

**B. TECH PROJECT
REPORT**

On

**Thermal Properties of
Polycrystalline carbon
nanotubes: A computational
study**

BY
CH AJAY SIMHA (ME150003009)
K DASARATH SANKAR SAI (ME150003015)



**DISCIPLINE OF MECHANICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY INDORE**

May 2018

Thermal Properties of Polycrystalline carbon nanotubes: A computational study.

A PROJECT REPORT

*Submitted in partial fulfillment of the
requirements for the award of the degrees
of*

**BACHELOR OF TECHNOLOGY
in
MECHANICAL ENGINEERING**

Submitted by:

**CH AJAY SIMHA (ME150003009)
K DASARATH SANKAR SAI (ME150003015)**

Guided by:

DR. SHAILESH I. KUNDALWAL



**INDIAN INSTITUTE OF TECHNOLOGY INDORE
November 2018**

CANDIDATE’S DECLARATION

We hereby declare that the project entitled “**Thermal Properties of Polycrystalline carbon nanotubes: A computational study**” submitted in partial fulfillment for the award of the degree of Bachelor of Technology in ‘Mechanical Engineering’ completed under the supervision of Dr. Shailesh Ishwarlal Kundalwal, Assistant Professor of Mechanical Engineering, IIT Indore is an authentic work.

Further, I/we declare that I/we have not submitted this work for the award of any other degree elsewhere.

CH AJAY SIMHA

K DASARATH SANKAR SAI

CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the students is correct to the best of my/our knowledge.

Dr. Shailesh Ishwarlal Kundalwal

Assistant Professor

Mechanical Engineering

Preface

This report on “**Thermal Properties of Polycrystalline carbon nanotubes: A computational study**” is prepared under the guidance of Dr. Shailesh Ishwarlal Kundalwal.

Through this report, we have developed a computational model for determining thermal conductivity and thermal expansion of carbon nanotubes. Carbon nanotubes with different grain distributions are developed for simulation purposes.

This was an attempt to understand the behavior of thermal properties at molecular scales which has been explained clearly to the best of our knowledge.

CH AJAY SIMHA

B.Tech. IV Year

Discipline of Mechanical Engineering

IIT Indore

K DASARATH SANKAR SAI

B.Tech. IV Year

Discipline of Mechanical Engineering

IIT Indore

Acknowledgements

We sincerely thank Dr. Shailesh Ishwarlal Kundalwal for giving us the opportunity to take on this project.

We would also like to specially mention Vijay Choyal for helping us with technical issues which were encountered during the project.

It is their help in providing the pre-requisites of the project that led us to the project completion.

In the absence of their guidance we would not have accomplished what we have now.

CH AJAY SIMHA

B.Tech. IV Year

Discipline of Mechanical Engineering

IIT Indore

K DASARATH SANKAR SAI

B.Tech. IV Year

Discipline of Mechanical Engineering

IIT Indore

Abstract

Carbon nanotubes (CNTs) do not exist in their pristine form naturally and they have certain types of defects like the atom vacancy and grain boundary defect. In comparison to all other types of defects, grain boundary defects affect the thermal conductivity of CNTs significantly and the study of thermal properties of polycrystalline CNTs is essential. In this work, Fourier's law and Reverse Non-Equilibrium Molecular Dynamics (RNEMD) method have been applied for various lengths of (10,10) chirality pristine and polycrystalline CNTs based on adaptive intermolecular reactive empirical bond order force field potential to calculate their thermal conductivities. The current results reveal the deviation in thermal properties of polycrystalline CNTs with different grain boundaries compared to that of pristine.

Table of Contents

Candidate's Declaration

Supervisor's Certificate

Preface

Acknowledgments

Abstract

Table of Contents

Chapter 1 Overview

1.1 Introduction

1.2 History

1.3 Motivation

Chapter 2 Theoretical Background

2.1 Carbon Nanotubes(CNTs)

2.1.1 Chirality

2.1.2 Pristine CNTs

2.1.3 Polycrystalline CNTs

2.2 Thermal Properties

2.2.1 Thermal Conductivity (Fourier's Law)

2.2.2 Coefficient of Thermal Expansion

2.2.3 Specific Heat

2.2.4 Equipartition Theorem

2.3 Molecular Dynamics

2.3.1 Newtonian Equations of Motion

2.3.2 Velocity Verlet Method

2.3.3 Interatomic Potentials

Literature Review

Chapter 3 Tools used for simulation.

3.1 NanoEngineer

3.2 LAMMPS

3.3 OVITO

3.4 Python and C++

3.5 Flow Chart

Chapter 4 Algorithmic System Design

4.1 Parameters of Interest

4.1.1 Boundary Conditions

4.1.2 Simulation Box

4.1.3 Potential File

4.1.4 Units Conversion to SI

4.2 Thermal Conductivity

4.2.1 Fourier's Law

4.2.2 Programming Logic

4.3 Coefficient of Thermal Expansion

4.3.1 Definition

4.3.2 Programming Logic

Chapter 5 Formulae used for Calculation

5.1 Thermal Conductivity

5.2 Coefficient of Thermal Expansion

Chapter 6 Results and Discussions

6.1 Thermal Conductivity

6.1.1 Conductivity versus Length

6.1.2 Temperature versus position on CNT

6.2 Coefficient of Thermal Expansion

Chapter 7 Conclusions and Scope for future work

References

List of Figures

Fig.1.1: Nanomaterial applications

Fig 2.1: Roll up vector and Unit vector

Fig 2.2: Polycrystalline CNT when cut along the length

Fig 2.3: Polycrystalline CNT with transverse GB

Fig 2.4: Polycrystalline CNT with parallel GB

Fig 2.5: Variation of simulation parameters across timesteps

Fig 3.1: Steps followed

Fig 4.1: Statistically averaged T vs position graph for pristine 60nm

Fig 4.2: Temperature of CNT vs time

Fig 4.3: Temperature of hot and cold ends vs time

Fig 6.1: Thermal Conductivity plots for different GBs

Fig 6.2: Temperature on various position on CNT for 60nm pristine

Fig 6.3: Temperature on various position on CNT for 60nm parallel GB

Fig 6.4: Temperature on various position on CNT for 60nm transverse GB

Fig 6.5: Pristine Thermal Expansion plot

Fig 6.6: Polycrystalline Thermal Expansion plot

List of Tables

Table 6.1: Thermal Conductivity values for different GBs

Table 6.2: Thermal Conductivity values from reference [12]

Table 6.3: Thermal Expansion values for different GBs

Table 6.4: Thermal Expansion values from reference [7]

Chapter 1 Overview

1.1 Introduction

1.2 History

1.3 Motivation

1.1 Introduction

Enormous developments has been made in area of carbon-based materials and new exotic materials like Bucky ball C_{60} and carbon nanotubes are discovered which created a great scientific curiosity because of its unique properties. These materials have shown excellent electrical properties, which are a foundation for nanomaterials based electronics. As experiments are hard to conduct on the nanomaterial, computer simulations are a powerful tool in studying the properties of nanomaterials to gain proper understanding of the structural properties and stability conditions. In this thesis, we create computational models to find out thermal conductivity and coefficient of thermal expansion for carbon nanotubes.

1.2 History

Only carbon forms or allotropes known until 1980's are the carbon, graphite, diamond. Then bucky ball C_{60} and carbon nanotubes were discovered. Carbon nanotubes (CNTs) are known as rolled up graphene (a single layer of graphite) sheets discovered by Iijima experimentally with transmission electron microscopy (TEM) Multi-walled Carbon nanotubes (MWCNTs) were observed [1]. Since then, the study of mechanical, thermal and electrical properties of carbon nanotubes is being conducted extensively. CNTs demonstrated exceptionally high elastic and thermal properties. The global market for carbon nanotubes in 2015 has been estimated to be worth about \$2.26 billion¹; an increase of 45% from 2009 (i.e. ~ \$ 1.24 billion). This was due to the growing potential of CNTs in electronics, plastics and energy storage applications and the projected market of CNTs is expected to be around \$ 5.64 billion in 2025.

1.3 Motivation

With the advent of science and technology, there is so much research going on the nano-sized materials to use nanomaterials in real life applications. Carbon nanotubes are believed to have exceptional thermal and mechanical properties, which makes them a suitable replacement for their counterparts that are being used now, to increase the efficiency and lifetime of the technological products. So, the study of properties carbon nanotubes and their defects is necessary for their complete exploitation of the their properties and their defects for their real life applications.

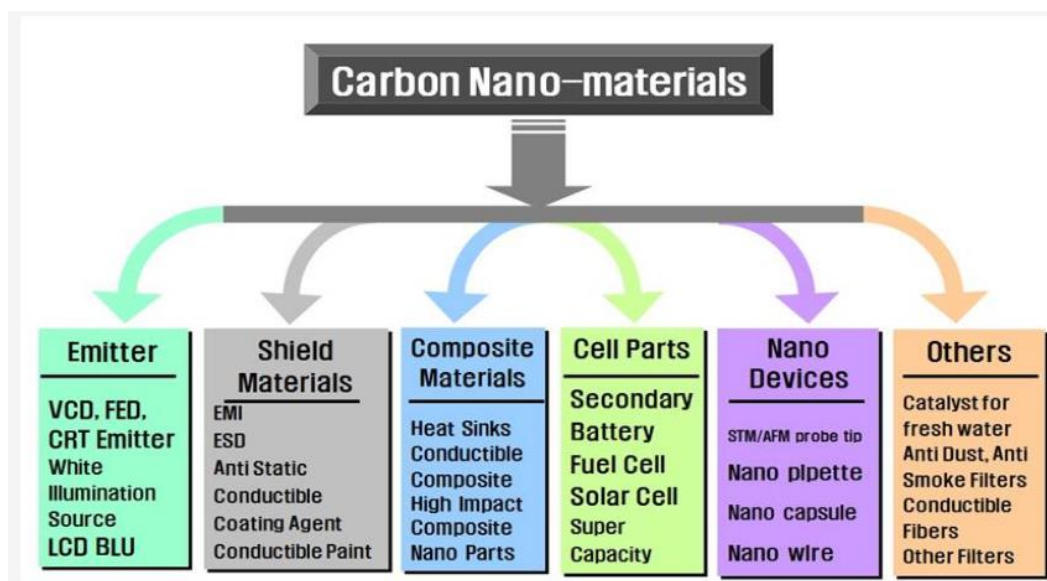


Fig.1.1: Nanomaterial applications

Chapter 2 Theoretical Background

2.1 Carbon Nanotubes (CNTs)

2.1.1 Chirality

2.1.2 Pristine CNTs

2.1.3 Polycrystalline CNTs

2.2 Thermal Properties

2.2.1 Thermal Conductivity (Fourier's Law)

2.2.2 Coefficient of Thermal Expansion

2.2.3 Specific Heat

2.2.4 Equipartition Theorem

2.3 Molecular Dynamics

2.3.1 Newtonian Equations of Motion

2.3.2 Velocity Verlet Method

2.3.3 Interatomic Potentials

Literature Review

2.1 Carbon Nanotubes (CNTs)

2.1.1 Chirality

There are various ways of defining a unique structure for each carbon nanotube. One way is to think of each CNT as a result of rolling a graphene sheet, by specifying the direction of rolling and the circumference of the cross-section [2].

The roll-up vector C_h , which can be expressed as the linear combination of the lattice basis (a_1 and a_2) is given as follows.

$$C_h = na_1 + ma_2$$

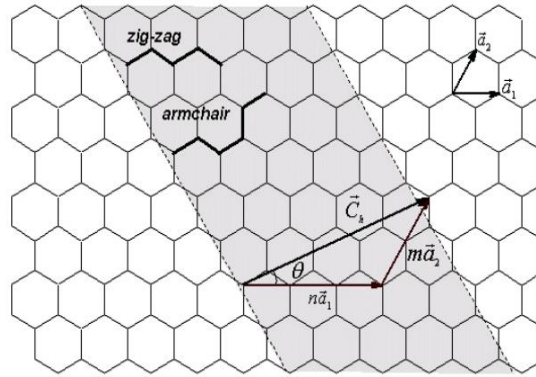


Fig 2.1: Roll up vector and Unit vector

$$D = \frac{\sqrt{3}\alpha \sqrt{m^2 + mn + n^2}}{\pi}$$

Where D is the diameter of the final rolled nanotube.

m, n are coefficients of lattice basis which determine rollup vectors.

α is the bond length of C-C interaction.

2.1.2 Pristine CNTs

The most narrow definition of pristine CNTs, to be used throughout this work, is of seamless and undistorted graphitic cylinders with no vacancy/grain boundary defects. They can also be classified as a group of CNTs with perfectly repeating unit cell of a hexagon which is repeated throughout the structure.

2.1.3 Polycrystalline CNTs

Polycrystalline CNTs are solids that are composed of many crystallites of varying size and orientation. These crystallites are known as grain boundaries. Grain boundary is an inherent structural impurity and very challenging to avoid. Polycrystalline CNTs can be viewed as the polycrystalline graphene sheet with different types of grain distribution rolled to form a tube.

In this work pentagons, heptagons are created in different combinations along a line to produce different types of the grain boundaries [5]. These polycrystalline carbon nanotubes are obtained by manipulation of bonds that is breaking and joining of bonds to form a pentagon-heptagon-heptagon family. This family is repeated until a grain boundary is formed. Quadrilaterals, octagons and nonagons are not considered in this work due to their higher formation energy and are rarely observed in experiments [6].

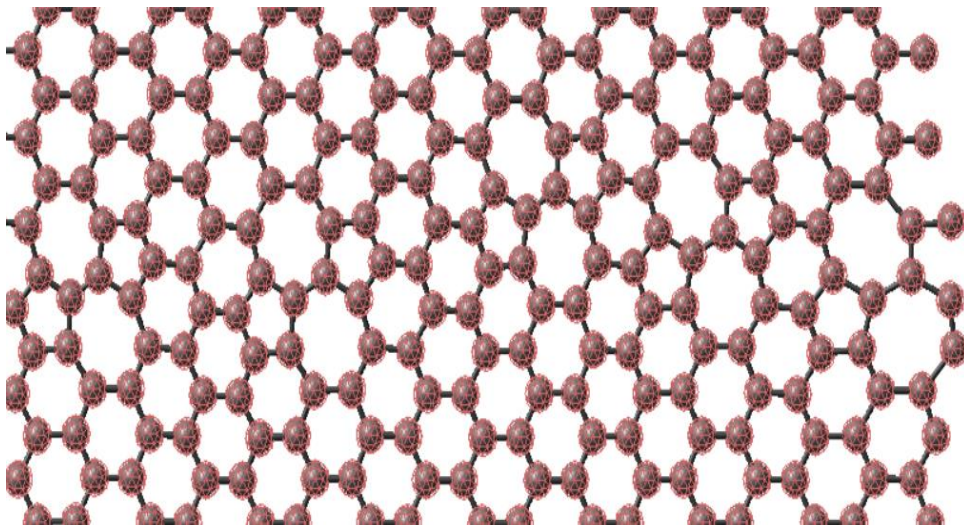


Fig 2.2: Polycrystalline CNT when cut along the length

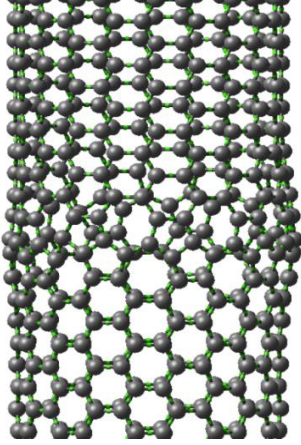


Fig 2.3: Polycrystalline CNT with transverse GB

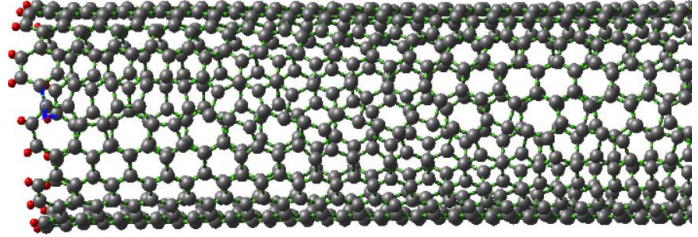


Fig 2.4: Polycrystalline CNT with parallel GB

2.2 Thermal Properties

2.2.1 Thermal Conductivity

Heat conduction occurs when thermal energy is transported by the random motion of heat carriers. Heat conduction can be described by Fourier's law that states the heat flux is proportional to the temperature gradient [3].

$$q = -k\nabla T$$

where q is the local heat flux, k is thermal conductivity, ∇ is the gradient operator. Thermal conductivity is dependent on the direction of the material; therefore, it can be written as a tensor. This directional property is estimated/predicted to help exceptionally in case of CNTs or any one dimensional for that matter as there are no other dimensions for the acoustic vibrations to disturb.

In this work, as Single Walled CNTs can be considered to have negligible radial propagation of heat we can write the ∇ operator directly as derivative in z direction as other components will be zero.

2.2.2 Coefficient of Thermal Expansion

Coefficient of thermal expansion is given as the fractional change in size per degree change in temperature at same pressure conditions.

This can be written mathematically as,

$$\alpha_v = \frac{1}{V} \left(\frac{\Delta V}{\Delta T} \right)_P$$

Since in our case area of cross-section does not change by a significant amount we can takeout area term from both numerator and denominator terms and cancel it which gives us the following result [7].

$$\alpha = \frac{\Delta L}{L \Delta T}$$

α is the coefficient of linear thermal expansion.

ΔL is the change in length of the system.

L is the initial length and ΔT is the change in temperature.

2.2.3 Specific Heat

Specific heat is the amount of thermal energy required to raise the temperature of unit mass substance through 1K. The relationship does not apply if a phase change is encountered, because the heat added or removed during a phase change does not change the temperature [4].

Although in this work, specific heat is not calculated it is one of the thermal properties.

Specific heat is given as,

$$Q = mc\Delta T$$

Where, Q is the amount of heat added/subtracted,

m is the mass of the system ,

ΔT is the temperature change in the system,

and c is the specific heat.

2.2.4 Equipartition Theorem

The equipartition energy theorem states that the total energy is equally shared among all of its degree of freedoms, when a system is in thermal equilibrium. The equipartition energy theorem relates the average energies of a system to the temperatures [3].

In case of non-rotational scenarios we can consider the Equipartition Theorem to result in the following conclusion that average kinetic energy of atoms in all the three axes is $(3/2)k_B T$.

Kinetic energy can be written as $\frac{1}{2}mv^2$. So on equating we get,

$$T_k = \frac{1}{3n_k k_B} \sum_{i \in k}^{n_k} m_i v_i^2$$

Thus, we have a relation between temperature and kinetic energy which proves to be helpful when calculating temperature values for a given system at any instant by just knowing their velocities from simulations.

2.3 Molecular Dynamics

Molecular Dynamics is a powerful tool in studying the behavior of systems in molecular level where the actual measurement of the properties is not possible. Molecular Dynamics are the numerical computations of an estimated path of atoms. Classical MD simulations are based on Newton's second law of motion and an inter-atomic potential. If the mass and the inter-atomic potential are known, then the next position in time can be determined. Results of the calculated trajectory can be analyzed to determine properties, like thermal conductivity [3]. Molecular dynamics (MD) is a technique where the time evolution of a set of interacting atoms is followed by numerical integration of Newton's equation of motion [8].

2.3.1 Newtonian Equations of Motion

The trajectory of an atom is estimated by solving Newton's second law of motion. This simple equation becomes a complex computation since each atom's equation of motion must be solved. The general Newtonian equation of motion for a system of N atoms is shown.

$$\sum_{\substack{j=1 \\ j \neq i}}^N F_{ij} = m_i \frac{d}{dt} \left(\frac{dr_i}{dt} \right)$$

$$i=1,2,3,4,5,6,\dots,N$$

where F_{ij} is the force exerted on atom i caused by atom j and m_i and r_i are the mass and position of atom i , respectively. A limitation of the Newtonian equation is it requires additional equations to describe rotational motion. By using the Lagrangian or Hamiltonian equations of motion, all the degrees of freedom of an atom's trajectory can be obtained in one vector of generalized coordinates, r .

The system's Lagrangian is defined as the difference of the kinetic energy and potential energy,

$$L(t, r, dr / dt) = K(r, dr / dt) - U(r)$$

dr/dt is the time derivative of r or the generalized velocity. The Lagrange equation of motion is

$$\frac{d}{dt} \left(\frac{\partial L}{\partial (dr_i / dt)} \right) - \frac{\partial L}{\partial r_i} = 0$$

the subscript i denotes the generalized coordinates for each atom.

Similarly, the Hamiltonian describes the energy of the system; however, it describes the total energy of the system

$$H(t, r, p) = K(p) + U(r)$$

Hamiltonian is a function of the generalized coordinate vector \mathbf{r} and a generalized momentum \mathbf{p} . The generalized momentum is derived from the Lagrangian by differentiating with respect to the generalized velocity

$$p = \frac{\partial L}{\partial (dr_i / dt)}$$

Hamilton equations of motion are

$$\frac{dp_i}{dt} = - \frac{\partial H}{\partial r_i}$$

$$\frac{dr_i}{dt} = \frac{\partial H}{\partial p_i}$$

Any of the three equations of motion can be used to describe the atom's trajectory.

2.3.2 Velocity Verlet Method

Velocity Verlet Integration technique is used in this MD simulations to determine the velocity from accelerations of the particle at the end of each and every iteration from the above equations. The determined velocities and positions at the end of every iteration are used to find out the values for the next iteration till the simulation is complete.

$$V(t_0 + \frac{\Delta t}{2}) = V(t_0) + a(t_0) \frac{\Delta t}{2}$$

$$r(t_0 + \frac{\Delta t}{2}) = r(t_0) + V(t_0 + \frac{\Delta t}{2})\Delta t$$

Where $V(t_0)$ is the velocity at instant t_0 .

$a(t_0)$ is the acceleration at instant t_0 .

$r(t_0)$ is the position at instant t_0 .

Δt is the timestep interval.

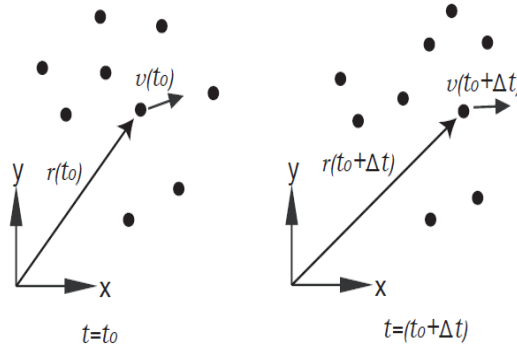


Fig 2.5: Variation of simulation parameters across timesteps

2.3.3 Interatomic Potentials

Interatomic potentials are mathematical functions for calculating the potential energy of a system of atoms with given positions. These potential energy values are then used to calculate individual

accelerations for each timestep/iteration so as to get velocity and corresponding new position which are then used to calculate potentials till the simulation ends.

In case of the AIREBO potential files which are known for their precision and are used in this work interatomic potential function is given as

The LJ used in above equation is given as MD simulations. The Lennard-Jones potential is used in MD simulations to describe non-bonded interactions[9-11]. The Lennard-Jones potential is defined as,

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} E_{kijl}^{TORSION} \right]$$

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where σ is the finite distance at which the inter-particle potential is zero,

ϵ is the depth of the potential well,

r is the distance between the particles.

More information can be found on the AIREBO pairwise interactions manual page on the LAMMPS website mentioned in references.

Literature review

References	K(W/mK)	System Length (nm)	Potential function	Method
Padgett and Brenner [13]	~35–350	~10–310	Brenner--II	NEMD
Eric Pop[14]	~3500	2600	-----	Joule-self heating
Hone [15]	~225	5000	-----	Comparative: constantan rod
Lukes and Zhong [16]	20–160	5–40	Brenner-II + LJ	EMD
Grujicic et al. [17]	~173-179	~2.5-40	AIREBO	EMD
Feng et al. [18]	~50-590	6.52-34.57	Brenner -II	NEMD

Early experiments used samples of CNT mats, which would show a lower thermal conductivity than an individual CNT due to the interaction between the multiple CNTs [19]. Padgett and Brenner et al. [11] studied the effect of thermal conductivity on the degree of functionalization. They have found that the thermal conductivity degrades in presence of functionalization. Eric et al. [14] showed that the thermal conductivity of CNT of 2.6 μm and 1.7 nm is nearly 3500 W/mK approximately by joule self heating process. Hone et al. [15] measured thermal conductivity parallel to the axis of a SWNT mat to have a thermal conductivity of ~225 W/m/K. Lukes and Zhong et al [16] determined the thermal conductivity values to be in the range of 20-160 W/mK for lengths in 5-40 nm using modified Brenner potential. Feng et al [18] studied the effect of doping and vacancies on

thermal conductivity of carbon nanotubes. Leendertjan Karssemeijer et al. [7] determined the coefficient of thermal expansion for (10,10) chirality CNT to be $2.24 \cdot 10^{-6} \text{ K}^{-1}$ for a length of 54.1 nm.

Chapter 3 Tools Used for Simulations

3.1 NanoEngineer

3.2 LAMMPS

3.3 OVITO

3.4 Python and C++

3.5 Flow Chart

3.1 NanoEngineer

A software which is primarily used to construct/modify a variety of geometric configurations consisting of atoms. Many features available are completely assisted with GUI (Graphical User Interface) which makes constructing molecules with desired configuration and geometry, very easy. In this work, NanoEngineer was used to manufacture pristine carbon nanotubes with 10-10 chirality with sp² hybridisation of C atoms. Once CNTs were generated they were used for pristine thermal property calculations. Pristine carbon nanotubes are also used to make vacancy defects in the CNT such that we end up getting a transverse or longitudinal grain boundary. The structural configuration of grain boundaries is well discussed in section 2.1.3.

3.2 LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)

This package is the key ingredient to perform molecular dynamics simulations. This software models ensembles/assembly of particles in various states of matter and can perform various physical phenomenon on them to calculate the desired quantities. In short, LAMMPS is a nano-laboratory for which the user can access anything. It's current limitation is it is a classical model so quantum mechanisms cannot be simulated using this software. In this work, LAMMPS was used to perform various kinds of actions on CNTs such as minimizing energy, altering temperature, applying heat flux etc. One can even dump the whole configuration as if you were taking snapshots of system and play those pictures in sequence using packages such as OVITO.

3.3 OVITO (Open Visualization Tool)

As pointed out in section 3.2 this software's primary moto is to provide GUI for the user to visualize various molecular phenomenon. This is the whole and sole purpose of this tool.

3.4 Python and C++

These are programming languages which were used in this work to perform plotting of graphs for huge datasets and compute averages over various window sizes over data generated through LAMMPS respectively.

3.5 Flow Chart

This is the sequence of packages used from the beginning to the end for all the results obtained in this work.

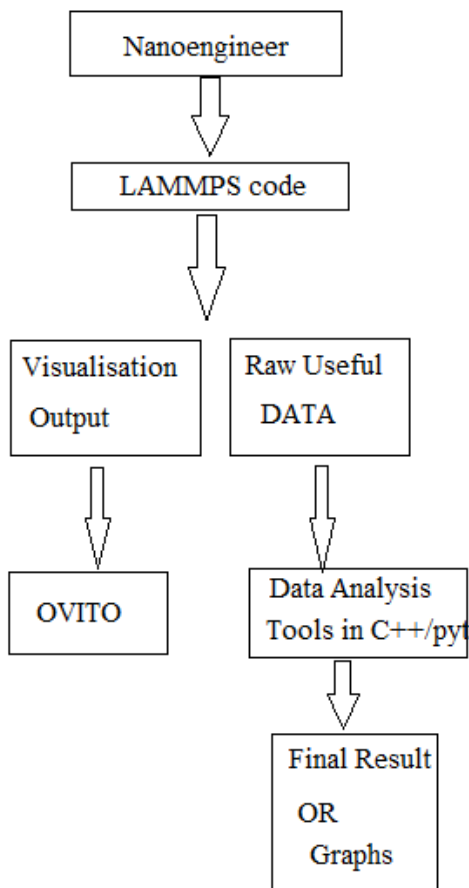


Fig 3.1 : Steps followed

Chapter 4 Algorithmic System Design.

4.1 Parameters of Interest

4.1.1 Boundary Conditions

4.1.2 Simulation Box

4.1.3 Potential File

4.1.4 Units Conversion to SI

4.2 Thermal Conductivity

4.2.1 Fourier's Law

4.2.2 Programming Logic

4.3 Coefficient of Thermal Expansion

4.3.1 Definition

4.3.2 Programming Logic

4.1 Parameters of Interest

While doing simulations in any molecular dynamics we observed that various parameters affect the whole course of the simulations, which must be considered carefully according to our case or else we end up getting incorrect values. Following are the Parameters affecting simulations in LAMMPS :

4.1.1 Boundary Conditions

For our case we chose periodic boundary conditions on all x, y and z directions. We did test non-periodic and fixed boundary condition although it didn't change our conductivity value by a huge amount. In fact, the value obtained was within the uncertainty.

4.1.2 Simulation Box

Both shape and size of the simulation box must be taken according to our system's structure as we observed a huge deviation in the values obtained once we changed the size of the simulation box. In our case, we chose a rectangular simulation box and saw that as the simulation box size decreases to the actual space occupied by our system the values obtained used to converge, which led us to the conclusion that taking simulation box a little bit bigger than system's size is the correct choice.

4.1.3 Potential file

We chose the AIREBO(Adaptive Intermolecular Reactive Empirical Bond Order) potential file as we had only one type of atom i.e. C-atom and this is the potential file that was closest to reality when it comes to pairwise molecular interactions as mentioned in theory. It takes Lenard Jones potential, Rebo potential as well as torsional effects which makes it accurate over others.

4.1.4 Units

LAMMPS, by default uses metal units for all the physical quantities generated computationally. So, to calculate we converted all the measured values to SI from metal. For thermal conductivity the converting factor was found to be 1602, whereas in case of thermal expansion converting factor is exactly 1.

4.2 Thermal Conductivity

4.2.1 Fourier's Law

One might think Fourier's Law cannot be applied at molecular level but we observed the following position vs Temperature graph while trying out. (Graph shown below is for pristine 10-10 chirality and 60nm CNT length. X-axis denotes discrete values of positions on CNT every 5nm regions. Y-axis denotes Temperature of corresponding region in Kelvin.)

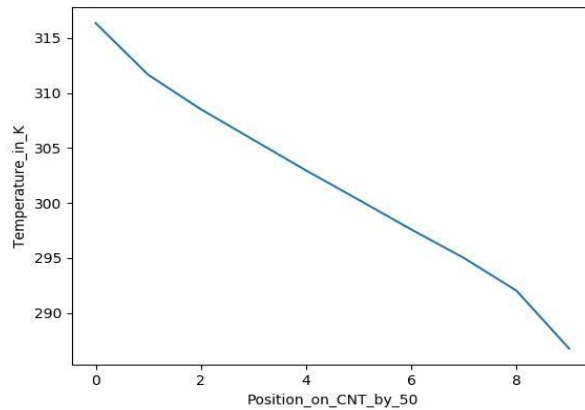


Fig 4.1: Statistically averaged T vs position graph for pristine 60nm

This result was a confirmation to various papers which already used Fourier's law for systems of the size greater than or equal to 10nm. It can also be concluded that heat current is nothing but an acoustic wave passing throughout the region due to interatomic interactions.

4.2.2 Programming Logic

Once applicability of Fourier's Law was satisfactory, we just had to implement it in order to get the values of thermal conductivity for various CNTs. This implementation was accomplished in the following manner.

- Energy Minimization – Whatever system is present in the simulation box, first it was cooled down to very low temperatures in order to ensure that there were no residual stresses/forces inside the CNT wherein some energy might come from, when time-integration algorithms are applied. (This was the equivalent Temperature(K) versus simulation time(ps) graph for this step when performed on 15nm 10-10 chirality CNT.)

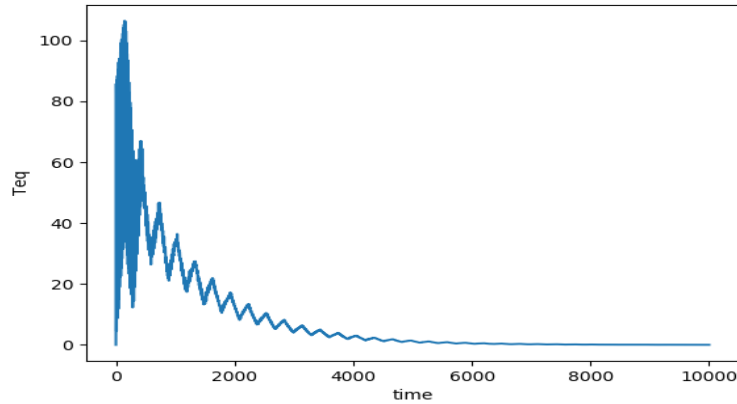


Fig 4.2: Temperature of CNT vs time

- Temperature Stabilization – Once the system was rid of any residual acoustic waves with high amplitudes, the target was to achieve room temperature as we had to calculate thermal conductivity values at room temperature for any structure. This is done by rescaling the velocity of atoms every 10 timesteps wherein each timestep was equivalent to 1 femtosecond. Boltzmann Energy Equipartition Theorem is behind the whole assignment of adjusting the temperature just by changing the velocities. Note : Velocities of atoms were rescaled in such a way that the linear and angular momentum are conserved for the whole group of atoms to which this operation is applied.
- Heat current application – Once we have a CNT at room temperature we added heat to one end and removed heat from the other. Note that added and removed amount at each timestep is exactly same. The system was given enough time to reach to a steady state. (Here steady state is defined as the state wherein properties don't change with time after averaging a collection of many timesteps.) Once steady state is reached Temperatures were calculated and Fourier's law was applied. (Following is the graph of Temperature(K) vs time(ps) of 10-10 chirality, 60nm CNT after coming to steady state. Hot end's temperature is blue in colour and cold end's temperature is orange in colour.)

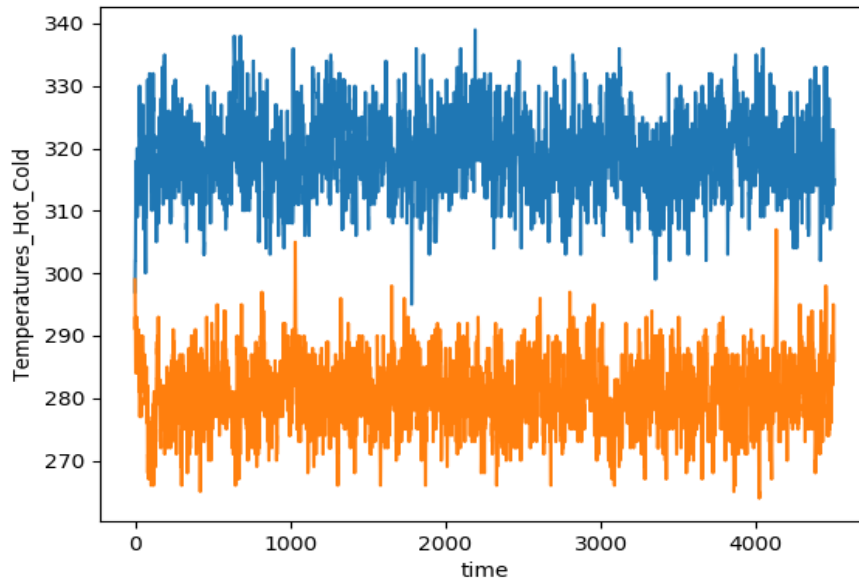


Fig 4.3: Temperature of hot and cold ends vs time

4.3 Coefficient of Thermal Expansion

4.3.1 Definition

The coefficient of thermal expansion describes how the size of an object changes with a change in temperature. Specifically, it measures the fractional change in size per degree change in temperature at a constant pressure.

Apparently for our simulations assuming pressure to be constant area of the carbon nanotube is invariant in our working limits which is then fair to say that coefficient of thermal expansion is equal to linear expansion coefficient.

4.3.2 Programming Logic

Once the above inference was concluded we had to find out the length of given CNT for two temperatures deviated by same amount above and below 300K. This was accomplished in the following manner.

- Energy Minimization – This was explained in 4.2.2 section. This is necessary no matter what quantity we want to measure as we don't want any errors coming in values due to initial leftover stresses due to geometry of the structure.
- Temperature Stabilization – This time we would take the CNT up to 325K and 275K in two different simulations as we want to measure the lengths at two different temperatures separately. The procedure on how to do was pointed out in section 4.2.2.
- Data Collection – Once we had our CNT at required temperature (325K or 275K) the target was to let the acoustic waves propagate throughout the CNT and measure the length of CNT at each timestep and average this length over a huge window which does not change its value significantly over time.

Chapter 5 Formulae Used for Calculations.

5.1 Thermal Conductivity

5.2 Coefficient of Thermal Expansion

5.1 Thermal Conductivity

$$KA = q \frac{\Delta T}{\Delta x}$$

where all the physical quantities have their usual meanings.

$$K_{SI} = K_{\text{metal}} \times \text{Scale}_{\text{metal to SI}}$$

where $\text{Scale}_{\text{metal to SI}} = 1602$

Temperature gradient of hot and cold ends in the Fourier's law can be found by determining individual temperatures of both heatbaths using Equipartition Theorem; as we already know number of particles in each region, Boltzmann constant, mass of each carbon atom before the simulation and velocities of each atom can be known from the simulations.

$$T_k = \frac{1}{3n_k k_B} \sum_{i \in k}^{n_k} m_i v_i^2$$

where all relevant terms are explained in section 2.2.4.

5.2 Coefficient of Thermal Expansion

From the very definition of coefficient of thermal expansion we can write the following.

$$\alpha_v = \frac{1}{V} \left(\frac{\Delta V}{\Delta T} \right)_P$$

As area of cross section available for phonon propagation doesn't change by significant amount in the simulations, we can consider the following cancelling area from above equation in numerator and denominator.

So,

$$\alpha = \frac{\Delta L}{L \Delta T}$$

where all the physical quantities have their usual meanings.

Note that,

$$\alpha_{SI} = \alpha_{\text{metal}}$$

as Temperature units are in Kelvin for both metal and SI. (As strain is a dimensionless quantity it won't change over various units.)

Chapter 6 Results

6.1 Thermal Conductivity

6.1.1 Conductivity vs Length

6.1.2 Temperature vs position on CNTs.

6.2 Coefficient of Thermal Expansion

6.1 Thermal Conductivity

6.1.1 Conductivity vs Length

<i>Length (nm)</i>	Kpristine (W/mK) No GB	Kpolycrystalline (W/mK) Transverse GB	Kpolycrystalline (W/mK) Parallel GB
10	80.286	43.983	57.156
25	112.456	77.714	69.321
55	146.228	123.0388	83.764
80	160.4045	137.7809	95.253

Table 6.1: Thermal Conductivity values for different GBs

<i>Length</i> <i>(nm)</i>	Kpristine (W/mK) No GB
10	85
25	110
55	140
80	165

Table 6.2: Thermal Conductivity values from reference [12]

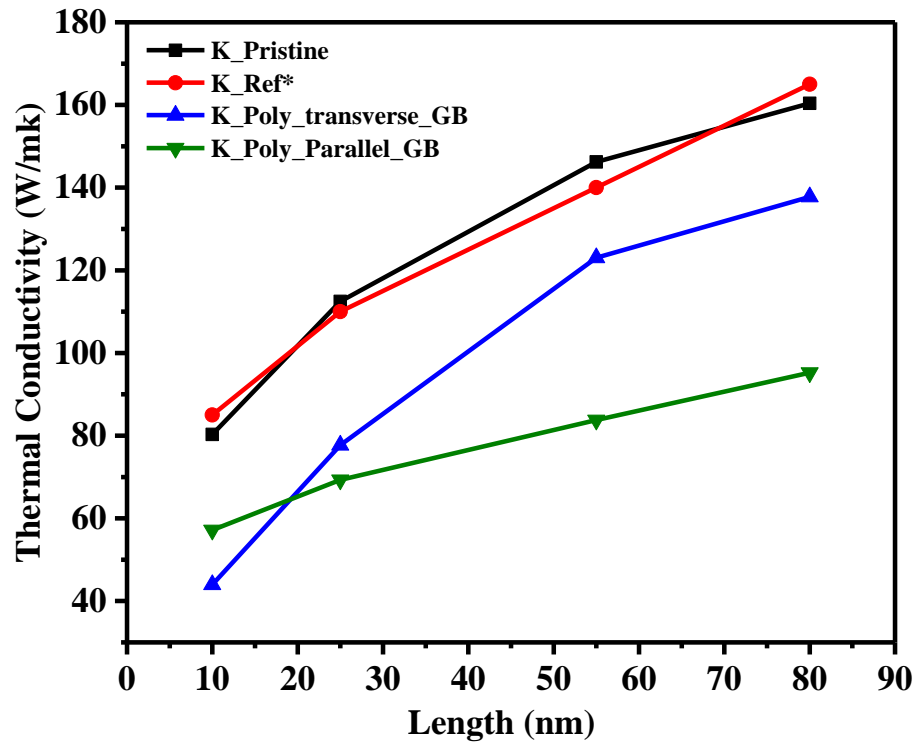


Fig 6.1: Thermal Conductivity plots for different GBs

6.1.2 Temperature vs Position on CNTs

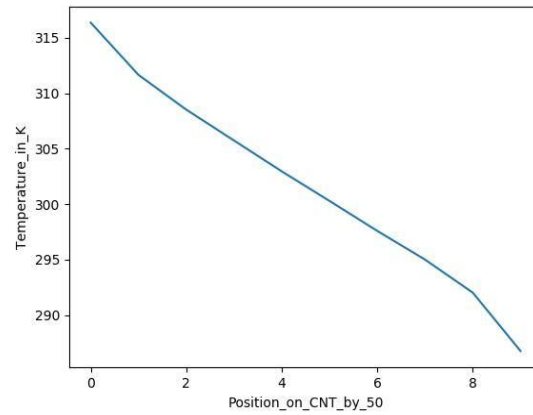


Fig 6.2: Temperature on various position on CNT for 60nm pristine

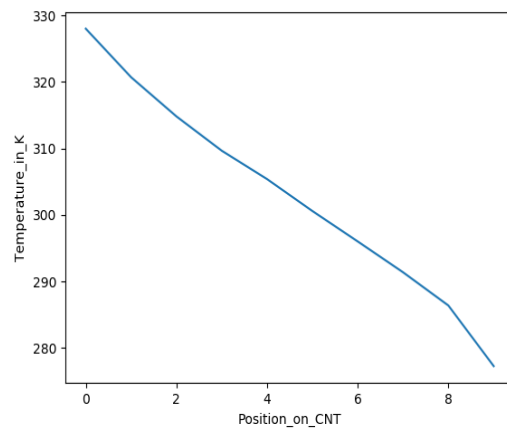


Fig 6.3: Temperature on various position on CNT for 60nm parallel GB

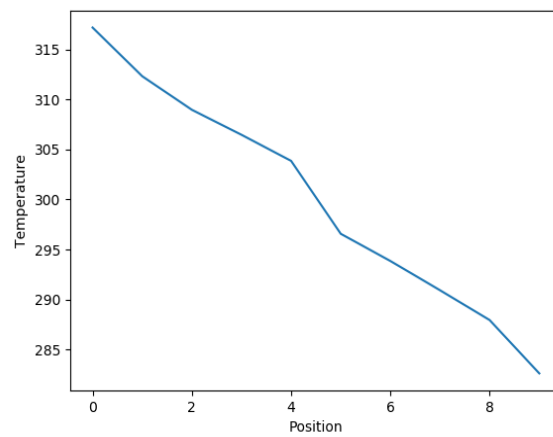


Fig 6.4: Temperature on various position on CNT for 60nm transverse GB

6.2 Coefficient of Thermal Expansion

<i>Length(nm)</i>	<i>$\alpha_{pristine} (K^{-1})$</i>	<i>$\alpha_{poly} (K^{-1})$</i>
15	1.400×10^{-6}	1.508×10^{-6}
30	2.082×10^{-6}	1.975×10^{-6}
60	2.125×10^{-6}	2.072×10^{-6}
85	2.206×10^{-6}	2.265×10^{-6}

Table 6.3: Thermal Expansion values for different GBs

<i>Length (nm)</i>	<i>$\alpha_{pristine_ref}$ (K^{-1})</i>
54.101	2.24×10^{-6}
108.219	2.38×10^{-6}

Table 6.4: Thermal Expansion values from reference [7]

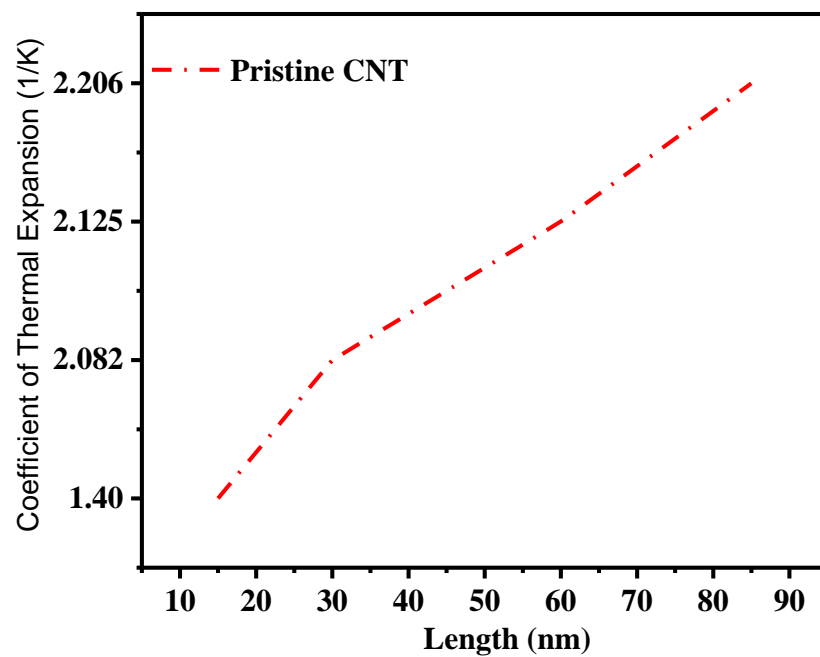


Fig 6.5: Pristine Thermal Expansion plot

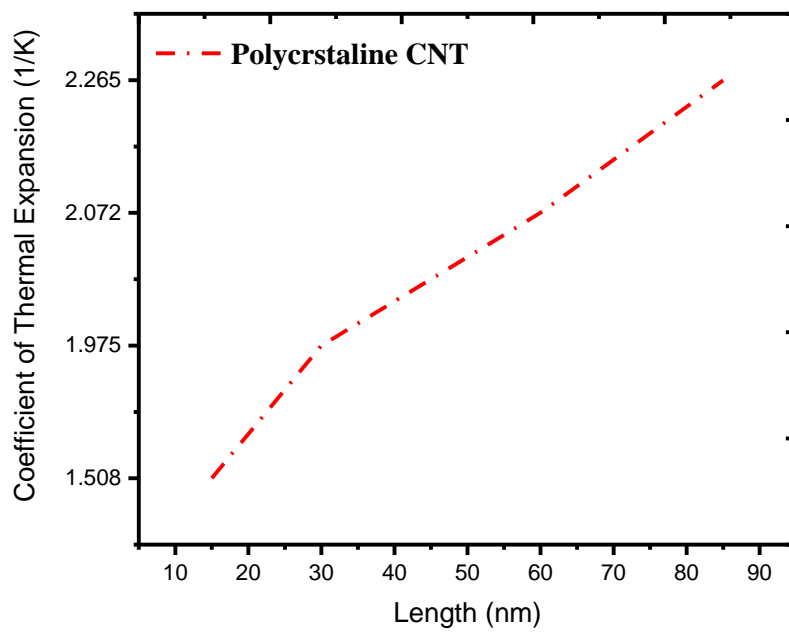


Fig 6.6: Polycrystalline Thermal Expansion plot

Chapter 7 Conclusion and Scope for future work

Conclusions

- Thermal Conductivity of carbon nanotubes is observed to increase with increasing length, which implies to the fact that more possible phonon/acoustic wavelengths are available for kinetic energy transmission from hot end to the cold end.
- Degradation of thermal conductivity occurs at grain boundaries which is the possible result of scattering of acoustic waves which are hit by these boundaries. This conclusion is justified from Fig 6.4 which has an abrupt change in temperature near the grain boundary.
- Axial Coefficient of Thermal Expansion does not follow a rigid trend though it increases over most of the lengths. This anomaly is the result of possibility of significant pressure variations on the system, wherein the definition of thermal expansion coefficient changes.

Scope for future work

- The general idea used to develop algorithms in this work can be used to study thermal properties of CNTs with various chirality.
- One might even go on further and apply the reasoning done in this work on not only CNTs but also other elemental structures such as BNNTs etc.
- Specific Heat calculations can also be done for CNTs in this manner.

References

- [1]. S. Iijima, “Helical microtubules of graphitic carbon,” *Nature*, vol. 354, pp. 56–58, 1991.
- [2]. Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)
- [3] J. Fourier, *The Analytical Theory of Heat*. London: Cambridge, 1878.
- [4] R. F. Pierret, *Advanced Semiconductor Fundamentals*, 2nd ed. Prentice Hall, 2002
- [5] T. Lehmann, D.A. Ryndyk, G. Cuniberti, Enhanced thermoelectric figure of merit in polycrystalline carbon nanostructures, *Phys. Rev. B* 92 (3) (2015), 035418.
- [6] P.Y. Huang, C.S. Ruiz-Vargas, A.M. van der Zande, W.S. Whitney, M.P. Levendorf, J.W. Kevek, S. Garg, J.S. Alden, C.J. Hustedt, Y. Zhu, J. Park, P.L. McEuen, D.A. Muller, Grains and grain boundaries in single-layer graphene atomic patchwork quilts, *Nature* 469 (7330) (2011) 389e392
- [7] Thermal expansion of carbon structures, Leendertjan Karssemeijer
- [8] Adcock and McCammon, 2006, *Encyclopedia of Bio-informatics and Computational Biology*, 2019
- [9] S. J. Stuart, A. B. Tutein, and J. A. Harrison, “A reactive potential for hydrocarbons with intermolecular interactions,” *J. Chem. Phys.*, vol. 112, no. 14, p. 6472, 2000.
- [10] J. Tersoff, “New empirical approach for the structure and energy of covalent systems,” *Phys. Rev. B*, vol. 37, no. 12, p. 6991, Apr. 1988.
- [11] D. W. Brenner, “Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films,” *Phys. Rev. B*, vol. 42, no. 15, p. 9458, Nov. 1990
- [12] R.N. Salaway, L.V. Zhigilei/*International Journal of Heat and Mass Transfer* 70 (2014) 954–964

[13] Influence of Chemisorption on the Thermal Conductivity of Single-Wall Carbon Nanotubes
Clifford W. Padgett* and Donald W. Brenner

[14] Pop, Eric; Mann, David; Wang, Qian; Goodson, Kenneth; Dai, Hongjie (22 December 2005). "Thermal conductance of an individual single-wall carbon nanotube above room temperature". *Nano Letters*. 6 (1): 96–100. arXiv:cond-mat/0512624. Bibcode:2006NanoL...6...96P. doi:10.1021/nl052145f. PMID 16402794.

[15] Electrical and Thermal Transport Properties of Magnetically Aligned Single-Wall Carbon Nanotube Films *Applied Physics Letters* 77(5):666-668 · July 2000

[16] Thermal Conductivity of Individual Single-Wall Carbon Nanotubes ,Jennifer R. Lukes and Hongliang Zhong ,J. Heat Transfer 129(6), 705-716

[17] Atomic-scale computations of the lattice contribution to thermal conductivity of single-walled carbon nanotubes, M Grujicica ,G Caoa ,BonnieGersten

[18] Effects of doping, Stone—Wales and vacancy defects on thermal conductivity of single-wall carbon nanotubes Feng Dai-Li, Feng Yan-Hui, Chen Yang, Li Wei and Zhang Xin-Xin.

[19] Hone J, Whitney M, Piskoti C and Zettl A 1999 Thermal conductivity of single-walled carbon nanotubes *Phys. Rev. B* 59 R2514

https://lammmps.sandia.gov/doc/pair_airebo.html

https://lammmps.sandia.gov/doc/fix_ehex.html

https://lammmps.sandia.gov/doc/fix_temp_rescale.html

https://lammmps.sandia.gov/doc/fix_viscous.html
