A HEAT CONDUCTION STUDY AT NON-CONTINUUM SCALES

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by

Alejandro Guajardo Cuéllar.

Mhir Sen, Co-Director

David B. Go, Co-Director

Graduate Program in Aerospace and Mechanical Engineering
Notre Dame, Indiana
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Abstract

by

Alejandro Guajardo Cuéllar

An extensive and detailed description of heat conduction at the micro- and nano-scale is presented. During the last two decades this phenomenon has become very attractive to study because of the shrinking in size of thermoelectric technologies and electronic devices. These newer technologies are at the micro- and nano-scale. Due to the small size, a power dissipation problem has presented itself in these applications. The proper thermal performance is related with the performance of the technology. Because of these facts a description of the thermal transport in different materials at these scales is required. This problem is important because understanding the energy transport will allow engineers to design faster electronic devices and more efficient thermoelectric applications.

For macro-scale it is known that diffusive behavior is presented in heat conduction; here models that show different behavior than diffusive such as wave-like are presented. One extra tool to understand heat conduction is to calculate the thermal conductivity. Equilibrium molecular dynamics combined with the Green-Kubo formula can be used to calculate the thermal conductivity of materials such as germanium and carbon. The foundation of this calculation is extracting the heat current from the results, and implementing it into the Green-Kubo formula. This work considers all formulations from the literature that calculate the
heat current for the Tersoff potential, the interatomic potential most applicable to semiconductor materials. The formulations for the heat current are described, and results for germanium and carbon are presented. The formulations are compared with respect to how well they capture the physics of the Tersoff potential and how well the calculated value of the thermal conductivity reflects the experimentally-measured value.

The second part of this work deals with heat transport in low dimensions at the nano-scale. The energy transport in a two dimensional graphene sheet is studied and compared to that in a one dimensional chain. The equations of motion for each individual atom of the sheet are solved numerically to generate the distribution of kinetic energy in the structure. The distribution of kinetic energy in the sheet shows two different characteristics of the transport. The components of frequency of the kinetic energy in the graphene structure are identified. The components allow the identification under which potential more low frequency carriers are expected. The presence of chaos in the graphene sheet using the anharmonic potential is identified. Finally, conclusions and recommendations for the study of heat conduction at the nano-scale are presented.
A mis papás que son mi ejemplo a seguir y siempre les estaré infinitamente agradecido por lo que me han dado en la vida.
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SYMBOLS

\( a \) lattice constant Chapter Two
\( a \) parameter Tersoff potential
\( a \) acceleration
\( A \) parameter Tersoff potential
\( b \) parameter Tersoff potential
\( B \) parameter Tersoff potential
\( c \) specific heat
\( c \) parameter Tersoff potential Chapter Three
\( C \) quantity of transport in Modified Cattaneo’s equation
\( C \) spring constant Chapter Three
\( d \) parameter Tersoff potential
\( d \) orbit to study Chapter Four
\( D \) density of states
\( f \) distribution function
\( f_b \) distribution function ballistic part
\( f_m \) distribution function diffusive part
\( F \) force
\( f_A \) attractive term potential
\( f_C \) cut off function potential
$f_R$ repulsive term potential

$g$ parameter Tersoff potential

$h$ Planck’s constant Chapter Two

$h$ parameter Tersoff potential

$H$ Hamiltonian

$H.c.$ Hermitian conjugate

$i$ index

$I_\omega$ Intensity phonons

$f^0_\omega$ equilibrium intensity phonons

$j$ index

$j$ heat flux

$J$ heat current

$J_{\text{kin}}$ heat current due to kinetic energy

$J_{\text{pot}}$ heat current due to potential energy

$k$ wave vector Chapter Two

$k$ index

$k_b$ Boltzmann constant

$k_1$ spring constant harmonic

$k_2$ spring constant anharmonic

$KE$ kinetic energy

$L$ length

$m$ mass

$M$ large number to represent integration to infinity

$n$ total number of atoms

$n_i$ parameter Tersoff potential
\( N \) total number of time steps
\( p \) absolute value momentum Chapter Three
\( p \) arbitrary variable telegraph equation Chapter Four
\( \mathbf{p} \) momentum
\( q \) one dimension heat flux
\( q \) lattice constant Chapter Three
\( \mathbf{q} \) heat flux vector
\( \mathbf{r} \) position vector
\( r \) distance
\( R \) parameter Tersoff potential
\( S \) parameter Tersoff potential
\( \mathbf{S} \) heat flux operator
\( t \) time
\( T \) temperature
\( U \) potential energy
\( v \) absolute value velocity vector
\( \mathbf{v} \) velocity
\( V \) volume
\( x \) spatial direction
\( y \) spatial direction
\( z \) spatial direction

**Greek**

\( \beta \) order of the derivative
\( \beta \) Parameter Tersoff potential Chapter Four
\( \epsilon \) parameter Lennard-Jones potential
\( \epsilon \) internal energy Chapter Three
\( \zeta \) parameter Tersoff potential
\( \gamma \) multi-body term Tersoff potential
\( \Gamma \) gamma function
\( \theta \) angle Tersoff potential Chapter Four
\( \lambda \) thermal conductivity
\( \lambda \) Lyapunov exponent Chapter Six
\( \mu \) cosine of an angle in the EPRT
\( \sigma \) parameter Lennard-Jones potential
\( \tau \) time in autocorrelation function
\( \tau_q \) phase lag
\( \tau_R \) Relaxation time
\( \tau_T \) phase lag
\( \chi \) parameter Tersoff potential
\( \omega \) parameter Tersoff potential
\( \omega \) frequency Chapter Four
\( \Omega \) natural frequency

*other symbols*

\( \langle \rangle \) autocorrelation function
\( \hbar \) reduced Planck’s constant
\( \hat{x} \) coefficient traveling wave phonons Chapter Two
\( \hat{\Omega} \) unit vector
CHAPTER 1

INTRODUCTION

During the last 20 years there has been an exponential growth of devices and technologies built from materials at the nano-scale. Gordon E. Moore, co-founder of Intel Co., predicted this growth with his famous Moore’s law [1] approximately 46 years ago. Semiconductor materials have had a huge impact in this development. Semiconductor materials can be used for transistors because their unique electrical behavior allows them to be a conductor or an insulator. This makes them perfect candidates for applications where ones and zeros process the information, such as transistors. For example, in the last 26 years carbon-related materials had the following development. During the 80’s Kroto et al. [2] discovered the so-called fullerenes, a molecule of 60 carbon atoms with the shape of a soccer ball. Then in the 90’s Iijima [3] reported measurements of multi-walled carbon nanotubes. This had a huge impact in the nano-technology field that marked the trend of devices in the last 20 years. Finally Novoselov and Geim [4], discovered graphene in 2004. This is a two-dimensional (2-d) sheet of carbon atoms in a honeycomb array. This novel material is supposed to be the “rock star” of the next generation of nano-technology devices/applications due to its excellent mechanical and electrical properties. Graphene has been shown to have excellent electrical properties including an extremely high electron mobility [5]. It also has good mechanical properties including a large Young’s modulus that makes it a rigid
and strong material [6]. These properties, as well as favorable optical [7, 8] and magnetic [5] properties, open a large window of possibilities for the exploration of new graphene-based materials and devices. Graphene-composite materials, for example, have been shown to have high electrical conductivity [9]. The discovery of fullerenes and graphene was awarded with the Nobel prize. Carbon was not the only material that became popular. Germanium and silicon also have been tremendously popular in the last 50 years. Integrated circuited fabrication methods that have become more available in industry have allowed a huge development of devices based on these materials. Industry has shown a shrinking size trend as predicted by Moore.

The discovery of these novel materials and the appearance of the new semiconductors technologies also brought into the picture new phenomena that were new or not completely understood by the scientific community. Most of these materials presented excellent mechanical and electrical properties, so questions arose about the limits and physical description of these materials. Heat transport was one of the new challenges that showed up with the boom of the new nanomaterials/applications. A result of this shrinking in size was a heat dissipation problem in the new technologies due to the small area. The scientists and engineers realized that this phenomenon cannot be described the same way as the macro-scale. This constraint was marking a limit in the new nano-technologies; a limit that the scientists of the final part of the last century and the beginning of this recent century bravely were, are, and will be eager to challenge.

One of the pioneers in the heat transfer area at the nano-scale was C.L. Tien at the University of California Berkeley at the beginning of the 90’s, leaving behind a rich school of researchers in the field such as A. Majumdar and G. Chen. After
this, the spread of knowledge in the field has been great, but, because of the
constant growth of nano-technology, heat conduction at the nano-scale is still a
rich field and not completely understood by the community.

The understanding of heat conduction at the nano-scale is the main motivation
of this work. This mechanism of transport is important in the proper working of
electronic and mechanical devices that are built at the nano-scale. Power dissipa-
tion in devices at the nano-scale is a significant challenge due to the inherently
small area leading to very high power densities. The understanding of the energy
transport in these systems represents an exciting and challenging problem.

Different strategies can be used to study the transport phenomenon. Fourier’s
law describes energy transport linearly relating the heat flux vector and the tem-
perature distribution. This constitutive law is successful in describing heat con-
duction at the continuum-scale. However for transport at the nano-scale further
detail than the one captured by Fourier’s law is required. At the continuum scale
temperature is the average value of the energy of small regions. At the nano-scale,
the average of energy of small regions is not possible because the domain is at the
atomic scale. Cahill et al. [10] reported values for the mean free path of phonons
for non-metallic materials in the range of 1 to 100 nm. This value is compared
with the characteristic length of systems at the nano-scale. Fourier’s law does
not capture these two effects, therefore further study is required. One strategy
that helps describe the transport of energy without assuming a constitutive law
is to study the dynamics of the atoms. The vibrations of the atoms produce
quantized energy packages called phonons. The phonons are one of the carriers
in heat conduction. In some materials such as semiconductor materials, phonons
are the main carriers. Information about these carriers can be obtained by solv-
ing the equations of motion of the atoms. This can be achieved using numerical
techniques such as molecular dynamics, (MD).

In this work heat conduction at the nano-scale is studied. To achieve the
understanding of the problem, and to propose a new contribution in the field, the
following is done. First a literature review on the field is provided. Next, the
thermal conductivity of crystals is calculated and a new formulation is proposed
to calculate this property for a specific potential for semiconductor materials.
Finally, the transport of energy in 1-d and 2-d structures is described.

The Chapters of this work deal with the following. Chapter Two is a literature
review of the topic. Chapter Three provides the necessary theoretical background
to attack the problem; concepts such as potentials, Green-Kubo, and MD are dis-
cussed. The Chapter is a link between heat conduction and the thermal conductivity; this study is performed in 3-d crystals. The materials studied are germanium
and carbon. These two semiconductor materials have been used for electronics
applications in the past 20 years and the description of the thermal behavior is
still a controversy. The Chapter also compares different methods to calculate the
thermal conductivity in these materials and proposes a new formulation to per-
form the calculation. This new formulation is compared with experimental results.
Chapter Four deals with energy transport in low dimensional systems (1-d and
2-d) and identifies characteristics of the transport. The study of low dimensional
systems (1-d and 2-d) has become prominent because these systems are starting to
be present in applications related with nanotechnology. Different configurations
are studied to examine transport in these systems. The simplest low dimensional
system is a chain of atoms in 1-d allowing movement of the atom just in one di-
rection. A 2-d honeycomb array of the atoms such as graphene with movement
in three directions is also a candidate for study. Finally this work concludes with Chapter Five where the conclusions and future recommendations are given.
A good technical manuscript is like a mystery novel. At the beginning the author tells the reader what the mystery to solve is. Then all the previously known information to solve the mystery is presented. After that different theories to solve the mystery are proposed. Finally, it is found who the killer is. Here this sequence is followed. Previously it was discussed what this story was going to be about. It is time to show what the previous information available about the topic is.

2.1 Temperature description of heat conduction at the nano-scale

Heat conduction at the continuum scale is described by Fourier’s law given by

\[ \mathbf{q} = -\lambda \nabla T, \] (2.1)

where \( \mathbf{q} \) is the heat flux vector, \( \lambda \) is the thermal conductivity and \( T \) is the temperature. This constitutive law works properly to describe heat conduction at the macro scale, where the temperature is defined as the average energy of small regions. As described in the introduction Chapter, this model does not capture all the characteristics for scales where the characteristic time and length are at the same order of magnitude as the relaxation time and wave length of the phonons.
Phonons are the energy carriers in non metallic materials. They are the energy packages due to the vibrations of the atoms. Equation (2.1), also shows an infinite speed of the signal between the heat flux vector and the temperature gradient. This means that a heat flux perturbation is felt in the whole domain instantaneously. One of the first attempts to capture characteristics that Fourier’s law do not capture was proposed by Cattaneo [11] and Vernotte [12]. They proposed a constitutive model that takes into account a lag between the heat flux vector and the temperature gradient. This model does not present an infinite wave speed between heat flux and temperature gradient. The model is

\[ \mathbf{q} + \tau_R \frac{\partial \mathbf{q}}{\partial t} = -\lambda \nabla T, \quad (2.2) \]

where \( \tau_R \) is a lag time between the heat flux and the temperature gradient. These two previous models can be combined with conservation of energy and partial differential equations are obtained. Fourier’s law produces a parabolic equation, and Cattaneo’s model (2.2) produces a hyperbolic equation. In the context of heat conduction at the micro and nano-scale, Escobar et al. [13], proposed a time and space scale where Cattaneo’s model is valid. They found that it is valid for length scales larger than the mean free path of phonons and time scales comparable with the relaxation time of phonons. Besides the small range of applicability of the model, it has also been reported that the model is not compatible with the second law of thermodynamics [14, 15], and may produce a heat wave that travels from a cold spot to a hot spot. However Barletta and Zanchini [16] reported a time domain where the equation is in good agreement with the second law.

Tzou proposed a model that is similar to Cattaneo’s model [17–19]. The
constitutive equation proposed by Tzou is

\[ q + \tau_q \frac{\partial q}{\partial t} = -\lambda \left( \nabla T + \tau_T \frac{\partial}{\partial t} \nabla T \right), \]  

(2.3)

where \( \tau_q \) and \( \tau_T \) are phase lags. The difference between Tzou’s and Cattaneo’s model is that Tzou’s has also a relaxation time in the temperature gradient. The model was proposed for heat conduction at the micro-scale; however it has also been used at the nano-scale [20]. The model has two relaxation times, one in the heat flux vector and the second one in the temperature gradient. In this model the parabolic equation or the hyperbolic equation for temperature can be recovered using different values of the relaxation times. The model was compared with molecular dynamics simulations by Shiomi and Maruyama [20]. They compare the model with temperature distribution in a single wall carbon nanotube perturbed with a heat pulse at the middle of the tube. The model predicted the molecular dynamics simulations, while the hyperbolic equation does not.

These previous are constitutive models. A different strategy is to analyze the phonons as particles. An equation that describes phonon distribution is the Boltzmann equation. The equation is

\[ \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \mathbf{a} \cdot \frac{\partial f}{\partial \mathbf{v}} = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}, \]  

(2.4)

where \( f \) is the distribution function of the particles, \( \mathbf{v} \) is the velocity vector, and \( \mathbf{a} \) is the acceleration. The \( \mathbf{a} \cdot \frac{\partial f}{\partial \mathbf{v}} \) is the term due to an external field, and the \( \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} \) term is due to collisions between particles. This equation is used in transport at the nano-scale because phonons can be treated as particles, and they approximately follow this distribution. The distribution function \( f \) is the
number of phonons in the infinitesimal volume formed by the space and velocity space $dr \, dv$. It is common to approximate the collision term assuming that the particles relax to equilibrium with an exponential decay. The Boltzmann equation is a different strategy that allows capture of physics of the transport that the previous constitutive models may not capture.

Majumdar [21] proposed the equation of phonon radiative transfer (EPRT), based on the Boltzmann distribution equation. This model proposes a radiative transport of phonons between walls. A similar concept for intensity for photons using phonons is defined as [22]

$$I_\omega = \sum_p = \Phi \lambda \omega D(\omega),$$  \hspace{1cm} (2.5)

where $h$ is the Planck’s constant, $D(\omega)$ is the density of states and $p$ is the polarization. The EPRT is obtained by multiplying the Boltzmann equation (2.4) by $\Phi \lambda \omega D(\omega)$. The EPRT also assumes no external field and the relaxation time approximation. The EPRT is

$$\frac{1}{v} \frac{\partial I_\omega}{\partial t} + \mu \frac{\partial I_\omega}{\partial x} = \frac{I_0^0 - I_\omega}{v \tau},$$  \hspace{1cm} (2.6)

where $\mu$ is the cosine of the angle between the phonon propagation direction and the $x$ direction and $I_0^0$ is the equilibrium intensity corresponding to a black body intensity at temperatures below the Debye temperature. The Debye temperature is defined from the Debye approximation. The approximation assumes a linear dispersion relation of phonons [23]. The heat flux is calculated after the EPRT equation 2.6 is solved. The calculation of the heat flux from $I_\omega$ depends on the limit studied. Majumdar reported that at the macro-scale this model reduced to
Fourier's law. At the nano-scale, where the mean free path of the carriers is larger than the characteristic length, the transport is radiative. For the transient part he reported that the EPRT behaves as a wave. The hyperbolic heat equation can be derived from the EPRT in the limit where the characteristic nondimensional length is much smaller than one.

Chen [24, 25] also proposed a model based on the Boltzmann distribution equation. The distribution function $f$ of the Boltzmann equation is divided in two parts, the ballistic and the diffusive. The distribution function is the sum of ballistics and diffusive parts

$$f = f_b + f_m,$$  \hspace{1cm} (2.7)

where $f_b$ is the ballistic part and $f_m$ the diffusive. The equation for the ballistic part is

$$\frac{1}{|v|} \frac{\partial f_b}{\partial t} + \hat{\Omega} \cdot \nabla f_b = - \frac{f_b}{|v\tau|}.$$  \hspace{1cm} (2.8)

where $\hat{\Omega}$ is the unit vector in the direction of the carrier propagation. The diffusive part is

$$\frac{\partial f_m}{\partial t} + v \cdot \nabla f_m = - \frac{f_m - f_0}{\tau}.$$  \hspace{1cm} (2.9)

The ballistic part is the result of the transport between boundaries and the diffusive is the result of the transport of scattered and excited carriers. The temperature profiles reported in this work show a different behavior than Fourier’s law and Cattaneo’s equation. The solution of the Boltzmann transport equation can be a challenging problem due to the collision term and the dependence on seven
variables, three for position, three for velocity, and time. A numerical scheme to solve this equation was proposed by Escobar et al. [13]. Besides the novelty of the numerical scheme to solve the Boltzmann equation, this work compares the Boltzmann equation and shows that Fourier’s law and Cattaneo’s equation are specific cases recovered from the Boltzmann equation. As mentioned previously, Fourier and Cattaneo’s model are valid for different regimes. One of the conclusion of Escobar and co-workers is that the Boltzmann equation is able to capture the same physics as Fourier and Cattaneo (diffusion and wave-like), but also captures the physics of sub-continuum regimes that these models fail to capture. This conclusion is similar as the one reported by Majumdar [21].

The previous discussion showed that there are different models to describe heat conduction in temperature representation at different scales. Fourier describes conduction for scales where the the mean free path of phonons are much smaller than the characteristic length. For processes where the time scale is of the same order of magnitude as phonon relaxation time, Cattaneo’s is sufficient. A more general model is the Boltzmann equation that captures the physics at scales in the same order of magnitude as the mean free path of phonons and relaxation times, but also Fourier and Cattaneo are special cases of the Boltzmann equation.

2.2 Normal and anomalous diffusion in 1-d and 2-d systems at the nano-scale

The movement of the atoms in a lattice will produce energy, and this energy will be transported and transmitted throughout the lattice. Different studies to understand heat transport at the nano-scale that focused on the energy produced due to the movement of the atoms have been conducted. This dynamical approach is a different strategy than the previous models described, where in this case
the efforts are more focused in understanding under which condition diffusion is presented in a lattice of atoms.

The procedure followed to conduct these studies is the following. The equations of motion of the atoms in the lattice are solved using different potentials. The boundaries of the lattice are in contact with thermal reservoirs to impose a temperature gradient. Finally, with these conditions temperature profiles are obtained. These studies can be performed in 1-d chains of atoms or in 2-d lattices. As mentioned, the goal is to identify normal or anomalous diffusion in the lattice. For this discussion, anomalous diffusion is a process that does not follow a temperature distribution such as the one resulting from Fourier’s law. Lepri et al. [26] reported temperature profiles where it was evident that the steady state temperature distribution was not linear between the boundaries suggesting anomalous transport. Anomalous diffusion is reflected with a thermal conductivity that changes with length of the system. It is important to clarify thermal conductivity that depends on \( x \) versus a thermal conductivity that depends on size \( L \). Thermal conductivity that increases with size is not finite and this is a result of anomalous diffusion [27]. The calculation of the thermal conductivity from the dynamical simulations can be calculated with different procedures. Green-Kubo formula with equilibrium molecular dynamics is one option commonly used. This procedure will be explained in detail in future sections and Chapters. Also direct calculation from the temperature gradient and the heat flux is used.

Hu et al. [28] reported the validity of Fourier’s law by looking at the temperature profile of a 1-d chain using a harmonic potential. In the same study it was reported that an anharmonic potential does not obey Fourier’s law. The same authors [29] studied heat conduction in a 1-d chain in the Fermi-Pasta-Ulam (FPU)
and the discrete $\phi^4$ [30] models. The FPU model is a lattice of masses connected with weakly anharmonics springs. An external nonlinear field is added in the $\phi^4$ model. They found diffusion in the discrete $\phi^4$ model and anomalous diffusion using the Fermi-Pasta-Ulam (FPU) model. The conclusions were obtained with temperature distributions in real space. Lepri et al. [26, 31] have studied this problem extensively. In their first work, they studied the FPU model. The second work [26] is one of the most complete reports about the topic. In this work they analyze the breakdown of Fourier’s law related with size. Aoki et al. [32] studied 1-d chains and under which parameters they obey Fourier’s law. The energy diffusion of a diatomic chain was studied by Delfini et al. [33], and normal and anomalous diffusion were reported. A study in the heat conduction transport in 1-d and 2-d FPU chain and system respectively was performed by Dhar [27], once again anomalous transport were identified in these systems. One study that suggests anomalous heat conduction in 1-d chains was conducted by Li and Wang [34]. For 2-d systems, few previous works are found, as mentioned previously these studies were performed by Lepri et al. [26] and Dhar [27]. In both works, it was concluded that a divergent thermal conductivity depending in size is present in 2-d systems.

The main conclusion of all these previous studies is that there is a controversy still going on to describe transport at the nano-scale. Some models observed diffusion and some did not, depending on the potentials used and the non-linearity presented in the systems. However in general it can be concluded that small systems present anomalous diffusion reflected in the size dependent thermal conductivity. It is also important to be cautious when studying thermal transport at nano-scales, learning from this results that classical diffusive characteristics will
not describe the transport completely. There may be more behaviors than the
diffusive present in the transport. It is one of the goals of this work to identify
them.

2.3 Chaos in transport

One topic that is closely related with the previous section is chaos in the
transport. Chaos is a characteristic that might be present in dynamical systems.
The main characteristics of chaotic systems is that they are highly sensitive to
initial conditions. As explained previously it is a common practice to study the
transport by solving the dynamics of the atoms because the dynamics of the atoms
produce the energy transported. Then it is important to study if the systems are
chaotic or not, and this will provide more information in the understanding of
the transport. In the context of heat transport, this is important because efforts
have been conducted to relate diffusive behaviors in the transport with chaotic
systems. This relation will also be studied in this work.

Li et al. [35] suggested that there is no relation between chaos and normal or
anomalous diffusion. They calculated the Lyapunov exponents of three different
1-d channels where the Lyapunov exponents were zero and diffusive behavior was
observed. Modifications of the 1-d chain have been studied. Casati et al. [36]
proposed a many-body 1-d chain. The chain consists of hard body spheres, where
some of them are bonded with harmonic oscillators and some of them are free, the
so called “ding a ling model”. The system is non-linear and chaotic. They report
that Fourier’s law is obeyed in this system and therefore the conclusion that chaos
is important in diffusive transport. Later, Prosen and Robnik [37] reported similar
results as Casati et al. . Li and co-workers reported no relation between chaos
and the transport regime, however Casati et al. and Prosen and Robnik reported
that chaos is related with normal diffusion. In Chapter Four chaos will be tested
for a 1-d chain of atoms and for a 2-d sheet of graphene, and will be related with
observed behavior.

2.4 Thermal conductivity and molecular dynamics

The thermal conductivity of a material can be calculated using molecular
dynamics simulations. There are generally two different approaches used [38],
equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynam-
ics (NEMD). A third, less common approach called homogeneous non equilibrium
molecular dynamics (HNEMD) was used by Lukes and Zhong [39]. EMD is the nu-
merical solution of the equations of motion of the atoms of a material at constant
temperature. The difference with NEMD is that in NEMD the simulations are
performed under a temperature gradient. HNEMD solves the equation of motion
at constant temperature, but an external field is imposed to simulate the heat flow
without the presence of a temperature gradient. Equilibrium molecular dynam-
ics is used to calculate the displacements, velocities and forces of each individual
atom. The advantage of EMD is the use of periodic boundary conditions which
avoid boundary scattering. EMD has been used to calculate transport properties
of materials such as the thermal conductivity at the micro- and nano-scale by dif-
ferent authors, [38–45]. The calculation of the thermal conductivity using EMD
is done with the Green-Kubo formulation. The Green-Kubo formulation allows
for the calculation of the thermal conductivity of a system in equilibrium. The
derivation of the formulation is based in small perturbations in the temperature
of the system. The derivation is a well known procedure reported in text books
More details about this formulation is given in Chapter Three. The second procedure commonly used is NEMD; as explained a temperature gradient is imposed through the system and the calculation of the thermal conductivity is done directly from Fourier’s law, where the heat flux and the temperature gradient are known. The challenge in this procedure is the solution of the equations of motion with prescribed temperatures at the boundaries and the presence of a not uniform temperature field.

EMD and NEMD have been used to determine the thermal conductivity $\lambda$ of carbon nanotubes and other nano-scale materials. Che et al. [41] reported $\lambda$ values for a (10,10) carbon nanotube using EMD, while Berber et al. [40] found a higher value for a similar carbon nanotube using NEMD. Osman and Srivastava [50] found a different value for the same carbon nanotube with the same NEMD technique. Using NEMD, Maruyama [43] found that $\lambda$ increases linearly with the length of the nanotube, and this could be a possible cause of the discrepancy of the values reported earlier. Moreland et al. [51] also studied how $\lambda$ increased with the length of the nanotube. To date, there are still discrepancies found in the values obtained for the thermal conductivity of carbon nanotubes using EMD and NEMD. In other studies, NEMD has been utilized by Lukes and Tien [52], Abramson et al. [53], Daly et al. [54] to determine thermal conductivities of thin films and super lattices, while EMD has been used by Volz et al. [45] and Volz and Chen [44] for nanowires.

Using the results from EMD simulations, the Green-Kubo formula [55] is used to calculate the thermal conductivity $\lambda$. The Green-Kubo formula requires a quantity called the heat current $J$. The heat flux is the rate of heat per unit area. The heat current per unit volume is the heat flux. It is a vector quantity
and, as a consequence, has a direction. The behavior between atoms in a material is modeled with a potential that describes the interactions between them. The Tersoff potential is a potential that models the interactions of materials with covalent bonds such as semiconductors materials [56, 57]. Different formulations for the calculation of the heat current using the Tersoff potential are found in the literature and it is unclear which is most accurate. The first formulation using this potential was proposed by Li et al. [58], and was used to calculate the thermal conductivity of silicon carbide systems. A second formulation was proposed by Che et al. [41] to calculate the thermal conductivity of carbon-diamond like crystal. They reported different values depending on the size of the crystal. However, all the reported values are acceptable for the thermal conductivity of carbon. Dong et al. [59] proposed a different formulation to calculate the thermal conductivity of a germanium crystal. They reported values close to experimental values. Finally a theoretical work that does not include numerical calculations was done by Chen [60] who proposed a formulation of heat current using three body potentials such as the Tersoff potential. All these formulations are tested in Chapter Four.

2.5 Heat conduction in graphene

The study of heat conduction in graphene, in the literature, is mainly dominated with the estimation of the thermal conductivity of the material. Some theoretical work has focused on ballistic (rather than diffusive) thermal transport in graphene by calculating the thermal conductance (which is related to the thermal conductivity). Mingo and Broido [61] studied different carbon-based materials including nanotubes, graphite and graphene using the Landauer formalism assuming quasi-ballistic transport. They suggest that their calculations predict
the quantum limits of thermal conductance, and therefore the theoretical limits. While they do not explicitly state thermal conductance values for graphene, they do note that it is lower than that of single-walled carbon nanotubes (SWCNTs) at low temperature but that they are similar at room temperature and beyond. Saito et al. [62] also assumed ballistic transport by using the Landauer formalism in order to theoretically study the relative effects of the phonon and electron energy carriers. They showed that, in general, phonons are the primary conduction mechanism for graphene but that at low temperatures it is possible for the electron transport to become more significant than the phonon transport. To date the thermal conductivity of graphene has yet to be quantified definitively though it is understood that it is extremely high. Osman and Srivastava [50] calculated the thermal conductivity of different configurations of SWCNTs and graphene using non-equilibrium molecular dynamics (NEMD). They found the thermal conductivity of graphene to be approximately 1750 W/m·K and that beyond 400 K it decreased with temperature. One more calculation of the thermal conductivity using NEMD was done by Hu et al. [63]. They found a value of 2000 W/m·K for a graphene nanoribbon at 400 K. One group from the University of California-Riverside has used a novel, Raman-shift experiment to measure the thermal conductivity of graphene monolayers suspended between silicon dioxide posts [64, 65]. They irradiated the graphene with a laser, which served to heat the graphene, and the heat was transferred to heat sinks on the posts. They then measured the Raman-shift of the graphene sheet which is a function of the temperature rise due to the irradiation. Using a simple thermal analysis, they related this temperature rise (and measurable Raman-shift) to the thermal conductivity and reported a value of approximately 5000 W/m·K. They compared their
result with previous measurements for carbon nanotubes [66–68], and concluded that graphene has a higher thermal conductivity than carbon nanotubes. An accompanying, simplified order-of-magnitude analysis suggested their measured value was reasonable [65]. Cai et al. [69] reported a value of 2500 W/m·K for suspended graphene near 350 K and 1400 about 500 K. Even stacks of several graphene layers have also been shown to have high thermal conductivity; for 2 layers a value of 2800 W/m·K and for four layers 1300 W/m·K were reported by Ghosh et al. [70]. Seol et al. [71] reported a value of 600 Wm·K for graphene supported in silicon dioxide as well. Koh et al. [72] performed similar measurements with several layers, supported in silicon oxide and covered by a metal; they found that heat is mainly carried by phonons in these structures. The thermal conductance of graphene structures bridged with a graphene nanoribbon was studied by Huang et al. [73, 74], and they found that the thermal conductance of these unique structures was lower than homogeneous graphene. Table 2.1 summarizes recent results of the thermal conductivity of graphene. All these studies show the same trend of graphene as a good heat conductor with high values of the thermal conductivity compared with semiconductor bulk materials.
<table>
<thead>
<tr>
<th>Author</th>
<th>Material</th>
<th>Method</th>
<th>Temperature K</th>
<th>λ W/m·K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berber et al. [40]</td>
<td>graphene sheet</td>
<td>NEMD</td>
<td>300</td>
<td>≈ 6600</td>
</tr>
<tr>
<td>Osman and Srivastava [50]</td>
<td>graphene sheet</td>
<td>NEMD</td>
<td>300</td>
<td>1750</td>
</tr>
<tr>
<td>Hu et al. [63]</td>
<td>graphene sheet</td>
<td>NEMD</td>
<td>400</td>
<td>2000</td>
</tr>
<tr>
<td>Hu et al. [63]</td>
<td>graphene sheet with vacancies</td>
<td>NEMD</td>
<td>400</td>
<td>1200</td>
</tr>
<tr>
<td>Balandin et al. [64]</td>
<td>graphene sheet</td>
<td>Experimental</td>
<td>300</td>
<td>5000</td>
</tr>
<tr>
<td>Cai et al. [69]</td>
<td>suspended graphene</td>
<td>Experimental</td>
<td>350</td>
<td>2500</td>
</tr>
<tr>
<td>Cai et al. [69]</td>
<td>suspended graphene</td>
<td>Experimental</td>
<td>500</td>
<td>1400</td>
</tr>
<tr>
<td>Ghosh et al. [70]</td>
<td>two layers graphene</td>
<td>Experimental</td>
<td>300</td>
<td>2800</td>
</tr>
<tr>
<td>Ghosh et al. [70]</td>
<td>four layers graphene</td>
<td>Experimental</td>
<td>300</td>
<td>1300</td>
</tr>
<tr>
<td>Seol et al. [71]</td>
<td>Graphene supported in silicon dioxide</td>
<td>Experimental</td>
<td>300</td>
<td>600</td>
</tr>
</tbody>
</table>
2.5.1 Discussion about graphene as an effective heat conductor

Two questions arise from this previous studies. What are the main differences between 1-d, 2-d and 3-d structures? Why is graphene such a good heat conductor? The difference in the dimensionality can be identified analyzing the phonon dispersion relation.

Previously the concept of phonon was introduced; however, a detailed explanation of the concept is important. The simplest system to understand the concept is a 1-d chain of infinite atoms with equal masses. For an atom $n$ in the chain the equation of motion is

$$m \frac{d^2x_n}{dt^2} = k_1(x_{n-1} - 2x_n + x_{n+1}), \quad (2.10)$$

where $x$ is the position of the atom, $m$ is the mass, and $k_1$ is the spring constant. A solution of the following form is proposed to solve equation (2.10)

$$x_n = \hat{x} e^{i(nka - \omega t)}, \quad (2.11)$$

where $k$ is the wave vector, $a$ the lattice constant, and $\omega$ the frequency. This solution has the form of a traveling wave. Substituting the solution (2.11) in the equation (2.10) allows to find the dispersion relation given by

$$\omega = \sqrt{\frac{2k_1}{m} \left(1 - \cos ka\right)^{\frac{1}{2}}}. \quad (2.12)$$

Fig. 2.1 shows this relation. The group velocity is $\frac{d\omega}{dk}$. Phonons with high group velocity carry more heat. For the 1-d chain assuming a monoatomic chain, the dispersion relation has just one acoustic branch as shown in the figure, here the
transport is expected to be good due to the presence of just one branch and one dimension avoiding scattering events. From the figure it can also be observed that low frequency phonons have larger group velocity or slope. These phonons carry more heat due to the high group velocity.

For a 2-d structure such as graphene the dispersion relation has acoustic and optical branches [70, 75–78]. Because of the dimension there is one longitudinal acoustic (LA) branch and two transverse branches (TA, ZA). The ZA branch is the branch out of plane of the sheet. The contribution of this branch is small compared with the LA and the TA branches [71, 79]. The group velocity of this branch is small compared with the other two branches. In one of the more recent works, Ghosh and co-workers [70] reported the small slope (group velocity) of ZA for graphene and a slope almost zero for bilayer graphene confirming the 2-d
nature of the transport. This fact makes the transport in graphene nearly 2-d. Similar studies were reported for graphene nanoribbons. A graphene nanoribbon is a small graphene sheet where the edges of the sheet play an important role in the properties. For graphene nanoribbons, dispersion relations were reported by Yamada et al. [80], Huang et al. [74] and Gillen et al. [81]. In these works the small slope in the ZA branch is also observed. The pure 2-d transport in graphene is the reason why graphene shows higher values of thermal conductivity than bulk diamond. The transport in 3-d has LA, TA and ZA phonons therefore the occurrence of more scattering process within the phonons. In the last Chapter some complementary characteristics of the transport of graphene will be discussed. It will be shown how the energy is distributed in a graphene sheet after an initial perturbation.

2.6 Summary

These previous studies suggest the necessity of complementing the understanding of heat conduction in low dimensional systems without assuming a constitutive law. The works discussed previously assume a temperature gradient in the lattice. The thermal conductivity calculated assuming Fourier’s law describes conduction at those scales. A different strategy to study heat conduction without assuming a constitutive law will complement the description of the transport. Chapter Four describes the transport of kinetic energy in 1-d and 2-d lattices from the dynamics of the atoms. The work presented in this Chapter does not assume any constitutive law for the description.
CHAPTER 3
MOLECULAR DYNAMICS AND THERMAL CONDUCTIVITY

It is important to describe some of the techniques used to study heat transport at the atomic level. This Chapter is devoted to set the theoretical basis to study the thermal conductivity. Now is turn to study the transport in deep from the atomic level.

3.1 Molecular dynamics (MD)

Molecular dynamics is a computational technique that solves Newton’s equation of motion of each individual atom. Newton’s equation of atom $i$ in a material is

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j=1}^{n} \mathbf{F}_{ij},$$

(3.1)

where $m_i$ is the mass of atom $i$, $\mathbf{r}_i$ is the position of atom $i$, $t$ is time, $\mathbf{F}_{ij}$ is the force on atom $i$ because of atom $j$ and $n$ is the total number of atoms in the system. The summation is because the total force on atom $i$ is because of all the interactions of atom $i$ with the other atoms. The total force on atom $i$ due to all other atoms is given by

$$\mathbf{F}_i = -\sum_{j=1}^{n} \frac{dU_{ij}}{d\mathbf{r}_{ij}},$$

(3.2)

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ (same convention for the rest of this work), and $U_{ij}$ is the potential energy between atoms $i$ and $j$. 

24
Equations (3.1) and (3.2) can be solved with different numerical schemes, such as the Verlet and the Leapfrog schemes. Both of these methods are implicit, and a modification of the Verlet scheme called the velocity Verlet is commonly used. This modified scheme has third order of accuracy in both variables, the position and the velocity. The velocity Verlet scheme will be used here in the molecular dynamics simulation part because this method is good in preserving the energy of the system.

As mentioned in the Chapter Two, two different approaches are mainly used, EMD and NEMD. The numerical scheme of both approaches is the same, the difference is that EMD is at constant temperature and NEMD is under a temperature gradient. EMD is used because periodic boundary conditions can be imposed.

The initial conditions of the system are given after the system is equilibrated. The process of equilibration consists of randomly initializing the variables of the system and running the simulation until a Gaussian statistical distribution of the velocities of the atoms is reached.

Periodic boundary conditions are the most common in EMD because as mentioned boundary scattering is not present. A computational cell is defined for the material, and when one atom leaves one of the boundaries of the cell, the atom goes back into the material through the opposite boundary.

3.2 Interatomic potential

The interatomic potential is one of the most important quantities in the MD process. The correct choice of the potential is required for a good description of the material behavior.
3.2.1 Two-body potential

One of the most common potentials is the Lennard-Jones (LJ). This potential is mainly used to describe interactions within gases or liquids. The potential written in a general form is

\[ U_{ij} = 4\epsilon [f_R(r_{ij}) - f_A(r_{ij})], \]  

where \( U \) is the potential energy between atoms \( i \) and \( j \), \( \epsilon \) is the depth of the potential well, and \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The repulsive term is given by

\[ f_R(r_{ij}) = \left(\frac{\sigma}{r_{ij}}\right)^{12}, \]

and the attractive term is

\[ f_A(r_{ij}) = \left(\frac{\sigma}{r_{ij}}\right)^{6}, \]

where \( \sigma \) is a parameter. The total potential energy of the system is given by

\[ U = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} U_{ij}. \]

This is a two-body potential because the total potential energy of the system is the result of two-body interactions. When these two body interactions are calculated (i.e. the interaction of atom \( i \) with atom \( j \)), all the rest of the atoms in the system are ignored.

3.2.2 Tersoff potential

As Fig. 3.1(a) shows, for the LJ potential, the potential energy \( U_i \) of atom \( i \) is calculated from its interaction with atom \( j \), and the effect of any atom \( k \) on
the attraction or the repulsion between atoms \( i \) and \( j \) is negligible, because of the weakness of the bonds between those atoms. For this reason, the LJ potential is well-suited for liquids and gases but not for solids that have strong covalent bonds, such as semiconductors and carbon-based materials. The Tersoff potential, shown in Fig. 3.1(b), not only accounts for the interaction between atom \( i \) and its nearest neighbor \( j \) but also the interaction of \( i \) with all its neighbors \( k \).

The covalent bonds keep the geometry of the crystal of the material. The Tersoff potential is proposed to represent materials with covalent bonds and to represent the interactions between atoms that keep the crystal structure. The potential is given by

\[
U_{ij} = f_C(r_{ij})\left[f_R(r_{ij}) + \gamma_{ij}f_A(r_{ij})\right],
\]

(3.7)

\( f_R(r_{ij}) \) is a repulsive term, \( f_A(r_{ij}) \) is an attractive term and \( f_C(r_{ij}) \) is a cut-off function. The parameter \( \gamma_{ij} \) is a multi-body term that accounts for atom \( k \), and \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The multi-body term means that when the two-body interaction between atom \( i \) and atom \( j \) is calculated, the rest of the atoms of the system are not ignored. All the parameters in the next equations for the Tersoff potential are related to the specific material in question. The repulsive term is given by

\[
f_R(r_{ij}) = A_{ij} \exp(a_{ij}r_{ij}),
\]

(3.8)

where \( A_{ij} \) and \( a_{ij} \) are parameters. The attractive term is

\[
f_A(r_{ij}) = -B_{ij} \exp(b_{ij}r_{ij}),
\]

(3.9)
and similarly $B_{ij}$ and $b_{ij}$ are parameters. The cut-off term is given by

$$f_{C}(r_{ij}) = \begin{cases} 1 & : r_{ij} < R_{ij}, \\ \frac{1}{2} + \frac{1}{2} \cos \left[ \pi \frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}} \right] & : R_{ij} < r_{ij} < S_{ij}, \\ 0 & : r_{ij} > S_{ij}; \end{cases}$$

(3.10)

where $R_{ij}$ and $S_{ij}$ are parameters, these parameters are chosen to include the first neighboring shell in the crystal [56] and they have length units.

The multi-body term $\gamma_{ij}$ takes into account the interactions of atoms $i$ and $j$ with the all other atoms in the lattice. The term is given by

$$\gamma_{ij} = \chi_{ij}(1 + \beta_{i} n_{i} \zeta_{ij}^{n_{i}}) \frac{1}{\pi n_{i}},$$

(3.11)

where $\chi_{ij}$, $\beta_{i}$ and $n_{i}$ are parameters. The $\zeta_{ij}$ term is defined as

$$\zeta_{ij} = \sum_{k \neq i,j} f_{C}(r_{ik}) \omega_{ik} g(\theta_{ijk}),$$

(3.12)

where $\omega_{ik}$ is a parameter. The $g(\theta_{ijk})$ term is calculated as

$$g(\theta_{ijk}) = 1 + \frac{c_{i}^{2}}{d_{i}^{2}} - \frac{c_{i}^{2}}{d_{i}^{2} + (h_{i} - \cos \theta_{ijk})^{2}},$$

(3.13)

where $\theta_{ijk}$ is the angle formed between the bonds of atoms $ij$ and $ik$, and the rest of the terms are parameters. The parameters are given by Tersoff [57] for germanium and carbon. The values of the parameters are obtained from a fitting process of theoretical calculations. The numerical values of the parameters are shown in Table 3.1.

The Tersoff potential is a modified two-body potential because the $\gamma_{ij}$ factor
### Table 3.1

NUMERICAL VALUES FOR MATERIAL PARAMETERS TERSOFF POTENTIAL. CARBON AND GERMANIUM.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Carbon</th>
<th>Germanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (eV)</td>
<td>$1.3936 \times 10^3$</td>
<td>$1.769 \times 10^3$</td>
</tr>
<tr>
<td>B (eV)</td>
<td>$3.467 \times 10^2$</td>
<td>$4.1923 \times 10^2$</td>
</tr>
<tr>
<td>$\lambda$ (Å$^{-1}$)</td>
<td>3.4879</td>
<td>2.4451</td>
</tr>
<tr>
<td>$\mu$ (Å$^{-1}$)</td>
<td>2.2119</td>
<td>1.7047</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$1.5724 \times 10^{-7}$</td>
<td>$9.0166 \times 10^{-7}$</td>
</tr>
<tr>
<td>n</td>
<td>$7.2751 \times 10^{-1}$</td>
<td>$7.5627 \times 10^{-1}$</td>
</tr>
<tr>
<td>c</td>
<td>$3.8049 \times 10^4$</td>
<td>$1.0643 \times 10^5$</td>
</tr>
<tr>
<td>d</td>
<td>4.384</td>
<td>1.5652 $\times 10^4$</td>
</tr>
<tr>
<td>h</td>
<td>$-5.7058 \times 10^{-1}$</td>
<td>$-4.3884 \times 10^{-1}$</td>
</tr>
<tr>
<td>R (Å)</td>
<td>1.8</td>
<td>2.8</td>
</tr>
<tr>
<td>S (Å)</td>
<td>2.1</td>
<td>3.1</td>
</tr>
</tbody>
</table>
in equation (3.11) takes into account interactions with all the rest of the atoms through the $\zeta_{ij}$ term, equation (3.12). It is a two-body potential that takes into account the non-local environment (atom k) when defining the potential energy between atom i and atom j. The local environment is the atoms i and j. The Tersoff potential is going to be referred as a modified two-body potential to differentiate with a classical two-body potential such as the LJ. Ultimately, the Tersoff potential more accurately captures the physics of the materials of interest, germanium and carbon.

3.2.3 Green-Kubo formula for thermal conductivity

The Green-Kubo formula will be used to calculate the thermal conductivity ($\lambda$). The derivation of the formula assumes the validity of Fourier’s law [23]. The formula relates the thermal conductivity with the fluctuations of the heat current linearly. The linear relation results from Fourier’s law. The formula is derived for systems at equilibrium; however in the derivation the gradient is not of the temperature but of a small disturbance in the temperature. The gradient is in
a small thermal disturbance of the temperature $\delta T$. It is also assumed that the system is still in equilibrium after the small disturbance. The formula is given by

$$\lambda = \frac{1}{3Vk_bT^2} \int_0^\infty \langle J(t) J(0) \rangle \, dt,$$  \hspace{1cm} (3.14)

where $V$ is the volume of the material, $k_b$ is the Boltzmann constant, $T$ is the temperature and $J$ is the heat current. The heat current is defined by

$$J = \int_V j \, dV,$$ \hspace{1cm} (3.15)

where $j$ is the heat flux. The angular brackets denote the autocorrelation function defined by

$$\langle J(t + \Delta t) J(t) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau J(t + \Delta t) J(t) \, dt,$$ \hspace{1cm} (3.16)

where $\Delta t$ is a time delay over the origin. The autocorrelation function describes the relation of a variable at some time with the same variable at some time lag, sampling all possible origins, that is why the integration is over the time and not the time delay. This relation describes the fluctuation of the variable, in this case the heat current. The physical meaning of the fluctuation is the relation in time of the variable, i.e. how much a variable is related with the same variable at different time.

The discrete representation of equation (3.14) is

$$\lambda = \frac{1}{3Vk_bT^2} \sum_{m=0}^M \frac{1}{N-m} \sum_{n=1}^{N-m} J(n+m)J(n),$$ \hspace{1cm} (3.17)

where $N$ is the total number of time steps in the simulation, $M$ is a suitably large number to represent the integration up to infinity, constrained by $M < N$. 
One of the main topics of this work is the heat current, which has been derived for the classic two-body LJ [23, 82]. However, different definitions for \( J \) are found when using the Tersoff potential [41, 58–60]. The differences are in how they each account for the multi-body \( \gamma_{ij} \) factor. In the LJ potential, the derivation of heat current depends only on the particles \( i \) and \( j \). In the Tersoff, the derivation has to take into account \( i, j \) and \( k \) because of \( \gamma_{ij} \). In the next sections, the formulations available are presented.

3.3 Heat current formulations

EMD data at the molecular scale must be related somehow with the heat current at the continuum scale. If one can calculate \( J \) from the computational information, one can then use equation (3.17) to calculate the bulk thermal conductivity \( \lambda \). In the following, the differences between current approaches to calculating \( J \) will be identified and discussed.

Generally, the heat current may be broken up into two parts

\[
J = J_{\text{kin}} + J_{\text{pot}}.
\]

\( J_{\text{kin}} \) is the transport of the kinetic energy of the atoms, while \( J_{\text{pot}} \) is that of the potential energy.
3.3.1 Formulation A

Hardy [83] proposed a flux operator for a lattice using a quantum mechanics context. The Hamiltonian for the lattice is

\[ H = \sum_{i=1}^{n} \epsilon_i, \]

where \( \epsilon_i \) is the internal energy of atom \( i \)

\[ \epsilon_i = \frac{1}{2} m_i v_i^2 + U_i, \]  \(3.18\)

and \( m_i \) is the mass of atom \( i \), \( v_i \) is the velocity of atom \( i \), \( v_i = |v_i| \), and \( U_i \) is the potential energy of atom \( i \). From this Hamiltonian (see details in [83]), the heat flux operator \( S = J/V \) is obtained where

\[ S = \frac{1}{2V} \left\{ \sum_{i=1}^{n} v_i \left( \frac{1}{2} m_i v_i^2 + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{i\hbar} \left[ \frac{1}{2} m_i v_i^2, U_j \right] \right\} + H.c. \]  \(3.19\)

The commutator \([A, B] = AB - BA\), the \( i \) that is not an index is the imaginary number, \( \hbar \) is the reduced Planck’s constant, and \( n \) is the total number of atoms in the system. The Hermitian conjugate, indicated by \( H.c. \), is the transpose of the complex conjugate.

In the classical limit \( \frac{i}{\hbar} \left[ m_i v_i, U_j \right] \) is replaced by \( \partial U_j/\partial r_i \) and \( H.c. \) by the complex conjugate [83]. The heat flux operator for a lattice then becomes

\[ S = \frac{1}{V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_j - r_i) v_i \cdot \frac{\partial U_j}{\partial r_i} \right\}. \]  \(3.20\)

where the momentum \( p = mv \), \( p = |p| \) and the relation \([AB, C] = A[B, C] + \)
[A, C]B have been used. Appendix A explain in detail the procedure to get (3.20) from (3.19).

The heat current is obtained by simply multiplying this quantity by $V$, and an equation is obtained that is valid for any $n$-body potential including Tersoff

\[
J_{\text{kin}} = \sum_{i=1}^{n} v_i \epsilon_i \quad (3.21a)
\]

\[
J_{\text{pot}} = \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij} \left( \frac{\partial \epsilon_i}{\partial r_j} \cdot v_j \right), \quad (3.21b)
\]

where

\[
r_{ij} = r_i - r_j. \quad (3.22)
\]

Dong et al. [59] used this approach to calculate the thermal conductivity of germanium.

When implementing this Formulation, it is necessary to share the potential energy $U_{ij}$ between atoms $i$ and $j$. The general practice is to share it equally, that is $U_i = \frac{1}{2} \sum_{j=1}^{n} U_{ij}$. This approximation has been made here.

3.3.2 Formulation B

Li et al. [58] proposed using an expanded form of Hardy’s formulation when they calculated $\lambda$ for silicon carbide ($\beta$-SiC). In their work, they suggested that the potential term, Eq. (3.21)b, be expanded to formally include both the interaction of atom $i$ with atom $j$ and the interaction with all other atoms $k$, reflecting the modified two-body nature of the Tersoff potential. This results in a modification to the potential term where the contribution of the interaction of atom $i$ with
atom \( j \) and of atom \( i \) with atom \( k \) is

\[
\mathbf{r}_{ij} \left[ \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_j} \left( \frac{U_{ij}}{2} \right) \cdot \mathbf{v}_j \right] + \mathbf{r}_{ik} \left[ \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_k} \left( \frac{U_{ij}}{2} \right) \cdot \mathbf{v}_k \right],
\]

and a second contribution is the interaction of atom \( j \) with atom \( i \) and atom \( j \) with atom \( k \) given by

\[
\mathbf{r}_{ji} \left[ \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_i} \left( \frac{U_{ij}}{2} \right) \cdot \mathbf{v}_i \right] + \mathbf{r}_{jk} \left[ \frac{1}{2} \frac{\partial}{\partial \mathbf{r}_k} \left( \frac{U_{ij}}{2} \right) \cdot \mathbf{v}_k \right].
\]

The potential term is then obtained by adding these two contributions, and summing over all the interactions between \( i \) and \( j \) and \( i, j, k \) [84] that participate in the system to give

\[
\mathbf{J}_{\text{pot}} = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \left[ \frac{1}{2} \mathbf{r}_{ji} \left( -\frac{1}{2} \frac{\partial U_{ij}}{\partial \mathbf{r}_j} \cdot \mathbf{v}_j + \frac{1}{2} \frac{\partial U_{ij}}{\partial \mathbf{r}_i} \cdot \mathbf{v}_i \right) - \sum_{k \neq i,j}^{n} \frac{1}{2} (\mathbf{r}_{jk} - \mathbf{r}_{ki}) \left( -\frac{1}{2} \frac{\partial U_{ij}}{\partial \mathbf{r}_k} \cdot \mathbf{v}_k \right) \right].
\]

(3.23)

Compared to Eq. (3.21)b, \( \mathbf{J}_{\text{pot}} \) includes a summation over all \( k \) that explicitly accounts for interactions between atoms \( i, j, k \). The kinetic term \( \mathbf{J}_{\text{kin}} \) remains the same as in Eq. (3.21)a.

3.3.3 Formulation C

Che et al. [41] calculated the thermal conductivity of carbon using the Tersoff potential and the Green-Kubo formula, where they defined the heat current as the change in time of the energy moment,

\[
\mathbf{J} = \frac{d}{dt} \sum_{i=1}^{n} \mathbf{r}_i \epsilon_i.
\]

(3.24)
They suggest that, after some algebra, the kinetic term is the same as in Eq. (3.21)b but the potential term is

$$J_{\text{pot}} = -\frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{l=1}^{n} r_{ik} \left( \frac{\partial U_{kl}}{\partial r_{ij}} \cdot v_i \right).$$  

(3.25)

Eq. (3.25) has four indexes, but they can have the same value, (e.g., $i = l$) so this does not imply that they treat the Tersoff as a four-body interaction.

The present author also began with Eq. (3.24), but derived a different form of the potential term. The detailed derivation is presented in Appendix B. Using Eqs. (3.18) and (3.22), $mdv_i/dt = -\sum_{j=1}^{n} \partial U_{ij}/\partial r_{ij}$, and $v_i = dr_i/dt$, the potential term becomes

$$J_{\text{pot}} = -\sum_{i=1}^{n} r_i \left( \sum_{j=1}^{n} \frac{\partial U_{ij}}{dr_{ij}} \cdot v_i \right) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left( r_i \frac{\partial U_{ij}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial t} + \sum_{k\neq i,j}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ik}} \frac{\partial r_{ik}}{\partial t} \right),$$  

(3.26)

Note that the symmetry relation $\partial U_{ij}/\partial r_{ij} = -\partial U_{ji}/\partial r_{ji}$, appropriate only for a true two-body potential such as the LJ, has not been invoked. Equation (3.26), like Eq. (3.23), also includes a summation over all $k$ that explicitly accounts for interactions between atoms $i$, $j$, and $k$. Both Eq. (3.25), which will be referred to as Formulation C$_a$, and the present derivation Eq. (3.26), which is Formulation C$_b$, will be explored here. It must be emphasized that the former is from the literature and the latter is a new result; they are different and one cannot be reduced to the other.
3.3.4 Formulation D

In a theoretical work that did not include EMD results, Chen [60] proposed that

$$J_{\text{kin}} = -\sum_{i=1}^{n} v_i \left( \frac{1}{2} m v_i^2 + U_i \right) \delta(r_i - x),$$

$$J_{\text{pot}} = \frac{1}{2} \int_0^1 \sum_{i=1}^{n} \sum_{j \neq i} \sum_{k \neq i,j} \left[ r_{ij} \frac{\partial U_{ij}}{\partial r_j} \cdot v_j \delta(r_i \xi + r_j (1 - \xi) - x) + r_{ik} \frac{\partial U_{ij}}{\partial r_k} \cdot v_k \delta(r_i \xi + r_k (1 - \xi) - x) \right] d\xi,$$

where $\delta$ is the delta function and $\xi$ is an integration variable. In the form of a generalized equation, the heat current is obtained using

$$\int_0^1 \delta(r_k \xi + r_i (1 - \xi) - x) d\xi = \sum_{n=1}^{\infty} \frac{1}{n!} (r_{kl} \cdot \nabla x)^{n-1} \delta(r_k - x).$$

For practical implementation, the zeroth order approximation of the series is used, giving

$$J = -\sum_{i=1}^{n} v_i \epsilon_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j \neq i} \sum_{k \neq i,j} \left( r_{ij} \frac{\partial U_{ij}}{\partial r_j} \cdot v_j + r_{ik} \frac{\partial U_{ij}}{\partial r_k} \cdot v_k \right). \quad (3.27)$$

Note that the potential term includes two interactions - those between atoms $i$ and $j$ ($i/j$) and those between atoms $i$, $j$, and $k$ ($i/j/k$). However, by including the summation over $k$ outside the parenthesis, a multiplication of $k$ times the $i/j$ interaction is included, which leads to a significant over prediction of the thermal conductivity and appears to have no physical basis. After discussions with the
original author [85], it was agreed that the summation over $k$ to explicitly account for interactions between atoms $i$, $j$, and $k$ should be in the parentheses. The corrected form of Eq. (3.27) therefore becomes

$$ J = -\sum_{i=1}^{n} v_i \epsilon_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j \neq i}^{n} \left( r_{ij} \frac{\partial U_{ij}}{\partial r_j} \cdot v_j + \sum_{k \neq i, j}^{n} r_{ik} \frac{\partial U_{ij}}{\partial r_k} \cdot v_k \right), $$

(3.28)

This form is similar to Eqs. (3.23) and (3.26) in the way the $i/j/k$ interaction is handled. However, Eq. (3.28), which will be implemented as Formulation D, has both a different potential term and kinetic term from the earlier Formulations, whereas Formulations A, B, C$_a$, and C$_b$ all derived a common kinetic term.

3.4 Implementation

3.4.1 Verification

In order to verify the correct implementation of the computer codes that used the different Formulations to calculate the heat current, a toy problem was designed. This consisted of solving a system of three masses. It is possible to expand algebraically all the terms in each of the Formulations, where the indexes in the sums run from one to three. Assumptions, such as using the same value of velocities in one component or the same position of the masses in one component, were imposed to eliminate terms and simplify the result. The numerical result of the analytical expansion of the toy problem and the numerical result of the computer codes using the same conditions were compared. The same results were obtained, giving confidence that each of the Formulations was correctly implemented into computer codes for this study.
3.4.2 Molecular dynamics simulation parameters

Two model systems, diamond-like germanium and carbon, were studied to explore the validity of each formulation. The EMD simulations were performed using the software DL POLY [86] with the velocity Verlet scheme to obtain the displacements and velocities of the atoms in the lattice. The diamond-like crystal structure for germanium and carbon is face-centered cubic (fcc) with four interior atoms located along the main cube diagonals [87]. The diamond-like unit cell has 8 atoms, and a crystal with 4 units cell per side (512 atoms total, Fig. 3.2) was simulated. The system was first equilibrated using a time step of 1 fs for 100 ps, and then the simulation continued for a further 1500 ps. The ensemble was at constant energy ($nve$), the temperature was 300 K, and periodic boundary conditions were used.
The parameters used for the Tersoff potential for both germanium and carbon are the ones suggested in [57] listed in table 3.1. In order to confirm that the DL POLY EMD simulation was correctly implemented, the energy of the system was calculated at each time step using an in-house code. Constant energy for both germanium and carbon EMD simulations was confirmed. Figures 3.3 and 3.4 show the normalized difference between the energy at each time step and the average energy in time $\Delta \epsilon = (\epsilon(t) - \bar{\epsilon})/\bar{\epsilon}$. The energy at each time step should be very near the average energy ($\Delta \epsilon \approx 0$) due to the constant energy ensemble ($\epsilon(t) \approx \bar{\epsilon}$). This is confirmed in figures 3.3 and 3.4, verifying the correct simulation of the system for the $nve$ ensemble. The total energy for germanium is $-1931$ eV and for carbon it is $-3761.6$ eV. After the simulation, the heat current was calculated using formulations A through D.

3.4.3 Autocorrelation of heat current

For each of the Formulations, the autocorrelation $R_{JJ}$ was calculated. Fig. 3.5 shows a representative plot for germanium using Formulation A. It is clear that the autocorrelation has high frequency content, and it is questionable whether this represents numerical noise or real physics. As a first approximation, it can be assumed that the highest physical frequency in the system is the ‘natural frequency’ that exists because of the spring-like bond between two adjacent atoms. The spring constant can be approximated by $C = d^2U/dx^2|_{x=q}$, where $U$ is the potential energy of one atom, and $q$ is the lattice constant. The natural frequency of the system is therefore given by $\Omega = \sqrt{C/m} = \sqrt{a_{ij}^2 A_{ij}e^{-a_{ij}q}/m}$ for the Tersoff potential.

Using parameters for germanium and carbon, the natural frequencies were
Figure 3.3. Constant energy of the system for the simulation of germanium.
Figure 3.4. Constant energy of the system for the simulation of carbon.
Figure 3.5. Autocorrelation in germanium for Formulation A: unfiltered autocorrelation.

calculated to be 1.17 and 7.3 THz, respectively. These values were used as cut-off frequencies for a low-pass filter, where all content above these frequencies in Fig. 3.5 was assumed to be due to numerical fluctuations and not due to physical phenomena. Fig. 3.6 shows the result of the filtered autocorrelation, and an expected initial decay is observed. Fig. 3.7 shows a comparison of the unfiltered and filtered autocorrelations over a small period of the simulation. The filtered signal shows some amplitude loss, but it is also smoother and without abrupt high frequency changes. This filter was implemented for all Formulations for both germanium and carbon, and similar trends were observed.
Figure 3.6. Autocorrelation in germanium for Formulation A: filtered autocorrelation.
Figure 3.7. Autocorrelation in germanium for Formulation A: comparison of original signal (dashed line) and filtered signal (solid line).
3.5 Results

3.5.1 Autocorrelation for germanium

In the filtered autocorrelation of germanium, two different behaviors were observed for all five different Formulations A, B, C\textsubscript{a}, C\textsubscript{b}, and D. At short times, the autocorrelation has an exponential decay, which is typical for diffusion behavior. However, for long times there appears to be a slow wave-like behavior. The short-time diffusion behavior is the one required to calculate the thermal conductivity, because a diffusive behavior is assumed in the Green-Kubo formula based on Fourier’s law. Therefore, an exponential fitting function of the form $y(t) = D \exp(Et)$, where $D$ and $E$ are fitting parameters, was used to fit the filtered signal over the period of time where the diffusive behavior was observed. The cut-off time for the fit was determined by inspection, though different approaches to determining the cut-off of curve fits to autocorrelations have been employed by others \cite{58}, \cite{88}. The exponential decay in the filtered autocorrelation for Formulation A is shown in Fig. 3.8, and a comparison of both curves, the filtered signal and the exponential fit, is shown in Fig. 3.9. The same characteristics were observed for all other Formulations, and exponential fits were applied. Ultimately, the filtering and curve-fitting did not significantly impact the calculated values of the thermal conductivity. A comparison of calculated $\lambda$ using the raw signal and the filtered and curve-fit signal showed that, though final values changed, they were on the same order of magnitude.

Across all Formulations A-D, the order of magnitude of the filtered autocorrelations were similar. For A, B, C\textsubscript{a}, C\textsubscript{b}, and D they were $10^{-31}$, $10^{-30}$, $10^{-30}$, $10^{-31}$, and $10^{-31}$ (Wm/K)$^2$, respectively, and the similarity leads to similar, though not identical, calculations of $\lambda$, as shown later. (Note that if Eq. (3.27) was imple-
Figure 3.8. Exponential decay in the filtered autocorrelation in germanium for Formulation A.
Figure 3.9. Comparison of the filtered signal (labeled F) to the exponential fit (labeled E).
Figure 3.10. Filtered autocorrelations of heat current in germanium Formulation A.

mented as Formulation D, the order of magnitude for the autocorrelation would have been $10^{-25}$ leading to an overprediction of $\lambda$ by a few orders of magnitude). Figures 3.10, 3.11, 3.12, 3.13 and 3.14 shows the filtered autocorrelations for the different formulations.

3.5.2 Autocorrelation for carbon

An exponential fitting function was also applied to the autocorrelations of all the Formulations for the carbon simulations. Again, a diffusive behavior was observed in all cases. Fig. 3.15 shows a representative exponential fitting of the filtered signal for Formulation A. For Formulation $C_\alpha$ the integration was performed
Figure 3.11. Filtered autocorrelations of heat current in germanium
Formulation B.
Figure 3.12. Filtered autocorrelations of heat current in germanium
Formulation $C_a$
Figure 3.13. Filtered autocorrelations of heat current in germanium
Formulation $C_b$
Figure 3.14. Filtered autocorrelations of heat current in germanium
Formulation D.
Figure 3.15. Comparison of the filtered autocorrelation signal (labeled F) to the exponential fit (labeled E) for carbon using Formulation A.

in the filtered signal without applying an exponential function. The filtered signals are shown in Figures 3.16, 3.17, 3.18, 3.19, and 3.20.

3.5.3 Thermal conductivity

After calculating the autocorrelation of $J$, filtering this signal, and fitting this new signal to an exponential decay, $\lambda$ was determined using Eq. (3.17) as listed in Table 3.2. All formulations, A, B, $C_a$, $C_b$, and D, are in fairly good agreement with the experimental values. For germanium, Formulations A, $C_a$, $C_b$, and D while all being on the right order of magnitude, underpredict the experimental values, and Formulation B overpredicts. This can be attributed to the integration
Figure 3.16. Filtered autocorrelation of heat current in carbon for Formulations A.
Figure 3.17. Filtered autocorrelation of heat current in carbon for Formulation B
Figure 3.18. Filtered autocorrelation of heat current in carbon for Formulation C_a.
Figure 3.19. Filtered autocorrelation of heat current in carbon for Formulation C_b.
Figure 3.20. Filtered autocorrelation of heat current in carbon for Formulation D.
TABLE 3.2

THERMAL CONDUCTIVITY OF GERMANIUM AND CARBON
FOR THE DIFFERENT FORMULATIONS COMPARED WITH
EXPERIMENTAL RESULTS.

<table>
<thead>
<tr>
<th>Material</th>
<th>A</th>
<th>B</th>
<th>C_a</th>
<th>C_b</th>
<th>D</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>germanium</td>
<td>29</td>
<td>123</td>
<td>46</td>
<td>14</td>
<td>17</td>
<td>62 [89, 90]</td>
</tr>
<tr>
<td>carbon</td>
<td>922</td>
<td>4482</td>
<td>1472</td>
<td>1552</td>
<td>2207</td>
<td>900–2000 [91]</td>
</tr>
</tbody>
</table>

of the fitted function to the filtered signal, because one of the costs of the filter was a reduction in the amplitude. This is not readily apparent in the predictions for carbon because the experimental values of the thermal conductivity reported in the literature have a range from 900 to 2000 W/m·K.

3.6 Discussion

As shown in Table 3.2, Formulations A, B, C_a, C_b, and D all produce λ values on the same order of magnitude as the experimental values, however, it should be noted that each predicted value is different. That is, from the perspective of accurately predicting thermal conductivity, it is unclear which Formulation is correct (or most correct). For instance, Formulation A does not explicitly account for i/j/k interactions because those interactions are incorporated within the potential itself and therefore do not need to be explicitly incorporated in the
formulation. Formulations B, C\textsubscript{b}, and D, on the other hand, do explicitly account for these interactions (and Formulation C\textsubscript{a} does as well, though in a much different manner), with little impact on the final result. It has been suggested that the definition of heat current in Eq. (3.24), which is the basis for Formulations C\textsubscript{a} and C\textsubscript{b}, is not correct for systems with periodic boundary conditions such as those used in EMD [46], but it is not definitively clear that these formulations are necessarily incorrect. One challenge, though, encountered with Formulations B, C\textsubscript{a} and C\textsubscript{b} is that they require rederiving the heat current for the specific potential of interest (the Tersoff potential here), which, as shown by the difference between Formulations C\textsubscript{a} and C\textsubscript{b}, can result in a lack of agreement. As for Formulation D, the original formulation obtained is not practical for MD implementation, and an approximation using the first term of an infinite series must be used, and it is again unclear to what extent this impacts the solution. The derivation of Formulation A is essentially Hardy’s formulation, which sets the Hamiltonian as an operator that is the addition of the kinetic energy and the potential energy leading to the heat flux. In this way, it could be argued that Formulation A is derived from first principles, and it has the advantage that it is applicable for any potential without requiring special modification.

3.7 Conclusions

It is an ongoing hurdle in the physics and engineering communities to establish a clear path from molecular simulation data to physical properties such as the thermal conductivity, and the challenge of extracting bulk material properties from molecular information remains. This work demonstrates that there is no clear, single technique for the heat current - many variations exist in the literature
and these all are fairly accurate. From a practical standpoint, Formulation A is easy to implement, accurate, and has the advantage that any potential can be used in the EMD simulations. For this reason, Formulation A appears to be the strongest candidate when using EMD and the Green-Kubo formula to predict thermal conductivity. However, much more work is required to clearly establish how to correctly calculate the heat current.
CHAPTER 4

TRANSPORT OF ENERGY IN 1-D AND 2-D SYSTEMS

The goal of this Chapter is to compare transport of kinetic energy between atoms in 1-d structures and 2-d structures. In the previous Chapter the thermal conductivity of crystals was calculated from molecular dynamics simulations. The validity of Fourier’s law was assumed to calculate the property. In this Chapter the dynamics of the atoms will be studied. Fourier’s law will not be assumed to describe the transport as in the previous Chapter. Wave-like and diffusive characteristics of the transport will try to be identified in the two different structures. To compare these characteristics, a proposed modified Cattaneo’s equation will be used. Cattaneo’s Modified equation has a tuning parameter that allows for recovering the wave equation, the diffusion equation, or a combination of both. It is not the intent of this Chapter to use this equation to model the transport, it is just used as a comparison to describe the transport.

4.1 Theoretical background

4.1.1 Modified Cattaneo’s equation

A modification of the Cattaneo equation [11, 12] in 1-d is proposed

\[ \frac{\partial^2 C}{\partial t^2} + p \frac{\partial C}{\partial t} = (1 + p) \frac{\partial^2 C}{\partial x^2}, \]  

(4.1)
where $C$ is a scalar and $p$ is an arbitrary variable. The $p$ variable is introduced to recover different forms of the equation. For $p \gg 1$, the diffusion equation is recovered. Whereas for $p \rightarrow 0$, the wave equation is recovered. Both behaviors, diffusive + wave-like, can be present in the transport of $C$ using different values of $p$. To analyze equation (4.1) the following initial conditions are proposed

$$C(x, t = 0) = \delta(x - x_0),$$  \hspace{1cm} (4.2)$$

$$\frac{dC}{dt}(x, t = 0) = 0,$$  \hspace{1cm} (4.3)$$

and periodic boundary conditions imposed

$$C(x = 0, t) = C(x = L, t),$$  \hspace{1cm} (4.4)$$

where $L$ is the total length of the domain, and the delta function will be injected in the middle of the domain $x_0 = L/2$. The proposed initial and boundary conditions allowed for solving this equation numerically using finite difference methods. The discretized equation is shown in Appendix E.

The first behavior recovered from the Modified Cattaneo’s equation is the wave-like, $p = 0$. The solution in time for $C$ at $x = L/2$ is shown in Fig. 4.1 (a). In the next figures the quantity plotted is $C^2$; this is because this quantity will be compared with kinetic energy that must be a positive quantity. In the figure, wave-like behavior is observed. Up to $t = 0.1$ arbitrary units of time (au) the wave has one frequency. After the initial wave travels the whole domain, and because of the periodic boundary conditions, the wave hits $x = L/2$ again with a different phase. This is reflected by the different frequencies after 0.1 au. The wave-like
behavior is present for all the time. The next stage to test the equation is \( p = 1 \) that adds some damping to the wave. It can be observed in equation (4.1) that increasing \( p \) will increase the wave speed given by \( \sqrt{1 + p} \), compared with \( p = 0 \), where the wave speed was 1 and for this case is \( \sqrt{2} \). This is observed in Fig. 4.1 (b). This figure shows a similar behavior as Fig. 4.1 (a) with the difference previously mentioned in the wave speed. The wave travels the whole domain in approximately 0.07 au, compared with approximately 0.1 au for \( p = 0 \). Increasing from \( p = 0 \) to \( p = 1 \), still results in a wave-like behavior. The effect of the combination of wave-like + diffusive is more evident for \( p = 10 \) shown in Fig. 4.1 (c). In this figure a wave-like decaying behavior up to 0.03 au is observed. After that the initial wave hits the initial perturbed point. However the recovered wave slowly decays in a wave with smaller amplitude up to 0.3 au. This figure describes the combination of the two behaviors where the wave-like behavior diffuses slowly with time. A more diffusive transport is observed for \( p = 100 \), Fig. 4.1 (d). Here the diffusive part is dominant and the waves reach a steady state before 0.1 au. At the steady state part all the domain shares the same transport quantity \( C \). This quantity is different than zero. In Fig. 4.1 (d) the steady state part is different than zero, because of the scale used it looks that \( C^2 = 0 \), however this is not true. These plots 4.1 (a), (b), (c), and (d), show the transition from a wave behavior to a diffusive behavior and how different values of \( p \) affect the solution. This description is used in the results sections to identify these behaviors in the transport of kinetic energy where a 1-d chain of atoms with periodic boundary conditions and a 2-d structure with the same boundary conditions are studied.

As mentioned, a 2-d structure also will be studied to identify different behaviors. The Modified Cattaneo’s equation in 2-d has to be solved. The equation in
Figure 4.1. Solution of Modified Cattaneo’s equation at $x = L/2$ for different values of $p$. 
2-d is

\[ \frac{\partial^2 C}{\partial t^2} + p \frac{\partial C}{\partial t} = (1 + p)\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right), \]  

(4.5)

and as in the 1-d problem periodic boundary conditions are imposed

\[ C(x = 0, y, t) = C(x = L_x, y, t), \]  

(4.6)

\[ C(x, y = 0, t) = C(x, y = L_y, t), \]  

(4.7)

where \( L_x \) is the length in the \( x \) direction and \( L_y \) is the length in the \( y \) direction. The initial condition is given in the middle of the domain

\[ C(x, y, t = 0) = \delta(x = x_0, y = y_0), \]  

(4.8)

where \( x_0 = L_x/2 \), and \( y_0 = L_y/2 \). Fig. 4.2 shows the solution of equation (4.5) for \( x = L_x/2, y = L_y/2 \), in time, for different values of \( p \). In the figure the four different behaviors in 2-d can be observed. The plot for \( p = 0 \) (a) shows the pure wave-like solution. For short times, less than 0.05 au, it can be observed that the wave is traveling through the 2-d domain. This is the reason for the decay of the amplitude of the initial perturbation. It is important to point out that this traveling wave is a radial wave, traveling in all the directions as opposed to a longitudinal wave like in the 1-d case. Approximately for \( t = 0.05 \) au the wave comes back to the initial perturbed point. Adding some damping to the Modified Cattaneo’s equation is shown in Fig. 4.2(b), where \( p = 1 \), like in the 1-d problem.
Figure 4.2. Solution of Modified Cattaneo’s equation in 2-d at $x = L_x/2$, $y = L_y/2$ for different values of $p$.

the diffusive part is still not evident for this case. The main difference is the wave speed where in this case it is difficult to recognize when the initial wave traveled the whole domain and hits back the initial perturbed point. It takes approximately 0.03 au for the wave to travel the whole domain. The diffusive effects are evident for $p = 10$, Fig. 4.2 (c). This plot clearly shows the damping of the initial perturbation. Finally for $p = 100$, Fig. 4.2 (d) the time for the wave to diffuses is short, less than 0.1 au. This last behavior is dominated by diffusive effects.

After solving the Modified Cattaneo’s equation in 1-d and 2-d, the transport of kinetic energy in 1-d and 2-d structures can be compared with the available solutions present in this section. The description of the behaviors will be used in
the results section.

4.1.2 Harmonic and anharmonic potential

Two different artificial potentials and then a single more realistic potential will be used in this Chapter. The artificial harmonic potential in 1-d is defined as

\[
U_i = \frac{1}{2} k_1 x_i^2, \tag{4.9}
\]

where \( k_1 \) is a spring constant and \( x_i \) is the displacement of the spring attached to atom \( i \). An artificial anharmonic potential in 1-d is also studied by including a single anharmonic term,

\[
U_i = \frac{1}{2} k_1 x_i^2 + \frac{1}{3} k_2 x_i^3, \tag{4.10}
\]

where \( k_2 \) is the spring constant for the anharmonic term. For this study, equivalent spring constants were obtained by using the lower order terms of the Taylor series expansion of the Lennard-Jones potential. The actual values of the spring constants \( k_1 \) and \( k_2 \) were estimated by using Lennard-Jones parameters for carbon [92, 93]. The values for \( k_1 \) and \( k_2 \) are \( k_1 = 0.1922 \) N/m, \( k_2 = 0.5291 \) N/m and the ratio \( k_2/k_1 = 2.75 \).

The derivative of the potential with respect to the position is the force on the atom, \( \mathbf{F} = -\nabla U \). Both of these potentials will be used in order to analyze the effect of the nonlinearity in the systems proposed in the problem definition section. The position and the velocity of each atom in the system will be solved in time by integrating the force on each atom using the Gear-predictor numerical scheme (Appendix F), and then the kinetic energy of each individual atom is calculated.
4.1.3 Lyapunov exponents

A measure of chaos in a dynamical system is the Lyapunov exponents

\[ \lambda_i = \lim_{t \to \infty} \frac{1}{t - t_0} \log \left( \frac{d(t)}{d_0} \right), \]

where \( \lambda_i \) is the Lyapunov exponent, \( d \) stands for the orbit in the study, \( d_0 \) is the distance of separation in phase space of a different orbit at \( t_0 \), and \( i \) is the index for each one of the mathematical dimensions. If the system is chaotic the largest Lyapunov exponent is positive. This means that two neighboring orbits in phase space diverge exponentially in time. It is important to differentiate the physical dimension from the mathematical dimension for the discussion in this Chapter. The physical dimension represents the direction of the movement or the velocity, i.e. \( x \), \( y \) and \( z \). The mathematical dimension represents the number of dimensions that the system is handling for each solution of the system. For example for a 1-d chain of 8 atoms, the physical dimension is one, and the mathematical dimension is 16 \((2N)\), 8 dimensions for the position and 8 dimensions for the velocities of the atoms. The Lyapunov exponents can be calculated following the algorithm proposed by Wolf et al. [94]. The algorithm tests the separation of the linearized orbits at different times.

4.2 Problem definition

4.2.1 1-d structure

The first system studied is a 1-d chain of atoms. A single, one-dimensional (1-d) chain of 28 carbon atoms was studied as shown in Fig. 4.3. The length of this chain was approximately the same as the \( x \) dimension of the graphene sheet.
that will be studied later, and, for simplicity, only the longitudinal motion was studied. An initial velocity was given to the central atom. The evolution in time of the kinetic energy distribution through the chain is shown in Fig. 4.4. These plots show a spatial distribution of kinetic energy in the chain at different times. It should be noted that Aoki et al. [32] observed a similar behavior in the transport of the signal for the autocorrelation of the heat current in a 1-d chain. A wave is ejected from the perturbed atom and travels through the chain as shown. Later in the results section, the evolution in time of the kinetic energy of the perturbed atom will be analyzed and compared with previous identified behaviors given by the Modified Cattaneo’s equation, (4.1).

4.2.2 2-d structure

In this work, for the study of 2-d systems, a graphene model problem was used. A single graphene sheet with 1024 atoms and dimensions of approximately 40 by 70 Å was studied (Fig. 4.5). The graphene structure is 2-d; however the sheet is allowed to move in the $x$, $y$ and $z$ directions.

The dynamics of the atoms in the crystal lattice were solved numerically, and each atom was bonded to its closest neighbors through a potential energy (Fig. 4.6). Like in the Modified Cattaneo’s equation and the 1-d chain, periodic boundary conditions were used. Again both potentials, the harmonic and the anhar-
Figure 4.4. Kinetic energy distribution 1-d chain for different times using the harmonic potential.
monic potential, were used. In addition to these two potentials, a third more realistic potential, the Tersoff potential discussed in Chapter Three was used.

The basic strategy was to analyze the time variation of the spatial distribution of kinetic energy throughout the graphene sheet. An initial perturbation in velocity equally shared in all three dimensions was given to the atom at the middle of the structure, while all other atoms in the sheet were set in their equilibrium position with a zero initial velocity. At time \( t = 0 \) all the energy in the system is solely in the perturbed atom and the rest of the atoms are in equilibrium with no energy. For times \( t > 0 \), the energy is transferred from the central atom to its neighboring atoms and so on throughout the structure. This evolution is shown in figures 4.7, and 4.8 where the distribution of kinetic energy for two different times is shown. The first figure shows the initial distribution of kinetic energy.
The second one shows the distribution for time $t = 3$ ps; it can be observed how the magnitude of the initial peak decreased. These two plots provide a mental picture of the transport of kinetic energy in the graphene sheet.

4.2.3 Numerical verification

The numerical scheme was verified by comparing the numerical solution to an analytical solution when using the harmonic potential. A toy problem with 16 atoms was solved to perform the verification. The structure used is shown in Fig. 4.6. In the validation, units on the order of meters and seconds were used. The value for $k_1 = 10$ N/m, for verification purposes. The comparison between the analytical solution and the numerical solution is shown in Fig. 4.9. The figure shows the position of atom 7 in Fig. 4.6. The integration time step used was 1 fs, which was sufficient to avoid numerical diffusion in the scheme. To ensure that the solution was independent of the time step, it was varied from 0.5 fs to 1 fs for both the harmonic and anharmonic systems. Figures 4.10 and 4.11
Figure 4.7. Kinetic energy distribution at $t = 0$ ps for an initial energy of $19 \times 10^4$ eV. Harmonic potential.
Figure 4.8. Kinetic energy distribution at $t = 3$ ps for an initial energy at $t = 0$ ps of $19 \times 10^4$ eV. Harmonic potential.
show the kinetic energy of the initially perturbed atom of the graphene sheet as a function of time for both the 1 fs and 0.5 fs time steps. For both systems, harmonic and anharmonic, the solution was the same, confirming that the solution was independent of the time step. For the results shown in the remainder of this Chapter, a time step of 1 fs was used. A time step of 0.5 fs was used for the Tersoff potential, because this time step was required to keep the scheme stable using this potential.
4.3 Results

4.3.1 1-d chain

The kinetic energy evolution in time of a specific point of the chain was studied. The atom studied was atom 14. This was the atom initially perturbed. The two different potentials, the harmonic and the anharmonic, were tested. The left plot of Fig. ?? shows the solution of the Modified Cattaneo’s equation, recovering the wave equation for \( p = 0 \). This plot is included in order to compare this behavior with the kinetic energy of atom 14. The right plot shows the normalized kinetic energy of this atom. The normalized kinetic energy is defined as \( KE(t)/KE(0) \). The plots show that both behaviors compare well qualitatively.

The effect of the anharmonic potential was also evaluated. Despite the fact
that it was shown that the ratio of $k_2/k_1 = 2.75$ presented some anharmonicity, Fig. ?? shows that the kinetic energy using the anharmonic potential for this case does not represent a different behavior in the solution. The only difference between the solid line and the dashed line in the figure is the phase. After 20 ps it is clear how the solutions start to get out of phase each other, both still behaving wave-like.

### 4.3.2 Graphene

For graphene a similar comparison as for the 1-d problem was performed. Fig. 4.12 shows the comparison of the Modified Cattaneo’s equation in 2-d with the normalized kinetic energy of atom 544 using the harmonic potential. This atom is located at the middle of the sheet and was the initially perturbed atom. A value
of \( p = 0 \) is used in the Modified Cattaneo’s equation (left plot). In the Modified Cattaneo’s equation a decreasing wave up to 0.03 au is observed, then the wave starts increasing in amplitude. This is the result of the wave traveling through the periodic structure. A similar effect is observed in the actual simulation of kinetic energy, Fig. 4.12 (right plot). The wave decays up to 20 ps; however the wave starts recovering amplitude and wave-like behavior is again observed after 30 ps. Using the harmonic potential in 2-d compares well with a wave-like behavior such as the one presented in the Modified Cattaneo’s equation for \( p = 0 \).

The second potential compared is the anharmonic potential. When adding anharmonic terms, wave-like transport is still observed. In the Fig. 4.13 the anharmonic potential is also compared with the modified Cattaneo’s equation for \( p = 0 \). Up to now diffusive effects have been not observed.

Finally the Tersoff potential is analyzed. Despite the fact that the expression for the Tersoff potential is non-linear as described in the previous Chapter, Fig. 4.14 (right) shows that the behavior of the kinetic energy is wave-like. This plot shows the normalized kinetic energy for 0.5 ps. This short time compared with the previous potentials is enough to observe the wave effects. The wave decays really fast, in less than 20% of 0.5 ps, and then it is just wave behavior. Again the comparison is made with the Modified Cattaneo’s equation in 2-d for \( p = 0 \) (right figure).

The previous results suggest that the transport of kinetic energy in graphene is purely wave-like. A statistical tool to recognize different regimes or behaviors in a signal is the autocorrelation. The autocorrelation described in the previous Chapter, allows for the identification of hidden behaviors, and is a comparison of a signal in time with the same signal with some time lag \( \tau \). In order to com-
Figure 4.12. Behavior comparison between Modified Cattaneo’s equation in 2-d ($p = 0$) vs Kinetic energy atom 544 in graphene using the harmonic potential.
Figure 4.13. Behavior comparison between Modified Cattaneo’s equation in 2-d ($p = 0$) vs Kinetic energy atom 544 in graphene using the anharmonic potential.
Figure 4.14. Behavior comparison between Modified Cattaneo’s equation in 2-d ($p = 0$) vs Kinetic energy atom 544 in graphene using the Tersoff potential.
pletely analyze the signal and maybe identify more regimes, the autocorrelation of the kinetic energy was calculated. Fig. 4.15 shows the autocorrelation of the normalized kinetic energy of atom 544 using the three potentials. Fig. 4.15 (a) shows the autocorrelation for the harmonic potential. The wave-like behavior in the autocorrelation can be observed. A decaying wave is identified up to 5 ps. The wave starts to grow slowly and for long correlation times $\tau > 40$ ps; it is observed how the wave is more evident. Fig. 4.15 (b) shows the same result for the anharmonic potential; here the initial wave behaves different. It decays at $\tau = 10$ and then it seems that the wave is damped, showing small activity about 45 ps. The autocorrelation for the Tersoff potential is presented in Fig. 4.15 (c), here the result is similar to the normalized kinetic energy for this potential presented previously. The autocorrelation behaves purely wave-like.

With the wave-like part of the transport previously recognized it is important to analyze the components of frequency of these waves. The power spectral density (PSD) shows the frequencies of a signal. The PSD is calculated in Fourier space by

$$PSD = (\hat{KE}(\omega)\hat{KE}(\omega)^*)^2,$$  \hspace{1cm} (4.12)

where $\hat{KE}(\omega)$ is the kinetic energy in frequency space, and $\hat{KE}(\omega)^*$ is the complex conjugate. The components of frequency for the harmonic potential are shown in Fig. 4.16 (a). Using this potential, there are low frequency components up to 2.5 THz. The anharmonic potential also produces low frequency components, Fig. 4.17 (b). The Tersoff potential produces component of frequencies with an order of magnitude larger values compared with the harmonic and the anharmonic potential, with component of frequencies up to 35 THz. The value of the y axis
Figure 4.15. Autocorrelation function of the normalized kinetic energy of atom 544 in graphene.
in the PSD represents the square of the amplitude of the wave at that frequency. For example in Fig. 4.16 (b), at 1 THz the PSD is approximately 0.15, this means that in the normalized kinetic energy there is a wave with a frequency of 1 THz that has an amplitude of $\sqrt{0.15}$. From the figure it is observed that when using the harmonic and the anharmonic potentials there are few waves but with larger amplitude than the waves for the Tersoff potential. The Tersoff potential results in a broad band spectrum going up to 35 THz, however all these waves have a small amplitude compared with the waves of the harmonic and the anharmonic potential. This effect is evident in the difference of magnitude of the $y$ axis between the harmonic, the anharmonic, and the Tersoff potential. A more detailed comparison between the spectrum of the harmonic and the anharmonic potential is presented in Fig. 4.17. The figure shows that the potentials present different components of frequencies. From 0 to 1 THz both potentials have components of frequency; however the amplitude of those waves are slightly larger for the anharmonic. The same effect is more evident from 1 to 1.5 THz. From 1.5 THz to 3 THz the effect is the opposite, the anharmonic potential starts decreasing the components, while the harmonic potential still presents frequency components for this values. The anharmonic potential produces lower components of frequency with larger amplitude compared with the harmonic potential up to 2 THz.

4.3.3 Chaos

For a linear system, the Lyapunov exponents are zero. This is confirmed when using the harmonic potential in the 1-d chain. The exponents are shown in Fig. 4.19. It can be observed how the steady state exponents go to zero. Using the anharmonic potential in the same 1-d problem result in the same. Fig. 4.20 shows
Figure 4.16. Power spectral density of kinetic energy of atom 544 in graphene.
Figure 4.17. PSD comparison between the harmonic and the anharmonic potential.
the exponents for the anharmonic potential. Using the anharmonic potential in 1-d does not produce chaos. The results for the Lyapunov exponents does not vary with the size of the chain.

The harmonic and anharmonic potentials were also tested for a 2-d graphene model problem. The structure studied is shown in Fig. 4.18. This model problem structure has 8 atoms. Periodic boundary conditions were used in this model problem. The atoms are allowed to move in the three directions $x$, $y$ and $z$. This physical dimension produces 48 exponents ($8 \times 3 \times 2$). The exponents are shown in figures 4.21 and 4.22 for the harmonic and the anharmonic potential respectively. It can be observed that for the harmonic potential the exponents go to zero as in the 1-d problem and as expected for a linear system. However for the anharmonic potential one of the exponents is greater than zero, having an approximate value of 1.5. This suggests the presence of chaos for the anharmonic 2-d structure. Comparing with the 1-d chain this result suggests that increasing the dimension produces chaos in the system.

The increase in the dimension combined with the anharmonic potential produced a chaotic system in the dynamics of the atoms. It was observed that for the 1-d problem, despite the use of the anharmonic potential, no chaos was identified. This resulted in the values of zero for the Lyapunov exponent for the 1-d chain.
The use of an anharmonic potential in graphene resulted in a chaotic system as showed by the Lyapunov exponents. This suggests that similar systems but in different dimensions result in different characteristics in the dynamics.

4.4 Discussion

At the beginning of the Chapter a Modified Cattaneo’s equation was proposed. The equation (4.1) had a tuning variable $p$ that allows recovering of the wave equation, the diffusion equation, and a combination of both. The equation was solved for different $p$, and three different behaviors were identified, the wave-like, the diffusive and a combination of both behaviors, wave-like + diffusive. The next step was to propose two different problem models and to identify the behavior in the transport of kinetic energy of these models. A 1-d chain of carbon
Figure 4.20. Lyapunov exponents 1-d chain 8 atoms, anharmonic potential.
Figure 4.21. Lyapunov exponents 2-d graphene model problem 8 atoms, harmonic potential.
Figure 4.22. Lyapunov exponents 2-d graphene model problem 8 atoms, anharmonic potential.
atoms was proposed with periodic boundary conditions and a graphene sheet also with periodic boundary conditions. The 1-d chain of atoms showed pure wave-like behavior using both potentials. A pure wave-like behavior for the chain using the harmonic potential was expected due to the lack of defects. Without boundaries and random defects in the lattice, diffusive effects are not possible. Also it was shown that the anharmonic potential for this level of anharmonicity behaves similar to the harmonic.

The 2-d Modified Cattaneo’s equation was solved for different values of $p$. Similar to the 1-d case, three different behaviors were identified. Transport of kinetic energy in a graphene sheet (2-d) was compared with these behaviors. The harmonic potential, the anharmonic and the Tersoff potentials were used. All these behaviors presented a pure wave-like transport. Up to this point no diffusive effects were identified. The autocorrelation function was calculated to find hidden behaviors in the signal of the kinetic energy in the 2-d case. The autocorrelation showed differences between the harmonic and the anharmonic potential. The first presents a wave that decays with time but recovers some activity after some time. The autocorrelation of the anharmonic looks more as a damped wave. This damped wave was not identified in the kinetic energy where the transport was wave-like. The autocorrelation for the Tersoff potential was more wave-like.

With an evident wave-like nature of the transport in 2-d structure, the frequency spectra were analyzed. The power spectral density shows the frequencies for the harmonic and the anharmonic potential and showed components in the low frequency range. The anharmonic potential showed more components for lower frequencies. The Tersoff potential showed a broadband spectrum, with frequency components one order of magnitude higher than the previous potentials. The
phonons as described previously in the introduction Chapter are the vibrations of
the atoms in the lattice. The phonons with lower frequencies are the ones which
carry more heat. This is a result of the phonon dispersion relationship. In general
this relation shows that the phonons with low frequency have larger slope in the
relation. The slope \( \frac{d\omega}{dk} \) is the group velocity of the phonons, so phonons with
higher slope in the dispersion relationship have larger group velocity therefore
they transport more heat. Translating this fact with the results shown, and from
the PSD, it can be concluded that for graphene using an anharmonic potential will
translate in an enhanced transport compared with the harmonic potential. The
results showed the presence of more low frequency phonons using the anharmonic
potential than the harmonic potential. Conclusions about the Tersoff potential
are different because the results showed a PSD that is not even close to compare
with the previous potentials. However it is important to point out that the Tersoff
potential is not an artificial potential, it is intended to describe a real system with
covalent bonds such as carbon. The interactions described with the Tersoff po-
tential are more close to describe a real graphene system. This potential showed
a broad band spectrum in the PSD. There is no reference to be compared for this
potential. In the previous artificial potentials (harmonic and anharmonic) both
were compared to identify differences but for Tersoff this is not the case. There is
no reference to imply that 35 THz is a low or high frequency components. However
the PSD of graphene Tersoff shows an uniform distribution of frequencies at least
up to 15 THz. These frequencies are uniformly distributed and means that from
0 THz to 15 THz there will be phonons with this frequencies; these frequencies
can be considered low compared with the whole spectrum for the potential. This
means that for this low value of frequencies there are many phonons carrying heat.
This fact is a possible explanation of the previous reported results of graphene as a good heat conductor in the literature review Chapter. Better transport is expected with more low frequency phonons. Here it was shown that using a more realistic potential such as Tersoff produces a broad band spectrum with many low frequency components.

It was also a purpose of this Chapter to recognize the differences between the 1-d structure and the 2-d graphene sheet. The studies in real space of the distribution of kinetic energy showed that both structures behave wave-like and a diffusive behavior was not identified. Nevertheless differences between the structures were found when the dynamics of the system were analyzed through a chaos study. For chaos the dimensionality plays a role. Here the presence of chaos was a combination of two factors using the anharmonic potential and the 2-d structure. For the 1-d chain chaos was not reported even using the anharmonic potential. For graphene chaos was observed using the anharmonic potential.

4.5 Conclusions

The study of the 1-d chain of atoms and the graphene sheet showed that the transport of kinetic energy in real space is wave-like using different potentials. Diffusive characteristics in the transport were not identified. The graphene sheet showed different characteristics between potentials depending on which tool was analyzed. The evolution in time of kinetic energy of the perturbed atom in graphene showed just waves with the three proposed potentials. Differences were identified when the autocorrelation function was analyzed; it can be concluded that the harmonic and the Tersoff potential present a wave-like autocorrelation meanwhile the anharmonic presents a damped wave. This damped wave in the
autocorrelation may be the result of adding the non-linear anharmonic term. The main conclusion from the PSD of graphene is that there are many low frequency components in the three different potentials. This low frequency components are the carriers that carry more heat, therefore they are good for the transport. It can be concluded that low frequency phonons were identified in graphene using different potentials. One final conclusion is related with the effect of increasing the physical dimension of the lattice. The only effect identified was the presence of chaos. The graphene sheet presented chaos using the anharmonic potential. This characteristic was different compared with the 1-d chain.
CHAPTER 5

CONCLUSIONS

5.1 Conclusions

This work presented a study of heat conduction at the micro- and nano-scales. This phenomenon has a wide variety of branches and applications that can be studied. The literature review Chapter taught the reader about the previous work in this topic. First the review on temperature representation models were given. Then the tools used to study the thermal conductivity, such as molecular dynamics and the materials where it has been applied were also reviewed. The review also dealt with the available studies in low dimensional materials. These materials have a huge projection in future applications. Previous studies in heat conduction in 1-d chains were given. The reader learned that most of the previous studies linked the dynamics of the atoms directly with Fourier law. In most of these studies, a temperature distribution between two reservoirs was studied and normal and anomalous diffusion were identified. Similar studies have also been conducted for 2-d materials. From here, the necessity of studying the conduction problem with a different strategy without assuming a constitutive law was clear. The identification of transport regimes such as diffusive or wave-like in these low dimensional systems may provide more insight about the problem. Also the differences in the characteristics of the transport between dimensions was interesting.
One of the most promising candidates to study the transport in 2-d was graphene. The state of the art about this material and heat transport was also reported in the literature review Chapter.

The estimation of the thermal conductivity in crystal systems was also explored. It was found that for the Tersoff potential different formulations are available in the literature. These formulations were explored in detail pointing out weakness and strengths of each of them. A new formulation was also proposed. Comparing all the formulations it was recommended to use Formulation A, because this formulation is general and does not depend on the potential used. Also wave-like and diffusive behavior was observed in the autocorrelation function of the heat current. For the calculation of the thermal conductivity, just the diffusive part was used, because the estimation of the thermal conductivity assumes a diffusive behavior.

The previous results suggested that it was important to study the transport without assuming a constitutive law. The study of the dynamics of the atoms was a good candidate to achieve this. This part of this work taught the reader about the differences and similarities in the dynamics between the 1-d and 2-d systems studied through the distribution of kinetic energy in the systems. A Modified Cattaneo’s equation was proposed to identify wave-like and diffusive behavior. The 1-d problem showed waves that eject from the initial conditions through the domain and these waves lose amplitude while they redistribute. The kinetic energy of the perturbed atom compared well with the solution of the Modified Cattaneo’s equation in the limit of the wave equation \( p=0 \). Also the transport in 1-d was non-chaotic when using a harmonic and anharmonic potential. For the 2-d problem a similar problem was analyzed. The kinetic energy of the perturbed atom
in 2-d also compares well with the wave-like behavior of the Modified Cattaneo’s equation. Diffusion was not identified. The autocorrelation function of the kinetic energy was also calculated. Here the harmonic and the Tersoff potential presented wave-like characteristics. The autocorrelation for the anharmonic looks more like a damped wave. Finally the components of frequency of the kinetic energy were calculated. The PSD show that the transport is better for the anharmonic potential compared with the harmonic due to the presence of more low frequency components in the anharmonic potential. The Tersoff potential also presents favorable conditions for the transport due to the broad band spectrum presenting many components in the low frequency regime. It was also observed that the anharmonic potential in 2-d produces chaos in a graphene model-problem. This suggest that there is an effect in the dynamics of systems increasing the dimensionality and using an anharmonic potential. However no relation between chaos and diffusive behavior was identified. Previously Casati et al. [36] suggested that chaos was present for systems with normal diffusion. Similar conclusions were reported by Prosen and Robnik [37]. Li et al. [35] reported a different conclusion. They reported that there is no relation between the transport and the presence of chaos. The results presented here are more in agreement with this statement. Chaos was identified; the system with chaos also presented wave-like characteristics as the systems with no chaos. This does not allow conclusions about a relation between chaos and the regimes of the transport.

The following points are the main conclusions of this work:

1. There is no single technique for the calculation of thermal conductivity in crystals of germanium and carbon using EMD. Formulation A is simple and calculates the thermal conductivity for any potential. The autocorrelation
of the heat current in these crystals showed diffusive and wave-like parts.

2. The transport of kinetic energy in 1-d and 2-d systems is wave-like. This characteristic is observed using the harmonic, anharmonic and Tersoff potential.

3. The anharmonic potential presents more low frequency components than the harmonic potential. The spectrum of the Tersoff potential is broadband. Low frequency components and broadband spectrum are good for the transport.

5.2 Recommendations

The following recommendations would provide a better understanding of the phenomenon, complementing the work presented here.

- For the study of low dimensional systems, different recommendations can be made. The first one is related with the study of 1-d and 2-d systems such as the ones studied here but adding defects and vacancies to the lattice. It is important to study these systems with non perfect lattices because these systems tend to be more real and are present in nature. The identification of the effects of non-homogeneous lattices will allow for the design of materials that enhance or decrease the transport depending the application. With the increase of defects, diffusive behaviors may show in the transport. In this work the wave-like part of the transport was identified, due to the vibrational nature of the phonons. A study that identifies the reason for diffusive effects would complement a description of the transport in atomic systems.
• The previous point brings into the picture a new opportunity for the extension of the work presented here. With the knowledge of the effects of impurities in the lattice in the transport, design of 1-d or 2-d materials with specific thermal properties would be a large field to be explored.

• The effect of the 2-d geometry was discussed. The limit of 2-d materials and up to which point they behave as 2-d materials in the transport is a question that still needs to be addressed. Different problems can be proposed to understand this limit of dimensionality. For example, to perform a similar problem as the one solved here for the graphene sheet but adding extra layers. How do these layers compare with previously identified behaviors from the Modified Cattaneo’s equation? Up to how many layers is wave-like? Up to how many layers until the transport starts to be diffusive? Answering these questions will have a huge impact in the understanding of strictly 2-d materials vs 3-d materials.

• It is a good exercise to complement some of the previous results of the thermal conductivity of graphene using the technique developed here in Chapter Three. Green-Kubo and EMD has not been used to calculate $\lambda$ of graphene. This exercise will complement previous work and also will provide a value of $\lambda$ with no effect of the boundaries. This will allow for the understanding of $\lambda$ with only phonon-phonon scattering. The result can be compared with previously reported results for suspended graphene, supported graphene, and NEMD of graphene with armchair and zigzag edges. The comparison will allow for the measure of the effect of boundaries and edges.

• Extensions of the two previous points can also be studied in graphene with
• A curious observation is that the waves in Fig. 5.1 appear to propagate in an ordered fashion. The figure shows the contours of the distribution of kinetic energy of the graphene sheet studied in Chapter Four. The sheet was perturbed with an initial energy at the middle of the sheet. The figure implies that the geometry of the graphene structure plays a significant role in the nature of the energy transport. In graphene, the energy will travel almost evenly in all directions along the atomic bonds, an almost radial transport. However, the transport pattern has a different orientation than the original honeycomb array of the graphene sheet - it is rotated by 30°.

The anharmonic potential also presents a hexagonal wave front as shown in Fig. 5.2. The same behavior is observed using the Tersoff potential, which more realistically represents the potential in a graphene lattice. A similar, yet more diffuse hexagonal pattern is formed (Figure 5.3), suggesting that the hexagonal energy transport is independent of the potential used and is a facet of the honeycomb structure. This may explain the high values reported for the thermal conductivity of graphene. One possible reason that makes graphene such an interesting material is the hexagonal structure of the monolayer. This opens a new window in studying mechanical properties of graphene, and the effect of the geometry in these properties. A description of the depletion zone of kinetic energy in these figures is required. It is surprising that this depletion zone follows an hexagonal radial direction. Understanding this effect in graphene will provide more description of the transport in the material.
Figure 5.1. Contour lines of kinetic energy distribution at t=0.28 ps for an initial energy at t = 0 ps of $19 \times 10^4$ eV. Harmonic potential
Figure 5.2. Contour lines of kinetic energy distribution at $t=0.28$ ps. Anharmonic potential.
Figure 5.3. Contour lines of kinetic energy distribution at $t=0.29$ ps.
Tersoff potential
APPENDIX A

CLASSICAL LIMIT OF HARDY’S FORMULATION FOR HEAT FLUX OPERATOR

The heat flux operator for a lattice from Hardy [83] is

\[ S = \frac{1}{2V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{i\hbar} \left[ \frac{p_i^2}{2m_i}, U_j \right] \right\} + H.c., \quad (A.1) \]

where the momentum \( p = mv \) has been used. Expanding the momentum inside the commutator

\[ S = \frac{1}{2V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{2m_i} \frac{1}{i\hbar} \left[ p_i, p_i, U_j \right] \right\} + H.c., \quad (A.2) \]

and using the following identity of the commutator

\[ [AB, C] = A[B, C] + [A, C]B, \quad (A.3) \]

then the heat flux operator is

\[ S = \frac{1}{2V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{2m_i} \frac{1}{i\hbar} \left[ p_i, [p_i, U_j] + [p_i, U_j]p_i \right] \right\} + H.c.. \quad (A.4) \]
Then in the classical limit is

\[ \frac{i}{\hbar} [p_i, U_j] = \frac{\partial U_j}{\partial r_i}. \]  (A.5)

Using

\[ \frac{1}{i\hbar} = \frac{-i}{\hbar}, \]  (A.6)

the following can be written

\[ S = \frac{1}{2V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{2m_i} - \frac{i}{\hbar} \left( p_i [p_i, U_j] + [p_i, U_j] p_i \right) \right\} + H.c. \]  (A.7)

Going from the quantum mechanics context to the classical mechanics context using equation (A.5) and the fact that in the classical context the \( H.c. \) is the complex conjugate the following is obtained

\[ S = \frac{1}{V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{2m_i} (-1) \left( p_i \cdot \frac{\partial U_j}{\partial r_i} + \frac{\partial U_j}{\partial r_i} \cdot p_i \right) \right\}. \]  (A.8)

Rewriting the heat flux operator as

\[ S = \frac{1}{V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{2m_i} (-1)(2m_i) \cdot \frac{\partial U_j}{\partial r_i} \right\}. \]  (A.9)

\[ S = \frac{1}{V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_i - r_j) \frac{1}{2m_i} (-1)(2m_i) \cdot \frac{\partial U_j}{\partial r_i} \right\}. \]  (A.10)

finally having

\[ S = \frac{1}{V} \left\{ \sum_{i=1}^{n} \frac{p_i}{m_i} \left( \frac{p_i^2}{2m_i} + U_i \right) + \sum_{i=1}^{n} \sum_{j=1}^{n} (r_j - r_i) \cdot \frac{\partial U_j}{\partial r_i} \right\}. \]  (A.11)
if the heat flux is multiplied by the volume and after arranging the indexes the equation for the heat current in formulation A is recovered

\[
J = \sum_{i=1}^{n} v_i \epsilon_i + \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij} \left( \frac{\partial U_i}{\partial R_j} \cdot v_j \right). \tag{A.12}
\]
APPENDIX B

DERIVATION OF THE HEAT CURRENT FOR A TWO-BODY POTENTIAL

IN FORMULATION C_b

The equation for the heat current for the LJ potential can be derived starting from

\[ J = \frac{d}{dt} \sum_{i=1}^{n} r_i \epsilon_i, \quad \text{(B.1)} \]

\[ J = \sum_{i=1}^{n} \left( v_i \epsilon_i + r_i \frac{d}{dt} \left( \frac{1}{2} m v_i^2 + \frac{1}{2} \sum_{j=1}^{n} U_{ij} \right) \right), \quad \text{(B.2)} \]

\[ J = \sum_{i=1}^{n} v_i \epsilon_i + \sum_{i=1}^{n} r_i (F_i \cdot v_i) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_i \left( \frac{\partial U_{ij}}{\partial r_{ij}} \frac{\partial r_i}{\partial t} - \frac{\partial U_{ij}}{\partial r_{ij}} \frac{\partial r_j}{\partial t} \right), \quad \text{(B.3)} \]

defining

\[ F_i = - \sum_{j=1}^{n} \frac{\partial U_{ij}}{\partial r_{ij}}, \quad \text{(B.4)} \]

then the following is obtained

\[ J = \sum_{i=1}^{n} v_i \epsilon_i - \sum_{i=1}^{n} \sum_{j=1}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_j, \quad \text{(B.5)} \]

combining terms

\[ J = \sum_{i=1}^{n} v_i \epsilon_i - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_j. \quad \text{(B.6)} \]
In the last term index $i$ is changed by $j$ and $j$ by $i$, this can be done because the sum in each term is independent of the other sums in the other terms. In Appendix C a toy problem with three atoms is expanded to show that this exchange of indexes is correct.

$$
J = \sum_{i=1}^{n} v_i \epsilon_i - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij} \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i - \frac{1}{2} \sum_{j=1}^{n} \sum_{i=1}^{n} r_{ji} \frac{\partial U_{ji}}{\partial r_{ji}} \cdot v_i,
$$

(B.7)

using the fact that for some specific 2 body potentials such as the Lennard-Jones, the following is true

$$\frac{\partial U_{ij}}{\partial r_{ij}} = -\frac{\partial U_{ji}}{\partial r_{ji}},$$

(B.8)

then equation B.7 can be written as

$$
J = \sum_{i=1}^{n} v_i \epsilon_i - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ij} \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i + \frac{1}{2} \sum_{j=1}^{n} \sum_{i=1}^{n} r_{ji} \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i,
$$

(B.9)

and finally the equation for the heat current for the LJ potential is obtained

$$
J = \sum_{i=1}^{n} v_i \epsilon_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} r_{ji} \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_i.
$$

(B.10)

with $F_{ij} = -\frac{\partial U_{ij}}{\partial r_{ij}}$ and $r_{ij} = -r_{ji}$.

As mentioned before this procedure is valid for a potential like the Lennard-Jones potential where equation (B.8) is true. Equation (B.8) is not true for the Tersoff potential. If the same procedure is done for the Tersoff potential, knowing that the potential is a function of the vectors $r_{ij}$ and $r_{ik}$ where the $k$ index runs for all the atoms

$$U_{ij} = f(r_{ij}, r_{ik}).$$

(B.11)
Then the equation for the heat current for this potential starting from equation (B.1) is

\[ J = \sum_{i=1}^{n} v_i \epsilon_i + \sum_{i=1}^{n} r_i (F_i \cdot v_i) + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left( r_i \frac{\partial U_{ij}}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial t} + \sum_{k=1}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ik}} \frac{\partial r_{ik}}{\partial t} \right), \] (B.12)

where \( F_i \) is the total force of atom \( i \). This equation is different than Formulation C\(_a\) proposed by Che et al. starting the derivation from the same equation (B.1).
APPENDIX C

DUMMY INDEXES IN A SUM

The indexes in a sum are dummy and they can be switched. The following term is going to be expanded for a problem with three atoms \( n = 3 \) to prove this

\[
\sum_{i=1}^{n} \sum_{j \neq i}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_j = \sum_{i=1}^{n} \sum_{j \neq i}^{n} r_j \frac{\partial U_{ji}}{\partial r_{ji}} \cdot v_i; \quad (C.1)
\]

expanding the term in the left hand side of equation (C.1) for \( i = 1, 3 \) and \( j = 1, 3 \)

\[
\sum_{i=1}^{n} \sum_{j \neq i}^{n} r_i \frac{\partial U_{ij}}{\partial r_{ij}} \cdot v_j = r_1 \frac{\partial U_{12}}{r_{12}} \cdot v_2 + r_1 \frac{\partial U_{13}}{r_{13}} \cdot v_3 + r_2 \frac{\partial U_{21}}{r_{21}} \cdot v_1 \\
+ r_2 \frac{\partial U_{23}}{r_{23}} \cdot v_3 + r_3 \frac{\partial U_{31}}{r_{31}} \cdot v_1 + r_3 \frac{\partial U_{32}}{r_{32}} \cdot v_2; \quad (C.2)
\]

and expanding the right hand side of equation (C.1)

\[
\sum_{i=1}^{n} \sum_{j \neq i}^{n} r_j \frac{\partial U_{ji}}{\partial r_{ji}} \cdot v_i = r_2 \frac{\partial U_{21}}{r_{21}} \cdot v_1 + r_3 \frac{\partial U_{31}}{r_{31}} \cdot v_1 + r_1 \frac{\partial U_{12}}{r_{12}} \cdot v_2 \\
+ r_3 \frac{\partial U_{32}}{r_{32}} \cdot v_2 + r_1 \frac{\partial U_{13}}{r_{13}} \cdot v_3 + r_2 \frac{\partial U_{23}}{r_{23}} \cdot v_3; \quad (C.3)
\]

the same terms of (C.2) appear in (C.3), showing that the indexes can be swapped.
APPENDIX D

VELOCITY VERLET NUMERICAL SCHEME

The velocity Verlet scheme used in the DL POLY software uses the following algorithm [95]. The velocity is calculated at half the next time step

$$v(t + \frac{1}{2}\Delta t) = v(t) + \frac{1}{2}\Delta t \frac{F(t)}{m}. \quad (D.1)$$

Here the force $F$ is obtained from the gradient of the potential, $F = -\nabla U$. Next the position at the next time step is calculated

$$x(t + \Delta t) = x(t) + \Delta t v(t + \frac{1}{2}\Delta t). \quad (D.2)$$

The forces are updated at $t + \Delta t$ using the new positions with $F = -\nabla U$. The new velocity is calculated.

$$v(t + \Delta t) = v(t + \frac{1}{2}\Delta t) + \frac{1}{2}\Delta t \frac{F(t + \Delta t)}{m}. \quad (D.3)$$

At the end of the algorithm, positions, velocities and forces are known at $t + \Delta t$. 

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APPENDIX E

FINITE DIFFERENCE METHOD IN THE MODIFIED CATTANEO'S EQUATION

The Modified Cattaneo’s equation in 1-d is

\[
\frac{\partial^2 C}{\partial t^2} + p \frac{\partial C}{\partial t} = (1 + p) \frac{\partial^2 C}{\partial x^2}.
\]  \hspace{1cm} (E.1)

The discrete form of the equation using finite differences is

\[
\frac{C_{i}^{k+1} - 2C_i^k + C_i^{k-1}}{\Delta t^2} + p \frac{C_{i}^{k+1} - C_i^k}{\Delta t} = (1 + p) \frac{C_{i+1}^{k+1} - 2C_i^k + C_{i-1}^k}{\Delta x^2},
\]  \hspace{1cm} (E.2)

where the \(i\) index is related with \(x\) and \(k\) with time. The solution of \(C\) at time \(k+1\) is

\[
C_{i}^{k+1} = \left( \frac{\Delta t(1 + p)(C_{i+1}^k - 2C_{i}^k + C_{i-1}^k)}{\Delta x^2} + \frac{2C_i^k - C_{i-1}^k}{\Delta t} + pC_i^k \right) \left( \frac{1}{\Delta t} + p \right)^{-1}.
\]  \hspace{1cm} (E.3)

This equation allows solving for \(C\) advancing forward in time.

The Modified Cattaneo’s equation in 2-d is

\[
\frac{\partial^2 C}{\partial t^2} + p \frac{\partial C}{\partial t} = (1 + p) \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right),
\]  \hspace{1cm} (E.4)

and using finite differences as in the 1-d case the discrete equation is
\[
\frac{C_{i,j}^{k+1} - 2C_{i,j}^k + C_{i,j}^{k-1}}{\Delta t^2} + p \frac{C_{i,j}^{k+1} - C_{i,j}^k}{\Delta t} =
(1 + p) \left( \frac{C_{i+1,j}^k - 2C_{i,j}^k + C_{i-1,j}^k}{\Delta x^2} + \frac{C_{i,j+1}^k - 2C_{i,j}^k + C_{i,j-1}^k}{\Delta y^2} \right),
\]

(E.5)

where the \( j \) index is related with \( y \). The solution at time \( k + 1 \) is

\[
C_{i,j}^{k+1} = \Delta t (1 + p) \left( \frac{C_{i+1,j}^k - 2C_{i,j}^k + C_{i-1,j}^k}{\Delta x^2} + \frac{C_{i,j+1}^k - 2C_{i,j}^k + C_{i,j-1}^k}{\Delta y^2} \right) +
\frac{2C_{i,j}^k - C_{i,j}^{k-1}}{\Delta t} + p C_{i,j}^k \left( \frac{1}{\Delta t} + p \right)^{-1}.
\]

(E.6)
APPENDIX F

GEAR’S PREDICTOR-CORRECTOR ALGORITHM

The scheme uses the fifth order Taylor series of the position

\begin{align}
x(t + \Delta t) &= x(t) + \dot{x}(t)\Delta t + \ddot{x}(t)\frac{\Delta t^2}{2!} + \dddot{x}(t)\frac{\Delta t^3}{3!} + \\
& \quad + \ddddot{x}(t)\frac{\Delta t^4}{4!} + \dddot{\dddot{x}}(t)\frac{\Delta t^5}{5!}, \tag{F.1}
\end{align}

\begin{align}
\dot{x}(t + \Delta t) &= \dot{x}(t) + \ddot{x}(t)\Delta t + \dddot{x}(t)\frac{\Delta t^2}{2!} + \dddot{x}(t)\frac{\Delta t^3}{3!} + \dddot{x}(t)\frac{\Delta t^4}{4!}, \tag{F.2}
\end{align}

\begin{align}
\ddot{x}(t + \Delta t) &= \ddot{x}(t) + \dddot{x}(t)\Delta t + \ddddot{x}(t)\frac{\Delta t^2}{2!} + \ddddot{x}(t)\frac{\Delta t^3}{3!}, \tag{F.3}
\end{align}

\begin{align}
\dddot{x}(t + \Delta t) &= \dddot{x}(t) + \ddddot{x}(t)\Delta t + \ddddddot{x}(t)\frac{\Delta t^2}{2!}, \tag{F.4}
\end{align}

\begin{align}
\ddddot{x}(t + \Delta t) &= \ddddot{x}(t) + \ddddddot{x}(t)\Delta t, \tag{F.5}
\end{align}

\begin{align}
\ddddot{x}(t + \Delta t) &= \ddddot{x}(t). \tag{F.6}
\end{align}
The method implies that the values of $x$ and the first five derivatives are known at time $t = 0$. The force is calculated with the predicted position with $F = -\nabla U$. A new acceleration is evaluated with this force $\ddot{x}(t + \Delta t)$. The difference with the predicted acceleration is calculated

$$\Delta \ddot{x} = \ddot{x}(t + \delta t) - \ddot{x}^P(t + \delta t), \quad (F.7)$$

where $\ddot{x}^P(t + \delta t)$ is the predicted acceleration from the Taylor series. A new quantity is calculated

$$\Delta R^2 = \frac{\Delta \ddot{x} \Delta t^2}{2!}. \quad (F.8)$$

The predicted positions and derivatives from the Taylor series are corrected

$$x = x^P + \alpha_0 \Delta R^2, \quad (F.9)$$

$$\dot{x} \Delta t = \dot{x}^P + \alpha_1 \Delta R^2, \quad (F.10)$$

$$\frac{\ddot{x} \Delta t^2}{2!} = \frac{\ddot{x}^P \Delta t^2}{2!} + \alpha_2 \Delta R^2, \quad (F.11)$$

$$\frac{x^{iii} \Delta t^3}{3!} = \frac{x^{iii} \Delta t^3}{3!} + \alpha_3 \Delta R^2, \quad (F.12)$$

$$\frac{x^{iv} \Delta t^4}{4!} = \frac{x^{iv} \Delta t^4}{4!} + \alpha_4 \Delta R^2, \quad (F.13)$$
TABLE F.1

NUMERICAL VALUES FOR $\alpha$

<table>
<thead>
<tr>
<th>$\alpha_i$</th>
<th>$\alpha_0$</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_3$</th>
<th>$\alpha_4$</th>
<th>$\alpha_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>value</td>
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<td>1</td>
<td>$\frac{11}{18}$</td>
<td>$\frac{1}{6}$</td>
<td>$\frac{1}{50}$</td>
</tr>
</tbody>
</table>

\[
\frac{x^v \Delta t^5}{5!} = \frac{x^{v_p} \Delta t^5}{5!} + \alpha_5 \Delta R_2. \tag{F.14}
\]

The values used for $\alpha$ are given in table F.1. The algorithm described above was taken from Haile [46].
BIBLIOGRAPHY


