Monte Carlo Simulation of Phonon Transport in Uranium Dioxide

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MONTE CARLO SIMULATION OF PHONON TRANSPORT IN URANIUM DIOXIDE

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Heat is transferred in crystalline semiconductor materials via lattice vibrations. Lattice vibrations are treated with a wave-particle duality just like photons are quantum mechanical representations of electro-magnetic waves. The quanta of energy of these lattice waves are called phonons. The Boltzmann Transport Equation (BTE) has proved to be a powerful tool in modeling the phonon heat conduction in crystalline solids. The BTE tracks the phonon number density function as it evolves according to the drift of all phonons and to the phonon-phonon interactions (or collisions). Unlike Fourier’s law which is limited to describing diffusive energy transport, the BTE can accurately predict energy transport in both ballistic (virtually no collisions) and diffuse regimes. Motivated by the need to understand thermal transport in irradiated Uranium Dioxide at the mesoscale, this work investigates phonon transport in \( \text{UO}_2 \) using Monte Carlo simulation. The simulation scheme aims to solve the Boltzmann transport equation for phonons within a relaxation time approximation. In this approximation the Boltzmann transport equation is simplified by assigning time scales to each scattering mechanism associated with phonon interactions. The Monte Carlo method is first verified by comparing to similar models for silicon. Unlike most previous works on solving this equation by Monte Carlo method, the momentum and energy conservation laws for phonon-phonon interactions in \( \text{UO}_2 \) are treated exactly; in doing so, the magnitude of possible wave vectors and frequency space are all discretized and a numerical routine is then implemented which considers all possible phonon-phonon interactions and chooses those interactions which obey the conservation laws. The simulation scheme accounts for the acoustic and optical branches of the dispersion relationships of \( \text{UO}_2 \). The six lowest energy branches in the [001] direction are tracked within the Monte Carlo. Because of their predicted low group velocities, the three remaining, high-energy branches are simply treated as a reservoir of phonons at constant energy in K-space. These phonons contribute to the thermal conductivity only by scattering with the six lower energy branches and not by their group velocities. Using periodic boundary conditions, this work presents results illustrating the diffusion limit of phonon transport in \( \text{UO}_2 \) single crystals, and computes the thermal conductivity of the material in the diffusion limit based on the detailed phonon dynamics. The temperature effect on conductivity is predicted and the results are compared with experimental data available in the literature.
CHAPTER 1

INTRODUCTION

The intrinsic properties of Uranium Dioxide, \( UO_2 \), have been the subject of many studies for more than half a century [1], particularly those which define the behavior of the bulk material. Understanding the behavior of the bulk material is essential for engineering applications such as the use of \( UO_2 \) as a nuclear fuel. Within a nuclear reactor a pellet of the nuclear fuel, most commonly \( UO_2 \) [2], is heated by the nuclear reaction and the heat is transformed into electrical energy. A major issue concerning the use of \( UO_2 \) as a nuclear fuel is the conduction of heat from the core of the fuel pellet to its outer area. The low thermal conductivity of \( UO_2 \) leads to large temperature gradients across the fuel pellet which can result in cracking and premature degrading of the pellet. Such degradation necessitates replacement of the fuel before it is depleted. Because \( UO_2 \) is an electronic insulator, the heat transfer is governed solely by the dynamics of the atomic vibrations. The atomic vibrations result in traveling waves with various frequencies and speeds which carry energy through the system. The quanta of energy of these waves can be thought of as discrete energy packets known as phonons [3]. The interactions of these phonons with one another give the material a finite conductivity and completely determine its thermal properties. Thus, the understanding of these phonon interactions is of utmost importance for choosing and designing efficient nuclear fuels.

1.1 Review of Similar Works

A Monte Carlo method for generating lattice thermal conductivities in the diffusion regime was first presented by Peterson[4], which was based on a linear Debye approximation to phonon dispersion. Mazumder et al. [5] extended Peterson’s model by including the dispersion relations for the acoustic phonon branches in silicon and germanium crystals. One drawback of the latter model was that the energy was not conserved after the phonon scattering algorithm was completed at each time step. This problem required manually removing or adding phonons to conserve energy. Lacroix et al. [6] improved the phonon scattering algorithm by sampling back the scattered phonon frequencies into the simulation in such a way that the energy was conserved in a statistical manner. Lacroix’s model was used as the starting point for this study. Reproducing the results presented by Lacroix was the first goal of this work. These results are presented in Chapter 4. Mittal and Mazumder [7] extended Lacroix’s work by including the optical modes into their model. Until this
point the optical modes of silicon had been neglected on the assumption that their low group velocities made them inefficient energy carriers. Contrary to popular belief, Mittal and Mazumder were able to show that the group velocities of the longitudinal optical (LO) and transverse optical (TO) modes are of the same order of magnitude as those for the longitudinal acoustic (LA) and transverse acoustic (TA) modes. Their results also show that at higher temperatures the number density of optical phonons can be significant (roughly 12%), especially since the optical modes may take on much larger frequencies than their acoustic counterparts. Thus, despite their lower velocities, optical modes can contribute to energy transport at higher temperatures since they carry more energy per phonon.

After appropriate results had been reproduced for silicon, an important but tedious part in making the transition to modeling $UO_2$ has to do with accurately defining scattering time scales for all phonons within the simulation. The treatment of these time scales in each of the cited works in this section are reviewed next.

1.1.1 Review of Phonon Scattering Time-Scales

As phonons traverse the crystal, they can exchange energy with other phonons. These phonon-phonon interactions are classified as either a Normal (N) process or an Umklapp (U) process. This study, like all previous MC models, only considers 3-phonon processes on the basis that 4-phonon processes will only become significant at much higher temperatures than will be considered in this study [8]. Both processes are governed by conservation rules[3]:

\[ \omega + \omega' \leftrightarrow \omega'' \] (1.1)

\[ \mathbf{K} + \mathbf{K}' \leftrightarrow \mathbf{K}'' + \mathbf{b} \] (1.2)

$\omega$, $\omega'$, and $\omega''$ are the interacting phonon frequencies which correspond to the wave vectors $\mathbf{K}$, $\mathbf{K}'$, and $\mathbf{K}''$. $\mathbf{b}$ is a crystal reciprocal lattice vector where the 0 vector is included and represents a Normal process. Note the double arrows in Equations 1.1 and 1.2. Thus, a particular vibrational mode is allowed to either combine with a second mode to produce a third or simply annihilate to produce two lower energy modes. A phonon with wavevector $\mathbf{K}$ does not carry a physical momentum. However, Equation 1.2 can be thought of as a momentum conservation equation since the phonon will interacted with other phonons as if it carries a momentum of $\hbar \mathbf{K}$ [3]. This equation allows us to identify the U process as the sole mechanism for restoring thermodynamic equilibrium. If the 3-phonon interactions were limited to only N processes, equilibrium would never exist. As a result, the crystal would have infinite conductivity, since nothing would restrict the flow of energy from the hot regions to the cold regions of the material [3].

Phonon-phonon interactions are a result of the crystals anharmonic interatomic forces. The difficulty of modeling phonon time-scales is a consequence of the complexities of these forces. As a result the relaxation time approximation for the scattering term of the BTE can be found in most literature. The details of the BTE in the relaxation time approximation are presented in Chapter 2. Instead of scattering between different wave vectors explicitly, each phonon is assigned a relaxation time. Using this relaxation time, the phonons are assigned a probability, $P_{\text{scat}}$, of participating in a phonon-phonon scattering event. This probability is derived by saying that the probability of a particular phonon to be scattered between $t$
and $t + dt$ is $dt/\tau$.[6] During each time step $\Delta t$, the probability that a phonon participates in a scattering event is calculated using the phonons relaxation time, $\tau$, as

$$P_{\text{scat}} = 1 - \exp\left(\frac{-\Delta t}{\tau}\right) \quad (1.3)$$

Peterson’s model treats the crystal as a continuum, and so phonon dispersion is neglected, each phonon drifts with the same group velocity, and each phonon is assigned the same relaxation time. This is the simplest possible treatment of phonon collisions. This type of model should only be used as a starting point for building a more elaborate Monte Carlo model.

Mazumder and Majumdar developed the first comprehensive Monte Carlo model for the solution of the BTE for phonons[5]. Their model included only the acoustic phonon modes and frequency and temperature dependent expression for the associated relaxation times. Mazumder’s expressions for the three-phonon relaxation times were borrowed from Holland[9]:

$$\tau_{ NU}^{-1} = B_L \omega^2 T^3 \quad \text{(LA, Normal+Umklapp)} \quad (1.4a)$$

$$\tau_{ N}^{-1} = B_T N \omega^4 \quad \text{(TA, Normal)} \quad (1.4b)$$

$$\tau_{ U}^{-1} = \begin{cases} 0 & \text{(TA, Umklapp) for } \omega < \omega_{1/2} \\ B_T U \omega^2 / \sinh\left(\frac{\hbar \omega}{k_B T}\right) & \text{(TA, Umklapp) for } \omega > \omega_{1/2} \end{cases} \quad (1.4c)$$

where $\omega_{1/2}$ is the frequency corresponding to $K/K_{\text{max}} = 0.5$, with $K$ being a wavenumber and $K_{\text{max}}$ the wavenumber at the Brillouin zone boundary. $\omega_{1/2} = 2.417 \times 10^{13}$ radians/sec for silicon[5]. Lacroix also used these expressions. Unfortunately, using these equations require fitting three parameter ($B_L$, $B_T N$, $B_T U$) to experimental conductivity measurements. It is important to point out that the parameters presented in Holland’s work were found assuming constant group velocity on each branch. According to Chung et al.[10] when a full dispersion model is used, these parameters need to be refit. Neither Mazumder and Majumdar nor Lacroix report refitting these parameters. While benchmarking with results presented by Holland, this study found that using Holland’s original parameters leads to low conductivity at higher temperatures as suggested by Chung.

As previously mentioned, Mittal and Majumder added to the existing model of silicon by including optical phonons into the simulation. Holland’s relaxation time expressions were once again used to model the N processes scattering rates. Mittal borrowed from the work of Hans Klemens[11] and Narumanchi et al.[12] to define the scattering rates for U processes. A subset of all possible three-phonons interaction which are believed to be important for silicon were used for calculation of these U scattering rates. For example, the time scale for an interaction of type LA + TA $\leftrightarrow$ LO (BZB) can be calculated using the expression

$$\frac{1}{\tau_{LALO}} = \frac{\gamma^2}{3\pi \rho v_g^2 \omega_{LA} \omega_{LO} \omega_T^3} \left[ \frac{1}{\exp(\hbar \omega_{TA}/k_B T) - 1} - \frac{1}{\exp(\hbar \omega_{LO}/k_B T) - 1} \right] \quad (1.5)$$

where LA refers to the phonon for which the time-scale is to be calculated, and TA is a mode which could combine with the LA phonon resulting in the LO mode. $v_g$ is the phase
velocity of the LA mode, and \( v_g \) is the magnitude of the group velocity for the LO mode. \( \gamma \) is the Gruneisen constant. \( \rho \) is the crystal's mass density, and \( \omega_{LA}, \omega_{TA}, \omega_{LO} \) are the angular frequencies of the mode involved in the scattering event. By summing terms like Equation 1.5 over all scattering interactions involving the LA phonon, the total relaxation time can be calculated with Mathiessen's [3] rule:

\[
\frac{1}{\tau} = \sum \frac{1}{\tau_i}
\]

For each 3-phonon interaction considered by Mittal and Majumder's model, one of the participating phonons is always assumed to reside at the Brillouin zone edge. For the process described above, the LO mode is assumed to exist at the zone edge and the TA phonon frequency can be calculated as \( \omega_{TA} = \omega_{LO} - \omega_{LA} \). This assumption is more appropriate at relatively low temperatures.

This work presents results from the first Monte Carlo model for calculating temperature dependant conductivities for \( \text{UO}_2 \). For phonon relaxation time calculations, no assumption is made for phonon branches which are allowed to interact with one another or for the frequencies of the involved phonons. Only the universal conservation laws (Equations 1.1 and 1.2) and experimental dispersion curve data are used when considering possible 3-phonon interactions. The calculation of relaxation times for \( \text{UO}_2 \) is described in the next section.

### 1.2 Phonon Scattering Treatment for Uranium Dioxide

In the model for \( \text{UO}_2 \), the dispersion curves for each mode are scanned to find all possible 3-phonon interactions which adhere to both energy and crystal momentum conservation (Equations 1.1 and 1.2). Using this information we can then assign an appropriate scattering time-scale to each phonon of the simulation. This algorithm was first outlined by Wang[13] to study thermal transport in silicon. We have extracted dispersion data for \( \text{UO}_2 \) from the experimental results obtained by Dolling et al.[14]. Unlike Wang, we use the dispersion for \( \text{UO}_2 \) in the [001] direction and assume isotropy for our initial runs. Figure 1.1 plots the data extracted from Dolling’s paper, along with our cubic fits which are used in the simulations. The cubic fits satisfy the boundary condition of zero group velocity at the Brillouin zone edge. The larger slope LA and LO branches are fit by two cubics which are matched in value and slope at the Brillouin zone center \((K/K_{max} = 0.5)\). Dolling discusses some uncertainty for the data points of the LA and lowest-energy LO branch, as they approach the Brillouin zone edge. Future work is needed to assess how these uncertainties may influence the MC results.

The highest-energy TO and LO modes are not included in the simulation on the basis of their low group velocity, as seen in Dolling’s data. However, each of these branches is included in the scattering algorithm by considering each as a reservoir of phonons that can interact with the lower-energy, simulated phonons. We assign these branches a constant angular frequency in K-space, one at \(8.6 \times 10^{13}\) rad/sec and another at \(11.15 \times 10^{13}\) rad/sec.

The search for all phonon triplets that can participate in a 3-phonon scattering event is governed by the conservation of energy and crystal momentum (Equations 1.1 and 1.2).
From the initialization of our system, \( \omega \) and \( \mathbf{K} \) are given. Details of this initialization and the rest of the Monte Carlo algorithm can be found in Chapter 3. When a phonon scatters, we scan each dispersion branch giving of all possible vaues for \( \omega' \) and \( \mathbf{K}' \). We can now calculate \( \mathbf{K}'' \) from Equation 1.2 with \( b = 0 \). If \( \mathbf{K}'' \) is still contained in the first Brillouin zone, the process is considered Normal. If \( \mathbf{K}'' \) falls outside of the first Brillouin zone, a reciprocal lattice vector is then subtracted and the process is considered Umklapp. Figure 1.2 shows a representation of both Normal and Umklapp processes [15]. Note that all three wavevectors are treated as being in-line and so only suffices as a one-dimensional representation of phonon scattering. This is also how we treat the phonon scattering in Equation 1.2 for this work. Although this treatment neglects the complexities of scattering within a three-dimensional Brillouin zone, it still captures the essential physics that modes with larger wavevectors are more likely to scatter via a U-process. Knowing \( \mathbf{K}'' \), we then use each dispersion relations discussed above to get values for \( \omega'' \). We can now complete the energy conservation equation as

\[
\Delta \omega = \omega + \omega' - \omega''
\]

for a scattering of type \( \mathbf{K} + \mathbf{K}' \rightarrow \mathbf{K}'' + \mathbf{b} \). In Figure 1.3 (a) we plot \( \Delta \omega \) versus \( \mathbf{K}'' \) when scattering a low energy LA phonon. Figure 1.3 (b) shows the same for a LA phonon with a wavenumber of roughly one-third the length of K-space. Notice in (b) that once the resultant \( \mathbf{K}'' \) falls outside the first Brillouin zone, it is reflected back by the reciprocal
Fig 1.2: (Bejan and Kraus, Heat Transfer Handbook, 2003). (a) Normal process in which two phonons combine resulting in a wavevector still contained within the first Brillouin zone. (b) Umklapp process in which two phonons combine and a reciprocal lattice vector must be used to place the resulting wavevector back within the first Brillouin zone.

In this manner, we can find all possible phonon triplets which satisfy the conservation equations (Equation 1.1 and 1.2). If a curve crosses the line $\Delta \omega = 0$, then the phonon triplet is stored and used to calculate the phonon relaxation time.

Perturbation theory gives us an expression for the contribution to the relaxation time of a phonon with frequency $\omega$ as [15]:

$$\frac{1}{\tau_i} = \frac{\gamma^2 \hbar}{3\pi^2 \rho v^2_p v_g} \frac{\omega \omega' \omega''}{\omega_0^2} \left[ \frac{1}{\exp(\hbar \omega'/k_B T) - 1} - \frac{1}{\exp(\hbar \omega''/k_B T) - 1} \right] \int_{K'} dS' \tag{1.8}$$

where $S'$ is an area over which the conservation laws are satisfied for varying directions of $K'$. Wang[5] and Han and Klemens[11] present different approximations in calculating the area $S'$. Borrowing ideas from both works, we approximate $S'$ by the area fraction $(\Omega'/4\pi)$ of a spherical shell with a radius of $|K'|$ (area of $4\pi K'^2$). $\Omega$ is an approximation of the solid angle subtended by the surface face of the face-centered cubic (fcc) Brillouin zone which is perpendicular to the [100] direction. Following the description by Han and Klemens $\Omega = \pi/8$ giving the contribution to the phonons relaxation time as:

$$\frac{1}{\tau_i} = \frac{\gamma^2 \hbar}{24\pi \rho v^2_p v_g} \frac{\omega \omega' \omega''}{\omega_0^2} \left[ \frac{1}{\exp(\hbar \omega'/k_B T) - 1} - \frac{1}{\exp(\hbar \omega''/k_B T) - 1} \right] \tag{1.9}$$

Having already found all possible phonon triplets which satisfy the conservation laws, we simply implement Equation 1.9 for each scattered phonon as sum multiple contributions with Mathiessen’s rule (Equation 1.6). The contributions from N and U processes are stored separately and contributions from processes of type $K + K' \leftarrow K'' + b$ are also included.

The details of treating phonon scattering within the Monte Carlo will be presented in Chapter 3. Some details of lattice vibration theory, phonon modeling, and of the BTE for phonons are presented next in Chapter 3.
Figure 1.3: (a) $\Delta \omega$ versus $K''$ when scattering a low energy LA phonon. (b) $\Delta \omega$ versus $K''$ when scattering a LA phonon with a wavenumber of roughly one-third the length of K-space
CHAPTER 2

LATTICE VIBRATION AND PHONON THEORY

2.1 Heat Transport in Crystals

2.1.1 Wave Propagation on a Linear Chain

Imagine vibrations within a crystal lattice having two atoms, of differing masses, within the primitive cell. The solution to this problem is simplest in the [100], [110], and [111] directions in a cubic crystal [3]. These represent the direction of the cube edge, face diagonal, and body diagonal respectively. When a wave travels in one of these directions, entire planes of atoms are shifted simultaneously. If the plane of atoms shifts parallel to the wavevector, the wave is called a longitudinal wave. If the atomic displacement are perpendicular to the wavevector, the wave is transverse. For mathematical inspection, consider a longitudinal wave. Because planes of atoms are moving in phase, it makes sense to treat the problem as one-dimensional, as in Figure 2.1. The atoms of mass $m_1$ and $m_2$ form a primitive cell and are bound to each other via springs having spring constants $g$. When two neighboring atoms are in their equilibrium positions, the distance between them is $a$. $x_n$ and $y_n$ denote the displacements of mass $m_1$ and $m_2$, found in the $n$th primitive cell, from their equilibrium positions. It is also assumed that each atom interacts only with its two nearest neighbors. Thus, when an $m_1$ atom is displaced from equilibrium, a restoring force...
is supplied via interactions with its two $m_2$ nearest neighbors. Assuming that the force felt between adjacent atoms is described by Hooke’s law, we can write down the equations of motion for masses $m_1$ and $m_2$ as

$$m_1 \frac{d^2x_n}{dt^2} = g(y_n + y_{n-1} - 2x_n) \quad (2.1a)$$

$$m_2 \frac{d^2y_n}{dt^2} = g(x_n + x_{n+1} - 2y_n) \quad (2.1b)$$

If energy is added to the left side of the system, the atoms there will begin to vibrate about their equilibrium positions. This causes neighboring atoms to begin their own oscillations, and thus, transporting the energy throughout the system. For insulating materials, this is the sole mechanism by which energy transmitted. To further explore the system governed by Equations 2.1, we search for traveling wave solutions in which each atom oscillates at the same angular frequencies:

$$x_{n \pm 1} = A \exp[i((K(x \pm a)) - \omega t)] \quad (2.2a)$$

$$y_{n \pm 1} = B \exp[i((K(y \pm a)) - \omega t)] \quad (2.2b)$$

where the sign for $a$ will depend on the direction of $K$. $A$ and $B$ are vibrational amplitudes, and $K$ is the wavenumber. By substituting Equations 2.2 into Equations 2.1, we get:

$$A(m_1 \omega^2 - 2g) + gB(1 + \exp(-iKa)) = 0 \quad (2.3a)$$

$$gA(1 + \exp(iKa)) + B(m_2 \omega^2 - 2g) = 0 \quad (2.3b)$$

We will have non-trivial solutions for 2.3 if and only if the determinant is zero. This allows us to write:

$$m_1 m_2 \omega^4 - 2g \omega^2(m_1 + m_2) + 2g^2(1 - \cos(Ka)) = 0 \quad (2.4)$$

This equation is quadratic in $\omega^2$, and so, implementing the quadratic equation, we can solve for $\omega^2$ as

$$\omega^2 = g \left[ \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \pm \sqrt{\left( \frac{1}{m_1} + \frac{1}{m_2} \right)^2 - \frac{4}{m_1 m_2} \sin^2 \left( \frac{Ka}{2} \right)} \right] \quad (2.5)$$

The $\pm$ gives two solution when we only consider positive values for $\omega^2$. The two solutions, or dispersion relations, which defines the allowed angular frequencies associated with each wavenumber, are shown in Figure 2.2. The solutions repeat themselves when the wavenumber falls outside of $|K| < \pi/a$. This region is called the first Brillouin zone.

The lower frequency spectrum, or polarization, resembles sound wave in that the frequencies are small at longer wavelengths. Thus, this branch is termed the “acoustic branch”. Acoustic waves are associated with the movement of the center of mass of the primitive cell. The higher polarization is associated with the movement of atoms within the primitive cell. If both atoms carried opposite charge, this type of $\omega - K$ relation could be produced by the electric field of a light wave[3]. And so, this branch is termed the “optical branch” Within a three dimensional crystal, each atom then has three degrees of freedom. Uranium Dioxide consists of a $UO_2$ molecule arranged on a fcc lattice. The three atoms lead to nine equations.
of motion. There are nine polarizations, three acoustic and six optical. The branches are in sets of threes (one longitudinal and two transverse), and the transverse is often times degenerate due to symmetries within the crystal.

The transmission velocity of the wave packet is the group velocity $v_g$ of a branch[3], defined as

$$v_g = \frac{d\omega}{dK}$$

or

$$v_g = \nabla_K\omega$$

the gradient of the frequency $\omega$ with respect to the wave vector. This is the velocity at which energy is propagated through the crystal.

2.1.2 Discretized Energy

Treating a crystal lattice as a classical spring-mass system leads to a continuous energy as a function of atomic displacements. This is analogous to the treatment of an elastic continuum where the wavenumber $K$ is allowed an infinite number of values. However, the quantum mechanical treatment of the lattice gives us a discrete set of energy states limited in number by the number of atoms in the crystal.

The density of states is defined as the number of states per unit frequency range, given a phonon dispersion relation, $\omega(K)$. The number of allowed values of $K$ when the phonon frequency is between $\omega$ and $\omega + d\omega$ is[6]

$$D(\omega)d\omega = \frac{V}{(2\pi)^3}K^2 dK = \frac{V}{2\pi^2}K^2 dK$$

Figure 2.2: (Mittal[10]) The optical and acoustic vibrational modes associated with a one-dimensional spring-mass system with two atoms of differing mass within each primitive cell.
where $V$ is the crystal volume. Note that in reducing the second expression, we are assuming an isotropic Brillouin zone. Using the definition for the group velocity, Equation 2.6, gives

$$D(\omega)d\omega = \frac{V}{2\pi^2v_g}K^2d\omega$$

(2.9)

The quantum of energy is called a phonon and carries energy $\hbar\omega$. Thus, the total energy of all phonons with frequency $\omega$ can be summed as

$$E = \left(\langle n \rangle + \frac{1}{2}\right)\hbar\omega$$

(2.10)

where $\langle n \rangle$ is the occupancy of phonons with wavevector $K$ found in thermal equilibrium. Like photons, phonons are bosons, and $\langle n \rangle$ is governed by Bose-Einstein statistics as

$$\langle n \rangle = \frac{1}{\exp(\frac{\hbar\omega}{k_BT}) - 1}$$

(2.11)

If we now sum over all phonon polarizations and use the density of states to integrate over phonon frequencies, we get an expression for the total vibrational energy of the crystal

$$E = V\sum_p\int_0^\infty \left[\frac{\hbar\omega}{\exp(\frac{\hbar\omega}{k_BT}) - 1}\right] \frac{K^2}{2\pi^2v_g}g_p d\omega$$

(2.12)

where $g_p$ is the degeneracy of polarization $p$. Note that in Equation 2.12 we have neglected the zero-point energy found in Equation 2.10 since this term is not temperature dependent and will not affect thermal transport calculations.

### 2.2 Boltzmann Transport Equation and Relaxation Time Approximation

First used to describe the behavior of dilute gases, the Boltzmann Transport Equation (BTE) can be used to model the evolution of a particle distribution whose constituents interact with one another via short range forces. The power in implementing the BTE comes in its validity to describe systems at the microscale where assuming local thermodynamic equilibrium is invalid and Fourier’s Law of thermal conductivity breaks down. The BTE can generally be written as[16]

$$\frac{\partial N}{\partial t} + v \cdot \nabla N + a \cdot \frac{N}{v} = \left[\frac{\partial N}{\partial t}\right]_{\text{scat}}$$

(2.13)

where $v$ is particle velocity, $a$ is particle acceleration, and $N = N(r,v,t)$ is the particle distribution function (Bose-Einstein for phonons in thermal equilibrium). $N = N(r,v,t)$ has seven independent variables: time, three components for the position $r$, and three components for the velocity $v$. When no external forces are considered acting on the system the acceleration term in Equation 2.13 can be dropped. The left hand side is composed of
the transient and drift terms respectively, and the right hand side represents the change in the distribution function $N = N(r,v,t)$ due to the interactions, or scatterings, among its particles.

If we now consider $N$ as representing a distribution of phonons which departs from equilibrium in the presence of a temperature gradient, we can recast 2.13 as[17]:

$$\frac{\partial N}{\partial t} + \mathbf{v}_g \cdot \nabla T \frac{\partial N}{\partial T} = \left[ \frac{\partial N}{\partial t} \right]_{\text{scat}}$$

(2.14)

The difficulty in solving this equation exactly to find $N$, from which a heat current could be calculated, is the complexity of the scattering term for the phonons. Not only do we have to find the rate at which phonons are scattered in and out of mode $\mathbf{K}$, but these rates also depend on the number density found in all other modes, which is what we are trying to find in the first place.

The most common simplification for approximating the scattering term of the BTE is the relaxation time approximation. Here it is assumed that the scattering processes tend to restore a particular phonon distribution at a rate proportional to the departure from the equilibrium distribution

$$\left( \frac{\partial N}{\partial t} \right)_{\text{scat}} = \frac{N - N_0}{\tau}$$

(2.15)

where $N_0$ is the Bose-Einstein distribution and $\tau$ is the total relaxation time-scale of a phonon which depends on $\mathbf{K}$ and polarization[17]. Thus, this approximation linearizes the scattering term which implies that whenever a system is not in equilibrium, the scattering term tends to restore equilibrium via an exponential decay law: $N - N_0 = \exp(-t/\tau)$. The objective for modeling thermal transport with the BTE is to calculate the distribution $N$. Using this distribution the heat current through the system can then be computed as

$$h = \sum_p \sum_{\mathbf{K}} N(\mathbf{K}) h\omega \mathbf{v}_g(\mathbf{K})$$

(2.16)
CHAPTER 3
MONTE-CARLO SOLUTION MODEL

The Monte Carlo (or Stochastic) method is ideal for solving differential equations which involve a relatively large number of independent variables. It is then well suited for application to the BTE in which the distribution function $N(r, K, t)$ is a function of seven independent variables: three space variables, three wave-vector components, and time. The ability of the Monte Carlo to treat individual phonon scattering events, rather than the application of a universal scattering time-scale for all phonons, make the MC method much more attractive for application to the phonon BTE. The MC numerical scheme for modeling phonons is described in this chapter.

3.1 Phonon Numbers

The end boundaries of the computational domain are treated as blackbody sources. For conductivity calculations, the first cell is prescribed a “hot” temperature and the last cell, and all intermediate cells are prescribed a “cold” temperature. Any phonon which drifts into the first or last cell is deleted from the simulation. The first and last cells are then re-initialized to the hot and cold temperature after each time-step. In this way, the end boundaries of the simulation domain are treated as heat-sinks and sources, which are allowed to add and remove heat according to the prescribed temperature.

Based on the initial temperature prescribed to the system, the first step is to calculate the number of phonons within each control volume of the system. Given a temperature $T$ and dispersion curves, the vibration energy within a volume $V$ is given by Equation 2.12 as an integration over the full frequency space and summed over each dispersion branch (phonon polarization). The integration is performed numerically by discretizing the frequency space into $N_b$ number of equally spaced bins, with $\omega_i$ being the central frequency of the $p$th polarization branch in the $i$th frequency bin. Each bin has a width of $\Delta\omega$. Thus, the integration is reduced to a summation over discrete frequency bins as

$$E = V \sum_p \sum_{b=1}^{N_b} \left[ \frac{\hbar \omega_i}{\exp \left( \frac{\hbar \omega_i}{k_B T} \right) - 1} \right] \frac{K_{i,p}^2}{2\pi^2 v_{gi,p}} g_p \Delta\omega \tag{3.1}$$

Since each phonon carries an energy of $\hbar \omega$, the total number of phonon found in each spatial
volume can similarly be found as

\[ N = V \sum_p \sum_{b=1}^{N_b} \left[ \frac{1}{\exp \left( \frac{\hbar \bar{\omega}_b}{k_B T} \right) - 1} \right] \frac{K_{i,p}^2}{2\pi^2 v_{gi,p} g_p} \Delta \omega \]  

(3.2)

The number of phonons resulting from Equation 3.2 will be very large. For silicon at temperature between 10 K to 300 K, Equation 3.2 would predict roughly $10^6 - 10^9$ phonons per $\mu m^3$. Computation time and memory requirements restrain us from running simulation of this size. For this reason we introduce a weighting factor $W$ defined as

\[ W = \frac{N}{N^*} \]  

(3.3)

where $N^*$ is the number of phonon packets that will be initialized and traced within the simulation domain. Therefore, each stochastic sample traced within the simulation will represent an ensemble of $W$ phonons. $N^*$ is used as an input to the code. $W$ is then calculated from Equation 3.2 and 3.3 and stored for future calculations. For this study, $W$ is initialized such that the initial number of phonons is roughly 100,000. Once $W$ is calculated, the phonons are then initialized by sampling from six stochastic spaces: three position vector components, two angles to define direction, and propagation speed.

### 3.2 Initialization of Phonon Samples

#### 3.2.1 Position

The spatial sampling of phonons is achieved by dividing the computational domain into equally sized rectangular parallelepiped. Each cell has dimensions $L_x \times L_y \times L_z$. Thus, the simulation domain can be imagined as a stack of rectangular cells as in Figure 3.1. For three-dimensional simulations, the position of each phonon can be determined by drawing three random number $R$, $R'$, and $R''$ uniformly distributed between 0 and 1. The position is then calculated as

\[ \mathbf{r} = \mathbf{r}_c + L_x R \mathbf{i} + L_y R' \mathbf{j} + L_z R'' \mathbf{k} \]  

(3.4)

with $\mathbf{r}_c$ being the coordinates of the cell.
3.2.2 Direction

Assuming isotropy within the crystal, a direction $\Omega$ can be assigned to each phonon by generating two random numbers $R$ and $R'$, uniformly distributed between 0 and 1. The two random numbers are used to define $\cos \theta = 2R - 1$ and $\phi = 2\pi R'$. Each phonon’s direction of travel is then given by

$$\Omega = \begin{cases} 
\sin \theta \cos \phi \\
\sin \theta \sin \phi \\
\cos \theta 
\end{cases}$$

(3.5)

where $\theta$ and $\phi$ are angles in spherical coordinates. Sampling phonon directions in this way gives a uniform random sampling across the $4\pi$ full space solid angle[6].

3.2.3 Frequency

As mentioned in Section 3.1, the frequency space is discretized into $N_b$ number of bins. From Equation 3.2 we can define the number density of phonons within the $ith$ frequency bin as

$$N_i = \sum_p \left[ \frac{1}{\exp \left( \frac{h\omega_i}{k_BT} \right) - 1} \right] \frac{K_{i,p}^2}{2\pi^2 v_{gi,p}} g_p \Delta \omega$$

(3.6)

From this we then construct a normalized cumulative number density function $F$,

$$F_i = \frac{\sum_{j=1}^i N_j}{\sum_{j=1}^{N_b} N_j}$$

(3.7)

$F_i$ then represents the probability of a phonon having a frequency less than $\omega_{i+1}$ and $F_i - F_{i-1}$ is the probability of a phonon being in the $ith$ frequency bin. A phonon’s frequency can then be sampled by drawing another random number between 0 and 1. The phonon belongs to the $ith$ frequency bin provided $F_{i-1} < R_f < F_i$, which can be determined using a bisection algorithm. In the silicon model, the phonon frequency is given by

$$\omega = \omega_i + (2R - 1) \frac{\Delta \omega}{2}$$

(3.8)

which gives a continuous sample space. However, due to the need to store all phonon interaction in $UO_2$ prior to beginning the simulation, the frequencies in $UO_2$ are simply assigned the central frequency, $\omega_i$.

3.2.4 Polarization

Once a phonon’s frequency has been sampled, the phonon can then be assigned to a polarization branch. The process is similar to the way a phonon’s frequency is chosen. Using Equation 3.6 for the total number of phonons in the $ith$ frequency bin, the probability of finding a phonon in the $ith$ frequency bin with polarization, $p$, is given by[7]

$$P_{i,p} = \frac{N_{i,p}}{N_i}$$

(3.9)
where \( N_{i,p} \) gives the number of phonons in the \( i \text{th} \) spectral bin with polarization \( p \). Then, another random number, \( R \), is drawn. If the random number satisfies the condition \( P_{i,p-1} < R < P_{i,p} \), then the phonon is assigned to the \( p \text{th} \) polarization branch. Once the frequency and the polarization are determined, the magnitude of the group velocity can be assigned via Equation 2.6. This completes the initialization of the system and the phonons are allowed to drift and scatter.

### 3.3 Linear Drift of Phonons

Once the initialization of all phonons is achieved, they are allowed to drift according to their group velocities, \( v_g \), and the chosen time-step, \( \Delta t \). A time-step needs to be chosen for each material such that the fastest phonons are not allowed to traverse an entire cell length. At each time step, phonon positions are updated as

\[
\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + v_g \Delta t \tag{3.10}
\]

As the simulation progresses, phonons are allowed to pass in and out of neighboring cells. As a result, each cell’s energy and temperature will be changed. And so, at the end of each drift phase, each cell is assigned an energy, \( E_{\text{cell}} \), by summing the energies of all phonons it contains. Each cell is then assigned a “pseudo-temperature” \( \tilde{T} \) by performing a numerical inversion of Equation 3.1 as

\[
E_{\text{cell}} \cdot W = V \sum_p \sum_{b=1}^{N_b} \left[ \frac{\hbar \omega_i}{\exp \left( \frac{\hbar \omega_i}{k_B \tilde{T}} \right) - 1} \right] \frac{K^2_{i,p}}{2 \pi^2 v_{g_i,p}} g_p \Delta \omega \tag{3.11}
\]

We must use the term pseudo-temperature here since we are studying a system which is not in thermodynamic equilibrium. Thus, temperature has no physical meaning here except for a measure of energy content in the cells. The calculation of this pseudo-temperature is essential for the calculation of the phonon scattering time-scales that were discussed in Sections 1.1.1 and 1.2.

This completes the drift phase and the phonons are now allowed to scatter, which is described in the next section. Since the MC treats phonon drift and scattering sequentially, the BTE is essentially decoupled at each time step into two equations: a free-flow equation and a spatially homogeneous Boltzmann equation. The free-flow solution is then used as the initial condition for the second step. This splitting of the BTE introduces an error that is first-order in time[10].

### 3.4 Scattering of Phonons

In this study, the bulk hypothesis is assumed and there is no scattering from the cell boundaries. All boundaries are treated as being periodic with exception of the two end cells. A perfect crystal is also assumed, and so, defect and impurity scattering is not considered. Hence, three-phonon interactions are treated as the sole scattering mechanism.

As described in Section 1.1.1 and 1.2, each phonon is assigned a total relaxation time depending on its temperature and angular frequency. From this relaxation time, the probability, \( P_{\text{scat}} \),
that the phonon is scattered during the present time-step is calculated via Equation 1.3. A random number, \( R \), is generated. If \( R < P_{\text{scat}} \), the phonon is scattered. For silicon simulation half of the scattered phonon are treated as a Normal process, while the other half are considered to have undergone an Umklapp scattering\[6\]. For \( \text{UO}_2 \), the N and U contributions to the total scattering time-scales are summed up separately. This allows us to calculate the probability of an Umklapp scattering as

\[
P_U = \frac{1/\tau_U}{1/\tau_U + 1/\tau_N}
\]

(3.12)

An additional random number in then drawn to check for a U or N process. When a phonon scatters, its frequency, polarization, wave vector, and group velocity are all re-sampled. If the event is deemed an Umklapp process, then the phonon’s direction is also resampled.

However, because the scattering time-scales are frequency dependant, a scattered phonon’s frequency must be sampled from a new distribution function. Otherwise, the probability of destroying a phonon will be different from the probability of sampling that phonon back into the simulation. To remedy this, the cumulative distribution \( F \), given by Equation 3.7, is now modulated by the probability of scattering:

\[
F_{\text{scat}}(\tilde{T}) = \frac{\sum_{j=1}^{N_j} \tilde{T_j} \times P_{\text{scat},j}}{\sum_{j=1}^{N_b} \tilde{T_j} \times P_{\text{scat},j}}
\]

(3.13)

By re-sampling scattered phonons from an equilibrium distribution, the scattering processes serve to push the local thermodynamic state a bit closer to equilibrium. The use of the \( F_{\text{scat}} \) function to re-sample scattered phonon frequencies ensures that the simulation will conserve energy.

At the end of the scattering algorithm, the net heat current along the \( z \) direction is calculated as

\[
h_z = \sum_{n=1}^{N^*} \sum_{j=1}^{N_j} W_n \omega_n v_{gn} \cdot \hat{k}
\]

(3.14)

Average conductivities are then calculated by directly applying Fourier’s law of heat conduction for a prescribed temperature gradient. For example, the conductivity at 300K is estimated by a simulation in which the first cell is held at 310 K and the last cell is held at 290 K. A temperature difference of 20 K between the hot and cold cell is used for all simulations.
CHAPTER 4

RESULTS AND DISCUSSION

In building the Monte Carlo code for $UO_2$, we first needed to benchmark the code by running test cases for silicon which had already been presented in the literature. The model for Silicon aims to reproduce the work by Lacroix et al. [6] as closely as possible. Comparison between this study and Lacroix’s results are presented in Section 4.1. In Section 4.2, results for the temperature dependence of the thermal conductivity in $UO_2$ are presented and compared to experimental data.

4.1 Verification of the Monte Carlo Code

The first test case for benchmarking the Monte Carlo code for silicon was a ballistic regime simulation. In the ballistic regime, the phonon mean free path becomes larger than the structure length. Here, the hot and cold end boundaries are set at 11.88 K and 3.0 K, respectively. At such low temperatures, three-phonon scattering events can be neglected, and the phonons simply fly from the hot to cold extremities without colliding. This results in a uniform temperature profile at 10 K. The geometry used is a 40 cell stack with cell dimensions, $(L_x, L_y, L_z) = (5 \times 10^{-7}, 5 \times 10^{-7}, 2.5 \times 10^{-7})$. The time-step and number of frequency bins are set to 5 ps and 1000, respectively. As seen in Figure 4.1, Lacroix’s results are recovered.

Next, transient calculations were made for room temperature silicon. All parameters are the same except that the simulation domain is shortened to 2 microns $(L_z = 5 \times 10^{-8})$ and the hot and cold ends are held at 310 K and 290 K, respectively. These silicon results are compared to those obtained by Lacroix et al. for germanium in Figure 4.2.

Finally, nine separate silicon simulations were run at temperatures ranging from 100 K to 500 K. All parameters are the same as those from the transient room-temperature simulation except for the domain length. Here, the computational domain is extended to 3 micron, versus the 2 micron used by Lacroix, to achieve values closer to bulk. Our results along with those presented by Lacroix are shown in Figure 4.3. The deviations from bulk data found at lower temperature are due to ballistic effects which begin to appear at the hot and cold boundary ends.
Figure 4.1: (a) Ballistic regime temperature profile from Lacroix et al. [6] (b) This study

4.2 Thermal Conductivity Calculations for $UO_2$

Preliminary simulations for $UO_2$ were run at five different temperatures ranging between 100 K and 450 K. The results are compared to Molecular Dynamics and experimental results[18] in Figure 4.4. The computational domain is defined as $(L_x, L_y, L_z) = (5 \times 10^{-8}, 5 \times 10^{-8}, 1.0 \times 10^{-8})$ and $\Delta t = 0.5$ ps. Each simulation was set to run for 10,000 time steps. However, at the time that this paper was produced, the 400 K and 450 K runs had yet to finish the full 10,000 steps. These runs, most likely, have yet to reach a steady-state and the validity of these points is questionable. The heat current in each simulation is averaged over the last 1,000 time-steps completed. Despite this averaging, large statistical fluctuations were still seen in the 400 K and 450 K runs.

Although a limited number of conductivity measurements were obtained at the time of this writing, the agreement of these results with modern molecular dynamics simulations is very exciting. This is the first MC simulation ever attempted for modeling thermal transport in $UO_2$, thus, these preliminary results are promising. Future simulations at 400 K and above need to be ran with a reduce weighting parameter $W$ to reduce statistical fluctuations.
Figure 4.2: (a) Fourier regime temperature profile from Lacroix et al. [6] (b) This study

Figure 4.3: (a) Temperature dependence of thermal conductivity in silicon as presented by Lacroix et al. [6] (b) This study
Figure 4.4: (a) (Watanabe et al.[18]) Conductivity of $UO_2$ from MD simulations compared to experimental (b) This study
CHAPTER 5

SUMMARY AND CONCLUSIONS

In this chapter, a summary of this work is presented and the importance of the results is discussed. The future plans for continuing this research concludes the chapter.

5.1 Summary

The degrading of nuclear fuels due to large temperature gradients within the fuel pellets, makes the understanding of thermal transport in these fuels of utmost importance. A comprehensive understanding of all mechanisms that contribute to the transport properties of $UO_2$ is needed for its improvement as a fuel source. This work has presented a Monte Carlo (MC) model which solves the Boltzmann Transport Equation (BTE) for phonons in single-crystal $UO_2$. This model improves upon previous MC models by implementing both energy and momentum conservation in phonon-triplets to calculate the phonon scattering time-scales. The model is tested by calculating the temperature dependence of thermal conductivity in $UO_2$ near room temperature. These preliminary runs agree well with recent molecular dynamics simulations.

5.2 Importance of Results

This work is the first MC model for calculating thermal conductivities for $UO_2$. The model seems to properly account for the interactions among the phonon polarizations by implementing universal conservation rules instead of using fitting parameters as most previous works have done. Eliminating the need for these fitting parameters in the calculation of phonon time-scales is essential for a better understanding of thermal transport. Because the this work makes no assumption in the strengths of these time-scales, and only enforces conservation laws, the model can be applied to any crystal, not limited in application to $UO_2$.

5.3 Future Work

As mentioned this model only predicts $UO_2$ conductivities in defect-free crystals. The ultimate goal of this study is the understanding and inclusion of all phonon scattering
mechanisms present in irradiated $UO_2$. This would include scattering from various crystal impurities. This will require knowledge of how these various defects will affect the scattering time-scales for each polarization branch. Before the modeling of defects is considered, the present model needs to be run with larger phonon number to decrease the statistical fluctuation which come from increased temperature. A study of the effect the scaling factor $W$ has on the amount of statistical error at each temperature would is needed here. Also, a comparison of the magnitude of scattering time-scales in $UO_2$ as compared to those in $Si$ will be include in a future work.
BIBLIOGRAPHY


BIOGRAPHICAL SKETCH

The author graduated high school from Hampton High School (Hampton, TN) in Spring 2002 before entering East Tennessee State University (Johnson City, TN). A Bachelor of Arts degree in Physics and Mathematics was earned for ETSU during the Spring of 2008. The author then entered the Department of Physics at Florida State University (Tallahassee, FL) in Fall 2008 semester for graduate work. A Masters of Science degree in Physics was earned after the Fall of 2009. The author then entered the Department of Scientific Computing from which another Masters of Science degree was awarded in Fall 2011 upon completion of this work.