Thickness of oxide layer as a function of simulation time for the O$_2$ canonical simulation. The inner and outer radial extent of the oxide layer as a function of simulation time are shown in the inset.
During the first 100 ps the temperature in the oxide region increases to 1500 K, near the melting temperature of alumina, where it subsequently remains. Oxygen atoms in the nanocluster surface region diffuse predominantly along the surface; their tangential and radial diffusivities at 50 ps are \(4.4 \times 10^4\) cm\(^2\)/s and \(2.0 \times 10^4\) cm\(^2\)/s, respectively. This high surface diffusivity results in uniformity in the oxide thickness with respect to polar angles.

Saturation of the oxide growth during the first 260 ps is accompanied by a depletion of oxygen outside the nanocluster. In order to bring the oxide as close as possible to complete saturation, we continue the \(\text{O}_2\) canonical simulation to 466 ps while maintaining \(n_0\) outside the nanocluster in the range \(0.001 - 0.002\) Å\(^3\). A surface-oxide of 40 Å thickness is subsequently formed, as seen in Fig. 5.7, which is a snapshot of a small slice (115 Å \(\times\) 115 Å \(\times\) 8 Å) of the system at 466 ps. The outer radial extent of the oxide remains at 110 Å; however, the inner radial extent moves to 70 Å. The average mass density of the oxide is 2.9 g/cm\(^3\) \((n_{\text{Al}} = 0.042\) Å\(^3\) & \(n_0 = 0.038\) Å\(^3\)), which is about 75% of \(\alpha\)-\(\text{Al}_2\text{O}_3\) density. Significant charge transfer is observed in the oxide region, as can be seen from Fig. 5.7 where color represents the sign and magnitude of the charge on an atom. Maximum and average atomic charges in the oxide region are, respectively, 2.6 \(e\) and 1.7 \(e\) for Al and \(-2.0\) \(e\) and \(-1.8\) \(e\) for O.

Aluminum nanoclusters of diameters 100 - 700 Å are known to form oxide scales of thickness 20 - 50 Å in low-density oxygen gases at room temperature [14,51,120]. The surface-oxide thickness as a function of cluster size for aluminum clusters have been measured [51]. For a cluster of diameter 200 Å the thickness is 30 - 40 Å. Despite orders of magnitude difference in the oxygen-gas densities, remarkable similarity in the oxide thickness is found between the present simulation results and the experimental observations.
Figure 5.7 Snapshot of a small slice (150 Å × 150 Å × 8 Å) of the O₂ canonical system after 466 ps of simulation time. The larger spheres correspond to oxygen and smaller spheres to aluminum; color represents the sign and magnitude of the charge on an atom.
Experimentally, the structure of the oxide scale is not fully known. We analyze structural correlations in the oxide region through partial pair-distribution functions and coordination numbers. Figure 5.8(a) shows the Al-O pair-distribution function for three spherical shells in the oxide region. These results show a variation of structures as we pass through the oxide from the metal-oxide interface (70 – 83.3 Å) to the oxide interior (83.3 – 96.7 Å) and on to the oxide-environment interface (96.7 – 110 Å). In Fig. 5.8(a) we observe that the position of the $g_{\text{AlO}}(r)$ peak gives the Al-O bond length to be around 1.81 Å in the metal-oxide region. The Al-O peak shifts slightly toward larger $r$ in the interior and oxide-environment regions. Pair-distributions for Al-Al and O-O also show shifts in the peak positions related to the change in the relative Al and O densities in each region. The corresponding coordination numbers for Al in each region (obtained by integrating $g_{\text{AlO}}(r)$ up to 2.5 Å) are 3.1 for the metal-oxide interface, 3.9 in the interior of the oxide region, and 4.3 for the oxide-environment interface.

Figure 5.8(b) shows the O-Al-O bond-angle distribution for each region in the oxide. We see that throughout the oxide region there are two distinct peaks in the bond angle distribution. In the interior of the oxide the distribution shows two peaks at 90° and 109°. These peaks shift toward smaller angles in the oxide-environment interface, reflecting the decrease in aluminum density. In the metal-oxide interface where the oxygen density is lower, we observe that the peaks in the bond-angle distribution shift toward larger angles. The two peaks in the oxide region indicate mixed octahedral, Al($O_{1/6}$)$_6$, and tetrahedral, Al($O_{1/4}$)$_4$, configurations. It is interesting to compare the present results with those for liquid alumina, which is made up of tetrahedrally coordinated aluminum [130], and amorphous alumina, which consists of a mixture of tetrahedrally and octahedrally coordinated aluminum [131]. Additionally, aluminum atoms in porous alumina films are known to be predominately tetrahedrally (or even lower) coordinated [131].

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5.7 Summary

In conclusion, we have performed large-scale MD simulations on parallel computers to study the oxidation of an aluminum nanocluster of radius 100 Å. The simulations take into account the effect of charge transfer between Al and O based on the electronegativity equalization principle. Simulations have been carried out for both microcanonical and canonical ensembles and for atomic and molecular oxygen environments. In the microcanonical simulations the nanocluster melts, with the atomic case occurring 30% sooner than the molecular case due to the dissociation energy of the O₂ molecule. In the canonical simulations a passivating amorphous oxide layer of thickness ~ 40 Å is formed during 466 ps of simulation time. The calculated thickness of
the oxide scale is in excellent agreement with experimental results on Al nanoclusters. The average mass density in the oxide region is 75% of the bulk alumina density. Owing to variations in Al and O densities, structures in the oxide scale vary when passing through the oxide from the metal-oxide interface to the oxide-environment interface.
CHAPTER 6

NANOPHASE SILICA GLASSES

6.1 Background

Much of the research in nanophase materials has dealt with nanocrystalline solids containing randomly oriented and randomly positioned nanometer sized crystalline clusters. It is also of interest to consider non-crystalline nanophase solids formed by the consolidation of nanometer size amorphous (glassy) clusters. To date little work has been done on nanophase glasses. Jing et al. [52] have studied Pd-Fe-Si nanophase glasses using Mössbauer spectroscopy. They observe that the nanophase glass differs structurally from conventionally prepared glass of the same chemical composition. The differences have been attributed to a lower average density of atoms in the interfacial regions. Differences in structure have also been observed in X-ray diffraction experiments on a Si$_{75}$Au$_{25}$ nanoglass [53]. Recently, Tsuruta et al. [54] have reported large scale molecular-dynamics (MD) simulations of crack propagation in nanophase amorphous Si$_3$N$_4$ (a-Si$_3$N$_4$), which is able to withstand a much higher strain than conventional a-Si$_3$N$_4$.

To study how the behavior of nanophase glasses differs from that of conventional glasses, we have performed million atom MD simulations of nanophase amorphous silicon dioxide (a-SiO$_2$). SiO$_2$ is known to be an important material in various electronic, optical, chemical, and structural applications [46,47]. It can exist in numerous crystalline forms as well as in non-crystalline or amorphous form. Structurally, the predominant feature of crystalline and amorphous silica is the SiO$_4$ tetrahedron which establishes the short-range order (SRO) [132]. In amorphous silica, the intermediate-range order (IRO), 4 – 8 Å, is manifested as the first sharp diffraction peak (FSDP) in the neutron scattering static structure factor. The IRO arises from the connectivity of the SiO$_4$ tetrahedral units [133,134].
6.2 Simulation methods and setup

The MD simulations on a-SiO$_2$ are based on an effective interatomic potential that is expressed as a sum of 2-body and 3-body interactions:

\[
V = \sum_{j>i} V^{(2)}(r_{ij}) + \sum_{k>j>i} V^{(3)}(r_{ij}, r_{jk}),
\]

(6.1)

where \( r_{ij} = |r_i - r_j | \), \( r_{ij} = r_i - r_j \) \cite{135}. The 2-body contribution is written as

\[
V^{(2)}(r) = A \left( \frac{\sigma_i + \sigma_j}{r} \right)^6 + \frac{Z_i Z_j}{r} e^{-\eta_1} - \frac{\alpha_j Z_j^2 + \alpha_i Z_i^2}{2r^4} e^{-\eta_2}.
\]

(6.2)

The first term in (6.2) represents the steric repulsion, the second term the Coulomb interaction due to charge transfer, and the third term a charge-dipole interaction caused by electronic polarizabilities of the atoms. The 2-body contribution is truncated at \( r = r_c \) using the shifted force form (3.2).

The 3-body covalent contribution incorporates bond bending and bond stretching effects and is of the Stillinger-Weber form (2.14):

\[
V^{(3)}(r_{ij}, r_{jk}) = B_{jk} \exp \left[ \xi \left( r_{ij} - r_0 \right)^{-1} + \xi \left( r_{jk} - r_0 \right)^{-1} \right]
\times \left( \cos \theta_{jk} - \cos \bar{\theta}_{jk} \right)^2 \Theta (r_0 - r_{ij}) \Theta (r_0 - r_{jk}),
\]

(6.3)

where \( \theta_{jk} \) is the angle between \( r_{ij} \) and \( r_{jk} \) and \( \Theta(x) \) is the step function. The 3-body contribution is only calculated for Si-O-Si and O-Si-O triplets; other possible bond angles are not realized because of the strong Coulomb repulsion between atoms of the same species. The values for the parameters in (6.2) and (6.3) are found in \cite{135} and are also listed in Table 6.1.

This interaction scheme has been used in MD simulations for molten, crystalline and amorphous states of normal SiO$_2$ and also permanently densified amorphous SiO$_2$ \cite{132,136}. MD simulation results for pair-distribution functions, static structure factors, vibrational densities of states, bond-angle distributions, and elastic moduli in crystalline and amorphous SiO$_2$ are in good agreement with experimental results \cite{132,136,137}. The interatomic potential used in the work described here differs from the original form of
Ref. [132] in that the long-range Coulomb interaction of Ref. [132] is replaced by a screened Coulomb form (second term in (2.2)). Calculations of pair-distribution functions, static structure factor, and vibrational density of states for normal density SiO\textsubscript{2} glass are found to be the same for both forms of the potential [138].

Table 6.1 Parameters in the interaction potential for a-SiO\textsubscript{2} (See equations (6.2) and (6.3)). The unit of charge is the electron charge, $e$.

<table>
<thead>
<tr>
<th>$A$(eV)</th>
<th>$\lambda$(Å)</th>
<th>$\zeta$(Å)</th>
<th>$r_c$(Å)</th>
<th>$r_0$(Å)</th>
<th>$\xi$(Å)</th>
</tr>
</thead>
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<tr>
<td>1.592</td>
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<td>2.50</td>
<td>5.50</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\sigma$(Å)</th>
<th>$Z_i$($e$)</th>
<th>$\alpha_i$(Å$^3$)</th>
</tr>
</thead>
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<td>1.20</td>
<td>0.00</td>
</tr>
<tr>
<td>O</td>
<td>1.20</td>
<td>-0.60</td>
<td>2.40</td>
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</tbody>
</table>

<table>
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<tr>
<th>$i-j$</th>
<th>$\eta_{ij}$</th>
<th>$i-j-k$</th>
<th>$B_{ijk}$(eV)</th>
<th>$\theta_{ijk}$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>O-Si-O</td>
<td>4.993</td>
<td>109.47</td>
</tr>
<tr>
<td>Si-O</td>
<td>9</td>
<td>Si-O-Si</td>
<td>19.972</td>
<td>141.00</td>
</tr>
<tr>
<td>O-O</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The initial nanophase a-SiO\textsubscript{2} configuration was generated by first removing a spherical a-SiO\textsubscript{2} cluster 70 Å in diameter (10,905 atoms) from well-thermalized bulk a-SiO\textsubscript{2}. Subsequently, the steepest-descent quench was applied to bring the atoms in the cluster to the zero-force configuration. Then the cluster was heated gradually to 1000 K. The initial MD configuration was generated by randomly positioning (with random orientations) 100 of these spherical a-SiO\textsubscript{2} clusters at 1000 K in a cubic box 360 Å on the side. The initial mass density was 0.79 g/cm$^3$. The simulations were performed in the isothermal-isobaric ensemble. The equations of motion were integrated with a reversible multiple time-scale algorithm using a time step of 2 fs [105]. First, at zero pressure and 1000 K, the entire system was relaxed for 22,000 time steps. The pressure was then increased to 0.1 GPa and the system was further thermalized for 30,000 steps. Figure
6.1 shows a snapshot of the nanophase system during thermalization under 0.1 GPa of pressure. Subsequently, the pressure was increased to 0.8, 1.6, and 2.4 GPa and at each pressure the system was thermalized for 10,000 steps. The three systems at 0.8, 1.6, and 2.4 GPa were cooled slowly to 200 K and then the external pressures were removed gradually. In each case the volume increase upon removing the pressure was no more than 7%. In this manner, we obtained nanophase a-SiO$_2$ with mass densities of 1.73, 1.90, and 2.03 g/cm$^3$ at 200K. A fourth system with mass density of 1.65 g/cm$^3$ was obtained in a similar manner by thermalizing at a pressure of 0.6 GPa.

![Image](image.png)

Figure 6.1 Snapshot of the nanophase a-SiO$_2$ system at a density of 1.07 g/cm$^3$. The figure on the left shows the clusters in red. On the right is a 20 Å slice showing the pore regions in red.

6.3 Sintering and pore structure

Figure 6.2 shows a 3D-color plot of pores in four nanophase silica glasses. (Pores are shown in cyan and they are identified by subdividing the MD box into 4 Å voxels and then performing a clustering analysis on the empty voxels using a breadth-first-search algorithm; this analysis was done at 5 K.) The nanophase system at the lower
density (1.63 g/cm³) contains many pores including a percolating pore, which occupies 36% of the total pore volume. As the pressure is increased, we observe decrease in both the number and size of pores. Note that at a pressure of 2.4 GPa the system achieves 93% of the bulk silica glass density. This well consolidated system contains only small isolated pores.

Figure 6.2 Pores in nanophase a-SiO₂ at mass densities 1.63, 1.75, 1.92, and 2.05 g/cm³. The pores are shown in cyan.
Figure 6.3 Log-log plot of the average pore radius ($R$) and interface width ($W$) as a function of the pore volume ($V$). Solid lines are the best least-squares fits.

Despite the differences in the pore sizes and distribution, we find remarkable similarity in the morphology of pores in nanophase a-SiO$_2$ at different densities. The pore morphology is defined in terms of the fractal dimension of pores and the roughness exponents of pore/silica interfaces. The average pore radius is calculated from:

$$R^2 = \frac{1}{N_S} \sum_{i=1}^{N_S} |r'_i - r_0|^2, \quad r_0 = \frac{1}{N_V} \sum_{i=1}^{N_V} r_i,$$

(6.4)

where $r_0$ is the center of the pore and $\{ r_i \}$ and $\{ r'_i \}$ denote the centers of voxels inside and at the interface of the pore, respectively. The number of interface voxels is $N_S$ and $N_V$ is the number of voxels in the pore volume. The roughness of pore interfaces is obtained from the interface width $W$ [139],

$$W = \left\{ \frac{1}{N_S} \sum_{i=1}^{N_S} (|r'_i - r_0| - R)^2 \right\}^{1/2}.$$

(6.5)

Figure 6.3 shows a log-log plot of $R$ and $W$ as a function of the pore volume $V$ for the nanophase system at 1.92 g/cm$^3$. The MD results for the average radius and the interface...
width obey the power-law behavior: $R \sim V^n$ and $W \sim V^\mu$, with the best-fit being $\eta = 0.47 \pm 0.02$ and $\mu = 0.51 \pm 0.02$. The fractal dimension of the pores is $d = 1/\eta = 2.1 \pm 0.09$. Within the statistical uncertainty, we find no difference in the fractal dimension or the roughness exponent of pores in nanophase a-SiO$_2$ at different densities.

6.4 Structural correlations

The MD calculations reveal insignificant differences in the short-range order (SRO) of nanophase silica glasses when compared with the bulk glass. All of the nanophase systems have corner-sharing Si(O$_{1/2}$)$_4$ tetrahedral units similar to the bulk silica glass. We are also interested in how the structural correlations differ in the cluster interior and interfacial regions. The interior region of a cluster is defined to be a spherical volume of radius 32 Å measured from the center-of-mass (COM) of the cluster. This choice was made by calculating average density as a function of distance from the COM of each cluster (with an average over all clusters). The 32 Å radius corresponds to the distance at which the average density begins to decrease. This choice gives an average number of atoms in the interfacial regions to be about 25% of the total system.

In the nanophase systems the nearest-neighbor distances and coordinations, and bond-angle distributions in the cluster interiors and interfacial regions are very similar. The nearest neighbor Si-Si, Si-O, and O-O distances are found to be 3.10, 1.65, and 2.64 Å respectively. The Si-Si and O-O distributions for the interfacial regions are slightly broader in comparison to the interior regions. The O-Si-O and Si-O-Si bond angle distributions have peaks around 109 and 144° respectively. The bond-angle distributions for the interfacial regions are slightly broader than those for the interior regions.

The most dramatic change in structural correlations is observed in the first sharp diffraction peak (FSDP) in the neutron-scattering static structure factor, $S_n(k)$. The FSDP yields information about the intermediate-range order (IRO) in glasses [133,140]. In the past decade it has been the focus of many experimental and computer simulation studies of amorphous silica as well as other oxide and chalcogenide glasses. Figure 6.4 shows a

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comparison of $S_n(k)$ calculated from MD simulations (solid line) and neutron-scattering measurements (solid dots) [141] for bulk a-SiO$_2$. Our MD simulations for bulk a-SiO$_2$ have been shown previously to be of the highest quality by quantitatively comparing them with experiments in terms of the $R_x$ quality factor introduced by Wright [142]:

$$R_x = \left( \sum_i [T_{\text{exp}}(r_i) - T_{\text{MD}}(r_i)]^2 / \sum_i T_{\text{exp}}^2(r_i) \right)^{1/2},$$

where $T_{\text{exp}}(r_i)$ and $T_{\text{MD}}(r_i)$ represent the experimental and MD values of the neutron-scattering pair-correlation function (the Fourier transform of the neutron-scattering static structure factor) at the point $r_i$, respectively. The $R_x$ factor for our MD simulations is 4.4% [138], which is the lowest of all the available MD simulations of silica glasses.

Figure 6.4 also shows the MD results for $S_n(k)$ for nanophase silica glasses at various densities. Variations in $S_n(k)$ as a function of density are prominent in the wavenumber region $k < 2 \text{ \AA}^{-1}$, whereas no significant differences are found for $k > 2 \text{ \AA}^{-1}$. The insets (a) and (b) in Fig. 6.4 clearly show these features. As seen in Fig. 6.4(a) the height of the FSDP in the nanophase glasses is significantly smaller than that of the bulk silica glass. Additionally, the position of the FSDP in nanophase silica glasses shifts toward smaller $k$ with respect to the bulk. The mean cluster-radius in the nanophase a-SiO$_2$ can be estimated by analyzing the simulation results in the Fig. 6.4(b) in terms of the long-wavelength limit of $S_n(k)$ for an assembly of clusters (radius $r_0$) [143]:

$$S_n(k) \propto (\sin(kr_0) - kr_0 \cos(kr_0))^2 / (kr_0)^6.$$  

The open circles in Fig. 6.4(b) correspond to the case of $r_0 = 56 \text{ \AA}$ and the peak positions in $S_n(k)$ agree reasonably well with those of the MD results for $S_n(k)$ for all four densities. The value $r_0 \sim 56 \text{ \AA}$ implies that two clusters, each of radius of 35 \AA, have merged into each other.

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Figure 6.4 Neutron-scattering static structure factor, $S_n(k)$, for bulk and nanophase a-SiO$_2$. Solid and dashed lines denote the MD results; solid dots are the results of a neutron-diffraction experiments for bulk a-SiO$_2$ (Ref. [141]). Inset (a): magnification of the FSDP; inset (b): magnification of the $k < 0.2$ Å$^{-1}$ region showing correlations due to the nanoclusters. Open circles correspond to the small-$k$ limit of $S_n(k)$ for an assembly of clusters with a radius of 56 Å.
We have analyzed the differences in the IRO of nanophase and bulk silica glasses by examining the partial static structure factors. Figure 6.5 shows how the height and the position of the FSDP and the partial contributions to the FSDP vary as a function of the density. We note that in the nanophase silica glasses the height of the FSDP in $S_n(k)$ increases gradually with density. This behavior reflects the trend seen in the Si-O contribution to the height of the FSDP. The Si-Si and O-O contributions to the height of the FSDP are flat with respect to density. The most remarkable feature is that the height of the FSDP for bulk silica glass is at least 15% higher than that of the nanophase glasses. The position of the FSDP in the nanophase glasses is observed to move toward larger $k$. 

Figure 6.5 MD results for the height and position of the FSDP and the partial contributions (Si-Si, Si-O, and O-O) to the FSDP in $S_n(k)$ for bulk and nanophase a-SiO$_2$. Open symbols — nanophase a-SiO$_2$; solid symbols — bulk a-SiO$_2$. 

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as the density increases. This behavior is reflected in the Si-O and O-O contributions, whereas the Si-Si contribution to the FSDP position is almost unchanged with density.

![Graph showing Si-Si, Si-O, and O-O distributions](image)

Figure 6.6 Plot of $\langle n_{\alpha\beta}(r) \rangle = 4\pi\rho_\beta r^2 g_{\alpha\beta}(r)$ for bulk and nanophase a-SiO$_2$. The solid straight lines show the general trend of the peaks as the density varies.

The behavior of the position of the FSDP can be understood through detailed analyses of the partial pair-distribution function $g_{\alpha\beta}(r)$. Figure 6.6 shows a plot of $\langle n_{\alpha\beta}(r) \rangle = 4\pi\rho_\beta r^2 g_{\alpha\beta}(r)$ where $\rho_\beta$ is the partial number density of the species $\beta$. The
solid straight lines are drawn to show the general trend of the peaks in the 4 – 10 Å range as the density changes. In the case of Si-Si, the decrease in the density causes the second-peak position around 5 Å to shift toward larger distances and the third-peak and fourth-peak positions to shift toward smaller distances. These shifts in opposite directions nullify and hence the position of the Si-Si FSDP is insensitive to variations in the density of nanophasic silica glasses (Fig. 6.5 (bottom)). The second, third, and fourth peaks for the Si-O and O-O pair-distribution functions shift toward larger-r as the density decreases. This is consistent with the density-dependencies of the FSDP positions for Si-O and O-O pairs shown in Fig. 6.5 (bottom).

6.5 Vibrational properties

We have calculated the vibrational densities-of-states (DOS) of bulk and nanophasic silica glass from the Fourier transforms of velocity autocorrelation functions. The velocity autocorrelation functions were calculated at 100 K. The time interval was 1024 time steps, and the averaging was done over 41 time origins. Figure 6.7(a) shows the calculated DOS of bulk silica and nanophasic silica glasses at densities 2.03, 1.90, and 1.73 g/cm³. We observe an enhancement in the DOS at low energies that can be attributed to the vibrations of atoms in the interfacial regions. The enhancement is clearly revealed in Fig. 6.7(b) which shows a magnified view of the low-energy range (0 to 25 meV). The enhancement of the low-energy modes increases with decreasing density in the nanophasic glasses. In the 10 to 18 meV region there is a distinct drop in the DOS of the nanophasic glasses in comparison to the bulk glass. The DOS of the nanophasic glasses also appears to be independent of the density in the 10 to 18 meV region (see Fig. 6.7(b)). In addition to the low-energy enhancement, there is also a slight enhancement of the high-energy edge of the DOS.
Figure 6.7  (a) Vibrational DOS for bulk (solid line) and nanophase a-SiO_2 (dashed lines). (b) Magnified view of the low-energy range (0 to 25 meV) of DOS shown in (a).

We examine the behavior of the DOS by separately computing the local density of states (LDOS) for the cluster interior and interfacial regions. The LDOS of the interior and interfacial regions of 1.73 g/cm^3 nanophase glass, together with the DOS of the bulk glass are shown in Fig. 6.8(a). It can be seen that the enhancement of the low-energy modes is due mainly to atoms in the interfacial region. Figure 6.8(b) shows a magnification of the low frequency region (0 to 25 meV); the interfacial contribution is clearly seen to dominate the enhancement of low-energy modes. We also observe in Fig. 6.8(b) that the LDOS of the interfacial region changes toward a linear dependence on the frequency, indicating a softening of the force constants for atoms in the interfacial region. The shift of the peak around 95 meV is also due to atoms in the interfacial regions (see Fig. 6.8(a)). Contributions to the slight enhancement of the high-energy edge appear to come from both the interior and interfacial regions.
6.6 Mechanical behavior

We have also investigated the effect of densification on the elastic moduli of nanophase silica glasses. In order to calculate the elastic moduli, each nanophase system, initially thermalized at 100 K, was first brought to a zero-force configuration using the steepest-descent quench. The 21 elastic moduli were then calculated using the approach outlined in Section 2.4.4. This procedure was also used to calculate the elastic moduli for bulk silica. The calculated elastic moduli for bulk and nanophase silica glasses together with the experimentally determined values [144] are shown in Table 6.2. We find that the calculated elastic moduli for bulk silica are in excellent agreement with experiment.

Figure 6.9 shows a log-log plot of the bulk (\(K\)), shear (\(G\)), and Young’s (\(E\)) moduli for the nanophase and bulk silica systems as a function of the density, \(\bar{\rho}\), relative to the bulk silica density. The solid lines are the best least-squares fits for each of the moduli. We find that the elastic moduli scale as \(\bar{\rho}^{3.5 \pm 0.2}\). These simulation results are in excellent agreement with experimental measurements in silica aerogels, which show the
power-law dependence of elastic moduli on the density with the exponent for the high-density aerogels and non-porous silica being 3.49 [145].

Table 6.2 Elastic moduli of bulk and nanophase silica glass. Experimental values are from Ref. [144]. (\(\rho\): density, \(K\): bulk modulus, \(G\): shear modulus, \(E\): Young’s modulus)

<table>
<thead>
<tr>
<th>(\rho) (g/cm(^3))</th>
<th>2.20 (exp.)</th>
<th>2.20 (MD)</th>
<th>2.05</th>
<th>1.92</th>
<th>1.75</th>
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<td>41</td>
<td>33</td>
<td>25</td>
<td>19</td>
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<tr>
<td>(G) (GPa)</td>
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<td>30</td>
<td>23</td>
<td>18</td>
<td>13</td>
</tr>
<tr>
<td>(E) (GPa)</td>
<td>73</td>
<td>71</td>
<td>56</td>
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<td>32</td>
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</table>

Figure 6.9 Log-log plot of the bulk (\(K\)), shear (\(G\)), and Young’s (\(E\)) moduli for bulk and nanophase a-SiO\(_2\) as a function of the density relative to the bulk glass density. The solid lines are the best least-squares fits for each of the moduli.

6.7 Summary

In conclusion, using parallel computers we have carried out large-scale MD simulations to investigate the sintering, structure, vibrational properties, and mechanical behavior of nanophase silica glasses. The nanophase solids were synthesized by the consolidation of glassy silica nanoclusters 70 Å in diameter. The consolidation was
performed at a temperature of 1000 K and with pressure ranging from 0.6 to 2.4 GPa to produce nanophase silica glasses with densities ranging from 76 to 93% of the bulk amorphous density. During consolidation the size and spatial distribution of pores change dramatically. However, over all densities studied we find that the structure of pores is self-similar with a fractal dimension close to 2 and surface roughness exponents of pores to be always ~0.5. The short-range order (SRO) in nanophase glasses is similar to that of the bulk glass. Additionally, there is no real difference in the SRO in the cluster interior and interfacial regions of the nanophase glasses. The intermediate-range order (IRO) in nanophase silica glasses is quite different from that of the bulk silica glass. The first sharp diffraction peak (FSDP) in nanophase glasses is observed to have a much smaller height and is shifted toward smaller $k$ relative to the FSDP in the bulk silica glass. Calculation of vibrational density of states reveals an enhancement of the low-energy modes of the nanophase glasses, which can be attributed to the high percentage of atoms in the interfacial regions. The elastic moduli of nanophase silica glasses scale with the density as $M \sim \rho^{1.5}$. 

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CHAPTER 7

CONCLUSIONS

In this dissertation, we have presented the investigation of properties and processes in nanostructured oxide ceramic materials using the molecular-dynamics (MD) approach. These simulations involved the implementation of scalable and portable multiresolution algorithms on parallel computers.

We have investigated the oxidation of aluminum nanoclusters (20 nm diameter) using a parallel MD approach based on dynamic charge transfer among atoms. The interatomic potential used is capable of simultaneously treating both aluminum and aluminum oxide systems. We have implemented the $O(N)$ Fast Multipole Method in order to compute the Coulomb interaction that arises from the dynamic charge transfer. Simulations have been performed for both atomic and molecular oxygen environments in the canonical and microcanonical ensembles. In the canonical simulation an amorphous oxide scale with a thickness of 4 nm and an average mass density of 2.9 g/cm$^3$ is formed. The oxide thickness is in excellent agreement with experimental results on aluminum clusters of sizes similar to that used in the simulations. Analyses of the oxide scale reveal significant charge transfer and a variation of local structures when passing through the oxide from the metal-oxide interface to the oxide-environment interface. Simulations in the microcanonical ensemble with atomic and molecular oxygen show a continuous increase in the thickness and average temperature of the oxide layer with time. Subsequent melting of the nanocluster is observed in both settings, with the atomic case occurring 30% earlier than the molecular case due to the dissociation energy of the $O_2$ molecule.

The oxidation simulations have set the stage for future investigations of nanostructured composites. We propose to synthesize a nanostructured composite consisting of passivated aluminum nanoclusters. These simulations will involve around

84
40 million atoms (there are ~400,000 atoms in each passivated aluminum nanocluster). The computational resources to perform such large-scale MD simulations have only recently become available.

We have carried out large-scale MD simulations to investigate how solids synthesized by the consolidation of glassy silica nanoclusters are different from the bulk SiO$_2$ glass. The simulations are based on a reliable effective interatomic potential that consists of both 2-body and 3-body interactions. The nanophase systems are prepared by sintering nanoclusters of size 7 nm under pressures ranging from 0.6 to 2.4 GPa and at a temperature of 1000 K. In nanophase silica glasses with densities ranging from 76 to 93% of the bulk amorphous density, we find the structure of pores to be self-similar with a fractal dimension close to 2 and surface roughness exponents of pores to be always ~0.5. The short-range order in nanophase glasses is similar to that in the bulk glass. However, the intermediate-range order (IRO) is quite different in these two classes of solids. Investigations of the neutron-scattering static structure factor in nanophase silica glasses reveal that the first sharp diffraction peak (FSDP), which is the signature of IRO, in the nanophase glasses is much smaller in height and is shifted toward smaller wavevectors relative to the FSDP in the bulk silica glass. The low-energy modes in the vibrational density of states (DOS) of nanophase silica glass are enhanced relative to those for the bulk glass. Analyses of the local DOS of the cluster interior and interfacial regions show that the low-energy enhancement is mainly due to atoms in the interfacial regions. The elastic moduli of nanophase silica glasses scale with the density as $M \sim \rho^{3.5}$. The predictions of the MD simulations with regard to the IRO and mechanical behavior can be verified by neutron scattering experiments and measurement of elastic moduli of nanophase silica glasses.

Future work in nanophase silica glasses will involve the investigation of crack propagation. It is known that the presence of interfacial regions between grains affects the fracture behavior of a material. MD simulations of fracture in nanophase silica glasses
can provide a unique insight into the atomistic processes involved. Comparisons will be made with fracture simulations done in the crystalline SiO$_2$ and bulk silica glass.
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VITA


In 1984, Timothy began a four year enlistment in the U.S. Navy. He married Bonnie L. Passerrello in 1986. After his enlistment, Timothy studied at St. Norbert College in De Pere, Wisconsin from 1989 to 1993 and graduated with a Bachelor of Science degree in Physics.

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DOCTORAL EXAMINATION AND DISSERTATION REPORT

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Title of Dissertation: Nanostructure Modeling in Oxide Ceramics Using Large Scale Parallel Molecular-Dynamics Simulations

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