Classical Molecular Dynamics Simulations for Crystalline Solids using Truncated Taylor Series Interatomic Potential

by

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Abstract

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This thesis discusses a general method for constructing interatomic potentials for crystal lattices based on a truncated Taylor series expansion. Such an interatomic potential may be constructed analytically, as in the case of a Lennard-Jones solid, or using ab initio methods such as Density Functional Theory. Specifically, it addresses the scope of application of the method, and demonstrates its practical importance in capturing anharmonicity for a Lennard-Jones solid. In particular, the third-order terms in the truncated potential are shown to accurately approximate the thermal conductivity of the standard interaction Lennard-Jones potential. The thesis also describes an efficient algorithm for locating the equilibrium lattice site of an atom in a three-dimensional crystal lattice displaced from its equilibrium position.

In addition, a procedure is outlined to compute the coefficients in the truncated Taylor series expansion using Density Functional Theory, which is an ab initio method. The procedure is applied to germanium, a material for which, an exact analytical interatomic potential is not known. The computed coefficients may then be used to construct an interatomic potential for germanium of ab initio accuracy. This interatomic potential is then used in MD simulations to estimate various thermophysical properties of a germanium crystal lattice within the range of applicability of this method.
Dedicated to my family and mentors.
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To my family and all my mentors, I humbly dedicate this work.
Chapter 1

Introduction

Molecular Dynamics (MD) is an invaluable computational tool for bridging the gap between microscopic dynamics and macroscopic physical properties. MD has been utilized to study a wide variety of systems ranging from crystalline solids to gaseous mixtures. The ubiquity of MD simulations in the study of such diverse systems is mainly due to the ease with which MD can be scaled to very large systems containing thousands of atoms and molecules.

For crystalline solids, another popular simulation technique is known as lattice dynamics, in which the basic unit of analysis is a mode of lattice vibration, known as a phonon. A key advantage of MD over conventional lattice dynamics methods is that it allows for the natural inclusion of anharmonic effects, which can only be dealt with by introducing various hypotheses in lattice dynamics methods [51]. Since these anharmonic effects are crucial in estimating most thermophysical properties, MD acts an invaluable computational tool for the efficient estimation of thermophysical properties of materials.

In spite of its many advantages, MD is not particularly suitable for all simulating all kinds of systems. In particular, classical MD, which is based on the classical Maxwell-Boltzmann statistics, is inapplicable to systems where quantum effects are dominant. While it is possible to circumvent this limitation by supplanting classical statistics by quantum statistics, such as the Fermi-Dirac or the Bose-Einstein statistics, full quantum mechanical MD is currently prohibitively expensive computationally to implement for all but only smaller systems, containing at most a few hundred atoms, as further elaborated below.

The biggest drawback of MD arises from its reliance on semi-empirical potential functions, which are required for computing interatomic interactions in MD simulations. The application of MD to the quantitative analysis of material response and properties is predicated upon the availability of accurate and efficient potentials. In principle, such potentials are intended to represent interatomic interactions between charged atomic particles. While ab initio MD is possible, its scope is extremely limited due to its prohibitive computational cost. Moreover, potential energy surfaces, which are solutions of the electronic Schrödinger equation within the Born-Oppenheimer approximation, are not readily available for most interesting systems. For this reason, one typically relies on a coarse empirical approximation to the true quantum-mechanical potential. Ideally, empirical potentials should have
CHAPTER 1. INTRODUCTION

a simple functional form to speed up the evaluation of the forces acting on an atom and also be transferable to many systems under different loading conditions. Thus, designing a general empirical interatomic potential that approximates the actual (unknown) solution of the Schrödinger equation is a challenging task. In practice, the choice of functional form and parameters is often based on fitting to available experimental data (e.g. equilibrium geometry of stable phases, cohesive energy, elastic moduli, vibrational frequencies, temperatures of the phase transitions, etc.). Unsurprisingly, a potential that is tailored to one set of experimental data for a given material does not necessarily predict with accuracy the response of the same material beyond the narrow scope of this data. For example, if a potential has been designed to reproduce mechanical properties, such as the experimental values of the lattice constant and elastic constants for a crystal phase, one should not expect it to accurately predict thermal transport properties [50].

Recent analytical work has introduced a general method of constructing interatomic potentials based on a truncated Taylor series expansion of the (unknown) potential function of the crystal to a given order [14, 13]. The coefficients in the Taylor series may be obtained from a given interatomic potential or through ab initio methods, e.g. Density Functional Theory (DFT) calculations. The latter enables the use of interatomic potentials of ab initio accuracy for MD simulations, thereby removing one of the major limitations of classical MD, that is, the dependence on purely empirical potentials.

While past work [14, 13] focused on the application of the method of truncated Taylor series potential, it did not include any information on the conditions under which this method is applicable. Further, it is not clear how many terms in the Taylor series expansion are required to accurately estimate thermophysical properties of crystal lattices, such as heat capacity and thermal conductivity, the latter of which depends strongly on the degree of anharmonicity of the potential energy. This is particularly important because inclusion of higher-order terms becomes computationally expensive in terms of storage of force constants. In addition, calculating these higher-order force constants for real materials using an ab initio method such as DFT is extremely challenging. As a result, most DFT-based methods are currently limited to computation of terms up to the third-order in the Taylor series expansion.

This thesis extends the previous work by addressing the range of applicability of the truncated Taylor series expansion method. It also demonstrates the effectiveness of this method in yielding accurate estimates of equilibrium properties such as heat capacity as well as transport properties such as thermal conductivity. The latter affirms the sufficiency of the third-order terms in representing the anharmonicity of crystal lattices, thereby clarifying the importance of the third-order terms in relation to higher-order terms in the potential energy expression of solid crystals. For simplicity, the method is illustrated for an ideal Lennard-Jones (LJ) crystal, as the closed functional form of an LJ solid allows for an accurate determination of the error incurred in the estimation of thermophysical properties by approximating the potential energy with a truncated Taylor series. It must be noted that the predictive capacity of this method is not limited to materials whose potential is explicitly known. Indeed, the real utility of this method is in enabling the use of interatomic potentials of ab initio accuracy to make more accurate predictions of thermophysical properties for a
The thesis is organized as follows. Chapter 2 provides the required background from continuum mechanics that forms the framework for the rest of the results in this work. Chapter 3 derives the main results from the theory of statistical mechanics that are used in the MD simulations. Chapter 4 provides the details of the MD simulations performed in this work and some associated important concepts. Chapter 5 discusses the details of the truncated Taylor series potential introduced in this work for MD simulations of crystal lattices. This chapter also addresses the range of applicability of this technique and concludes with an application of this method to the case of LJ Ar. Chapter 6 discusses the details of the DFT computations for the case of Ge, which are required to determine the exact \textit{ab initio} interatomic potential for Ge. Finally, Chapter 7 summarizes the work and provides further scope of applications for this work.
Chapter 2

Continuum Mechanics

It is well-known that the thermomechanical response of most materials may be explained quite satisfactorily by modeling the material body as a continuous medium rather than as a collection of discrete atoms. The treatment of material bodies as continua forms the subject matter of Continuum Mechanics and is discussed in this chapter. On the other hand, describing the thermophysical properties of materials by accounting for the agglomeration of atoms composing the material body is the primary concern of the subject of Statistical Mechanics, which is discussed in the next chapter. The macroscopic balance laws of mass, linear and angular momenta and energy for a continuum, which together constitute some of the central results in continuum mechanics, are introduced below.

2.1 Kinematics

In continuum mechanics, a body \( \mathcal{B} \) is assumed to consist of a collection of material points, with a typical one denoted \( X \). If \( \mathcal{B} \) is finite in size, it occupies a bounded region \( \mathcal{R}_t \) in three-dimensional Euclidean space \( \mathbb{R}^3 \) at any time \( t \). The motion of the body \( \mathcal{B} \) in \( \mathbb{R}^3 \) is represented by the mapping \( \chi : \mathcal{B} \times t \rightarrow \mathcal{R}_t \subseteq \mathbb{R}^3 \), where \( \chi \) is assumed to be invertible and differentiable at each time \( t \). In other words, the current position \( x \in \mathcal{R}_t \) of any material point \( X \) at time \( t \) relative to the fixed origin \( o \) of an orthonormal basis in \( \mathbb{R}^3 \) is given by

\[
x = \chi(X,t).
\]  

(2.1)

The image \( \mathcal{R}_t \) of the body \( \mathcal{B} \) under the mapping \( \chi \) is known as the current configuration of the body. The velocity \( \mathbf{v} \) of any material point is defined as

\[
\mathbf{v} = \dot{x} = \frac{\partial \chi(X,t)}{\partial t},
\]

(2.2)

where the superposed “dot” denotes the material time derivative.

In order to describe the motion of the body succinctly, the image \( \mathcal{R}_0 \) under the mapping \( \chi \) at some fixed time \( t_0 \) is defined as the reference configuration of the body. The position
\( \mathbf{X} \) of any material point \( X \) in the reference configuration \( \mathcal{R}_0 \) is defined by

\[
\mathbf{X} = \mathbf{\chi}(X, t_0) = \mathbf{\chi}_0(X) \in \mathcal{R}_0 .
\] (2.3)

From the invertibility of \( \mathbf{\chi} \), it follows that \( \mathbf{\chi}_0 \) is invertible and hence, the current position \( \mathbf{x} \) of a material point is expressible in terms of its reference position \( \mathbf{X} \) using Equations (2.1) and (2.3) as

\[
\mathbf{x} = \mathbf{\chi}(\mathbf{\chi}_0^{-1}(X), t) = \mathbf{\chi}_{\mathcal{R}_0}(X, t) .
\] (2.4)

The displacement \( \mathbf{u} \) of a material point at time \( t \) from its reference position \( \mathbf{X} \) is given by

\[
\mathbf{u} = \mathbf{x} - \mathbf{X} .
\] (2.5)

The fundamental kinematic tensor underlying the local analysis of deformation is the deformation gradient \( \mathbf{F} \) defined by

\[
\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} .
\] (2.6)

For physically plausible deformations, it may be easily shown that \( J = \det \mathbf{F} > 0 \) for all time \( t \).

### 2.2 Kinetics

The linear momentum of an arbitrary subset \( \mathcal{S} \) of the body \( \mathcal{B} \) occupying the region \( \mathcal{P} \) at time \( t \) is defined by \( \int_{\mathcal{P}} \rho \mathbf{v} \, dv \). Similarly, the angular momentum of the subset \( \mathcal{S} \) of the body with respect to the origin \( o \) of the coordinate system is defined by \( \int_{\mathcal{P}} \mathbf{x} \times (\rho \mathbf{v}) \, dv \), where “\( \times \)” denotes the ordinary cross-product in \( \mathbb{R}^3 \).

In classical continuum mechanics, the action of the surroundings on the body is described by two kinds of forces: surface and body forces. The former one is mathematically represented as a vector \( \mathbf{t} \), called the traction vector, which is defined as the surface force acting per unit area of the boundary \( \partial \mathcal{P} \) of the region \( \mathcal{P} \). The latter is expressed as a vector \( \mathbf{b} \), which denotes the body force acting per unit mass of the body. Thus, the total force acting on the body \( \mathcal{S} \) is given by the sum of the surface and body forces acting on it, i.e.,

\[
\int_{\partial \mathcal{P}} \mathbf{t} \, da + \int_{\mathcal{P}} \mathbf{\rho b} \, dv .
\]

Similarly, the total torque with respect to the origin \( o \) acting on \( \mathcal{S} \) is given by

\[
\int_{\partial \mathcal{P}} \mathbf{x} \times \mathbf{t} \, da + \int_{\mathcal{P}} \mathbf{x} \times \mathbf{\rho b} \, dv .
\]

#### 2.2.1 Mass balance

The total mass \( m \) contained in an arbitrary subset \( \mathcal{S} \) of the body \( \mathcal{B} \) occupying the region \( \mathcal{P} \subseteq \mathcal{R}_t \) is defined as

\[
m(\mathcal{S}) = \int_{\mathcal{P}} \rho \, dv ,
\] (2.7)
where \( \rho \) is called the **mass density**. According to the law of conservation of mass, the total mass contained in \( \mathcal{P} \) does not change during the motion of the body in time, i.e.,

\[
\frac{d}{dt} \int_{\mathcal{P}} \rho \, dv = 0 .
\]  

(2.8)

Using the Reynold’s transport theorem [70], the law of mass conservation may be re-expressed as

\[
\int_{\mathcal{P}} \left( \dot{\rho} + \rho \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{v} \right) \, dv = 0 ,
\]  

(2.9)

where \( \frac{\partial}{\partial \mathbf{x}} \cdot \) denotes the spatial divergence operator with respect to the current position \( \mathbf{x} \).

Applying the classical localization theorem [70] yields the local form of mass balance as

\[
\dot{\rho} + \rho \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{v} = 0 ,
\]  

(2.10)

which, on expanding the material time derivative on the left-hand side, may be re-written as follows

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{v}) = 0 .
\]  

(2.11)

### 2.2.2 Balance of linear momentum

Euler’s first law of motion states that [70]

\[
\frac{d}{dt} \int_{\mathcal{P}} \rho \mathbf{v} \, dv = \int_{\partial \mathcal{P}} \mathbf{t} \, da + \int_{\mathcal{P}} \rho \mathbf{b} \, dv .
\]  

(2.12)

Now, Cauchy’s theorem [70] implies that

\[
\mathbf{t} = \mathbf{T} \mathbf{n} ,
\]  

(2.13)

where \( \mathbf{T} \) denotes the Cauchy stress tensor and \( \mathbf{n} \) denotes the unit normal to the boundary \( \partial \mathcal{P} \). Substituting \( \mathbf{t} \) from Equation (2.13) into Equation (2.12) and simplifying the resulting equation using the divergence theorem, followed by the localization theorem, as in the case of mass balance, results in the local form of linear momentum balance given by

\[
\rho \mathbf{\dot{v}} = \frac{\partial}{\partial \mathbf{x}} \cdot \mathbf{T} + \rho \mathbf{b} ,
\]  

(2.14)

where the Cauchy stress tensor \( \mathbf{T} \) is assumed to be continuously differentiable.
2.2.3 Balance of angular momentum

Euler’s second law of motion may be mathematically expressed as

\[
\frac{d}{dt} \int_{P} \mathbf{x} \times (\rho \mathbf{v}) \, dv = \int_{\partial P} \mathbf{x} \times \mathbf{t} \, da + \int_{P} \mathbf{x} \times \rho \mathbf{b} \, dv .
\] (2.15)

Using the laws of mass and linear momentum balance from equations (2.11) and (2.14) respectively, and the divergence and localization theorems, as in the case of linear momentum balance, the local form of Equation (2.15) is reduced to

\[
T^T = T ,
\] (2.16)

which expresses the symmetry of the Cauchy stress tensor \( T \).

2.3 Thermodynamics

From Equation (2.14), it is straightforward to derive the equation of mechanical energy balance, given by

\[
\frac{d}{dt} \int_{P} \rho \left( \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + T \cdot D \right) \, dv = \int_{\partial P} \mathbf{t} \cdot \mathbf{v} \, da + \int_{P} \rho \mathbf{b} \cdot \mathbf{v} \, dv ,
\] (2.17)

where \( D = \text{Sym} \left( \frac{\partial \mathbf{v}}{\partial \mathbf{x}} \right) \) denotes the symmetric part of the spatial velocity gradient. In Equation (2.17), the first term of the integrand on the left-hand side denotes the kinetic energy of the subset \( \mathcal{S} \) of the body, the second term denotes the stress power, while the sum on the right-hand side denotes the total power of the applied forces acting on \( \mathcal{S} \). The kinetic energy of a body forms only a part of its total energy content. In continuum mechanics, the remaining energy content of the body is defined to be its internal energy \( U \) and is given by

\[
U(\mathcal{S}) = \int_{P} \rho \epsilon \, dv ,
\] (2.18)

where \( \epsilon \) denotes the internal energy per unit mass of the body.

2.3.1 Energy balance

The law of conservation of energy for any subset \( \mathcal{S} \) of the body asserts that the change in the total energy content of \( \mathcal{S} \) must equal the rate at which energy is supplied to it through mechanical and thermal interactions, \( i.e., \)

\[
\frac{d}{dt} \int_{P} \rho \left( \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + \epsilon \right) \, dv = \int_{\partial P} (\mathbf{t} \cdot \mathbf{v} - h) \, da + \int_{P} \rho (\mathbf{b} \cdot \mathbf{v} + r) \, dv ,
\] (2.19)
where $h$ denotes the outward heat flux per unit area of the boundary $\partial\mathcal{P}$ and $r$ denotes the heat supply rate per unit mass. In analogy to Cauchy’s theorem, Equation (2.13), it may be shown that

$$h = q \cdot n,$$

(2.20)

where $q$ is known as the heat flux vector [70]. Substituting for $h$ from Equation (2.20) into Equation (2.19) and applying the divergence and localization theorems leads to the local form of energy balance given by

$$\rho\dot{e} = T \cdot D - \frac{\partial}{\partial x} \cdot q + \rho r.$$

(2.21)

Equation (2.21) may be alternatively expressed as

$$\rho\dot{e} = \frac{\partial}{\partial x} \cdot (Tv) - \frac{\partial}{\partial x} \cdot q + \rho b \cdot v + \rho r,$$

(2.22)

where $e$, defined as

$$e = \frac{1}{2}v \cdot v + \epsilon,$$

(2.23)

denotes the total energy per unit mass of the body.
Chapter 3

Statistical Mechanics

Statistical mechanics deals with collections of atoms or molecules, which make up material bodies, as mentioned in Chapter 2. In classical statistical mechanics, the dynamics of these constituent particles are assumed to be governed by Newton’s Laws with specified interparticle interactions. Since it is practically impossible to determine the state of the macroscopic system by determining the position and momenta of every atom or molecule, the state of the system is assumed to be completely characterized by a set of relatively few macroscopic observables (e.g., energy, temperature, etc.). Statistical mechanics is concerned with the relationship between the dynamics at the microscale and the macroscopic observables that characterize the system [10].

3.1 Microstates and macrostates

Consider a three-dimensional system consisting of \( N \) atoms with current positions \( \mathbf{r}_1, \ldots, \mathbf{r}_N \) and momenta \( \mathbf{p}_1, \ldots, \mathbf{p}_N \), collectively called the phase variables. The current configuration of the system characterized by these phase variables is termed a microstate. The \( 6N \)-dimensional space of all possible positions and momenta, denoted by \( \Gamma = \{(\mathbf{r}_i, \mathbf{p}_i), i = 1, \ldots, N\} \), is called the phase space. The phase space allows for the representation of the instantaneous state of the system by a point in \( \mathbb{R}^N \) whose motion in the phase space represents the time-evolution of the system, i.e., as a curve \( \Gamma(t) \) in phase space. The thermodynamic state of a system at any time \( t \) is characterized by a set of macroscopic variables, whose cardinality is much smaller than \( 6N \) (e.g., volume, pressure, temperature etc.). It follows that there are many possible microstates consistent with a given set of macroscopic variables that characterize the current thermodynamic state of the system; all of these states form an ensemble. This implies the existence of a phase-space distribution function \( f(\Gamma, t) \) that determines the probability of the system being a microstate \( \Gamma \) at time \( t \). The explicit time-dependence of \( f(\Gamma, t) \) accounts for the fact that the system may possibly not be in thermodynamic equilibrium. Being a probability distribution function, \( f(\Gamma, t) \) must be
normalized to unity, i.e.,
\[ \int_{\gamma} f(\Gamma, t) \, d\Gamma = 1 \quad (3.1) \]
where \( \gamma \) denotes the entire phase space of the system. It follows that for any subset \( \Omega \) of \( \gamma \),
\[ \int_{\Omega} f(\Gamma, t) \, d\Gamma \]
gives the fraction of members of the ensemble that are within \( \Omega \). If one follows this set in time, then the fraction of members within this set should remain constant in time, as members are neither created nor destroyed, Therefore,
\[ \frac{d}{dt} \int_{\Omega} f(\Gamma, t) \, d\Gamma = 0 \quad (3.2) \]
Assuming continuity of \( f(\Gamma, t) \), the use of Reynold’s transport theorem transforms Equation (3.2) to
\[ \int_{\Omega} \left[ \frac{\partial f(\Gamma, t)}{\partial t} + f(\Gamma, t) \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f(\Gamma, t) \right] \, d\Gamma = 0 \quad (3.3) \]
where \( \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = \sum_i \left( \frac{\partial}{\partial p_i} \cdot \dot{p}_i + \frac{\partial}{\partial r_i} \cdot \dot{r}_i \right) \). Since \( \Omega \) is any arbitrary subset of \( \Gamma \), application of the localization theorem \([70]\) yields
\[ \frac{\partial}{\partial t} f(\Gamma, t) = -iLf(\Gamma, t) \quad (3.4) \]
where \( iL = \left[ \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right] \) is called the \( f \)-Liouvillean operator. Equation (3.4) is called the Liouville equation for the phase space distribution function and its solution is formally given by
\[ f(\Gamma, t) = \exp(-iLt)[f(\Gamma, 0)] \quad (3.5) \]
where \( f(\Gamma, 0) \) is the initial phase space distribution consistent with the initial preparation of the system \([16]\). It is interesting to note that if \( \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = 0 \), the phase space is incompressible, which is conceptually analogous to material incompressibility in continuum mechanics.

Another kind of Liouvillean operator arises in connection with phase variables, i.e., variables that depend only on the microstate of the system and not explicitly on time. Consider a general phase variable \( G(\Gamma) = \tilde{G}(t) \). The time derivative of \( G \) is given by
\[ \dot{G}(\Gamma) = \left[ \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right] G(\Gamma) = iLG(\Gamma) \quad (3.6) \]
where \( iL \) is called the \( p \)-Liouvillean operator. The solution of Equation (3.6) is formally given by
\[ \tilde{G}(t) = \exp(itL)[\tilde{G}(0)] \quad (3.7) \]
The two Liouvillean operators are related by the following identity
\[ \int f(\Gamma, t) iLG(\Gamma) \, d\Gamma = - \int G(\Gamma) iLf(\Gamma, t) \, d\Gamma \quad (3.8) \]
which follows from a simple application of integration by parts, see [16, Chapter 3].

The ensemble average of the phase variable $G$ at any time $t$, $\langle G(t) \rangle$ can be evaluated in two equivalent ways. In the first approach, termed as the Heisenberg representation, an arbitrary configuration $\Gamma(0)$ is selected from the initial probability distribution with probability $f(\Gamma,0)$ and the phase variable $G$ is evaluated at time $t$ by following the trajectory of this configuration in time starting at $\Gamma(0)$, i.e.,

$$\langle G(t) \rangle_H = \int \tilde{G}(t) f(\Gamma,0) \, d\Gamma.$$  
(3.9)

Thus, the Heisenberg representation is analogous to the Lagrangian formulation in continuum mechanics, where one follows a material point. In the second approach, termed the Schrödinger representation, the phase variable $G$ is evaluated at time $t$ at an arbitrary configuration $\Gamma$ in the phase space chosen with probability $f(\Gamma,t)$, i.e.,

$$\langle G(t) \rangle_S = \int G(\Gamma) f(\Gamma,t) \, d\Gamma.$$  
(3.10)

Thus, the Schrödinger representation is analogous to the Eulerian formulation in continuum mechanics, where one monitors the particles passing through a fixed point.

Now suppose that the system is aged, i.e., a closed and isolated system in thermodynamic equilibrium, characterized by the macroscopic thermodynamic parameters $a_1, \ldots, a_n$ with equilibrium values $\bar{a}_1, \ldots, \bar{a}_n$. Let the fluctuations of these quantities from their equilibrium values at any instant of time $t$ be denoted $\{\alpha_1, \ldots, \alpha_n\} \equiv \alpha$, i.e.,

$$\alpha_i(t) = a_i(t) - \bar{a}_i, \quad (i = 1, \ldots, n).$$  
(3.11)

Since $a_1, \ldots, a_n$ are phase variables, it follows that $\alpha$ is a phase variable too, i.e., $\alpha \equiv \alpha(\Gamma)$.

At equilibrium, the phase space distribution function does not explicitly depend on time, i.e., $f(\Gamma,t) \equiv f(\Gamma)$. It follows that there exists a probability distribution function over $\alpha$ given by

$$W(\alpha') = \int_{\alpha(\Gamma)=\alpha'} f(\Gamma) \, d\Gamma.$$  
(3.12)

Being a probability distribution function, $W(\alpha)$ must satisfy

$$\int W(\alpha) \, d\alpha = 1.$$  
(3.13)

For an aged system, the probability distribution function $W(\alpha')$ decays to 0 extremely rapidly for even small deviations of $\alpha'$ from its equilibrium value (which is 0 by definition) [62], as illustrated in Figure 3.1. This is because the width of the distribution function near the maximum in Figure 3.1 is inversely proportional to the square root of the number of particles in the macroscopic system [62] and since the typical macroscopic system contains on the order of $10^{24}$ particles, the distribution function near the maximum is extremely narrow.
This implies that the total number \( g(\alpha) \) of microstates corresponding to a given macrostate characterized by \( \alpha \), termed as multiplicity of the state, drops off extremely rapidly away from equilibrium. The multiplicity \( g(\alpha) \) of a state is related to the entropy \( S \) of the state by the Boltzmann equation [62]

\[
S(\alpha) = k_B \ln g(\alpha) ,
\]

where \( k_B \) denotes the Boltzmann constant. This relation directly implies the well-known thermodynamic law that the equilibrium state of the system is characterized by maximum entropy and forms a crucial link between the statistical and classical theories of thermodynamics.

The probability distribution function \( W(\alpha) \) is quite useful as it allows a direct way to evaluate the ensemble average of any equilibrium thermodynamic quantity \( F(\alpha) \). Indeed, it may be seen that both the Heisenberg and the Schrödinger representations lead to the same expression for the ensemble average of \( F(\alpha) \), \textit{viz.,}

\[
\langle F(\alpha) \rangle = \int F(\alpha)W(\alpha) \, d\alpha .
\]

(3.15)
3.2 Heat Capacity

A fundamental result in statistical mechanics is the expression for heat capacity \( C_v \), an equilibrium property, in terms of fluctuations of energy in the canonical ensemble, where the prescribed set of macroscopic variables are the number of particles \( N \), volume \( V \) and temperature \( T \).

This result is based on the observation that a system for which a canonical ensemble is appropriate can be viewed as a subsystem of one for which the microcanonical ensemble, i.e., where the temperature is replaced by the total energy \( E \) in the governing set of macroscopic variables, is applicable. This observation is illustrated in Figure 3.2, where the system is kept in equilibrium at temperature \( T \) by being in contact with a heat bath. The bath is assumed to be much larger than the system, which justifies the assumption that the energy of the bath \( E_B \) is overwhelmingly larger than the energy of the system \( E_\Gamma \) in any microstate \( \Gamma \). The energy of the system fluctuates because the system is in contact with the bath, but the total energy of the system and the bath \( E = E_B + E_\Gamma \) remains constant.

\[ W_\Gamma \propto g_B(E - E_\Gamma). \]  
(3.16)

Since \( E_\Gamma \ll E \), the right-hand side can be approximated by a truncated Taylor series expansion. However, as discussed earlier, \( g_B(E - E_\Gamma) \) is a rapidly varying function of \( E - E_\Gamma \),
so it is better to expand \( \ln g_B(E - E_\Gamma) \) rather than \( g_B(E - E_\Gamma) \) itself. This is accomplished by rewriting the relation (3.16) as

\[
W_\Gamma \propto \exp \left[ \ln g_B(E - E_\Gamma) \right] \doteq \exp \left[ \ln g_B(E) - E_\Gamma \frac{d \ln g_B(E)}{d E} \right]. \tag{3.17}
\]

By definition, the equilibrium temperature \( T \) of a closed and isolated system at equilibrium satisfies

\[
\left[ \frac{\partial S}{\partial E} \right]_{eqb.} = \frac{1}{T}. \tag{3.18}
\]

Combining the definition of temperature with the Boltzmann equation (3.14) leads to

\[
W_\Gamma \propto \exp[-\beta E_\Gamma], \tag{3.19}
\]

where \( \beta = \frac{1}{k_B T} \). The constant of proportionality is obtained by simply normalizing \( W_\Gamma \) to unity, i.e.,

\[
W_\Gamma = \frac{\exp[-\beta E_\Gamma]}{Q}, \tag{3.20}
\]

where

\[
Q = \int \exp[-\beta E_\Gamma] \ d\Gamma, \tag{3.21}
\]

is called the canonical partition function.

The canonical partition function, with the aid of equations (3.20) and (3.21), allows for the direct evaluation of many other thermodynamic quantities. For instance, the ensemble average \( \langle E_\Gamma \rangle \) of the energy of the system in a canonical ensemble is given by

\[
\langle E_\Gamma \rangle = \int E_\Gamma W_\Gamma \ d\Gamma = \left( \frac{\int E_\Gamma \exp[-\beta E_\Gamma] \ d\Gamma}{\int \exp[-\beta E_\Gamma] \ d\Gamma} \right) = -Q^{-1} \left. \frac{\partial Q}{\partial \beta} \right|_{\beta} = - \left. \frac{\partial \ln Q}{\partial \beta} \right|_{\beta}. \tag{3.22}
\]

Similarly, the average squared fluctuation \( \langle (\delta E_\Gamma)^2 \rangle \) of the energy in the canonical ensemble
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is given by

\[
\langle (\delta E^2) \rangle = \langle (E_\Gamma - \langle E_\Gamma \rangle)^2 \rangle \\
= \langle E^2_\Gamma \rangle - \langle E_\Gamma \rangle^2 \\
= \int E^2_\Gamma W_\Gamma d\Gamma - \left( \int E_\Gamma W_\Gamma d\Gamma \right)^2 \\
= Q^{-1} \frac{\partial^2 Q}{\partial \beta^2} - Q^{-2} \frac{\partial Q}{\partial \beta} \\
= \frac{\partial^2 \ln Q}{\partial \beta^2} \\
= - \frac{\partial \langle E \rangle}{\partial \beta} ,
\]

(3.23)

where use is also made of Equation (3.22).

The heat capacity \( C_v \) of the system is defined as

\[
C_v = \frac{\partial \langle E_\Gamma \rangle}{\partial T} .
\]

(3.24)

Thus, inserting the definition of \( \beta \) in Equation (3.23), the heat capacity of the system may be computed from the average squared fluctuation of the energy in the canonical ensemble by the formula

\[
C_v = \frac{\langle (\delta E_\Gamma)^2 \rangle}{k_B T^2} .
\]

(3.25)

Equation (3.25) is a fundamental result since it represents the heat capacity, an equilibrium property, in terms of fluctuations of energy in the canonical ensemble.

3.3 Thermal Conductivity

In this section, a classical derivation of the Green-Kubo formulae for estimating thermal conductivity of any system is presented, while explicitly stating all the underlying assumptions involved. Starting from Onsager’s regression hypothesis, a general formula for transport coefficients is derived and is subsequently employed to deduce the Green-kubo formula for thermal conductivity. The derivation initially follows the same procedure outlined in [37] although it deviates slightly to arrive at the general form of the Green-Kubo formula for any transport coefficient. This result is then used to express the thermal conductivity for a closed and isolated system.

3.3.1 Green-Kubo formula for a general transport coefficient

According to Onsager’s regression hypothesis [55], the average behavior of fluctuations of a physical quantity in an aged system is governed by the same physical law which governs the
change of the corresponding macroscopic variable. This hypothesis may be mathematically expressed as follows: Let \( \alpha_j(t + \Delta t | \alpha'_t) \) denote the value of \( \alpha_j \) from Equation (3.11) at time \( t = t + \Delta t \) when the observed values of \( \{\alpha_1, \ldots, \alpha_n\} \) at time \( t \) are specified as \( \{\alpha'_1, \ldots, \alpha'_n\} \equiv \alpha' \). Then, Onsager’s regression hypothesis implies that

\[
\alpha_j(t + \Delta t | \alpha'_t) - \alpha'_j = \sum_k G_{jk} \left[ \frac{\partial S}{\partial \alpha_k} \right]_{\alpha'} \Delta t , \quad (j, k = 1, \ldots, n), \tag{3.26}
\]

where \( \alpha_j(t + \Delta t | \alpha'_t) \) denotes the average equilibrium value of the stochastic variable \( \alpha_j \) at time \( t = t + \Delta t \) for all initial states starting with \( \alpha(t) = \alpha' \) and \( G_{jk} \) denote some macroscopic coefficients. Since the entropy of a closed and isolated system is maximum at equilibrium \([62]\), the term \( \frac{\partial S}{\partial \alpha_k} \) denotes the \( k \)-th term of the driving force, which drives the variables \( \alpha_1, \ldots, \alpha_n \) to their equilibrium values, \( \text{viz.}, 0 \). For small deviations from equilibrium, the macroscopic coefficients \( G_{jk} \) may be taken to be constant since the relations between the velocity of regression of \( \alpha_j \)'s and the driving forces \( \frac{\partial S}{\partial \alpha_k} \) will be linear. Thus, the constants \( G_{jk} \) are the macroscopic coefficients which relate the rates of change of the macroscopic variables \( \alpha_j \) to the driving forces.

It may be noted that Equation (3.26) is a finite-difference equation and hence, is valid only if \( \Delta t \) is small in the macroscopic sense (\( i.e., \) of the order of the apparatus measurement time), but sufficiently large in the microscopic sense, the meaning of which may be made more precise by manipulating (3.26) as follows. The entropy \( S \) of the system may be expanded in a Taylor series about its equilibrium value as

\[
S = S_0 + \sum_k \left[ \frac{\partial S}{\partial \alpha_k} \right]_0 \alpha_k + \sum_{k,l} \left[ \frac{\partial^2 S}{\partial \alpha_k \partial \alpha_l} \right]_0 \alpha_k \alpha_l + \ldots , \tag{3.27}
\]

where \( S_0 \) denotes the equilibrium value of the entropy of the system. Each partial derivative in Equation (3.27) is evaluated at equilibrium. However, since the entropy of the system is a maximum at equilibrium, each of the first partial derivatives of \( S \) must vanish. Therefore,

\[
S = S_0 + \sum_{k,l} \left[ \frac{\partial^2 S}{\partial \alpha_k \partial \alpha_l} \right]_0 \alpha_k \alpha_l + \ldots . \tag{3.28}
\]

Using Equation (3.28), the term \( \frac{\partial S}{\partial \alpha_k} \) may be approximated at any value \( \alpha' \), assuming small deviations from equilibrium, as

\[
\left[ \frac{\partial S}{\partial \alpha_k} \right]_{\alpha'} = \sum_l \left[ \frac{\partial^2 S}{\partial \alpha_k \partial \alpha_l} \right]_0 \alpha'_l . \tag{3.29}
\]

Using Equation (3.29), Equation (3.26) may be recast into the form

\[
\alpha_j(t + \Delta t | \alpha'_t) - \alpha'_j = \sum_k M_{ji} \alpha'_i \Delta t , \tag{3.30}
\]
where \( M_{jl} = \sum G_{jk} \left( \frac{\partial S}{\partial \alpha_k} \right)_{\alpha_l} \). It may be seen that the coefficients \( M_{jl} \) are linearly related to the coefficients \( G_{jk} \). Now the condition for the finite difference equation (3.30) to hold may be formulated in terms of \( M_{jl} \) as \( M_{jl} \Delta t \ll 1 \) for all \( j, l \).

Multiplying Equation (3.26) by \( \alpha' \) and taking the average of the resulting equation over the equilibrium ensemble yields

\[
\langle \alpha_j (t + \Delta t | \alpha'_t) \alpha'_l = \sum G_{jk} \left( \frac{\partial S}{\partial \alpha_k} \right)_{\alpha'_k} \Delta t .
\]

To derive a formula for the macroscopic transport coefficients \( G_{jk} \), the left and right sides of Equation (3.31) are manipulated next.

By the definition of ensemble average in Equation (3.15), one may write

\[
\left( \frac{\partial S}{\partial \alpha_k} \right)_{\alpha'_k} = \int \frac{\partial S}{\partial \alpha_k} \alpha'_k W(\alpha') d\alpha',
\]

where \( d\alpha' \) is used as shorthand for \( d\alpha'_1 \ldots d\alpha'_n \). Since the probability of finding the system in any state characterized by \( \alpha \) is proportional to the multiplicity of that state, i.e.,

\[
W(\alpha) \propto g(\alpha),
\]

it follows using Equation (3.14) that

\[
\frac{\partial S}{\partial \alpha_k} = k_B \frac{\partial W}{W(\alpha) \partial \alpha_k}.
\]

Substituting the expression for \( \frac{\partial S}{\partial \alpha_k} \) from (3.34) into (3.32) gives

\[
\left( \frac{\partial S}{\partial \alpha_k} \right)_{\alpha'_k} = G_{jk} k_B \int \alpha'_k W(\alpha') d\alpha' .
\]

Using integration by parts in the right-hand side of Equation (3.35) leads to

\[
\int \alpha'_k \frac{\partial W}{\partial \alpha_k} d\alpha'_k = [W(\alpha') \alpha'_k]^{+\infty}_{-\infty} - \int W(\alpha') \frac{\partial \alpha'_k}{\partial \alpha_k} d\alpha'_k
\]

\[
= 0 - \int W \delta_{kl} d\alpha'_k
\]

\[
= -\delta_{lk} \int W d\alpha'_k ,
\]

where \( \delta_{lk} \) denotes the Kronecker delta function, which is defined as

\[
\delta_{lk} = \begin{cases} 
1 & \text{if } l = k \\
0 & \text{if } l \neq k ,
\end{cases}
\]
and “+∞” and “−∞” denote the upper and lower limits of integration respectively, i.e., the maximum and minimum values that the macroscopic variable α_k can take in thermodynamic equilibrium under the given conditions, where \( W(\alpha) \) is very nearly zero (see Figure 3.1).

Substituting (3.36) into the right-hand side of (3.35) and using the normalization condition Equation (3.13), the right-hand side of Equation (3.31) is transformed to

\[
\sum_k \left< G_{jk} \left[ \frac{\partial S}{\partial \alpha_k} \right] \alpha'_l \right> \Delta t = -k_B G_{jl} \Delta t .
\] (3.38)

Turning now to the left-hand side of Equation (3.31) and applying the Fundamental Theorem of Calculus gives

\[
\alpha_j(t + \Delta t | \alpha'_l) = \alpha'_j + \int_t^{t + \Delta t} \dot{\alpha}_j(s) \, ds ,
\] (3.39)

where \( \dot{\alpha}_j(s) \) denotes the rate of change of \( \alpha_j(s) \). Substituting Equation (3.39) into the left-hand side of Equation (3.31) leads to

\[
\left< \alpha_j(t + \Delta t | \alpha'_l) \alpha'_l - \alpha'_j \alpha'_l \right> = \int_t^{t + \Delta t} \left< \dot{\alpha}_j(s) \alpha'_l \right> \, ds .
\] (3.40)

The integrand may be made symmetric with respect to the two variables \( \alpha_j \) and \( \alpha_l \) using the principle of time invariance: since the system is in thermodynamic equilibrium, the average values of the various macroscopic quantities do not change with time, i.e.,

\[
\frac{d}{d\tau} \left< \dot{\alpha}_j(t + \tau) \alpha_l(t) \right> = \frac{d}{d\tau} \left< \dot{\alpha}_j(t) \alpha_l(t - \tau) \right>
\]

\[= - \left< \dot{\alpha}_j(t) \dot{\alpha}_l(t - \tau) \right>
\]

\[= - \left< \dot{\alpha}_j(t + \tau) \dot{\alpha}_l(t) \right> .
\] (3.41)

Using the Fundamental Theorem of Calculus to integrate Equation (3.41) yields

\[
\left< \dot{\alpha}_j(t + \tau) \alpha_l(t) \right> = \left< \dot{\alpha}_j(t) \alpha_l(t) \right> - \int_0^\tau \left< \dot{\alpha}_j(t + s) \dot{\alpha}_l(t) \right> \, ds .
\] (3.42)

The term on the left-hand side of Equation (3.42) may be evaluated by invoking Onsager’s reciprocal relations [55, 56] which imply that

\[
\left< \alpha_j(t + \Delta t) \alpha_l(t) \right> = \left< \alpha_j(t) \alpha_l(t + \Delta t) \right> ,
\] (3.43)

where we assume \( \Delta t \) is macroscopically small as discussed before. Differentiating Equation (3.43) with respect to \( \Delta t \) and using the principles of time invariance and Onsager’s reciprocal relations leads to

\[
\frac{d}{d\Delta t} \left< \alpha_j(t + \Delta t) \alpha_l(t) \right> = \frac{d}{d\Delta t} \left< \alpha_j(t) \alpha_l(t + \Delta t) \right> ,
\] (3.44)
which implies that
\[
\langle \dot{\alpha}_j(t + \Delta t) \alpha_l(t) \rangle = \frac{d}{d\Delta t} \langle \alpha_j(t - \Delta t) \alpha_l(t) \rangle
\]
\[
= - \langle \dot{\alpha}_j(t - \Delta t) \alpha_l(t) \rangle
\]
\[
= - \langle \dot{\alpha}_j(t) \alpha_l(t + \Delta t) \rangle
\]
\[
= - \langle \dot{\alpha}_j(t + \Delta t) \alpha_l(t) \rangle ,
\]
which finally yields
\[
\langle \dot{\alpha}_j(t + \Delta t) \alpha_l(t) \rangle = 0 .
\]

Using equations (3.45) and (3.42) in Equation (3.40) results in
\[
\langle \alpha_j(t + \Delta t) \alpha_l(t) | \alpha_j'(t) - \alpha_j'(t) \rangle = - \int_{t}^{t+\Delta t} \int_{0}^{\tau} \langle \dot{\alpha}_j(t + s) \dot{\alpha}_l(t) \rangle \, ds \, d\tau
\]
\[
= - \int_{0}^{\Delta t} \int_{0}^{\tau} \langle \dot{\alpha}_j(s) \dot{\alpha}_l(0) \rangle \, ds \, d\tau ,
\]
where the principle of time invariance has been used to derive the last equality. Using the identity
\[
\int_{0}^{a} \int_{0}^{y} f(x) \, dx \, dy = \int_{0}^{a} (a - y) f(y) \, dy ,
\]
Equation (3.46) may be rewritten as
\[
\langle \alpha_j(t + \Delta t) \alpha_j'(t) - \alpha_j'(t) \rangle = - \int_{0}^{\Delta t} (\Delta t - \tau) \langle \dot{\alpha}_j(\tau) \dot{\alpha}_l(0) \rangle \, d\tau .
\]

By virtue of Equation (3.31), the right-hand sides of equations (3.38) and (3.48) may now be equated resulting in
\[
G_{jl} = \frac{1}{k_B} \int_{0}^{\Delta t} \left( 1 - \frac{\tau}{\Delta t} \right) \langle \dot{\alpha}_j(\tau) \dot{\alpha}_l(0) \rangle \, d\tau .
\]

The term in the angle brackets in Equation (3.49) depends on the correlation time of \( \dot{\alpha}_j \) and \( \dot{\alpha}_l \). Assuming this correlation time to be much smaller than \( \Delta t \), the integrand will be nonzero only for a small time interval in which \( 1 - \tau/\Delta t \approx 1 \). Therefore, it follows that Equation (3.49) may be approximated as
\[
G_{jl} \approx \frac{1}{k_B} \int_{0}^{\infty} \langle \dot{\alpha}_j(\tau) \dot{\alpha}_l(0) \rangle \, d\tau .
\]

This is the formula derived by Kubo, Yokota and Nakajima [37] for a general transport coefficient.
3.3.2 Green-Kubo formula for thermal conductivity

In this section, we will apply the result derived in Section 3.3.1 to estimate the thermal conductivity of a closed and isolated system. To this end, consider such a system, where all the macroscopic thermodynamic parameters of the system (e.g., temperature, entropy etc.) depend only on the total energy of the system. In other words, the entropy density $s$ is taken to be a function of the internal energy density $\epsilon$ only (in other words, having been averaged over all other intrinsic or extrinsic variables it could depend on). Expanding the total entropy of the system in the form of a Taylor series in terms of fluctuations about the equilibrium value $s_0$ yields

$$
S = \int_V s(x) \, dV = \int_V \left( s_0 + \frac{\partial s}{\partial \epsilon} \delta \epsilon + \frac{\partial^2 s}{\partial \epsilon^2} (\delta \epsilon)^2 + \ldots \right) \, dV ,
$$

(3.51)

where, $x$ denotes the position vector with respect to a specified origin and $\delta \epsilon$ denotes the fluctuation of $\epsilon$ from its equilibrium value. The domain of integration is the entire volume $V$ of the system and all the partial derivatives appearing in Equation (3.51) are evaluated at equilibrium. Using the definition of temperature in Equation (3.18), the second term in the Taylor series expansion of Equation (3.51) reduces to

$$
\int_V \frac{\partial s}{\partial \epsilon} \delta \epsilon \, dV = \frac{1}{T} \int_V \delta \epsilon \, dV = 0 ,
$$

(3.52)

where the last equality is a consequence of the fact that since the system is closed and isolated, the total energy of the system at any time is constant and hence, the integral of $\delta \epsilon$ over the entire volume of the system must vanish. Thus, neglecting the higher order terms (since deviations from equilibrium are assumed to be small), Equation (3.51) reduces to

$$
S = S_0 - \frac{1}{2 T^2} \frac{\partial T}{\partial \epsilon} \int_V (\delta \epsilon)^2 \, dV ,
$$

(3.53)

where, $S_0 = \int_V s_0 dV$ represents the total entropy of the system at equilibrium.

Since the system has finite volume $V$, the fluctuations $\delta \epsilon$ may be expressed using a Fourier series as

$$
\delta \epsilon = \sum_k \epsilon_k \exp[\imath k \cdot x] ,
$$

(3.54)

where, $\epsilon_k = (1/V) \int_V \delta \epsilon \exp[-\imath k \cdot x] \, dV$ represent the Fourier coefficients. Here, $k$ is an index for the wave-number $k$. Using the orthogonality property of the set $\{\exp[\imath k \cdot x]\}$, i.e.,

$$
\int_V e^{\imath k \cdot x} e^{\imath k' \cdot x} \, dV = \begin{cases} V & \text{if } k = -k', \\ 0 & \text{otherwise}. \end{cases}
$$

(3.55)

the right-hand side of Equation (3.53) may be expressed in terms of the Fourier coefficients $\epsilon_k$ as

$$
S = S_0 - \frac{1}{2 T^2} \frac{\partial T}{\partial \epsilon} \left( \sum_k \epsilon_k \epsilon_{-k} \right) V .
$$

(3.56)
Now, the general thermodynamics of irreversible processes asserts that $\dot{\epsilon}_k$ is linearly related to the driving force $\partial S/\partial \epsilon_k$ for small deviations from equilibrium [62]. Therefore, the phenomenological equation for $\dot{\epsilon}_k$ may be written as

$$\dot{\epsilon}_k = \sum_{k'} G_{kk'} \frac{\partial S}{\partial \epsilon_{k'}}, \quad (3.57)$$

where $G_{kk'}$ is the coefficient relating the rate of change of the $k$-th Fourier coefficient of the fluctuations of energy density with the driving force $\partial S/\partial \epsilon_{k'}$. Thus it is seen that in this case, the coefficients $\alpha_k$ of Section 3.3.1, is taken to be $\epsilon_k$ and hence, $G_{kk'}$ has the units of $WK/m^6$. Using Equation (3.56) to evaluate the partial derivative in Equation (3.57), we get

$$\dot{\epsilon}_k = -\frac{V}{T^2} \frac{\partial T}{\partial \epsilon} \sum_{k'} G_{kk'} \epsilon_{-k'} . \quad (3.58)$$

Turning to the classical continuum case, assuming the system is at rest and there is no heat source within the system, the local form of macroscopic energy balance, Equation (2.21) reduces to

$$\dot{\epsilon} = -\frac{\partial}{\partial x} \cdot q. \quad (3.59)$$

Equation (3.59) may be decomposed into its Fourier components by expressing both $\dot{\epsilon}$ and $q$ using a Fourier series as

$$\dot{\epsilon} = \sum_k \dot{\epsilon}_k \exp[i\mathbf{k} \cdot \mathbf{x}] \quad (3.60)$$

and

$$q = \sum_k q_k \exp[i\mathbf{k} \cdot \mathbf{x}], \quad (3.61)$$

which implies that

$$\frac{\partial}{\partial \mathbf{x}} \cdot q = i \sum_k q_k \cdot \mathbf{k} \exp[i\mathbf{k} \cdot \mathbf{x}] . \quad (3.62)$$

Substituting $\dot{\epsilon}$ and $\frac{\partial}{\partial \mathbf{x}} \cdot q$ from (3.60) and (3.62) into Equation (3.59) and exploiting the orthogonality property of the set $\{\exp[i\mathbf{k} \cdot \mathbf{x}]\}$, allows the Fourier components of $\dot{\epsilon}$ and $q$ to be related as

$$\dot{\epsilon}_k = -i \mathbf{k} \cdot q_k . \quad (3.63)$$

By definition, the thermal conductivity tensor $\kappa$ of a system satisfies

$$q = -\kappa \frac{\partial T}{\partial \mathbf{x}}. \quad (3.64)$$

Since all thermodynamic quantities are assumed to depend only on $\epsilon$,

$$\frac{\partial T}{\partial \mathbf{x}} = \frac{\partial T}{\partial \epsilon} \frac{\partial \epsilon}{\partial \mathbf{x}}. \quad (3.65)$$
Equation (3.65) may be written in terms of Fourier coefficients by noting that the equilibrium energy density $\bar{\epsilon}$ is uniform throughout the system and so, the gradient of the local energy density is entirely due to the fluctuations in $\epsilon$, i.e.,

$$\frac{\partial \epsilon}{\partial x} = \frac{\partial (\bar{\epsilon} + \delta \epsilon)}{\partial x} = \frac{\partial (\bar{\epsilon})}{\partial x} = i \sum_k k \epsilon_k \exp[i k \cdot x],$$

(3.66)

where the Fourier representation in Equation (3.54) is used to derive the second equality.

Combining equations (3.64), (3.65) and (3.66) and comparing with the Fourier representation of $q$ from Equation (3.61) yields

$$q_k = -i \kappa k \epsilon_k \frac{\partial T}{\partial \epsilon}. \quad (3.67)$$

Substituting $q_k$ from equation (3.67) into equation (3.63) gives

$$\dot{\epsilon}_k = -(k \cdot \kappa k) \frac{\partial T}{\partial \epsilon} \epsilon_k. \quad (3.68)$$

Comparing equations (3.68) and (3.58), it may be concluded that

$$G_{kk'} = \left\{ \begin{array}{ll} 0 & (k + k' \neq 0) \\ \frac{T^2}{V} (k \cdot \kappa k) & (k + k' = 0). \end{array} \right. \quad (3.69)$$

Also, it is seen from Equation (3.57) that $G_{kk'}$ is the coefficient relating the rate of change of $\epsilon_k$ to $\epsilon_{k'}$, so the Green-Kubo formula Equation (3.50) for $G_{kk'}$ implies that

$$G_{kk'} = \frac{1}{k_B} \int_0^\infty \langle \dot{\epsilon}_k(0) \dot{\epsilon}_{k'}(\tau) \rangle \, d\tau. \quad (3.70)$$

Comparing equations (3.69) and (3.70) yields

$$\kappa \cdot (k \otimes k) = \frac{V}{k_B T^2} \int_0^\infty \langle \dot{\epsilon}_k(0) \dot{\epsilon}_{-k}(\tau) \rangle \, d\tau. \quad (3.71)$$

Using Equation (3.63), the term in the integrand of (3.71) may be expressed as

$$\dot{\epsilon}_k(0) \dot{\epsilon}_{-k}(\tau) = (q_k(0) \otimes q_{-k}(\tau)) \cdot (k \otimes k). \quad (3.72)$$

Substituting the expression for $\dot{\epsilon}_k(0) \dot{\epsilon}_{-k}(\tau)$ from Equation (3.72) into Equation (3.71) and noting that the resulting equation holds for all values of $k$ leads to the result

$$\kappa = \frac{V}{k_B T^2} \int_0^\infty \langle q_k(0) \otimes q_{-k}(\tau) \rangle \, d\tau. \quad (3.73)$$

It may be recalled that the application of the Green-Kubo formula for $G_{kk'}$ requires that $M_{kk'} \Delta t \ll 1$, where $M_{kk'} = \sum_{k'} G_{kk'} \left[ \frac{\partial^2 S}{\partial \alpha_k \partial \alpha_{k'}} \right]_0$. From Equation (3.69), it may be seen
that if \( k \to 0 \), then \( G_{kk'} \to 0 \) and hence, the aforementioned condition on \( M_{kk'} \) will be automatically satisfied for any value of \( \Delta t \). Therefore, the Green-Kubo formula for thermal conductivity may be expressed in the form

\[
\kappa = \lim_{k \to 0} \frac{V}{k_B T^2} \int_0^\infty \langle q_k(0) \otimes q_k(\tau) \rangle \, d\tau ,
\]

where \( -k \) has been replaced by \( k \) in the subscript of the second term of the integrand since in the limit \( k \to 0 \), it is also true that \( -k \to k \).

### 3.4 Irving-Kirkwood procedure

In this section, the local forms of balance of mass, linear momentum and energy are derived under the assumption that the particles obey Newton’s laws of motion and in the absence of thermal interactions with the environment, following a generalization of Irving and Kirkwood’s procedure [28]. The expressions for the stress tensor and body force are derived in terms of molecular variables from the balance of linear momentum, while the derivation of the balance of energy yields corresponding expressions for the heat flux vector and heat supply, following the procedure outline in [45].

Newton’s laws of motion relate the rates of change of the phase variables as

\[
\begin{align*}
\dot{r}_i & = \frac{p_i}{m_i} , \\
\dot{p}_i & = F_i ,
\end{align*}
\]

where \( m_i \) denotes the mass of the \( i \)-th atom and \( F_i \) is the total force on atom \( i \). We assume the existence of a potential function \( \Phi(r_1, \ldots, r_N) \) of the general form

\[
\Phi(r_1, \ldots, r_N) = \frac{1}{1!} \sum_i u_1(r_i) + \frac{1}{2!} \sum_{i,j} u_2(r_i, r_j) + \frac{1}{3!} \sum_{i,j,k} u_3(r_i, r_j, r_k) + \ldots ,
\]

where \( u_1(r_i) \), \( u_2(r_i, r_j) \) and \( u_3(r_i, r_j, r_k) \) denote the one-, two- and three-body contributions to the total potential energy. In Equation (3.76), the constant term, \( i.e. \), the zero-body contribution to the total potential energy has been set to zero without any loss of generality, as it is simply a constant additive term with no physical significance. Using Equation (3.76), the total interaction force \( F_i \) on atom \( i \) may be obtained as follows

\[
F_i = -\frac{\partial \Phi}{\partial r_i} = \frac{1}{0!} F_{i0} + \frac{1}{1!} \sum_j F_{ij} + \frac{1}{2!} \sum_{j,k} F_{ijk} + \ldots ,
\]
where
\[
F_{i0} = -\frac{\partial u_1(r_i)}{\partial r_i}, \quad (3.78)
\]
\[
F_{ij} = -\frac{\partial u_2(r_i, r_j)}{\partial r_i}, \quad (3.79)
\]
\[
F_{ijk} = -\frac{\partial u_3(r_i, r_j, r_k)}{\partial r_i}, \quad (3.80)
\]
denote the one-, two- and three-body contributions to \( F_i \) respectively.

In order to obtain the local forms of balances of mass, linear momentum and balance of energy from the principles of classical statistical mechanics, the macroscopic variables that characterize the system must be related to the atomic positions and momenta. From the observation that the probability per unit volume of finding an atom \( i \) at the macroscopic position \( x \) is given by \( \int \delta(x - r_i)f(\Gamma, t)\,d\Gamma \), where \( \delta(x) \) denotes the Dirac delta function, it seems reasonable to define the total mass density at \( x \) due to the contribution from all atoms at time \( t \) as
\[
\rho(x, t) = \int \sum_i m_i \delta(x - r_i)f(\Gamma, t)\,d\Gamma. \quad (3.81)
\]
In a similar manner, the linear momentum density at the macroscopic position \( x \) at time \( t \) is defined as
\[
\rho(x, t)v(x, t) = \int \sum_i p_i \delta(x - r_i)f(\Gamma, t)\,d\Gamma. \quad (3.82)
\]
In order to define the energy density \( e(x, t) \), a definition of the total energy \( e_i \) of an atom \( i \) is required. This is simply taken to be the sum of the kinetic and the attributed potential energy due to interparticle interactions, \( i.e., \)
\[
e_i = \frac{p_i \cdot p_i}{2m_i} + \frac{1}{2!} \sum_j u_2(r_i, r_j) + \frac{1}{3!} \sum_{j,k} u_3(r_i, r_j, r_k) + \ldots. \quad (3.83)
\]
For this choice of \( e_i \), the energy density at \( x \) at time \( t \) is defined as
\[
\rho(x, t)e(x, t) = \int \sum_i e_i \delta(x - r_i)f(\Gamma, t)\,d\Gamma. \quad (3.84)
\]
3.4.1 Balance of Mass

Taking the partial time derivative of (3.81) yields

\[
\frac{\partial \rho}{\partial t} = \int \sum_i m_i \delta(x - r_i) \frac{\partial f(\Gamma, t)}{\partial t} \, d\Gamma \\
= - \int \sum_i m_i \delta(x - r_i) L f(\Gamma, t) \, d\Gamma \\
= \int f(\Gamma, t) L \left( \sum_i m_i \delta(x - r_i) \right) \, d\Gamma \\
= \int f(\Gamma, t) \sum_i m_i \frac{\partial \delta(x - r_i)}{\partial x} \cdot \dot{r}_i \, d\Gamma \\
= - \int f(\Gamma, t) \sum_i m_i \frac{\partial \delta(x - r_i)}{\partial x} \cdot \frac{p_i}{m_i} \, d\Gamma \\
= - \frac{\partial}{\partial x} \cdot \int \sum_i p_i \delta(x - r_i) f(\Gamma, t) \, d\Gamma \\
= - \frac{\partial}{\partial x} \cdot (\rho v),
\]

on utilizing equations (3.4), (3.6), (3.8) and the chain rule. Comparison with Equation (2.11) shows that the local form of mass balance is identically satisfied by the definitions of mass and momentum density given in equations (3.81) and (3.82).

3.4.2 Balance of Momentum

Following the same procedure as for the balance of mass, the partial time derivative of Equation (3.82) yields

\[
\frac{\partial}{\partial t} (\rho v) = \int \sum_i p_i \delta(x - r_i) \frac{\partial f(\Gamma, t)}{\partial t} \, d\Gamma \\
= - \int \sum_i p_i \delta(x - r_i) L f(\Gamma, t) \, d\Gamma \\
= \int f(\Gamma, t) L \left( \sum_i p_i \delta(x - r_i) \right) \, d\Gamma.
\]
Hence,

\[
\frac{\partial}{\partial t}(\rho \mathbf{v}) = \int f(\Gamma, t) \sum_i \left( \mathbf{p}_i \delta(\mathbf{x} - \mathbf{r}_i) + \mathbf{p}_i \left( \frac{\partial \delta(\mathbf{x} - \mathbf{r}_i)}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i \right) \right) d\Gamma \\
= \int f(\Gamma, t) \sum_i \mathbf{F}_i \delta(\mathbf{x} - \mathbf{r}_i) d\Gamma - \frac{\partial}{\partial \mathbf{x}} \cdot \int f(\Gamma, t) \sum_i \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{m_i} \delta(\mathbf{x} - \mathbf{r}_i) d\Gamma \\
= \int f(\Gamma, t) \sum_i \mathbf{F}_i \delta(\mathbf{x} - \mathbf{r}_i) d\Gamma - \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{v} \otimes \mathbf{v}) \\
- \frac{\partial}{\partial \mathbf{x}} \cdot \int f(\Gamma, t) \sum_i m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \right) \otimes \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \right) \delta(\mathbf{x} - \mathbf{r}_i) d\Gamma,
\]

(3.87)

on utilizing equations (3.4), (3.6), (3.8), (3.82) and the chain rule. Therefore,

\[
\frac{\partial}{\partial t}(\rho \mathbf{v}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \rho \dot{\mathbf{v}} = \\
\int f(\Gamma, t) \sum_i \mathbf{F}_i \delta(\mathbf{x} - \mathbf{r}_i) d\Gamma - \frac{\partial}{\partial \mathbf{x}} \cdot \int f(\Gamma, t) \sum_i m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \right) \otimes \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \right) \delta(\mathbf{x} - \mathbf{r}_i) d\Gamma.
\]

(3.88)

In order to bring Equation (3.88) to the standard form of linear momentum balance in continuum mechanics, given by Equation (2.14), the first term is manipulated as follows.

\[
\sum_i \mathbf{F}_i \delta(\mathbf{x} - \mathbf{r}_i) = \sum_i \delta(\mathbf{x} - \mathbf{r}_i) \left( \frac{1}{0!} \mathbf{F}_{i0} + \frac{1}{1!} \sum_j \mathbf{F}_{ij} + \frac{1}{2!} \sum_{j,k} \mathbf{F}_{ijk} + \ldots \right) \\
= \frac{1}{1!} \sum_i \delta(\mathbf{x} - \mathbf{r}_i) \mathbf{F}_{i0} + \frac{1}{2!} \sum_{i,j} \delta(\mathbf{x} - \mathbf{r}_i) (\mathbf{F}_{ij} - \mathbf{F}_{ji}) \\
+ \frac{1}{3!} \sum_{i,j,k} \delta(\mathbf{x} - \mathbf{r}_i) (2 \mathbf{F}_{ijk} - \mathbf{F}_{jik} - \mathbf{F}_{kij}) + \ldots \\
= \frac{1}{1!} \sum_i \delta(\mathbf{x} - \mathbf{r}_i) \mathbf{F}_{i0} + \frac{1}{2!} \left( \sum_{i,j} \delta(\mathbf{x} - \mathbf{r}_i) \mathbf{F}_{ij} - \sum_{i,j} \delta(\mathbf{x} - \mathbf{r}_j) \mathbf{F}_{ij} \right) \\
+ \frac{1}{3!} \left( 2 \sum_{i,j,k} \delta(\mathbf{x} - \mathbf{r}_i) \mathbf{F}_{ijk} - \sum_{i,j,k} \delta(\mathbf{x} - \mathbf{r}_j) \mathbf{F}_{ijk} - \sum_{i,j,k} \delta(\mathbf{x} - \mathbf{r}_k) \mathbf{F}_{ijk} \right) + \ldots
\]

(3.89)
Hence,

\[
\sum_i F_i \delta(x - r_i) = \frac{1}{1!} \sum_i \delta(x - r_i) F_{i0} + \frac{1}{2!} \sum_{i,j} (\delta(x - r_i) - \delta(x - r_j)) F_{ij} \\
+ \frac{1}{3!} \sum_{i,j,k} (\delta(x - r_i) - \delta(x - r_j)) F_{ijk} + \frac{1}{3!} \sum_{i,j,k} (\delta(x - r_i) - \delta(x - r_k)) F_{ijk} + \ldots
\]

\[
= \frac{1}{1!} \sum_i \delta(x - r_i) F_{i0} + \frac{1}{2!} \sum_{i,j} \frac{\partial}{\partial x} \cdot (r_{ij} b_{ij}) F_{ij} \\
+ \frac{1}{3!} \sum_{i,j,k} \frac{\partial}{\partial x} \cdot (r_{ij} b_{ij} + r_{ik} b_{ik}) F_{ijk} + \ldots
\]

\[
= \frac{1}{1!} \sum_i \delta(x - r_i) F_{i0} \\
+ \frac{\partial}{\partial x} \cdot \left( \frac{1}{2!} \sum_{i,j} F_{ij} \otimes r_{ij} b_{ij} + \frac{1}{3!} \sum_{i,j,k} F_{ijk} \otimes (r_{ij} b_{ij} + r_{ik} b_{ik}) \right) + \ldots.
\]

(3.90)

In this derivation, the two- and three-body force contributions are assumed to be central forces, which implies that they satisfy

\[
F_{ij} + F_{ji} = 0,
\]

(3.91)

\[
F_{ijk} + F_{jik} + F_{kij} = 0,
\]

(3.92)

and the following identity is also utilized

\[
\delta(x - r_i) - \delta(x - r_j) = \frac{\partial}{\partial x} \cdot (r_{ij} b_{ij}),
\]

(3.93)

where \( r_{ij} = r_j - r_i \) and \( b_{ij} = \int_0^1 \delta(x - r_i + \lambda r_j) \, d\lambda \) is called the bond function \[70\].

Comparing equation (3.88) to equation (2.14) yields the following expressions for the macroscopic body force and stress tensor in terms of the molecular variables. Firstly, the body force is given by

\[
\rho b(x, t) = \int f(\Gamma, t) \sum_i \delta(x - r_i) F_{i0} \, d\Gamma.
\]

(3.94)

Also, to within a divergence-free function, the pointwise stress tensor \( T(x, t) \) may be looked upon as composed of two parts, \( i.e., \)

\[
T(x, t) = \int (T_K + T_V) f(\Gamma, t) \, d\Gamma,
\]

(3.95)
where
\[
T_K = - \sum_i m_i \left( \frac{p_i}{m_i} - v \right) \otimes \left( \frac{p_i}{m_i} - v \right) \delta(x - r_i) ,
\]
(3.96)
\[
T_V = \frac{1}{2!} \sum_{i,j} F_{ij} \otimes r_{ij} b_{ij} + \frac{1}{3!} \sum_{i,j,k} F_{ijk} \otimes (r_{ij} b_{ij} + r_{ik} b_{ik}) + \ldots ,
\]
(3.97)
denote the kinetic and virial contributions to \( T(x, t) \), respectively. It may be seen that \( T_K \) is always symmetric, while \( T_V \) is symmetric when the interatomic interactions are given by central forces, which is almost always the case [2]. It follows that \( T(x, t) \) is also almost always a symmetric tensor, consistent with the balance of angular momentum, given by Equation (2.16), as required.

### 3.4.3 Balance of Energy

Repeating the same exercise as for the balance of linear momentum, starting with taking the partial time derivative of Equation (3.84) yields
\[
\frac{\partial}{\partial t}(pe) = \int \sum_i e_i \delta(x - r_i) \frac{\partial f(\Gamma, t)}{\partial t} \, d\Gamma
\]
\[
= - \int \sum_i e_i \delta(x - r_i) L f(\Gamma, t) \, d\Gamma
\]
\[
= \int f(\Gamma, t) L \left( \sum_i e_i \delta(x - r_i) \right) \, d\Gamma
\]
\[
= \int f(\Gamma, t) \sum_i \dot{e}_i \delta(x - r_i) \, d\Gamma + \int f(\Gamma, t) \sum_i e_i \left( \frac{\partial \delta(x - r_i)}{\partial r_i} \cdot \dot{r}_i \right) \, d\Gamma
\]
\[
= \int f(\Gamma, t) \sum_i \dot{e}_i \delta(x - r_i) \, d\Gamma - \frac{\partial}{\partial x} \left( \int f(\Gamma, t) \sum_i e_i \delta(x - r_i) \, d\Gamma \right) .
\]
(3.98)

To cast Equation (3.98) into the standard form of energy balance in continuum mechanics, given by Equation (2.22), the first term is manipulated as follows:
\[
\sum_i \dot{e}_i \delta(x - r_i) = \sum_i \left( \frac{p_i}{m_i} \cdot \dot{p}_i + \frac{1}{2!} \sum_j \ddot{u}_2(r_i, r_j) + \frac{1}{3!} \sum_{j,k} \ddot{u}_3(r_i, r_j, r_k) + \ldots \right) \delta(x - r_i)
\]
\[
= \sum_i \left( \frac{p_i}{m_i} \cdot \mathbf{F}_{ij} \right) \delta(x - r_i) + \frac{1}{2!} \sum_{i,j} \left( \frac{2 p_i}{m_i} \cdot \mathbf{F}_{ij} + \ddot{u}_2(r_i, r_j) \right) \delta(x - r_i)
\]
\[
+ \frac{1}{3!} \sum_{i,j,k} \left( \frac{3 p_i}{m_i} \cdot \mathbf{F}_{ijk} + \ddot{u}_3(r_i, r_j, r_k) \right) \delta(x - r_i) + \ldots
\]
(3.99)
Hence,
\[
\sum_i \dot{\epsilon}_i \delta(x - r_i) = \sum_i \delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \cdot F_{i0} + \sum_i \delta(x - r_i) F_{i0} \cdot v \\
+ \frac{1}{2!} \sum_{i,j} \left( 2 \frac{p_i}{m_i} \cdot F_{ij} + \frac{\partial u_2(r_i, r_j)}{\partial r_i} \cdot \dot{r}_i + \frac{\partial u_2(r_i, r_j)}{\partial r_j} \cdot \dot{r}_j \right) \delta(x - r_i) \\
+ \frac{1}{3!} \sum_{i,j,k} \left( 3 \frac{p_i}{m_i} \cdot F_{ij} + \frac{\partial u_3(r_i, r_j, r_k)}{\partial r_i} \cdot \dot{r}_i + \frac{\partial u_3(r_i, r_j, r_k)}{\partial r_j} \cdot \dot{r}_j + \frac{\partial u_3(r_i, r_j, r_k)}{\partial r_k} \cdot \dot{r}_k \right) \delta(x - r_i) + \ldots \\
= \sum_i \delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \cdot F_{i0} + \sum_i \delta(x - r_i) F_{i0} \cdot v \\
+ \frac{1}{2!} \sum_{i,j} \left( 2 \dot{r}_i \cdot F_{ij} - F_{ij} \cdot \dot{r}_i - F_{ji} \cdot \dot{r}_j \right) \delta(x - r_i) \\
+ \frac{1}{3!} \sum_{i,j,k} \left( 3 \dot{r}_i \cdot F_{ijk} - F_{ijk} \cdot \dot{r}_i - F_{jik} \cdot \dot{r}_j - F_{kij} \cdot \dot{r}_k \right) \delta(x - r_i) + \ldots \\
= \sum_i \delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \cdot F_{i0} + \sum_i \delta(x - r_i) F_{i0} \cdot v \\
+ \frac{1}{2!} \sum_{i,j} \dot{r}_i \cdot F_{ij} (\delta(x - r_i) - \delta(x - r_j)) \\
+ \frac{1}{3!} \sum_{i,j,k} \left( \dot{r}_i \cdot F_{ijk} (2 \delta(x - r_i) - \delta(x - r_j) - \delta(x - r_k)) \right) + \ldots \\
= \sum_i \delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \cdot F_{i0} + \sum_i \delta(x - r_i) F_{i0} \cdot v \\
- \frac{\partial}{\partial x} \cdot \left( \sum_i \left( \frac{1}{2!} \sum_j r_{ij} b_{ij} \otimes F_{ij} + \frac{1}{3!} \sum_{j,k} (r_{ij} b_{ij} + r_{ik} b_{ik}) \otimes F_{ijk} \ldots \right) \frac{p_i}{m_i} \right) \\
= \sum_i \delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \cdot F_{i0} + \sum_i \delta(x - r_i) F_{i0} \cdot v \\
- \frac{\partial}{\partial x} \cdot \left( \sum_i \dot{T}_i \left( \frac{p_i}{m_i} - v \right) \right) + \frac{\partial}{\partial x} \cdot (T_i^T v) ,
\]

(3.100)

where equations (3.78), (3.79), (3.80) and (3.97) have been used and \( \hat{T}_i = \frac{1}{2!} \sum_j r_{ij} b_{ij} \otimes F_{ij} + \frac{1}{3!} \sum_{j,k} (r_{ij} b_{ij} + r_{ik} b_{ik}) \otimes F_{ijk} + \ldots \).
Similarly, the second term in Equation (3.98) is recast as

\[
\int f(\Gamma, t) \sum_i e_i \dot{r}_i \delta(x - r_i) \ d\Gamma = \int f(\Gamma, t) \sum_i e_i \left( \frac{p_i}{m_i} - v \right) \delta(x - r_i) \ d\Gamma + \rho ev
\]

\[
= \int f(\Gamma, t) \sum_i \left( \frac{m_i}{2} \left( \frac{p_i}{m_i} - v \right) \cdot \left( \frac{p_i}{m_i} - v \right) + \frac{1}{3!} \sum_j u_2(r_i, r_j) + \frac{1}{3!} \sum_{j,k} u_3(r_i, r_j, r_k) + \ldots \right) \delta(x - r_i) \ d\Gamma - T_K^T v + \rho ev
\]

\[
\delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \ d\Gamma - T_K^T v + \rho ev,
\]

using equations (3.84) and (3.96) and where \( \hat{e}_i = \frac{m_i}{2} \left( \frac{p_i}{m_i} - v \right) \cdot \left( \frac{p_i}{m_i} - v \right) + \frac{1}{3!} \sum_j u_2(r_i, r_j) + \frac{1}{3!} \sum_{j,k} u_3(r_i, r_j, r_k) + \ldots \). Substituting from equations (3.100) and (3.101) into Equation (3.98) and comparing to Equation (2.22) yields

\[
q(x, t) = \int \sum_i \left( \hat{e}_i I \delta(x - r_i) + \hat{T}_i \left( \frac{p_i}{m_i} - v \right) \right) f(\Gamma, t) \ d\Gamma,
\]

(3.102)

where \( I \) denotes the 3-by-3 identity tensor, and

\[
\rho r(x, t) = \int f(\Gamma, t) \sum_i \delta(x - r_i) \left( \frac{p_i}{m_i} - v \right) \cdot F_{i0} \ d\Gamma.
\]

(3.103)

### 3.4.4 Macroscopic continuum quantities

In order to obtain the macroscopic balance laws, an appropriate spatial averaging must be taken over a microscopically large though macroscopically small domain, determined by the resolving power of measuring instruments [28]. Thus, averaging over a spatial domain of volume \( V \) and specializing to any one system in the ensemble leads to the following expressions for the macroscopic continuum quantities. The expression for the instantaneous macroscopic density \( \tilde{\rho}(t) \) from Equation (3.81) reduces to

\[
\tilde{\rho}(t) = \frac{1}{V} \int_\Omega \rho(x, t) \ dV = \frac{1}{V} \sum_i m_i,
\]

(3.104)

where the sum is over all the atoms in the macroscopic volume \( V \). In an exactly similar manner, the expression for the instantaneous macroscopic velocity \( \tilde{v}(t) \) may be seen from
Equation (3.82) to be
\[ \tilde{v}(t) = \frac{1}{\tilde{\rho}(t)V} \int_V \rho(x,t)v(x,t) \, dV = \frac{\sum_i p_i}{\sum_i m_i}, \tag{3.105} \]
while the instantaneous macroscopic energy density \( \tilde{e}(t) \) from Equation (3.84) takes the form
\[ \tilde{e}(t) = \frac{1}{\tilde{\rho}(t)V} \int_V \rho(x,t)e(x,t) \, dV = \frac{\sum_i e_i}{\sum_i m_i}. \tag{3.106} \]

Similarly, the expressions for the instantaneous macroscopic body force \( \tilde{b}(t) \), stress tensor \( \tilde{T}(t) \), heat flux vector \( \tilde{q}(t) \) and heat supply \( \tilde{r}(t) \) may be deduced, akin to those deduced earlier (see equations (3.94), (3.95), (3.102) and (3.103)) to be as follows
\[ \tilde{b}(t) = \frac{1}{\tilde{\rho}(t)V} \int_V \rho(x,t)b(x,t) \, dV = \frac{\sum_i F^{0}_i}{\sum_i m_i}, \tag{3.107} \]
\[ \tilde{T}(t) = \frac{1}{V} \int_V T(x,t) \, dV \]
\[ = -\frac{1}{V} \sum_i m_i \left( \frac{p_i}{m_i} - v \right) \otimes \left( \frac{p_i}{m_i} - v \right) \tag{3.108} \]
\[ + \frac{1}{V} \left( \frac{1}{2!} \sum_{i,j} F_{ij} \otimes r_{ij} + \frac{1}{3!} \sum_{i,j,k} F_{ijk} \otimes (r_{ij} + r_{ik}) \cdots \right). \]
\[ \tilde{q}(t) = \frac{1}{V} \int_V q(x,t) \, dV \]
\[ = \frac{1}{V} \sum_i \left( \tilde{e}_i I + \frac{1}{2!} \sum_j r_{ij} \otimes F_{ij} + \frac{1}{3!} \sum_{j,k} (r_{ij} + r_{ik}) \otimes F_{ijk} + \cdots \right) \left( \frac{p_i}{m_i} - v \right), \tag{3.109} \]
\[ \tilde{r}(t) = \frac{1}{\tilde{\rho}(t)V} \int_V \rho(x,t)r(x,t) \, dV = \frac{\sum_i F_{i0} \cdot \left( \frac{p_i}{m_i} - v \right)}{\sum_i m_i}. \tag{3.110} \]
Chapter 4

Molecular Dynamics Simulations

Molecular Dynamics (MD) is a computer simulation method for studying the physical movements of material particles (atoms and molecules). In MD, the particles are allowed to interact for a period of time according to specified laws giving a view of the dynamical evolution of the system. In classical MD, the trajectories of atoms and molecules are determined by numerically solving Newton’s equations of motion (3.75) for a system of interacting particles, where forces between the particles are calculated using interatomic potentials or molecular mechanics force fields.

The MD method was originally developed within the field of theoretical physics in the late 1950s [3, 61], but today its range of application spans chemical physics, materials science and the modeling of biomolecules [4]. In addition, MD is also an invaluable computational tool for the bridging of real- and phonon-space analysis techniques [51].

In the statistical analysis of computational physics methods such as MD, the ergodic hypothesis is often assumed. The hypothesis simply states that over long periods of time, the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the volume of this region, *i.e.*, that all accessible microstates are equiprobable over a long period of time [62]. This hypothesis implies that the average of a phase variable over a long period of time and its average over the statistical ensemble are equal, *i.e.*, it is as good to simulate a single sample of a system over a long time as it is to make many independent samples of the same statistical ensemble and average over the response of all of them at any given time.

The MD methods that may be used to compute the thermal conductivity fall primarily in two categories: non-equilibrium MD (NEMD) and equilibrium MD methods. These two categories of MD simulations are discussed in this chapter.

4.1 Direct Method

NEMD is also known as the direct method since it is analogous to the experimental methods used for the measurement of thermal conductivity [64]. In this method, a known value of
heat flux $\mathbf{q}$ is constantly driven through the system, which is then left to evolve by Newton’s equations of motions resulting in a constant temperature gradient when the system reaches steady state. The value of thermal conductivity $\kappa$ is then obtained by using Fourier’s law (3.64). A detailed explanation and the application of the method is given in [64].

![Diagram](image)

Figure 4.1: Schematic representation of the molecular dynamics system in the direct method

Figure 4.1 shows a schematic representation of the MD system used to compute the thermal conductivity. The heat flux in the system is driven by the addition and removal of energy from the system at two different locations. The energy is added or removed by appropriate scaling of the velocities of atoms in the system. Although only kinetic energy, and not potential energy, is added to or subtracted from the system, we expect that within a typical vibrational period ($<1$ ps), equilibration between kinetic and potential energy will occur.

As shown in Figure 4.1, energy $\Delta\epsilon$ is added by rescaling the velocities of atoms at every time step in the slab of thickness $w$ centered at $z = -\frac{L_z}{4}$ and removed from the slab of same thickness $w$ centered at $z = \frac{L_z}{4}$. Applying energy balance to the slab of width $w$ around $z = \frac{L_z}{4}$ when the system reaches a steady state, it can be seen that

$$\frac{\Delta\epsilon}{wA\Delta t} = \frac{q - (-q)}{w},$$

where $\Delta t$ denotes the time step used in the MD simulation, $A$ is the cross-sectional area of the MD system and $q$ is the heat flux along the axis of the slab in the $z$-direction. Thus, the heat flux driven through the system is given by

$$q = \frac{\Delta\epsilon}{2A\Delta t}.$$
chosen to mimic the presence of an infinite bulk surrounding the model system in order to obtain the bulk estimates. In the case of PBCs, all atoms that exit the system from one side enter it again from the opposite side with the same momentum and forces \(^4\). To determine the temperature as a function of \(z\), the system is divided into small blocks along the \(z\)-axis. The temperature at \(z\) is then defined in terms of the kinetic energies of the atoms in the block centered at \(z\) using the equipartition theorem \(^62\) as
\[
T(z) = \left\langle \sum_{i \in \text{block}} \frac{m_i \mathbf{v}_i \cdot \mathbf{v}_i}{3N_z k_B} \right\rangle = \left\langle T_b(z) \right\rangle, \tag{4.3}
\]
where \(k_B\) denotes the Boltzmann constant and the summation is on the atoms in the block, \(\left\langle \cdot \right\rangle\) denotes the ensemble average corresponding to the steady state phase space distribution, and \(N_z\) is the number of atoms in the block. Furthermore, assuming the system to be ergodic, the ensemble average in Equation (4.3) is evaluated as a time average of the kinetic energy once the steady state is reached, \(i.e.,\)
\[
\left\langle T_b(z) \right\rangle = \lim_{Y \to \infty} \frac{1}{Y} \int_{t_0}^{t_0 + Y} \tilde{T}_{bz}(t) \, dt, \tag{4.4}
\]
where \(T_b(z) = \tilde{T}_{bz}(t)\). Using Equation (4.4), a typical temperature profile for the case of silicon modeled by the Stillinger-Weber potential at 500 K as is shown in Figure 4.2. The temperature profile in the center region of the slab is fitted to a straight line to estimate the temperature gradient, as illustrated in Figure 4.3. The temperature gradient thus obtained and the heat flux given by Equation (4.2) can be used along with Fourier’s law to obtain an estimate of the thermal conductivity \(\kappa_z\) along the axis of the induced flux. Thus, one of the drawbacks of this method is that it can only provide the normal component of thermal conductivity along the direction of the induced flux. Another difficulty arises from the fact that to produce an appreciable heat flux, the temperature gradients required in the method are very high, of the order of \(10^9\) K/m as may be seen from Figure 4.3, where the validity of Fourier’s law for thermal conductivity becomes questionable. The large temperature gradients introduce the additional complication of making it difficult to identify precisely the temperature for which the computed value of thermal conductivity is obtained.

In this method, it is observed that the computed value of thermal conductivity, which is a material constant, depends on the values chosen for the rescaling energy \(\Delta \epsilon\) and the total length of the system \(L_z\), as shown in Figures 4.4 and 4.5 respectively. The dependence of \(\kappa_z\) on \(\Delta \epsilon\) shows that there is a range of values of \(\Delta \epsilon\) in which the former is independent of the latter. Identifying the appropriate range for the rescaling energy adds substantially to the total computational cost of the direct method. The size dependence of the computed value of \(\kappa_z\) makes it necessary to perform several simulations of increasing length and then extrapolate to the infinite-size limit. The thermal conductivity at infinite length \(\kappa_{z\infty}\) may then be obtained from linear extrapolation, as illustrated in Figure 4.5, using
\[
\frac{1}{\kappa_z(L_z)} = \frac{1}{\kappa_{z\infty}} + \frac{\alpha}{L_z}, \tag{4.5}
\]
where $\kappa_z(L_z)$ is the thermal conductivity corresponding to a length $L_z$ and $\alpha$ is a length-independent coefficient, which corresponds to the slope of the best fit straight line. In order to obtain meaningful values of $\kappa_z$ that may be compared to experimental results, the length of the system in the direction along which $\kappa_z$ is estimated must be much larger than the mean-free path of the phonons, in order to avoid scattering of phonons with the heat source ($+\Delta \epsilon$) and sink ($-\Delta \epsilon$) [64]. For Si at 500 K, the phonon mean free path is of the order of 100 nm [64] and hence, the system needs of the order of $3 \times 10^5$ atoms to avoid size effects, making the simulation computationally costly in spite of imposing PBCs.

### 4.1.1 HNEMD method

The homogeneous non-equilibrium molecular dynamics (HNEMD) method, proposed by Evans [15], and extended in [47], [48], [46] and [45], employs a mechanical analogue to the thermal transport process and the linear response theory to calculate the transport coefficients. This method is synthetic, in the sense that a fictitious force field is used to mimic the effect of a thermal gradient, thereby reducing the thermal transport problem to a mechanical problem. Using the linear response theory [16], the long-time ensemble average of the heat
Figure 4.3: Linear fit to the temperature profile in Figure 4.2 for a $4 \times 4 \times 288$ unit cells Si system at an average temperature of 500 K, from [64].

Figure 4.4: Effect of changing the rescaling energy for a $4 \times 4 \times 96$ unit cells Si system at an average temperature of 500 K, from [64].
Figure 4.5: System size dependence of \(1/\kappa_z\) on \(1/L_z\) for Si and diamond, from [64].

flux vector for the resulting non-equilibrium system can be shown to be proportional to the external force field (when the latter is sufficiently small), with the constant of proportionality being the Green-Kubo (GK) formula for the heat transport coefficient tensor.

In contrast to the non-equilibrium methods outlined above, equilibrium methods employ fluctuations from the average value of certain thermodynamic quantities, e.g., heat flux at thermodynamic equilibrium to obtain estimates of non-equilibrium transport properties such as thermal conductivity. As a result, equilibrium methods do not suffer from the drawback of having very large thermal gradients as seen in NEMD. One of the most widely used equilibrium methods is the Green-Kubo method, which is described next.

### 4.2 Green-Kubo Method

In the Green-Kubo (GK) method, the MD system of fixed volume \(V\) is allowed to reach equilibrium at a certain temperature \(T\) by imposing PBCs in all three directions. As the system is at equilibrium, the average heat flux \(\bar{q}\) in the system is zero, nevertheless the instantaneous value of \(\tilde{q}(t)\) fluctuates about the mean value. Using \(\tilde{q}(t)\), the heat flux autocorrelation function may be computed as a function of correlation time \(\tau\) by

\[
C_q(\tau) = \langle \tilde{q}(\tau) \otimes \tilde{q}(0) \rangle = \lim_{Y \to \infty} \frac{1}{Y} \int_0^Y \tilde{q}(\tau + s) \otimes \tilde{q}(s) \, ds ,
\]

where the second equality is obtained by invoking the ergodic hypothesis. The autocorrelation function is used in the GK formula (3.74) to obtain the thermal conductivity \(\kappa\).
The main advantage of the GK method is the rapid convergence of $\kappa$ with system size. In the case of Si at 1000 K, convergence is attained for a system size of the order of only 2000 atoms \[^{[64]}\]. Also, unlike the direct method, the GK method yields all the components of $\kappa$ in a single simulation. However, the most important limitation of the GK method is the convergence of the thermal conductivity with respect to simulation time for a given system size. The relative error $\Delta \kappa$ in the computed value of any component $\kappa$ of $\kappa$ is bounded as

$$\frac{\Delta \kappa}{\kappa} \leq 2 \sqrt{\frac{\tau_c}{\tau_M}},$$

(4.7)

where $\tau_c$ denotes the maximum correlation time and $\tau_M$ denotes the total simulation time \[^{[29]}\]. The maximum correlation time must be chosen large enough so that the heat flux autocorrelation function $C_q$ becomes negligibly small. From the relation (4.7), it may be observed that the relative error depends on the ratio of $\tau_c$ to $\tau_M$. The maximum correlation time $\tau_c$ required for a given MD simulation decreases with the temperature of the simulation. This implies that as the temperature at which the GK method is applied to compute $\kappa$ decreases, it is necessary to simultaneously increase the total simulation time in order to keep the relative error in $\kappa$ the same. This clearly increases the computational expense of the method.

Since the application of the GK method requires an $NVT$ ensemble, the temperature of the system must be held constant during the course of the MD simulation. This is accomplished by using the Nosé-Hoover (NH) thermostat, which is described in the next section.

### 4.2.1 Nosé-Hoover Thermostat

The NH thermostat is a deterministic algorithm for MD simulations based on a canonical ensemble. It was originally developed by Nosé \[^{[53]}\] and was improved further by Hoover \[^{[26]}\]. The NH thermostat has been commonly used in MD as one of the most accurate and efficient methods for performing $NVT$ simulations.

The $N$-body dynamics evolving according to Newton’s laws given by equations (3.75) correspond to a system whose total energy is conserved, \textit{i.e.}, a microcanonical ensemble. However, in problems associated with the canonical ensemble, such as the GK method, it is essential that the equations of motion used to model the system preserve the canonical phase space distribution function given by Equation (3.20), which differs from the microcanonical distribution function. The total energy $E_T$ appearing in Equation (3.20) is simply the sum of the kinetic and potential energies of the $N$-body system, \textit{i.e.},

$$E_T = \sum_i \frac{p_i \cdot p_i}{2m_i} + \Phi(r_1, \ldots, r_N),$$

(4.8)

where $\Phi(r_1, \ldots, r_N)$ is the interatomic potential energy given by Equation (3.76).
The NH equations of motion corresponding to the canonical ensemble are given by

\[ \dot{r}_i = \frac{p_i}{m_i}, \]
\[ \dot{p}_i = F_i - \zeta p_i, \]
\[ \dot{\zeta} = \frac{1}{Q} \left( \sum_{i=1}^{N} \frac{p_i \cdot p_i}{m_i} - 3Nk_B T \right), \]

(4.9)

where \( \zeta \) is the thermodynamic friction coefficient and \( Q \) is an arbitrary parameter chosen to yield the canonical phase space distribution [26]. The equations follow the integral feedback mechanism to generate the canonical distribution. From Equations (4.9), it may be observed that the NH equations effectively extend the \( N \)-body system by introducing an additional degree of freedom \( \zeta \) that represents the heat bath. It may be shown that the NH equations give rise to the canonical phase space distribution with temperature \( T \) as argued below.

Applying the Liouville equation (3.4) to the extended phase space distribution function \( f(\Gamma, \zeta, t) \) gives

\[ \frac{\partial f(\Gamma, \zeta, t)}{\partial t} = - \left[ \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \frac{\partial}{\partial \Gamma} \cdot \dot{\zeta} + \frac{\partial}{\partial \zeta} \right] f(\Gamma, \zeta, t), \]

(4.10)

which can be rewritten in terms of the total time derivative as

\[ \frac{df(\Gamma, \zeta, t)}{dt} = - \left[ \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \frac{\partial}{\partial \zeta} \right] f(\Gamma, \zeta, t). \]

(4.11)

Using the NH equations of motion (4.9), the operator on the right hand side of Equation (4.11) can be simplified to

\[ \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} + \frac{\partial}{\partial \zeta} = \sum_{i=1}^{N} \frac{\partial}{\partial \Gamma} \cdot \dot{r}_i + \sum_{i=1}^{N} \frac{\partial}{\partial p_i} \cdot \dot{p}_i + \frac{\partial}{\partial \zeta} \]
\[ = -3N\zeta, \]

(4.12)

thereby reducing equation (4.11) to

\[ \frac{\partial f(\Gamma, \zeta, t)}{\partial t} = 3N f(\Gamma, \zeta, t). \]

(4.13)

Defining the total energy of the extended NH thermostatted system by \( E_\Gamma + \frac{1}{2} Q \zeta^2 \), the time derivative of the total energy of the extended system is given by

\[ \frac{d}{dt} \left( E_\Gamma + \frac{1}{2} Q \zeta^2 \right) = \sum_{i=1}^{N} \left( \frac{p_i \cdot \dot{p}_i}{m_i} + \frac{\partial \Phi}{\partial r_i} \cdot \dot{r}_i \right) + Q \dot{\zeta} \]
\[ = -3Nk_B T, \]

(4.14)
where the NH equations of motion (4.9) and the definition of \( F_i \) (3.77) have been employed. Comparing equations (4.13) and (4.14) yields the following differential equation for the phase distribution function of the extended system

\[
\frac{1}{f(\Gamma, \zeta, t)} \frac{df(\Gamma, \zeta, t)}{dt} = -\beta \frac{d}{dt} \left( E_{\Gamma} + \frac{1}{2} Q \zeta^2 \right), \tag{4.15}
\]

where the definition of \( \beta = \frac{1}{k_B T} \) has been utilized. The solution to the differential equation (4.15) is given by

\[
f(\Gamma, \zeta, t) = \frac{\exp[-\beta(E_{\Gamma} + \frac{1}{2} Q \zeta^2)]}{\int \exp[-\beta(E_{\Gamma} + \frac{1}{2} Q \zeta^2)] d\Gamma d\zeta}, \tag{4.16}
\]

which coincides with the canonical phase space distribution for the extended system. Thus, the NH equations of motion (4.9) accurately reproduces the canonical phase distribution as desired.
Chapter 5

Truncated Taylor Series Interatomic Potential

5.1 Background on interatomic potentials

In any crystal at finite temperature, the atoms undergo small-amplitude vibrations about their equilibrium lattice positions. This allows the potential energy $U$ to be expanded in a Taylor series about its equilibrium value $U_0$ in terms of the displacements of the atoms from their equilibrium positions, in the form

$$U = U_0 + \sum_{i,\alpha} \Pi_{i}^{\alpha} u_{i}^{\alpha} + \frac{1}{2!} \sum_{i,j;\alpha,\beta} \Phi_{ij}^{\alpha\beta} u_{i}^{\alpha} u_{j}^{\beta} + \frac{1}{3!} \sum_{i,j,k;\alpha,\beta,\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_{i}^{\alpha} u_{j}^{\beta} u_{k}^{\gamma} + \ldots . \quad (5.1)$$

Here, $u$ denotes the atomic displacement, $i, j, k$ label the different atoms and $\alpha, \beta, \gamma$ denote the Cartesian directions. In addition, the force constants (FCs) $\Pi_{i}^{\alpha}$, $\Phi_{ij}^{\alpha\beta}$, $\Psi_{ijk}^{\alpha\beta\gamma}$ denote respectively the first, second and third partial derivatives of $U$ with respect to the displacements evaluated in the equilibrium configuration. Without loss of generality, the constant term $U_0$ may be set to 0 by adjusting the reference level of the potential energy. Furthermore, $\Pi_{i}^{\alpha} = 0$ since the equilibrium configuration corresponds to a minimum of the potential energy, Equation (5.1) may be reduced to

$$U = \frac{1}{2!} \sum_{i,j;\alpha,\beta} \Phi_{ij}^{\alpha\beta} u_{i}^{\alpha} u_{j}^{\beta} + \frac{1}{3!} \sum_{i,j,k;\alpha,\beta,\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_{i}^{\alpha} u_{j}^{\beta} u_{k}^{\gamma} + \ldots . \quad (5.2)$$

The components $F_{i}^{\alpha}$ of the total force acting on atom $i$ may be obtained from Equation (5.2) as

$$F_{i}^{\alpha} = -\frac{\partial U}{\partial u_{i}^{\alpha}} = -\sum_{j;\beta} \Phi_{ij}^{\alpha\beta} u_{j}^{\beta} - \frac{1}{2!} \sum_{j,k;\beta,\gamma} \Psi_{ijk}^{\alpha\beta\gamma} u_{j}^{\beta} u_{k}^{\gamma} + \ldots . \quad (5.3)$$

For simple systems (e.g., an LJ crystal) the FCs may be calculated analytically. However, for many realistic systems, where highly accurate interatomic potentials are not known, ab
**CHAPTER 5. TRUNCATED TAYLOR SERIES POTENTIAL**

*initio* methods based on DFT may be employed to compute the FCs in Equation (5.3). In this manner, one may, in principle, construct interatomic potentials of *ab initio* accuracy up to any given order.

### 5.2 Range of validity

Classical MD simulations are meaningful when the temperature is high enough to render the classical Maxwell-Boltzmann distribution of atomic velocities a good approximation to the corresponding quantum statistical distribution. This is the case when the temperature is at least in the range of the Debye temperature of the material [5, Chapter 23], [67].

For the purpose of accurately estimating many thermophysical properties of materials, including transport properties such as thermal conductivity, it is sufficient to include the effect of anharmonicity of the potential and truncate the Taylor series in Equation (5.2) at the third order [13]. This truncation is predicated on the assumption that the displacement $u$ of the atoms about their equilibrium positions is “small” in the sense that

$$\max_{i,j}(||u_i||, ||u_j||) \ll ||R_j - R_i|| \equiv ||R_{ij}||,$$

(5.4)

for all pairs of atoms $(i, j)$ with equilibrium positions $R_i$ and $R_j$. This truncation also serves the purpose of limiting the computational expense of the resulting MD simulations. For solids, condition (5.4) is typically satisfied unless the temperature is close to the melting point.

The precise meaning of the inequality condition (5.4) may be articulated as follows: the temperature of the solid must remain low enough so that no atom displaces so far away from its equilibrium position that the resultant force on it is directed away from that position. Figure 5.1 illustrates, for the simple case of a single-variable potential, the existence of a critical displacement beyond which an initially restoring force on an atom becomes disturbing in the case of an anharmonic potential. It can be seen from the figure that while this issue does not arise for purely harmonic potentials, all higher-order approximations suffer from this phenomenon. In general, the addition of a fourth-order term has minimal effect on the critical displacement because: (a) the FCs are typically much smaller in magnitude than their third-order counterparts and (b) the correction provided by the fourth-order is only appreciable at displacements much larger than the critical one, where anyway inequality (5.4) is violated. Therefore, if there exists a critical displacement in the third-order truncation, then it will persist even in the presence of higher-order terms. Figure 5.1 further suggests this point by showing the effect of a fourth-order term to the Taylor series expansion of a general potential energy for a crystal lattice.

In summary, the proposed method is most applicable in a range of temperatures bounded from below by the Debye temperature of the material and from above by the temperature for which condition (5.4) no longer holds for any given atom in the crystal. The latter temperature depends on the width of the interatomic potential function well at the global
minimum corresponding to the equilibrium configuration and, hence, must be determined by trial-and-error for each material.

Figure 5.1: Pure harmonic and an anharmonic potential

5.3 Truncated statistical mechanics expressions

The expressions derived in Section 3.4.4 are now specialized to the case of the truncated Taylor series based interatomic potential. It may be observed that in the expressions for macroscopic continuum stress tensor and heat flux given by equations (3.108) and (3.109), it suffices to consider terms up to third order only. Hence, for the case of the truncated Taylor series based interatomic potential

\[
\tilde{T}(t) = -\frac{1}{V} \sum_i m_i \left( \frac{p_i}{m_i} - \mathbf{v} \right) \otimes \left( \frac{p_i}{m_i} - \mathbf{v} \right) \\
+ \frac{1}{V} \left( \frac{1}{2!} \sum_{i,j} \mathbf{F}_{ij} \otimes \mathbf{r}_{ij} + \frac{1}{3!} \sum_{i,j,k} \mathbf{F}_{ijk} \otimes (\mathbf{r}_{ij} + \mathbf{r}_{ik}) \right)
\]  

(5.5)

and

\[
\tilde{q}(t) = \frac{1}{V} \sum_i \left( \dot{\mathbf{r}}_i \delta(\mathbf{x} - \mathbf{r}_i) + \frac{1}{2!} \sum_j \mathbf{r}_{ij} \otimes \mathbf{F}_{ij} + \frac{1}{3!} \sum_{j,k} (\mathbf{r}_{ij} + \mathbf{r}_{ik}) \otimes \mathbf{F}_{ijk} \right) \left( \frac{p_i}{m_i} - \mathbf{v} \right) .
\]

(5.6)
5.4 Implementation as an interatomic potential for MD

The proposed technique is implemented for a crystal lattice in LAMMPS [60], a widely used general-purpose classical molecular dynamics code which runs on a multitude of serial and parallel computer architectures. The primary utility of any interatomic potential is in the computation of the total potential energy of the system and the total force on every atom at each time-step. For the truncated Taylor series potential, these quantities are computed according to Equations (5.2) and (5.3), respectively. The FCs appearing in these equations are obtained simply by accessing a lookup table of FCs, which may be generated analytically, or by *ab initio* methods (e.g. based on DFT simulations). This lookup table must provide the values of the FCs between an atom and each of its neighbors.

Unlike a conventional LJ potential, which depends exclusively on the current distance between atoms, the truncated Taylor series potential of Equation (5.2) depends on the displacement of atoms from their equilibrium lattice positions. Since most MD codes do not store the equilibrium positions, these need to be extracted from information contained in the current atomic positions. This is possible as long as assumption (5.4) holds true, since, in that case, the equilibrium position of an atom is the nearest lattice site. The resulting map of atoms to lattice sites is represented by a table, termed here “TableID”.

This approach is analogous to the total Lagrangian finite element formulation in continuum mechanics [6]. The algorithm implemented in the interatomic potential consists of the following key steps:

1. At each time-step, the equilibrium lattice position of every atom, which is the nearest lattice site to its current position, is identified.

2. For each atom, a list of all of its neighbors within a given cutoff distance is compiled by a low-cost binary search, such as binning. This is a standard feature available in all MD codes.

3. For each neighbor of a given atom, its TableID is determined with respect to the given atom using the lattice equilibrium positions of the two atoms.

4. TableID is used to identify the appropriate FCs from the lookup table for computing the force on a given atom due to each of its neighbors.

5. The resultant force on each atom and the total energy of the crystal lattice are computed according to Equations (5.2) and (5.3).

The algorithm to determine the equilibrium lattice position of every atom is detailed in Appendix A.
5.5 Application to Lennard-Jones potential

The proposed technique of expanding potentials in a Taylor series is illustrated by application to a solid described by the Lennard-Jones interatomic potential. The simple analytical form of the LJ potential allows the exact computation of the expressions for the FCs in the Taylor series expansion up to a given order, thereby serving as a very good test model for this technique.

By way of background, recall that in an LJ solid the potential energy between two atoms $i$ and $j$, separated instantaneously by distance $r_{ij}$, is defined as

$$U_{ij}(r_{ij}) = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}},$$

(5.7)

where $A$ and $B$ are constants. These constants are related to the standard LJ parameters as $A = 4\epsilon\sigma^{12}$ and $B = 4\epsilon\sigma^{6}$, where $\epsilon$ and $\sigma$ are the standard LJ parameters. Consequently, the total potential energy of an LJ crystal is given by the sum of all pairwise interaction energies between the atoms in the crystal according to

$$U = \frac{1}{2} \sum_i \sum_{j \neq i} U_{ij},$$

(5.8)

where the factor $\frac{1}{2}$ compensates for the double-counting of the pairwise interactions.

To expand $U$ in a Taylor series as in Equation (5.1), it is first necessary to express $U_{ij}$ in terms of the displacements $u_i$ and $u_j$. This can be achieved by noting that

$$r_{ij}^2 = ||R_{ij} + u_{ij}||^2 = R_{ij}^2 \left(1 + 2 \frac{R_{ij} \cdot u_{ij}}{R_{ij}} + \frac{u_{ij}^2}{R_{ij}^2}\right) = R_{ij}^2 \left(1 + 2 \frac{u_{ij}}{R_{ij}} \cos \theta_{ij} + \frac{u_{ij}^2}{R_{ij}^2}\right),$$

(5.9)

where $u_{ij} = u_j - u_i$ and $\theta_{ij}$ is the angle between $R_{ij}$ and $u_{ij}$, as shown in Figure 5.2. Substituting the expression for $r_{ij}$ in Equation (5.7) allows for expanding $U_{ij}$ in a Taylor series around $u_{ij} = 0$. This series may be truncated at third order, leading to
\[ U_{ij} = \frac{A}{R_{ij}^{12}} \left( 1 + 2 \frac{u_{ij}}{R_{ij}} \cos \theta_{ij} + \frac{u_{ij}^2}{R_{ij}^2} \right)^6 - \frac{B}{R_{ij}^6} \left( 1 + 2 \frac{u_{ij}}{R_{ij}} \cos \theta_{ij} + \frac{u_{ij}^2}{R_{ij}^2} \right)^3 \]

(5.10)

Thus, the pairwise potential term \( U_{ij} \) has been approximated in terms of ascending powers.
of \( u_{ij} \) in the form

\[
U_{ij} = U_{0,ij} + U_{1,ij} + U_{2,ij} + U_{3,ij} .
\] (5.11)

According to Equation (5.2), the constant term \( U_{0,ij} \) and the linear term \( U_{1,ij} \) do not contribute to the total crystal potential energy, hence they are ignored. The quadratic term \( U_{2,ij} \) may be compactly expressed as

\[
U_{2,ij} = \left[ \frac{A}{R_{ij}^{12}}(-6 + 84 \cos^2 \theta_{ij}) - \frac{B}{R_{ij}^{6}}(-3 + 24 \cos^2 \theta_{ij}) \right] \frac{u_{ij}^2}{R_{ij}^2}.
\] (5.12)

where

\[
C_{ij} = - \frac{6A}{R_{ij}^{14}} + \frac{3B}{R_{ij}^{8}},
\] (5.13)

and

\[
D_{ij} = \frac{84A}{R_{ij}^{16}} - \frac{24B}{R_{ij}^{10}}.
\] (5.14)

Likewise, the cubic terms \( U_{3,ij} \) may be written as

\[
U_{3,ij} = \left[ \frac{A}{R_{ij}^{12}}(84 \cos \theta_{ij} - 448 \cos^3 \theta_{ij}) - \frac{B}{R_{ij}^{6}}(24 \cos \theta_{ij} - 80 \cos^3 \theta_{ij}) \right] \frac{u_{ij}^3}{R_{ij}^3}.
\] (5.15)

where

\[
E_{ij} = - \frac{448A}{R_{ij}^{18}} + \frac{80B}{R_{ij}^{12}}.
\] (5.16)

Substituting the expression for \( U_{ij} \) from Equation (5.11) to Equation (5.8) leads to a representation of the total crystal energy in terms of ascending powers of \( u \) in the form

\[
U = \frac{1}{2} \sum_i \sum_{j \neq i} U_{ij} = \frac{1}{2} \sum_i \sum_{j \neq i} (U_{2,ij} + U_{3,ij}) = U_2 + U_3 ,
\] (5.17)

where \( U_2 = \frac{1}{2} \sum_{ij} U_{2,ij} \) and \( U_3 = \frac{1}{2} \sum_{ij} U_{3,ij} \) contain the quadratic and cubic terms in \( u_{ij} \), respectively. For notational simplicity, the self-interaction terms (corresponding to \( i = j \)) in Equation (5.17) are set to zero, thus allowing the elimination of the extra condition \( j \neq i \) henceforth.
The quadratic term $U_2$ in (5.17) may be expressed in Cartesian component form as

$$U_2 = \frac{1}{2} \sum_{ij} \left[ C_{ij} u_{ij}^2 + D_{ij} (u_{ij} \cdot R_{ij})^2 \right]$$

$$= \frac{1}{2} \sum_{ij} C_{ij} \left[ \sum_{\alpha} (u_{ij}^\alpha - u_{ij}^\alpha)^2 \right] + \frac{1}{2} \sum_{ij} D_{ij} \left[ \sum_{\alpha} R_{ij}^\alpha \left(u_{ij}^\alpha - u_{ij}^\alpha\right)\right]^2$$

$$= \frac{1}{2} \sum_{ij} C_{ij} \left[ \sum_{\alpha} (u_{ij}^\alpha)^2 - 2u_{ij}^\alpha u_{ij}^\alpha + (u_{ij}^\alpha)^2 \right] + \frac{1}{2} \sum_{ij} D_{ij} \left[ \sum_{\alpha\beta} R_{ij}^\alpha R_{ij}^\beta \left(u_{ij}^\alpha u_{ij}^\beta - 2u_{ij}^\alpha u_{ij}^\beta + u_{ij}^\alpha u_{ij}^\beta\right)\right]. (5.18)$$

Since the order of $i$ and $j$ in the sums may be interchanged without altering the values of $C_{ij}$ and $D_{ij}$, it follows that

$$\sum_{ij,\alpha} C_{ij} (u_{ij}^\alpha)^2 = \sum_{ij,\alpha} C_{ji} (u_{ij}^\alpha)^2 = \sum_{ij,\alpha} C_{ij} (u_{ij}^\alpha)^2, \quad \sum_{ij,\alpha\beta} D_{ij} u_{ij}^\alpha u_{ij}^\beta = \sum_{ij,\alpha\beta} D_{ji} u_{ij}^\alpha u_{ij}^\beta = \sum_{ij,\alpha\beta} D_{ij} u_{ij}^\alpha u_{ij}^\beta. \quad (5.19)$$

Therefore, it follows from Equation (5.18) that

$$U_2 = \sum_{ij} C_{ij} \left[ \sum_{\alpha} (u_{ij}^\alpha)^2 - u_{ij}^\alpha u_{ij}^\alpha \right] + \sum_{ij} D_{ij} \left[ \sum_{\alpha\beta} R_{ij}^\alpha R_{ij}^\beta (u_{ij}^\alpha u_{ij}^\beta - u_{ij}^\alpha u_{ij}^\beta)\right]. \quad (5.21)$$

Comparing the preceding expression to the quadratic term in Equation (5.2) leads to the representation of the harmonic FC $\Phi_{ij}^{\alpha\beta}$ for an LJ crystal in the form

$$\Phi_{ij}^{\alpha\beta} = 2 \left[ \sum_k \left( C_{ik} \delta^{\alpha\beta} + D_{ik} R_{ik}^\alpha R_{ik}^\beta \right) \delta_{ij} - C_{ij} \delta^{\alpha\beta} - D_{ij} R_{ij}^\alpha R_{ij}^\beta \right], \quad (5.22)$$

where $\delta^{\alpha\beta}$ and $\delta_{ij}$ both denote the Kronecker delta symbol. It can be readily concluded that the expression for the harmonic FC in (5.22) satisfies the Acoustic Sum Rule (ASR), which is a statement of translation-invariance of the potential energy of the crystal [59]. Furthermore, it is also easy to verify that the harmonic FCs automatically satisfy the linearized version of rotational invariance, which is sufficient, insofar as the linear theory of elasticity gives physically reasonable results [38].
A similar procedure may be carried out for the cubic term \( U_3 \) in Equation (5.17), leading to

\[
U_3 = \frac{1}{2} \sum_{ij} \left[ D_{ij} u_{ij}^2 (\mathbf{u}_{ij} \cdot \mathbf{R}_{ij}) + E_{ij} (\mathbf{u}_{ij} \cdot \mathbf{R}_{ij})^3 \right]
\]

\[
= \frac{1}{2} \sum_{ij} D_{ij} \left[ \sum_{\alpha\beta} R_{ij}^\beta \left( (u_i^\alpha - u_i^\beta)^2 (u_j^\beta - u_j^\gamma) \right) \right] + \frac{1}{2} \sum_{ij} E_{ij} \left[ \sum_{\alpha} R_{ij}^\alpha (u_i^\alpha - u_i^\beta) \right]^3
\]

\[
= \frac{1}{2} \sum_{ij} D_{ij} \left[ \sum_{\alpha\beta} R_{ij}^\beta \left( (u_i^\alpha - u_i^\beta)^2 - 2u_i^\alpha u_j^\alpha + (u_j^\alpha)^2 \right) (u_j^\beta - u_j^\gamma) \right]
\]

\[
+ \frac{1}{2} \sum_{ij} E_{ij} \left[ \sum_{\alpha\beta\gamma} R_{ij}^\alpha R_{ij}^\beta R_{ij}^\gamma (u_i^\alpha - u_i^\beta) (u_j^\beta - u_j^\gamma) (u_j^\gamma - u_j^\delta) \right].
\]

Simplifying the preceding expression using the symmetries of \( D_{ij} \) and \( E_{ij} \) results in

\[
U_3 = \sum_{ij} D_{ij} \left[ \sum_{\alpha\beta} R_{ij}^\beta (-(u_i^\alpha)^2 u_i^\beta + (u_i^\alpha)^2 u_j^\beta + 2u_i^\alpha u_j^\beta u_j^\gamma) \right]
\]

\[
+ \sum_{ij} E_{ij} \left[ \sum_{\alpha\beta\gamma} R_{ij}^\alpha R_{ij}^\beta R_{ij}^\gamma (u_i^\alpha u_i^\beta u_i^\gamma + 3u_i^\alpha u_i^\beta u_j^\gamma) \right].
\]

Comparing (5.24) to the cubic term in Equation (5.2) results in an expression for the anharmonic FC \( \Psi_{ijk}^{\alpha\beta\gamma} \) for a LJ crystal in the form

\[
\Psi_{ijk}^{\alpha\beta\gamma} = -2 \left[ \delta_{ij} \left( D_{ik}(\delta^{\alpha\beta} R_{ik}^\gamma + \delta^{\beta\gamma} R_{ik}^\alpha + \delta^{\alpha\gamma} R_{ik}^\beta) + 3E_{ik} R_{ik}^\alpha R_{ik}^\beta R_{ik}^\gamma \right) \right]
\]

\[
+ \delta_{jk} \left( D_{ji}(\delta^{\beta\gamma} R_{ji}^\alpha + \delta^{\alpha\gamma} R_{ji}^\beta + \delta^{\alpha\beta} R_{ji}^\gamma) + 3E_{ji} R_{ji}^\beta R_{ji}^\gamma R_{ji}^\alpha \right)
\]

\[
+ \delta_{ki} \left( D_{kj}(\delta^{\gamma\alpha} R_{kj}^\beta + \delta^{\alpha\beta} R_{kj}^\gamma + \delta^{\beta\gamma} R_{kj}^\alpha) + 3E_{kj} R_{kj}^\gamma R_{kj}^\alpha R_{kj}^\beta \right) \right].
\]

It may be again verified that this expression for the cubic FC satisfies the ASR as generalized to higher-order FCs [14].

From Equations (5.22) and (5.25), it can be seen that the FCs between an atom and its neighbors depend on the components of the relative equilibrium positions. To compute the FCs for a solid LJ crystal, a supercell needs to be considered with all atoms at their equilibrium positions so that the FCs between the central atom and all other atoms in the supercell are determined according to Equations (5.22) and (5.25). This supercell should be large enough to take into account all the significant interatomic interactions between any two atoms of the LJ crystal. This condition is satisfied if the length of the supercell along each Cartesian direction is at least twice the cutoff distance for interatomic interactions. For LJ solids, it is sufficient to take the cutoff distance to be greater than \( 2.5 (\frac{4}{\pi})^{1/6} \) [50].
CHAPTER 5. TRUNCATED TAYLOR SERIES POTENTIAL

5.5.1 Specific heat capacity of LJ Ar

To assess the numerical accuracy of the proposed technique, solid Ar is chosen as a test material. Ar (atomic mass = 39.948 gm/mol) is well-described with the LJ potential with the LJ parameters $\epsilon = 0.0104 \text{ eV}$ and $\sigma = 3.40 \text{ Å}[5]$. As argued in Section 5.2, the temperature range within which condition (5.4) remains valid depends on the width of the potential well at equilibrium. For solid Ar modeled using LJ with the potential function truncated at third order it was observed that the MD simulations become unstable at temperatures above 10 K. The instability is due to the thermal motion of atoms past a critical distance from their equilibrium positions at some point of time during the simulation.

The crystal structure of solid Ar is a face-centered cubic (FCC) lattice with one basis atom per lattice site. The lattice constant for FCC Ar is determined by performing NPT simulations at a constant pressure of 1 bar and at temperatures ranging from 2 K to 10 K, as discussed in [49]. All of the MD simulations were performed with a time-step of 4 fs, which is found to be sufficient to resolve all the lattice vibrations, and cutoff of 3.1$\sigma$ [49].

The specific heat of solid Ar may be estimated from MD simulations using a formula which relates it to the fluctuations of the total energy of the system under thermodynamic equilibrium in a canonical (i.e., NVT) ensemble according to Equation (3.25).

The FCs used in the computation of energy are taken from a lookup table based on Equations (5.22) and (5.25). This table is constructed outside the MD code and contains all harmonic and anharmonic FCs generated between the central atom and all other atoms in a supercell whose size is at least twice the typical LJ cutoff distance.

A Nosé-Hoover thermostat [53, 27] is employed in the NVT system to ensure that when the temperature of the system reaches beyond a certain window around the target temperature it is restored back to the target temperature by the application of appropriate fictitious forces. One of the critical thermostat parameters in an NVT simulation is the rate $\zeta$ at which the system is restored to the target temperature, as this determines the magnitude of the fluctuations in the total energy of the system at equilibrium. Since the computed value of the heat capacity and other thermophysical properties determined from equilibrium fluctuations (e.g. thermal conductivity using the Green-Kubo formula [16]) depend on the size of these fluctuations, the thermostat parameter $\zeta$ should be set to an appropriate value while performing MD simulations in an NVT ensemble. To determine the appropriate value of $\zeta$ for the NVT ensemble of LJ Ar, a pure harmonic crystal of solid Ar is considered, for which the heat capacity $C_v$ is derived by the Dulong-Petit law as

$$C_v^h = 3Nk_B,$$  \hspace{1cm} (5.26)

where $N$ denotes the total number of atoms in the system [58]. The pure harmonic crystal is simply realized by using the truncated Taylor series interatomic potential, where the cubic FCs are set to zero. MD simulations are then performed in the NVT ensemble for different values of $\zeta$ and different temperatures and the resulting values of $C_v$ are compared to the
Dulong-Petit value. The value of $\zeta$ that yields the closest match to the theoretical estimate is selected for all subsequent MD simulations in NVT ensembles.

Each MD simulation was run for 7,000,000 time steps and each of the results obtained are averaged over an ensemble of 10 independent runs, while the errors reported are taken to be the standard deviation in the result over the 10 runs. Figure 5.3 shows a plot of the specific heat capacity obtained from MD simulations on pure harmonic Ar in an NVT ensemble. The specific heat capacity (including error bars indicating its standard deviation) is computed using Equation (3.25) for temperatures ranging from 2 to 10 K and for different values of $\zeta$ [36]. A comparison of the computed values of $C_v$ to the one obtained from the Dulong-Petit law shows that beyond a certain value of $\zeta$, $C_v$ is fairly close to the expected value. Of the three values of $\zeta$ that yield the smallest deviation of the average value of $C_v$ from (5.26), the optimal ($\zeta = 8$ ps) is selected to be the one that minimizes the standard deviation.

![Graph showing variation of specific heat capacity with thermostat parameter $\zeta$ in NVT ensemble](image)

Figure 5.3: Variation of specific heat capacity with thermostat parameter $\zeta$ in NVT ensemble

Using the optimal value of $\zeta$, MD simulations are performed for a solid crystal of Ar using the standard LJ potential and the one obtained from the Taylor series based potential truncated at third order for different unit cell sizes of 4, 5 and 6 unit cells in each direction to confirm size convergence. It was found that by the difference between the values of $C_v$ computed for these different unit cell sizes converged to within 10% by 6 unit cells. This showed that size convergence had been attained by the largest domain size. Figure 5.4 shows the values of the $C_v$ for 6 unit cells [36]. The figure demonstrates that the maximum deviation between the computed values of $C_v$ for the two potentials across all temperatures from 2 to 10 K is less than 10%.
The difference in the specific heat capacities of the pure harmonic crystal and the LJ crystal is due to the anharmonicity in the latter [5, Chapter 22]. Thus, the excellent agreement between the values of \( C_v \) for the standard LJ potential and its truncated counterpart shows that, within the given temperature range, the cubic terms are sufficient to capture the anharmonicity of the LJ Ar crystal.

### 5.5.2 Thermal conductivity of LJ Ar

To test the efficiency of this method in capturing anharmonicity, a transport property such as the bulk thermal conductivity \( \kappa \) may be employed, as its value depends strongly on the anharmonic terms in the potential energy. The thermal conductivity of a material is computed from an NVT ensemble using the Green-Kubo formula Equation \( (3.74) \). In practice, the upper limit of the integral in Equation \( (3.74) \) is replaced by a finite time \( (\tau_C) \), which must be taken to be long enough for the correlations between the heat flux to decay to nearly zero in that time interval [4].

The relative error in the computed value of a transport property computed by the Green-Kubo method is given by Equation \( (4.7) \). Hence, having chosen a suitable correlation time \( \tau_C \), the total simulation time \( \tau_M \) for a desired accuracy \( a = \frac{\Delta \kappa}{\kappa} \) is given by

\[
\tau_M \geq \frac{4\tau_C}{a^2}. \tag{5.27}
\]
Using this result, it is possible to estimate the minimum simulation time required to obtain the thermal conductivity to any desired accuracy.

To confirm the effectiveness of this method in capturing the anharmonicity of LJ Ar, the thermal conductivity for solid Ar obtained for the truncated potential is compared to that obtained for the standard LJ potential. To this end, first the correlation time to be used as the upper limit of the integral in Equation (3.74) is determined by noting the value at which the heat flux autocorrelation function \( C_q(\tau) \) from Equation (4.6) decays to zero. The correlation time \( \tau_C \) is not a constant but depends on the temperature of the simulation and must be determined by trial and error. For instance, it was found that at 2 K, \( \tau_C \) must be taken to be 1024 ps, whereas at 6 K, it is sufficient to take \( \tau_C \) to be 256 ps. Then, the total number of time-steps required to be performed for the relative error in the computed value of thermal conductivity to be about 10% is determined according to (5.27). This procedure is repeated for the same unit cell sizes in order to ensure convergence with respect to domain size to within 10%. Figure 5.5 shows the decay of the heat flux autocorrelation function \( C_q(\tau) \) with correlation time \( \tau_C \) for the truncated Taylor series-based potential at 6 K for 6 unit cells, while Figure 5.6 shows the integral of the same autocorrelation function with respect to the correlation time [36]. The difference between the two conductivity estimates in 5.6 is due to the Taylor series truncation relative to the standard LJ potential. Figure 5.7 demonstrates that the maximum deviation between the computed values of \( \kappa \) for the two potentials across all temperatures from 2 to 10 K is less than 20% [36].
Figure 5.6: Integral of the heat flux autocorrelation function for the standard potential and the truncated Taylor series-based potential for a $6 \times 6 \times 6$ unit cells with respect to correlation time at 6 K

Figure 5.7: Comparison of thermal conductivity for standard LJ and the truncated Taylor series based potentials for solid Ar at different temperatures for $6 \times 6 \times 6$ unit cells
Chapter 6

First-principles Calculations

6.1 Motivation

To test the utility of the method of truncated Taylor series potential for practical materials, it is applied to the estimation thermophysical properties in germanium (Ge), which is a technologically important material \cite{63}. Currently, MD simulations for Ge are performed using the Stillinger-Weber (SW) potential \cite{66} with the parameters given in \cite{11}. The SW potential is semi-empirical and is known to be unable to accurately reproduce all the thermophysical properties of the material, as mentioned in Chapter 1. This limitation is inherent to the functional form of the potential, which is postulated on the basis of certain physical hypotheses, that cannot be rigorously justified. Specifically, one of the main assumptions is that the total potential energy of interaction is the sum of two-body and three-body terms, both of which decay to zero smoothly at a specified cutoff distance and where the latter takes its minimum value for the tetrahedral bond angle (109.5°) found in diamond crystal lattice of Ge \cite{66}. One of the goals of the thesis is to try and remove the need of such hypotheses in the case of crystal lattices, by replacing the expression for the potential energy with a general form which is mathematically applicable to all smooth potential functions, \textit{viz.}, a truncated Taylor series based potential, with the coefficients computed from first-principles \textit{ab initio} methods such as DFT. To this end, it is necessary to first compute the FCs in the truncated Taylor series expansion of the potential energy using DFT, which is described in the following Section.

6.2 Background on quantum mechanics

In standard quantum mechanics, any system is assumed to be completely characterized by a complex-valued wavefunction \( \Psi(r, t) \) of unit norm at any instant of time \( t \). In other words, all the physical properties of a system that can be experimentally measured are assumed to be functions of the wavefunction \( \Psi \). The wavefunction characterizing a system is assumed
to evolve according to Schrödinger’s time-dependent equation
\[ i\hbar \frac{\partial}{\partial t} \Psi(r, t) = \hat{H} \Psi(r, t) , \]
where \( \hbar \) denotes the reduced Planck’s constant \( (\hbar = \frac{\hbar}{2\pi} \), where \( \hbar \) is the Planck’s constant) and \( \hat{H} \) denotes the Hamiltonian operator of the system. In the non-relativistic domain, for a system of interacting particles in an external potential field \( U(r, t) \), the Hamiltonian operator takes the form
\[ \hat{H} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + U(r, t) , \]
where \( \nabla_i^2 \) denotes the Laplacian operator in three dimensions with respect to the \( i \)-th particle coordinates, \( m_i \) denotes the mass of \( i \)-th particle and the sum runs over all the particles in the system.

In the usual case where the Hamiltonian operator does not explicitly depend on time, the standard technique to solve Schrödinger’s equation involves separating the spatial and temporal parts of the wavefunction as
\[ \Psi(r, t) = \psi(r) \tau(t) . \]

Substituting for \( \Psi(r, t) \) from Equation (6.3) into Equation (6.1) leads to a separation of variables, as follows:
\[ \frac{1}{\psi(r)} \hat{H} \psi(r) = \frac{i\hbar}{\tau(t)} \frac{d}{dt} \tau(t) . \]

Since each side of Equation (6.4) depends on only one of the two variables \( r \) and \( t \), each side must be equal to the same constant, say \( E \). Thus, we obtain
\[ \hat{H} \psi(r) = E \psi(r) , \quad \frac{d\tau(t)}{dt} = -\frac{iE\tau(t)}{\hbar} . \]

Equation (6.5) is known as the \textit{time-independent Schrödinger’s equation}. Since \( \hat{H} \) is the Hamiltonian operator of the system, the constant \( E \) in Equation (6.5) has the physical interpretation of the total energy of the system. Equation (6.5) is a simple first-order differential equation for \( \tau(t) \), which may be easily solved to obtain
\[ \tau(t) = \exp \left[ -\frac{iEt}{\hbar} \right] . \]

Thus, the total wavefunction \( \Psi(r, t) \) may be cast, using equations (6.6) and (6.4), in the form
\[ \Psi(r, t) = \psi(r) \exp \left[ -\frac{iEt}{\hbar} \right] , \]
where \( \psi(r) \) satisfies Equation (6.5). Thus, the solution of Schrödinger’s equation (6.1) reduces to solving the time-independent Schrödinger’s equation (6.5). It may be noted
that Equation (6.5) represents an eigenvalue problem for the Hamiltonian operator $\hat{H}$. It is well known that an eigenvalue problem has multiple solutions, in general. The solution of Equation (6.5)$_1$ corresponding to the lowest value of the energy $E$ is called the ground state of the system.

6.2.1 Born-Oppenheimer approximation

All materials are composed of a multitude of atoms, which in turn, consist of nuclei and electrons orbiting the nuclei. For a system composed of many atoms, the complete solution to Equation (6.5) is practically intractable. To simplify the process of obtaining a solution to Equation (6.5)$_1$, the Born-Oppenheimer approximation, also known as the adiabatic approximation, is often invoked [5, Chapter 22]. The adiabatic approximation is based on the fact that the typical velocity of electrons is orders of magnitude higher than the velocity of the nuclei (typically of the order of $10^3$ [5, Chapter 2]). Since the nuclei move so slowly compared to the electrons, it is assumed that at any instant of time, the electrons are in their ground state for the configuration of the nuclei at that instant of time. The foregoing assumption allows the wavefunction of the full system to be decomposed into two wavefunctions - one describing the electrons and one describing the nuclei. Furthermore, the electrons may be assumed to be in motion in a positive field arising from the stationary nuclei at any instant of time. The electronic wavefunction can then, in principle, be obtained by solving Equation (6.5)$_1$ with the Hamiltonian operator given by Equation (6.2), in which, the potential function $U(r, t)$ corresponds to the instantaneous configuration of the nuclei. Thus, the Born-Oppenheimer approximation reduces the problem of computing the total wavefunction of the full system consisting of multiple nuclei and electrons, to simply computing the wavefunction for all the electrons for a given static configuration of the nuclei.

6.2.2 Pauli’s exclusion principle

In quantum mechanics, all the electrons in a material body are assumed to be exactly identical to each other, in the sense that it is experimentally impossible to distinguish one electron from another. The wavefunction $\psi$ characterizing a system of identical charged particles possesses an important mathematical property which is discussed below. As mentioned earlier, in quantum mechanics, the state of a system is assumed to be completely determined by a wavefunction of unit norm. In other words, two wavefunctions that differ by a phase factor, i.e., a complex number of unit norm, represent the same system. Now, it is obvious that in a system of identical particles, interchanging any number of particles among each other does not change the state of the system. Mathematically, the operation of interchanging particles in the system may be represented by the action of a permutation operator $\hat{P}$ acting on the wavefunction describing the system. Since the permutation operator does not change the state of the system, the wavefunction resulting from the application of this operator to the original wavefunction of the system may differ from the latter by at most a phase factor,
CHAPTER 6. FIRST-PRINCIPLES CALCULATIONS

\[ i.e., \quad \hat{P} \psi = k_P \psi , \] (6.8)

where \( k_P \) is a complex number of unit norm. Now, by observing that a successive operation of the same permutation operator to the system brings it back to its original state, it may be concluded that

\[ \hat{P} (\hat{P} \psi) = k_P^2 \psi = \psi , \] (6.9)

from which it follows that

\[ k_P^2 = 1 , \] (6.10)

and hence,

\[ k_P = \pm 1 . \] (6.11)

Therefore, the result of the permutation operator on the wavefunction characterizing a system of identical particles is given, with the aid of equations (6.8) and (6.11), by

\[ \hat{P} \psi = \pm \psi . \] (6.12)

In other words, the wavefunction of a system of identical particles must be either symmetric or antisymmetric under a single permutation of the particles. Thus, we obtain one of the fundamental results of quantum mechanics, \( \textit{viz.} \), that there are only two kinds of particles in nature – those for which \( k_P = 1 \) and those for which \( k_P = -1 \). The former are called \textit{bosons}, while the latter are called \textit{fermions}. A basic result of quantum mechanics is that the \textit{spin quantum number} of any particle, which corresponds to its \textit{spin angular momentum} (a quantum-mechanical property) along a given axis, can only take integer multiple values of \( \frac{1}{2} \) \footnote{12}. Furthermore, according to relativistic quantum theory, the spin quantum number of bosons must be an integer, while fermions have half-integer value of spin. It is experimentally found that electrons can only have spin values of either \( +\frac{1}{2} \) or \( -\frac{1}{2} \) and hence, fall under the category of fermions. Now, suppose in a system of identical fermions, two fermions, say \( i \) and \( j \), occupy the same position \( r \) at some instant of time. Then, the wavefunction describing the system takes the form

\[ \psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots) = \psi(\mathbf{r}_1, \ldots, \mathbf{r}, \ldots, \mathbf{r}, \ldots) , \] (6.13)

whereas, on interchanging the particles \( i \) and \( j \), it takes the form

\[ \psi(\mathbf{r}_1, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots) = \psi(\mathbf{r}_1, \ldots, \mathbf{r}, \ldots, \mathbf{r}, \ldots) . \] (6.14)

But since the wavefunction characterizes a system of identical fermions, it must be antisymmetric under an interchange of the particles \( i \) and \( j \), \( i.e., \)

\[ \psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots) = -\psi(\mathbf{r}_1, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots) , \] (6.15)

From equations (6.13), (6.14) and (6.15), it may be concluded that

\[ \psi(\mathbf{r}_1, \ldots, \mathbf{r}, \ldots, \mathbf{r}, \ldots) = 0 , \] (6.16)
which shows that in a system of identical fermions, if two fermions have the same position in space, the wavefunction vanishes and hence, cannot correspond to any physically plausible state of the system, as its norm is not unity. In other words, two electrons cannot occupy the same spatial position in a system at any instant of time. This important result is known as Pauli’s exclusion principle and is an important criterion that must be satisfied by any solution of Equation (6.5) for a many-electrons system.

Most of the approaches to solving Schrödinger’s time-independent wave equation for a many-electrons system involve reducing it through various approximations to a set of one-electron-like equations of the form

\[ \hat{H}(r)\psi = E\psi, \] (6.17)

where the Hamiltonian operator is given by

\[ \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(r), \] (6.18)

where \( m \) denotes the electron mass. The total wavefunction for the many-electrons system is then constructed from the solutions of Equation (6.17), called as one-electron wavefunctions, by taking linear combinations of their products for different energy values \( E \). The total wavefunction for the many-electrons system constructed this way must satisfy Pauli’s exclusion principle, viz., it must be antisymmetric under the interchange of any two one-electron wavefunctions.

### 6.2.3 Bloch’s theorem

In the case of a crystal lattice, the one-electron wavefunctions satisfy a fundamental property given by Bloch’s theorem, as shown below. Since a crystal lattice is periodic in space, the potential energy \( U(r) \) in the Hamiltonian of Equation (6.17) is a periodic function, i.e.,

\[ U(r + R) = U(r), \] (6.19)

where \( R \) denotes a Bravais vector associated with the crystal lattice and is expressed in terms of the basis vectors of the crystal lattice \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \) as

\[ R = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \] (6.20)

for some integers \( n_1, n_2 \) and \( n_3 \), as shown in figure 6.1. In this case, a fundamental theorem of solid state physics, called as Bloch’s theorem, states that with every solution of Equation (6.17), a wave-vector \( \mathbf{k} \) may be associated such that

\[ \psi(r + R) = \exp[i\mathbf{k} \cdot \mathbf{R}]\psi(r), \] (6.21)

for all Bravais vectors \( R \). The proof of Bloch’s theorem follows very simply from one of the fundamental theorems of quantum mechanics, as shown below.
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Figure 6.1: Schematic representation of a Bravais lattice in 3 dimensions

Corresponding to each Bravais vector $\mathbf{R}$, a translation operator $\hat{T}_\mathbf{R}$ is defined such that its action on any function $f(\mathbf{r})$ is given by

$$\hat{T}_\mathbf{R} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}). \quad (6.22)$$

It is easy to see that for any two Bravais vectors $\mathbf{R}$ and $\mathbf{R}'$, the corresponding translation operators $\hat{T}_\mathbf{R}$ and $\hat{T}_{\mathbf{R}'}$ satisfy

$$\hat{T}_\mathbf{R} \hat{T}_{\mathbf{R}'} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R} + \mathbf{R}') = \hat{T}_{\mathbf{R}'} \hat{T}_\mathbf{R} f(\mathbf{r}) = \hat{T}_{\mathbf{R} + \mathbf{R}'} f(\mathbf{r}), \quad (6.23)$$

which, being an identity for any function $f(\mathbf{r})$, implies that

$$\hat{T}_{\mathbf{R}'} \hat{T}_\mathbf{R} = \hat{T}_\mathbf{R} \hat{T}_{\mathbf{R}'} = \hat{T}_{\mathbf{R} + \mathbf{R}'} \quad (6.24)$$

Now, it follows from Equation (6.18) that if the potential energy $U(\mathbf{r})$ is periodic, then the total Hamiltonian $\hat{H}(\mathbf{r})$ is also a periodic function with the same period as $U$. The periodicity of the Hamiltonian $\hat{H}$ implies that for any function $f(\mathbf{r})$

$$\hat{T}_\mathbf{R}(\hat{H}(\mathbf{r})f(\mathbf{r})) = \hat{H}(\mathbf{r} + \mathbf{R})f(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})f(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})(\hat{T}_\mathbf{R}f(\mathbf{r})), \quad (6.25)$$
where the definition of \( \hat{T}_R \) from Equation (6.22) has been used for the first and last equalities, while the middle equality follows from the periodicity of the Hamiltonian operator \( \hat{H}(\mathbf{r}) \). Since Equation (6.25) holds for any function \( f(\mathbf{r}) \), the following operator identity is established

\[
\hat{T}_R \hat{H} = \hat{H} \hat{T}_R ,
\]

i.e., the translation and Hamiltonian operators are commutative. From a fundamental theorem in quantum mechanics, it follows that the eigenstates of the Hamiltonian, given by solutions of Equation (6.17), are also eigenstates of the translation operator [12]. Hence, any solution \( \psi \) of Equation (6.17) also satisfies

\[
\hat{T}_R \psi = c_R \psi ,
\]

where \( c_R \) denotes an eigenvalue of the translation operator \( \hat{T}_R \). Equation (6.24) may be used to obtain an important property of the eigenvalue \( c_R \) according to which

\[
\hat{T}_R (\hat{T}_{R'} \psi) = \hat{T}_R c_{R'} \psi = c_R c_{R'} \psi = \hat{T}_{R+R'} \psi = c_{R+R'} \psi ,
\]

from where, it follows that

\[
c_R c_{R'} = c_{R+R'} .
\]

Now, the eigenvalues for the basis vectors of the crystal lattice \( \mathbf{a}_i \) for \( i = 1, 2, 3 \) may be expressed as

\[
c_{a_i} = \exp[2\pi i x_i]
\]

for some \( x_1, x_2 \) and \( x_3 \). From Equations (6.20) and (6.29), it follows that

\[
c_R = c_{a_1} c_{a_2} c_{a_3} ,
\]

which, on using Equation (6.30), may be re-expressed as

\[
c_R = \exp[i \mathbf{k} \cdot \mathbf{R}] .
\]

Here, \( \mathbf{k} \) is defined as

\[
\mathbf{k} = x_1 \mathbf{b}_1 + x_2 \mathbf{b}_2 + x_3 \mathbf{b}_3 ,
\]

where \( \mathbf{b}_1, \mathbf{b}_2 \) and \( \mathbf{b}_3 \) denote the reciprocal lattice vectors satisfying \( \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi i \delta_{ij} \), where \( \delta_{ij} \) denotes the Kronecker delta. Finally, from Equations (6.22), (6.27) and (6.32), it follows that

\[
\hat{T}_R \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}) = c_R \psi(\mathbf{r}) = \exp[i \mathbf{k} \cdot \mathbf{R}] \psi(\mathbf{r}) ,
\]

which completes the proof of Bloch’s theorem.

It may be noted that Bloch’s theorem may also be expressed in the alternative form

\[
\psi(\mathbf{r}) = \exp[i \mathbf{k} \cdot \mathbf{R}] u_k(\mathbf{r}) ,
\]
where \( u_k \) is a periodic function with the same period as the potential energy, \( i.e., \)
\[
 u_k(r + R) = u_k(r), \tag{6.36}
\]
for all Bravais lattice vectors \( R \). An important consequence of Bloch’s theorem is that it
suffices to obtain the one-electron wavefunction within the Brillouin zone of a lattice to com-
pletely determine it over the entire crystal lattice. This affords an enormous simplification
for the computation of the electronic wavefunctions by the approximate methods described
next.

6.3 First-principles methods

In spite of the simplification provided by the Born-Oppenheimer approximation, it is pro-
hibitively expensive to obtain a complete analytical solution to Equation (6.5)\( _1 \) for a many-
atom system, as is the case for most materials, and further approximations are required.
There are many approaches for determining the ground state of many-electrons systems by
solving the Schrödinger wave equation based on various approximations. All these methods,
which regard a many-atom system as a many-body system composed of nuclei and electrons,
and treat everything on the basis of first principles of quantum mechanics without introduc-
ing any empirical parameters, are known as \textit{ab initio} methods or \textit{first-principles} methods.
The various \textit{ab initio} approaches may be classified into three broad categories \cite{54}, based on:

1. the Hartree-Fock (HF) approximation,
2. the Density Functional Theory (DFT), and
3. Monte Carlo methods.

These approaches are discussed in the next subsections.

6.3.1 Hartree-Fock approximation

One of the simplest methods for calculating the electronic states of many-electrons systems
is a one-electron approximation, called the Hartree-Fock (HF) approximation.

The expectation value of the Hamiltonian operator \( \hat{H} \) for a \( N \)-electron system is defined
by
\[
 \langle \psi | \hat{H} | \psi \rangle = \sum_{s_1} \ldots \sum_{s_N} \int_{r_1} \ldots \int_{r_N} \psi^*(1, \ldots, N) \hat{H} \psi(1, \ldots, N) \ dr_1 \ldots dr_N, \tag{6.37}
\]
where the superposed "*" denotes complex conjugate, \( s_i \) denotes the spin of the \( i \)-th electron
and \( \psi(1, \ldots, N) \) denotes the total wavefunction of the system \cite{12}. According to standard
quantum mechanics, the ground state of the system may be determined by a variational
principle, \( \textit{viz.} \), that the expectation value of the Hamiltonian operator takes its minimum value \( E_0 \) in the ground state of the system \([22]\). In the HF approximation, the electrons are supposed to move independently of each other \([23, 24, 18]\). In this case, if \( \hat{H}(i) \) denotes the Hamiltonian operator for the \( i \)-th electron, the total Hamiltonian of the \( N \)-electron system may be decomposed into a sum of commutative operators as

\[
\hat{H} = \hat{H}(1) + \ldots + \hat{H}(N), \quad (6.38)
\]

and the total wavefunction of the \( N \)-electron system may, in general, be written as a sum of the product of \( N \) one-electron wavefunctions. By Pauli’s exclusion principle, the total wavefunction of the \( N \)-electron system must be antisymmetric under the interchange of any two electrons. One such antisymmetric solution for the total wavefunction of the \( N \)-electron wavefunction in terms of \( N \) one-electron wavefunctions is given by the \textit{Slater determinant} of the one-electron wavefunctions \([65]\)

\[
\psi(1, \ldots, N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{ccc}
\psi_1(1) & \ldots & \psi_N(1) \\
\vdots & \ldots & \vdots \\
\psi_1(N) & \ldots & \psi_N(N)
\end{array} \right|, \quad (6.39)
\]

where \( \psi_\lambda(i) \) denotes the \( \lambda \)-th solution of the one-electron Equation (6.17) for the one-electron wavefunction for electron \( i \). It may be noted that the one-electron wavefunctions form an orthonormal set \([54]\), \( i.e., \)

\[
\langle \psi_\lambda(i) | \psi_\nu(i) \rangle = \sum_{s_i} \int \psi_\lambda^*(i) \psi_\nu(i) \, dr_i = \delta_{\lambda\nu}. \quad (6.40)
\]

A one-electron Hamiltonian \( \hat{H}_1 \) for the \( i \)-th electron is defined in a similar way as Equation (6.18), \( \textit{viz.} \),

\[
\hat{H}_1(i) = -\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i), \quad (6.41)
\]

in which, the potential energy \( U(r_i) \) is given by

\[
U(r_i) = -\sum_J \frac{Z_J}{4\pi\epsilon_0 |r_i - R_J|}, \quad (6.42)
\]

where \( Z_J \) denotes the nuclear charge on the \( J \)-th nucleus, \( \epsilon_0 \) denotes the electrical permittivity of vacuum and \( R_J \) denotes the position of the \( J \)-th nucleus. Then, the Hamiltonian for the \( N \)-electron system may be decomposed as

\[
\hat{H} = \sum_i \hat{H}_1(i) + \frac{1}{2} \sum_{i,j} U_C(i, j). \quad (6.43)
\]
Here, $U_C(i, j)$ denotes the electron-electron Coulomb interaction between electrons $i$ and $j$ given by

$$U_C(i, j) = \frac{1}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}.$$ \hfill (6.44)

Substituting for the Hamiltonian operator $\hat{H}$ from Equation (6.43) and for the $N$-electron wavefunction from the Slater determinant Equation (6.39) in Equation (6.37), and using the orthonormality property Equation (6.40), the expectation value of the Hamiltonian operator takes the form

$$\langle \psi | \hat{H} \psi \rangle = \sum_{\lambda=1}^{N} \langle \psi_\lambda | \hat{H}_1 \psi_\lambda \rangle + \frac{1}{2} \sum_{\lambda, \nu} \langle \psi_\lambda \psi_\nu | \hat{U}_C \psi_\lambda \psi_\nu \rangle - \frac{1}{2} \sum_{\lambda, \nu} \langle \psi_\lambda \psi_\nu | \hat{U}_C \psi_\lambda \psi_\nu \rangle - \sum_{\lambda} \epsilon_\lambda \langle \delta \psi_\lambda | \psi_\lambda \rangle.$$ \hfill (6.45)

To minimize the expectation value of the Hamiltonian operator $\hat{H}$ under the normalization condition given by Equation (6.40), a Lagrange multiplier $\epsilon_\lambda$ may be used with the normalization condition to yield the variational problem

$$\sum_{\lambda=1}^{N} \langle \delta \psi_\lambda | \hat{H}_1 \psi_\lambda \rangle + \frac{1}{2} \sum_{\lambda, \nu} \langle \delta \psi_\lambda \psi_\nu | \hat{U}_C \psi_\lambda \psi_\nu \rangle - \frac{1}{2} \sum_{\lambda, \nu} \langle \delta \psi_\lambda \psi_\nu | \hat{U}_C \psi_\lambda \psi_\nu \rangle - \sum_{\lambda} \epsilon_\lambda \langle \delta \psi_\lambda | \psi_\lambda \rangle = 0.$$ \hfill (6.46)

Since Equation (6.46) must hold for arbitrary variation of the one-electron wavefunction $\psi_\lambda$, it must satisfy

$$\hat{H}_1 \psi_\lambda(i) + \sum_{\nu=1}^{N} \sum_{s_j} \int \psi^*_\nu(j) U_C(i, j) \psi_\nu(j) \, d\mathbf{r}_j \psi_\lambda(i) - \sum_{\nu=1}^{N} \sum_{s_j} \int \psi^*_\nu(j) U_C(i, j) \psi_\lambda(j) \, d\mathbf{r}_j \psi_\nu(i) = \epsilon_\lambda \psi_\lambda(i),$$ \hfill (6.47)

where $s_j$ denotes the spin of the $j$-th electron, known as the Hartree-Fock equation. Thus, the Hartree-Fock equation is a rigorous one-electron approximation for a system of interacting electrons, which takes into account the antisymmetry of the wavefunction describing the many-electrons system, also known as the exchange energy. However, it neglects the electron-electron correlation energy, which is a quantum mechanical effect, due to its assumption of independent electrons.

The HF equation is only tractable for a system comprising a small number of atoms, but becomes too complex for crystals. Using the HF approximation in metals results in a zero density of states at the Fermi level (i.e., the highest partially filled energy level), in contradiction with experiments. Further, the HF approximation overestimates the energy gap between the occupied and unoccupied states of a semiconductor, as it is unable to properly describe electron screening [54].
6.3.2 Density Functional Theory

In contrast to the HF approximation, Density Functional Theory (DFT) explicitly takes into account all the electrons in a many-electrons system. To simplify the problem of solving Schrödinger’s equation for a many-electron system in DFT, the mutual interactions between the electrons is replaced by an effective potential acting on the electrons as described below.

In 1964, Hohenberg and Kohn [25] made a breakthrough in calculating properties of materials by proving that all properties of a non-degenerate ground state of a system of interacting electrons in an external potential $U(\mathbf{r})$ are completely determined by its electron density $n(\mathbf{r})$, and furthermore, the ground state energy given by

$$E_0 = \int U(\mathbf{r})n(\mathbf{r}) \, d\mathbf{r} + F[n(\mathbf{r})], \quad (6.48)$$

where $F[n(\mathbf{r})]$ denotes a universal functional of the electron density $n(\mathbf{r})$ that is independent of the external potential $U(\mathbf{r})$, is minimized by the true electron density. The latter result gives the Hohenberg-Kohn theorems the character of a variational principle. Even though the Hohenberg-Kohn results do not provide a direct solution to the many-electrons problem, they cast the calculation of electronic energy into the slightly more manageable form of the electron density $n(\mathbf{r})$, which is a function of only three spatial coordinates, rather than a single wavefunction for all the electrons, which is a function of the $3N$ spatial coordinates of all the electrons in the body. This tremendous reduction in the number of independent parameters of the function to be determined in DFT makes the problem tractable, especially for systems with large number of atoms, such as crystals. Thus, the results of Hohenberg and Kohn gave rise to a practically useful technique for determining the properties of many-electrons systems. These properties can be calculated from first principles, i.e., DFT calculations do not need any experimental input or adjustable parameters to accurately predict many physical properties [42]. One of the great advantages of DFT is that the error in the electronic energy reduces quadratically with respect to the error in the electron density, which implies that the electron density need not be calculated very accurately in order to obtain a fairly accurate estimate of the electronic energy [7].

The proof of Hoheberg-Kohn theorems proceeds by reductio ad absurdum, as sketched below. The electron density $n(\mathbf{r})$ is related to the $N$-body wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ by [25]

$$n(\mathbf{r}) = \int \psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, N)\psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_2 \ldots \mathbf{r}_N. \quad (6.49)$$

Since $\psi$ is a solution of Schrödinger’s Equation (6.5)$_1$, where the Hamiltonian operator depends on the external potential, as given by Equation (6.2), it follows that the ground state electron density $n(\mathbf{r})$ is determined uniquely by the external potential $U(\mathbf{r})$. The converse of this statement is also true, as shown below. For two different external potentials $U(\mathbf{r})$ and $U'(\mathbf{r})$ that do not differ by merely a constant, the ground state electron wavefunctions $\psi$ and $\psi'$ respectively cannot be the same, as they satisfy two different Schrödinger’s equations

$$\hat{H}\psi = E\psi$$

$$(6.50)$$
and
\[
\hat{H}'\psi' = E'\psi',
\]
where \(\hat{H}\) and \(\hat{H}'\) correspond to the potentials \(U(r)\) and \(U'(r)\) respectively. If the two potentials \(U\) and \(U'\) lead to the same ground state electron density \(n(r)\), it follows from the variational principle of the ground state, that
\[
\langle \psi' | \hat{H}' \psi' \rangle = \langle \psi' | \hat{H} + U' - U \psi' \rangle = \langle \psi | \hat{H} \psi \rangle + \int [U'(r) - U(r)] n(r) \, dr.
\]
(6.52)

Using Equations (6.50) and (6.51), it follows that
\[
E' \leq E + \int [U'(r) - U(r)] n(r) \, dr.
\]
(6.53)

Similarly, interchanging the primed and unprimed quantities, it may be deduced that
\[
E \leq E' + \int [U(r) - U'(r)] n(r) \, dr.
\]
(6.54)

Addition of the inequalities (6.53) and (6.54) leads to the contradictory result
\[
E + E' < E' + E.
\]
(6.55)

Thus, it has been proved that two potentials that do not differ by only a constant, must lead to two different ground state electron densities. In other words, the external potential \(U(r)\) is uniquely determined by the ground state electron density \(n(r)\). Hence, it follows that the Hamiltonian \(\hat{H}\) of the system is also uniquely determined by the ground state electron density. Since, the ground state wavefunction is a solution to Schrödinger’s Equation (6.5), it follows that all properties of the ground state are uniquely determined by the ground state electron density. In particular, the ground state energy \(E_0\) may be expressed as a function of the electron density \(n(r)\) as given in Equation (6.48), where
\[
F[n(r)] = \langle \psi | \hat{H}_0 \psi \rangle,
\]
(6.56)

where \(\hat{H}_0\) denotes the Hamiltonian of the system in the absence of any external potential. From the variational principle of the ground state, it follows that the ground state energy given by Equation (6.48) takes its minimum value when the wavefunction \(\psi\) coincides with the true ground state wavefunction of the system. Since the ground state wavefunction is uniquely determined by the ground state electron density, it follows that the ground state energy takes its minimum value when the ground state electron density coincides with the true ground state electron density, thus proving the second Hohenberg-Kohn theorem.

In 1965, using the variational principle of Hohenberg and Kohn, Kohn and Sham [30] derived a system of one-electron equations of the form
\[
\hat{H}_{KS}\psi_\lambda = \epsilon_\lambda \psi_\lambda,
\]
(6.57)
where $\psi_\lambda$ denotes the one-electron wavefunction or a Kohn-Sham orbital and $\epsilon_\lambda$ denotes the corresponding eigenvalue of the Kohn-Sham one-electron equation. The operator $\hat{H}_{KS}$ appearing in the Kohn-Sham equation is given by

$$\hat{H}_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + U_{\text{ext}} + \frac{\delta E_I[n]}{\delta n(r)},$$

where $\frac{\delta}{\delta n(r)}$ denotes a functional derivative and $E_I[n]$ denotes the “interaction energy” functional defined as

$$E_I[n(r)] = \frac{1}{2} \int \frac{n(r)n(r')}{4\pi \epsilon_0 |r-r'|} \, dr \, dr' + E_{xc}[n(r)].$$

Here, $E_{xc}$ denotes the electron exchange-correlation energy functional, which arises due to electron-electron exchange and correlation effects. The solutions to the Kohn-Sham equations may be used to construct the electron density for the many-electrons problem as follows

$$n(r) = \sum_\lambda \psi^*_\lambda(r) \psi_\lambda(r),$$

where the sum runs over all the occupied (i.e., valence) Kohn-Sham orbitals. The total energy of the many-electron system is given by

$$E[n] = \sum_\lambda \epsilon_\lambda - \frac{1}{2} \int \frac{n(r)n(r')}{4\pi \epsilon_0 |r-r'|} \, dr \, dr' + E_{xc}[n(r)] - \int \frac{\delta E_{xc}[n]}{\delta n(r)} \, n(r) \, dr.$$

The Kohn-Sham equations are solved self-consistently as follows. Starting from a trial electron density $n(r)$, Equation (6.57) is solved with the operator $\hat{H}_{KS}$ given by equations (6.58) and (6.59). Using the solution obtained to Equation (6.57), the electron density $n(r)$ is computed using Equation (6.60), using which the total energy is computed Equation (6.61). With this new density, Equation (6.57) is solved once again and the cycle is iterated over and over again until a self-consistent solution is obtained or the desired tolerance for the total energy of the system is attained.

Whereas the Kohn-Sham equations furnish the exact solution to the many-electrons problem in principle, it requires knowing the exact exchange-correlation energy functional in Equation (6.59) for a given material. Since it is very difficult to compute this functional for every material, various approximations are used. Kohn and Sham introduced an approximation that is still widely used and is known as the local density approximation (LDA). In LDA approximation, the exchange-correlation energy functional for any material is approximated by that of a homogeneous electron gas, which has been calculated quite accurately using various techniques. In other words, the exchange-correlation energy at any spatial position $r$ is replaced with the corresponding value for an electron gas system, which has a homogeneous charge density $n = n(r)$ everywhere. Thus, the exchange-correlation energy functional takes the form

$$E_{xc}[n(r)] = \int E_{xc}[n(r)]n(r) \, dr,$$
where \( E_{xc}^0[n(r)] \) is the exchange-correlation energy functional of a homogeneous electron gas with density \( n(r) \). Although by construction, the local density approximation should work well only for materials with slowly varying electron densities, it has been found to give accurate atomic configurations and energies for a relatively wide range of materials in practice.

### 6.3.2.1 All-electron approaches

In the case of a crystal lattice, a standard approach to solve the Kohn-Sham equations (6.57) is to expand the Kohn-Sham orbitals in terms of some basis functions, such that the expansion is consistent with Bloch’s theorem. The two most commonly basis functions are:

1. **Localized orbitals** \( \phi_\lambda \), centered at each unit cell

   \[
   \psi_{k\lambda}(r) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp[i\mathbf{k} \cdot \mathbf{R}] \phi_\lambda(r - \mathbf{R}),
   \]

2. **Plane waves** expansion given by

   \[
   \psi_{k\lambda}(r) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \tilde{u}_{k\lambda}(\mathbf{G}) \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}],
   \]

   where \( \tilde{u}_{k\lambda}(\mathbf{G}) \) denotes the Fourier coefficient of a periodic function \( u_{k\lambda}(r) \), which is used to express the electron wavefunction in Bloch’s theorem in Equation (6.36), \( \mathbf{G} \) denotes a reciprocal lattice vector given by

   \[
   \mathbf{G} = l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + l_3 \mathbf{b}_3
   \]

   for some integers \( l_1, l_2 \) and \( l_3 \) and \( \Omega \) denotes the volume of the unit cell.

From a computational point of view, the infinite sums in Equations (6.63) and (6.64) must be truncated only a finite number of terms, corresponding to a finite number of the basis functions. It is easy to see that in both these cases, the electronic wavefunction \( \psi_{k\lambda}(r) \) satisfies Bloch’s theorem.

As the name suggests, in all-electron approaches the wavefunction for each electron in the crystal is determined by solving the Kohn-Sham equations self-consistently and using the self-consistent wavefunctions to determine the ground state electron density and energy. As a result, all-electron approaches are computationally very expensive, especially for systems with a large number of atoms.

### 6.3.2.2 Pseudopotential approach

Usually, the core electrons do not play an important role in describing the nature of bonding between the atoms in a crystal. This observation is the basis of a widely technique for \( ab \)
initio computations, in which the core electrons are neglected completely in the calculation scheme, termed as the pseudopotential approach.

The basic idea of this approach is to modify the effective one-electron potential, the modified potential being termed as a pseudopotential, in the Kohn-Sham equations by including a term which describes the Coulomb potential due to the core electrons. Since the pseudopotential includes the effect of all the core electrons, it is a non-local function. The solution of the modified Kohn-Sham equations is termed as a pseudo-wavefunction and it is typically expressed in terms of plane waves basis functions for crystal lattices. As in the case of all-electron approaches, the number of plane waves basis functions used in the expansion of the pseudo-wavefunction is limited to a finite number, given in terms of a plane-wave energy cutoff. It turns out that to include only the nonvalence electron orbitals in the pseudo-wavefunction, it suffices to include only a finite number of plane waves.

Commonly, the pseudopotential function is constructed in such a way that the pseudo-wavefunction outside a cutoff radius, which is taken to be the core radius, has the same value as the true wavefunction, as well as connects smoothly to it at the cutoff radius, while being as smooth as possible inside the cutoff radius. As there are many parameters involved in the construction of pseudopotentials, such as the cutoff radius, the connectivity conditions at the cutoff radius, the choice of the pseudo-wavefunction inside the cutoff radius, the number of plane waves used in the expansion of the pseudo-wavefunction etc., there are correspondingly many pseudopotentials that have been constructed for most materials.

The advantage of the pseudopotential approach is that it leads to a simple and fairly accurate method for computing the ground state properties of many-electron systems. Due to its relatively low computational cost, the pseudopotential approach may be successfully applied to perform ab initio calculations for a wide variety of crystals, surface, clusters etc. For the same reason, there are many DFT software packages, such as Vienna ab initio Simulation Package (VASP) [34, 35, 32, 33], Abinit [21] and Quantum Espresso [19], based on the pseudopotential approach, which are widely used to perform DFT calculations.

6.3.2.3 Other approaches

Instead of expanding the Kohn-Sham orbitals in terms of basis functions, there are other approaches based on the cellular method. In these approaches, a simplified form of the potential function is utilized. For example, in the muffin-tin approximation, the potential felt by an electron is decomposed into two regions: a spherically symmetric part around each atom, called a “muffin-tin” and an outer region, termed as a “muffin-pan”, where it is constant. There are a variety of methods, e.g., “augmented plane wave” (APW), KKR, LMTO, ASW etc., that are based on such approximations.

6.3.3 Quantum Monte Carlo

A common computational problem that arises when dealing with many-body systems in quantum mechanics is the evaluation of multi-dimensional integrals in a large number of
dimensions. A large family of computational methods have been implemented for the evaluation of such complex integrals using the Monte Carlo method [10], which relies on repeated random sampling to obtain numerical results. All such methods are collectively termed as Quantum Monte Carlo methods. The quantum Monte Carlo methods allow for a direct treatment of complex many-body effects encoded in multi-dimensional integrals involving the wavefunction of a many-body system, which is a function of $3N$-spatial coordinates. In some circumstances, quantum Monte Carlo methods may produce an exact solution of the quantum many-body problem. Some of the main flavors of quantum Monte Carlo methods are [54] as follows

1. variational Monte Carlo,
2. diffusion Monte Carlo, and
3. path-Integral Monte Carlo.

To obtain good quality numerical results from Monte Carlo methods, typically, a tremendous amount of random sampling and hence, computational resources are required. Hence, the use of these methods are currently limited to simpler systems.

### 6.4 Computation of Force Constants using DFT

There are many parameters that affect the quality of a DFT calculation using the pseudopotential approach with plane wave basis. Some of the most important ones are [34]:

- the particular choice of pseudopotential used,
- the total number of plane waves used in the expansion of the one-electron wavefunctions, expressed in terms of the plane-wave energy cutoff, and
- the number of grid points, called $k$-points, used in the reciprocal lattice for performing numerical integration of various expressions in the reciprocal space, which is required to compute some physical quantities in DFT calculations, e.g., total energy.

For a given pseudopotential, the accuracy of a DFT calculation increases as the plane-wave energy cutoff and the number of $k$-points used increases. In order to ensure that the results obtained from DFT calculations for a given pseudopotentials are reliable, it is necessary to ensure their convergence with respect to the plane-wave energy cutoff and the number of $k$-points. Typically, every pseudopotential prescribes, among other things, the minimum value of the energy cutoff for the plane waves to be used in conjunction with that pseudopotential for performing DFT calculations. In practice, to ensure convergence of the various quantities calculated with the pseudopotential approach in DFT, it is frequently necessary to increase the energy cutoff beyond the prescribed minimum.
All DFT calculations were performed using the software package VASP. VASP is one of the oldest and most widely used software packages for performing DFT calculations and has an extensive library of pseudopotentials for most elements in the periodic table. All the pseudopotentials used in the DFT calculations are of the LDA type \[57\]. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1053575 \[69\] as well as the resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

### 6.4.1 Lattice constant of Ge

Just as in the case of LJ Ar, it is important to first compute the lattice constant of Ge, in order to correctly determine the harmonic and cubic FCs for Ge, as the lattice constant determines the distances between an atom and its neighbors, which has an important effect on the FCs themselves.

VASP provides three different pseudopotentials of the LDA type for Ge, referred to here as “soft”, “moderate” and “hard”. From a computational point of view, the major difference between these pseudopotentials is the prescribed value of the minimum plane-wave energy cutoff to be used with each of these pseudopotentials, with the soft pseudopotential having the lowest prescribed value (174 eV), the hard pseudopotential having the highest (411 eV) and the moderate pseudopotential somewhere in between the two (311 eV). Since a lower value of the plane-wave energy cutoff corresponds to a fewer number of plane waves included in the DFT calculations, it is expected that the DFT calculations using the soft pseudopotential would be computationally cheapest, while those using the hard pseudopotential would be the most expensive. It was also found that the number of \(k\)-points used in the DFT calculations did not affect the computational cost as significantly as the plane-wave energy cutoff, which may be attributed to the fact that most DFT packages, including VASP, use crystal symmetry considerations to significantly reduce the actual number of \(k\)-points used in the numerical integration of various quantities in DFT. The symmetry-reduced set of \(k\)-points used in DFT calculations is together referred to as the irreducible Brillouin zone.

To determine the lattice constant for Ge, a series of DFT calculations is performed to compute the total energy of Ge for different values of the lattice constant and find the value of the lattice constant that minimizes the total energy. A representative result of a series of such computations is shown in Figure 6.2, which represents the values of the total energy of Ge obtained using the moderate pseudopotential with a plane-wave energy cutoff that was chosen to be 30% higher than the prescribed minimum cutoff, which amounts to a cutoff of 405 eV, and with 15 \(k\)-points along each axis. As may be seen from this figure, the lowest energy of the crystal lattice is obtained for a lattice constant of 5.65 Å. This observation was consistent across all the three pseudopotentials employed in this study, and it is also consistent with the experimental value of the lattice constant for Ge (5.658 Å) \[31\]. This
result shows that each of the three pseudopotentials tested reproduces the experimental value of the lattice constant of Ge quite accurately.

A convergence study was performed for the total energy of the crystal at its minimum value, which is always found to be when the lattice constant is 5.65 Å, with respect to the number of $k$-points and plane-wave energy cutoff for each of the three pseudopotentials. Representative results of these convergence studies are shown in Figures 6.3 and 6.4 for the soft pseudopotential, Figures 6.5 and 6.6 for the moderate pseudopotential, and Figures 6.7 and 6.8 for the hard pseudopotential respectively. In Figure 6.8, even though a slight variation is seen in the computed total energy of Ge with respect to the plane wave energy cutoff, the actual variation is only 0.03%.

To assess the convergence of the total energy of Ge at a lattice constant of 5.65 Å with respect to the DFT parameters, viz., number of $k$-points and plane-wave energy cutoff, the relative difference between the maximum and minimum values of the total energy of Ge was computed as the aforementioned DFT parameters were varied. The results of these computations are is shown in Table 6.1 for each of the pseudopotentials. These results show that for all the three pseudopotentials, a sufficient level of convergence for the total energy has been attained with respect to each of the two important DFT parameters, viz., the number of $k$-points and the plane-wave energy cutoff. Thus, the converged values of the lattice constant and the ground-state energy of Ge has been determined.
Figure 6.3: Variation of total energy of Ge crystal lattice with number of k-points for the soft pseudopotential with plane-wave energy cutoff of 227 eV

Figure 6.4: Variation of total energy of Ge crystal lattice with plane-wave energy cutoff for the soft pseudopotential with 11 k-points
Figure 6.5: Variation of total energy of Ge crystal lattice with number of k-points for the moderate pseudopotential with plane-wave energy cutoff of 405 eV

Figure 6.6: Variation of total energy of Ge crystal lattice with plane-wave energy cutoff for the moderate pseudopotential with 11 k-points
Figure 6.7: Variation of total energy of Ge crystal lattice with number of k-points for the hard pseudopotential with plane-wave energy cutoff of 535 eV.

Figure 6.8: Variation of total energy of Ge crystal lattice with plane-wave energy cutoff for the hard pseudopotential with 11 k-points.
**Variation of total energy with respect to**

<table>
<thead>
<tr>
<th></th>
<th>for soft pseudopotential</th>
<th>for moderate pseudopotential</th>
<th>for hard pseudopotential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of $k$-points</td>
<td>0.01909%</td>
<td>0.01917%</td>
<td>0.01923%</td>
</tr>
<tr>
<td>Plane wave energy cutoff</td>
<td>0.1041%</td>
<td>0.03138%</td>
<td>0.06687%</td>
</tr>
</tbody>
</table>

Table 6.1: *Variation of total energy of Ge crystal for the lattice constant of 5.65 Å with respect to the DFT parameters for the different pseudopotentials*

### 6.4.2 Force constants for Ge

Having determined the lattice constant of Ge, it is now possible to use it in DFT simulations to determine the harmonic and cubic FCs for a Ge crystal lattice. The values of these FCs depend on the number of neighbors included in the DFT computations of the FCs. Therefore, in addition to the aforementioned DFT parameters important in any convergence study, viz., number of $k$-points and the plane-wave energy cutoff, it is additionally important to study the convergence of the FCs with respect to the number of neighbors included in the DFT computations. The number of neighbors included in the DFT calculations depends directly on the number of unit cells of the crystal lattice included in a single supercell on which the DFT computations are performed, since in all of these DFT computations, periodic boundary conditions are imposed by the DFT software package in all three directions.

#### 6.4.2.1 Harmonic Force Constants

To reduce the computational expense of calculating the harmonic FCs, crystal symmetry is utilized to relate the harmonic FCs of different atoms to each other. Using this set of relationships, a set of linearly independent harmonic FCs is established, and the rest of the harmonic FCs of the crystal lattice are calculated from the values harmonic FCs in this linearly independent set. There are two standard procedures to compute the harmonic FCs:

- finite-difference method, and
- density functional perturbation theory (DFPT).

In the first approach, a single atom in a supercell of the crystal lattice is displaced by a small amount from its equilibrium position and the forces on all the other atoms in the supercell are calculated from DFT simulations. This information provides an equation relating the harmonic FCs of the various atoms according to Equation (5.3). This procedure is repeated for a series of atomic displacements, until enough equations are obtained to determine all the linearly independent harmonic FCs, from which the entire set of harmonic FCs between all the atoms of the crystal may be computed. In the second approach, a perturbation method is applied to the Kohn-Sham equations to obtain the first-order response in the change in the total energy of the supercell due to an infinitesimal displacement of an atom, from which
the harmonic FCs may be calculated directly [54]. Although the second approach is more accurate than the first one in principle, it is relatively very expensive computationally and hence, in practice, can be only applied for small systems, i.e., for smaller supercells. In the case of Ge, it was found, by trying to run simulations using VASP, that the DFPT method for computation of the harmonic FCs worked only for a supercell with 2 unit cells in each direction.

The actual computation of the harmonic FCs from the results of the DFT simulations was performed using the software package phonopy [68]. Phonopy has the capability to compute the harmonic FCs using both the finite-difference and the DFPT approaches, as well as many other features such as determining the phonon density of states (PDOS), band structure, etc.

Representative results of the convergence studies for the harmonic FCs with respect to the number of \( k \)-points, plane-wave energy cutoff and number of unit cells for the soft pseudopotential are shown in Figures 6.9, 6.10 and 6.11, respectively. It may be seen from Figure 6.10 that there is some oscillation in the computed value of the maximum harmonic FC as the plane-wave energy cutoff is increased continuously. This implies the need for DFT calculations with higher values of plane-wave energy cutoff to ensure convergence of the harmonic FCs. However, it was found that for the purposes of this study, the accuracy of the harmonic FCs obtained from the DFT calculations was sufficient.

![Figure 6.9: Variation of maximum harmonic FC of Ge crystal lattice of 4 unit cells in each direction with number of \( k \)-points for the soft pseudopotential with plane-wave energy cutoff of 174 eV](image)

Since it is impractical to show the convergence of each of the multitude of harmonic FCs for each case, the convergence of only the maximum harmonic FCs is shown in Figures 6.9, 6.10 and 6.11.
Representative results of the convergence studies for the harmonic FCs with respect to the number of $k$-points, plane-wave energy cutoff and number of unit cells for the moderate pseudopotential are shown in Figures 6.12, 6.13 and 6.14, respectively. From Figure 6.13, it may be seen that there is some oscillation in the computed value of the maximum harmonic FC as the plane-wave energy cutoff is increased continuously, as in the case of the
soft pseudopotential. However, it was found that for the purposes of this study, the accuracy of the harmonic FCs obtained from the DFT calculations was sufficient.

Figure 6.12: Variation of maximum harmonic FC of Ge crystal lattice of 2 unit cells in each direction with number of $k$-points for the moderate pseudopotential with plane-wave energy cutoff of 311 eV

Figure 6.13: Variation of maximum harmonic FC of Ge crystal lattice of 2 unit cells in each direction with plane-wave energy cutoff for the moderate pseudopotential with 11 $k$-points
Representative results of the convergence studies for the harmonic FCs with respect to the number of \( k \)-points and plane-wave energy cutoff for the hard pseudopotential are shown in figures 6.15 and 6.16 respectively. From Figure 6.16, it may be seen that there is some oscillation in the computed value of the maximum harmonic FC as the plane-wave energy cutoff is increased continuously, as in the case of the soft and moderate pseudopotential. However, it was found that for the purposes of this study, the accuracy of the harmonic FCs obtained from the DFT calculations was sufficient.

To assess the convergence of the harmonic FCs with respect to the DFT parameters and the number of unit cells, the relative difference between the maximum values of the computed harmonic FCs for the finest two refinements was computed in each case. Table 6.2 shows the results of these computations for three pseudopotentials. It may be seen from Table 6.2 that

<table>
<thead>
<tr>
<th>Variation of maximum harmonic FC with respect to</th>
<th>for soft pseudopotential</th>
<th>for moderate pseudopotential</th>
<th>for hard pseudopotential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of ( k )-points</td>
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<td>0.04386%</td>
<td>0.09481%</td>
</tr>
<tr>
<td>Plane wave energy cutoff</td>
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<td>0.0143%</td>
<td>0.01382%</td>
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<tr>
<td>Number of unit cells</td>
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<td>1.051%</td>
<td>2.502%</td>
</tr>
</tbody>
</table>

Table 6.2: Variation of maximum harmonic FCs for Ge crystal for the lattice constant of 5.65 \( \text{Å} \) with respect to the DFT parameters and the number of unit cells for the various pseudopotentials
the maximum error in the harmonic FCs is higher for the soft pseudopotential than for the moderate pseudopotential, which may be due to the fact that the soft pseudopotential, having a lower plane-wave energy cutoff, is more inaccurate than the moderate pseudopotential.
6.4.2.2 Cubic Force Constants

The computation of the cubic FCs follows a similar procedure to that of the harmonic FCs. First, crystal symmetry is utilized to relate the cubic FCs of the different atoms to each other and a set of linearly independent cubic FCs is determined. This computation is accomplished by using the Python module third-order, which is part of the software package ShengBTE [40, 41]. In addition to the parameters used in the computation of the harmonic FCs, there is also an option to supply the number of nearest neighbor interactions to be included in the calculation of the cubic FCs in the third-order module of ShengBTE package. However, it is important to ensure that the number of nearest neighbors specified for the computation of cubic FCs lies within the supercell domain specified in the computation, as, otherwise, periodic images of some of the nearest neighbors would also affect the values of the cubic FCs, leading to unphysical results. For example, in the case of a Ge crystal lattice, for a supercell consisting of 2 unit cells in each direction, only nearest neighbor interactions may be included in the computation of cubic FCs.

To compute the cubic FCs using the third-order module of ShengBTE, the following work-flow is recommended. The program is first supplied with the size of the supercell and the number of nearest neighbor interactions to be included in the computation of the cubic FCs for a given crystal lattice. The program uses this information along with the symmetries of the given crystal lattice to determine the minimal set of distorted supercells required for the computation of the entire set of cubic FCs between all the basis atoms of a central unit cell and all of their neighbors up to the specified nearest neighbor interaction cutoff. For example, in the case of a Ge crystal lattice with 2 unit cells in each direction, to determine all the cubic FCs in the case of only first nearest neighbor interactions, the program determines a set of 8 distorted supercells on which DFT computations must be performed, whereas in the case of 3 unit cells in each direction and accounting for first and second nearest-neighbor interactions, the program determines a set of 52 distorted supercells for performing the same DFT computations. Then, DFT computations are performed on the distorted supercells to compute the forces on each atom. This information is fed back to the third-order module, which then produces as the output, the entire set of cubic FCs for the given supercell with the specified nearest neighbor interactions.

In order to ensure the reliability of the results obtained from the aforementioned procedure, it is necessary to study the convergence of the computed cubic FCs with respect to the DFT parameters, supercell size (specified in terms of the number of unit cells in each direction) and the number of nearest neighbor interactions to be included. Representative results for the convergence of cubic FCs of Ge with respect to the number of $k$-points and plane-wave energy cutoff are shown in Figures 6.17 and 6.18 respectively for the soft pseudopotential. As in the case of harmonic FCs, only the convergence of the maximum value of the cubic FCs is shown in each case, as it is impractical to show the values of the multitude of cubic FCs between each atom and its neighbors. For the moderate pseudopotential, representative results for the convergence of cubic FCs of Ge with respect to the number of $k$-points and plane-wave energy cutoff Figures 6.19 and 6.20 respectively. For the hard pseudopotential,
representative results for the convergence of cubic FCs of Ge with respect to the number of \( k \)-points and plane-wave energy cutoff. Figures 6.21 and 6.22 respectively. Also, in order to perform meaningful convergence studies with respect to the number of nearest neighbor interactions, it is necessary to perform DFT computations for a supercell with at least 3 unit cells in each direction; however, of the order of 100 DFT computations are required to be performed for each pseudopotential and those computations is still in progress.

![Graph of Max. cubic FC vs. Number of \( k \)-points](image)

Figure 6.17: Variation of maximum cubic FC of Ge crystal lattice of 2 unit cells in each direction with number of \( k \)-points for the soft pseudopotential with plane-wave energy cutoff of 174 eV

To assess the convergence of the cubic FCs with respect to the DFT parameters and the number of unit cells, the relative difference between the maximum values of the computed cubic FCs for the finest two refinements was computed in each case. Table 6.3 shows the results of these computations for three pseudopotentials.

<table>
<thead>
<tr>
<th>Variation of cubic FC with respect to</th>
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<th>for hard pseudopotential</th>
</tr>
</thead>
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<tr>
<td>Number of ( k )-points</td>
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<td>0.0001%</td>
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<tr>
<td>Plane wave energy cutoff</td>
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<td>0.0158%</td>
<td>0.0811%</td>
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Table 6.3: Variation of maximum cubic FCs of Ge for the lattice constant of 5.65 Å with respect to the DFT parameters for the various pseudopotentials
Figure 6.18: Variation of maximum cubic FC of Ge crystal lattice of 2 unit cells in each direction with plane-wave energy cutoff for the soft pseudopotential with 15 k-points

Figure 6.19: Variation of maximum cubic FC of Ge crystal lattice of 2 unit cells in each direction with number of k-points for the moderate pseudopotential with plane-wave energy cutoff of 311 eV
Figure 6.20: Variation of maximum cubic FC of Ge crystal lattice of 2 unit cells in each direction with plane-wave energy cutoff for the moderate pseudopotential with 15 k-points.

Figure 6.21: Variation of maximum cubic FC of Ge crystal lattice of 2 unit cells in each direction with number of k-points for the hard pseudopotential with plane-wave energy cutoff of 311 eV.
6.4.3 MD simulations on Ge with truncated Taylor series potential

The harmonic and cubic FCs computed from DFT calculations on Ge are used in Equations (5.2) and (5.3) to determine the potential energy of the Ge crystal and the forces acting on the Ge atoms respectively. Using the same code for the interatomic potential that was used for LJ Ar, MD simulations are performed on Ge. A procedure similar to the one carried out for LJ Ar is used to estimate the thermophysical properties of Ge from MD simulations.

First, the optimum value of the parameter $\zeta$ of the Nosé-Hoover thermostat of the canonical ensemble is determined by comparing the specific heat capacity of the pure harmonic part of Ge to the Dulong-Petit value. The specific heat capacity (including error bars indicating its standard deviation) is computed using Equation (3.25) for temperatures ranging from 100 to 700 K and for different values of $\zeta$. Figures 6.23, 6.24 and 6.25 show the results of these simulations for the soft, moderate and hard pseudopotentials respectively. From Figures 6.23, 6.24 and 6.25, it is clear that the optimum value of the parameter $\zeta$ is 2.5 ps for all the three pseudopotentials.

Using the optimum value of $\zeta$, MD simulations are performed for Ge with the truncated Taylor series potential. It was found that inclusion of the third order terms in the potential energy made the MD simulations unstable at a temperature of 400 K and above. It is hoped that as the cubic FCs are obtained with more accuracy, these instabilities will disappear, as Ge has a melting point of 1210 K [1].

Figure 6.26 shows a comparison of the specific heat capacity for Ge obtained from the MD simulations using the truncated Taylor series potential for each of the three pseudopo-
Figure 6.23: Variation of specific heat capacity with thermostat parameter $\zeta$ in NVT ensemble for Ge with the soft pseudopotential

Figure 6.24: Variation of specific heat capacity with thermostat parameter $\zeta$ in NVT ensemble for Ge with the moderate pseudopotential

tentials to the experimental values from [1, 17]. The harmonic and cubic FCs used in the MD simulations for each of the pseudopotentials was the most accurate obtained from DFT calculations. For the soft pseudopotential, the harmonic FCs used are those obtained from DFT
CHAPTER 6. FIRST-PRINCIPLES CALCULATIONS

Figure 6.25: Variation of specific heat capacity with thermostat parameter $\zeta$ in NVT ensemble for Ge with the hard pseudopotential

Figure 6.26: Comparison of specific heat capacity for Ge with the truncated Taylor series based potentials with experimental values at different temperatures
calculations for a 4 by 4 by 4 supercell with 15 \( k \)-points along each direction and plane wave energy cutoff 30\% higher than the one recommended in the corresponding pseudopotential file, while the cubic FCs are those obtained from DFT calculations for a 2 by 2 by 2 supercell with 19 \( k \)-points along each direction and a plane wave energy cutoff 80\% higher than the recommended value from the pseudopotential file. For the moderate pseudopotential, the harmonic FCs used are those obtained from DFT calculations for a 4 by 4 by 4 supercell with 11 \( k \)-points along each direction and the recommended plane wave energy cutoff from the corresponding pseudopotential file, while the cubic FCs are those obtained from DFT calculations for a 2 by 2 by 2 supercell with 19 \( k \)-points along each direction and a plane wave energy cutoff 80\% higher than the recommended value from the pseudopotential file. For the hard pseudopotential, the harmonic FCs used are those obtained from DFT calculations for a 3 by 3 by 3 supercell with 13 \( k \)-points along each direction and the recommended plane wave energy cutoff from the corresponding pseudopotential file, while the cubic FCs are those obtained from DFT calculations for a 2 by 2 by 2 supercell with 19 \( k \)-points along each direction and a plane wave energy cutoff 80\% higher than the recommended value from the pseudopotential file. As may be seen from Figure 6.26, with the exception of 100 K, the specific heat capacity computed using the truncated Taylor series potential is within the experimental range of values at all temperatures. Since the Debye temperature of Ge is 374 K [43], it is expected that the fit with experimental data will become progressively poorer as the temperature goes below the Debye temperature, due to the increasing importance of quantum statistics. This expectation is borne out in Figure 6.26. The difference in the specific heat capacities of the pure harmonic Ge crystal and the experimental values is due to the anharmonicity in the latter [5, Chapter 22]. Thus, the excellent agreement between the values of \( C_v \) for the truncated Taylor series potential and the experimental values shows that, within the given temperature range, the cubic terms for all three pseudopotentials are sufficient to capture the anharmonicity of the Ge.

To confirm the effectiveness of this method in capturing the anharmonicity of Ge, the thermal conductivity for Ge obtained for the truncated potential is compared to the experimental values. To this end, first the correlation time to be used as the upper limit of the integral in Equation (3.74) is determined by noting the value at which the heat flux autocorrelation function \( C_q(\tau) \) from Equation (4.6) decays to zero. Figure 6.27 shows the decay of the heat flux autocorrelation function \( C_q(\tau) \) with correlation time \( \tau_C \) for the truncated Taylor series-based potential for Ge with the FCs computed using the moderate pseudopotential at 200 K for 4 unit cells. Figure 6.28 shows the integral of the same autocorrelation function with respect to the correlation time, which shows that the maximum correlation time of Figure 6.28 is sufficient for the heat flux autocorrelation function to decay to zero.

The same FCs that were used for the MD simulations for computing specific heat capacity were also used for the MD simulations for computing thermal conductivity. Figure 6.29 shows the values of thermal conductivity computed for a Ge crystal of 4 unit cells using the truncated Taylor series potential with the FCs derived from the three pseudopotentials compared to the experimental values from [20]. It is observed that the values of thermal conductivity computed using classical MD are closer to the experimental values above 100
Figure 6.27: Decay of the heat flux autocorrelation function for Ge with the truncated Taylor series-based potential computed using the moderate pseudopotential with correlation time at 200 K for a $4 \times 4 \times 4$ unit cells

Figure 6.28: Integral of the heat flux autocorrelation function for the Ge with the truncated Taylor series-based potential for a $4 \times 4 \times 4$ unit cells computed using the moderate pseudopotential with respect to correlation time at 200 K

K, which is consistent with the results observed for the heat capacity. This is again due to the neglect of quantum statistics in classical MD, which becomes very important at 100 K. It must be noted that the value of thermal conductivity computed for Ge is very sensitive to the accuracy of the cubic FCs obtained from DFT calculations, since for a pure harmonic crystal, it is known that the thermal conductivity is infinite [5]. It is expected that as more accurate
values of cubic FCs obtained from DFT simulations, the thermal conductivity computed from MD simulations will match more closely with the experimental results.
Chapter 7

Conclusions and Scope

A method for determining and implementing a truncated interatomic potential using a Taylor series expansion of any general potential has been detailed. The coefficients in this expansion may be derived analytically, as illustrated in this work for the case of LJ Ar or, in the case of real materials where the interatomic potential is not known, through \textit{ab initio} methods such as DFT simulations. Restrictions in the use of the truncated potential (evidenced by limits on the temperature range) are shown to arise from the existence of critical atomic displacements beyond which the resulting material model becomes unstable. Thus, there exists a range of temperatures for which the proposed method is readily applicable. The practical limitation in determining higher-order FCs in the Taylor series expansion of the crystal potential energy necessitates the investigation of how many higher-order terms are required to accurately estimate thermophysical properties such as heat capacity and thermal conductivity that depend on the higher-order terms of the crystal potential energy. It has been shown that for LJ Ar, the method of truncated Taylor series potential produces a reasonably accurate estimate of the heat capacity, which shows its effectiveness in modeling a bulk equilibrium property. To further test the utility of this method, it is also shown for LJ Ar that the effect of anharmonicity in thermal conductivity may be well captured by merely truncating the Taylor series.

The real power of the method of truncated Taylor series potential is expressed when applied to materials whose exact interatomic potential energy is unknown. Such is the case for Ge and it becomes necessary to perform \textit{ab initio} DFT simulations to determine its FCs. The details of these \textit{ab initio} calculations are provided and the most important parameters affecting the accuracy of the calculations are reported. The FCs computed from the DFT calculations are used in MD simulations to estimate the specific heat capacity of Ge. The good fit between the specific heat values predicted from MD simulations using the truncated Taylor series potential and the experimental values indicates that the third order terms are sufficient to capture the anharmonicity of Ge above its Debye temperature. To further test the accuracy of the cubic FCs for Ge, the thermal conductivity of Ge computed using the truncated Taylor series potential are compared with the experimental values. It was found that when the temperature of the MD simulation was appreciably lower than the
Debye temperature for Ge, the fit with experimental data was not good due to the effect of quantum statistics. On the other hand, around the Debye temperature of the material and above, the proposed method, within its range of applicability, allowed estimation of thermal conductivity closer to the experimental values than that produced using the semi-empirical Stillinger-Weber potential for Ge. The fact that this method reproduces the thermal conductivity values close to the experimental range of values even with the slightly inaccurate cubic FCs shows that this method is robust and likely to produce more results more closely matched with experiments as the accuracy of the FCs is improved.

Further work is being done to perform more DFT calculations on Ge to get the FCs to the desired accuracy level, using which, it is expected that the fit of the computed values of the heat capacity and thermal conductivity with the experimental values will be better. This same technique may also be applied to study thermophysical properties of many other crystalline materials, which would otherwise be too expensive computationally to study using other techniques such as Lattice Dynamics. In addition, this method may also be used to explain the observed unusual temperature dependence of thermal conductivity of nanowires [9, 44, 39]. In a nanowire, it would be inappropriate to use periodic boundary conditions in all directions, as in the case of bulk. Instead, due to the presence of the free surface, it would be more appropriate to impose free boundary conditions for the surface atoms. It is expected that the imposition of the right boundary conditions in the MD simulations of nanowires will help explain the observed unusual behavior of thermal conductivity in nanowires.
Bibliography


Appendix A

An efficient algorithm for computing equilibrium positions in a crystal lattice

The problem of computing the nearest equilibrium lattice position of an atom is a special case of the Closest Vector Problem (CVP) for three dimensions [52].

Any crystal lattice in three dimensions may be completely specified by listing its basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ and the positions $\mathbf{b}_i$ ($i = 1, \ldots, N$) of the basis atoms within a unit cell. Then, the position of any lattice site is given by

$$\mathbf{R} = m_1 \mathbf{a}_1 + m_2 \mathbf{a}_2 + m_3 \mathbf{a}_3 + \mathbf{b}_i,$$

where $m_1$, $m_2$ and $m_3$ denote some integer values.

To describe the algorithm succinctly, let $\mathbf{A}$ denote the matrix whose columns are the components of the lattice basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. The problem is to find the nearest lattice site to a given arbitrary position vector $\mathbf{r}$. Let $m_1$, $m_2$ and $m_3$ denote integers representing the unit cell of the lattice site $\mathbf{R}$ nearest to the current position $\mathbf{r}$. The algorithm consists of the following steps:

1. For each basis atom $i$, solve the linear system of equations given by

$$\mathbf{r} = \mathbf{A} \mathbf{n} + \mathbf{b}_i,$$  \hspace{0.5cm} (A.2)

where $\mathbf{n} = [n_1, n_2, n_3]^T$ represents the solution to the aforementioned linear system. Note that $\mathbf{n}$ will have non-integral components in general.

2. Set $m_i$ to the nearest integer to the corresponding $n_i$ by rounding for $i = 1, 2, 3$ and set $\mathbf{R} = \sum_i \mathbf{A} \mathbf{m} + \mathbf{b}_i$, where $\mathbf{m} = [m_1, m_2, m_3]^T$ is the vector containing the integer values $m_1$, $m_2$, $m_3$, which represent the tentative unit cell of the lattice site $\mathbf{R}$ nearest to the current position $\mathbf{r}$. 
APPENDIX A. COMPUTING EQUILIBRIUM POSITIONS IN A CRYSTAL LATTICE

3. If the distance between \( r \) and \( R \) is less than half the nearest-neighbor distance in the crystal lattice, then \( R \) is the desired nearest equilibrium lattice position to the current position.

4. If the aforementioned condition is not satisfied, then a series of parallelepipeds of increasing sizes centered at \( R \) are constructed. For each parallelepiped, the distance between each lattice site on the surface of the parallelepiped and \( r \) is computed and the smallest distance for that parallelepiped is noted. If this smallest distance is larger than the smallest distance between \( r \) and a lattice site found so far, this means that the parallelepiped completely envelopes the sphere with center at \( r \) and radius equal to this shortest distance. This implies that no parallelepiped of larger size can contain the nearest lattice site on its surface and so the search is terminated with the lattice site \( R \) giving the shortest distance so far.

This algorithm is found to be very efficient in practice as it always terminates within two to three steps.