Study of the Anharmonicity of Vibrational Modes in Carbon Nano-Materials Using a Moments-Based Approach

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Study of the anharmonicity of vibrational modes in carbon nano-materials using a moments-based approach

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In Partial Fulfillment
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Abstract

Thermal properties of solids are one of the most important features studied in solid state physics, and many of the thermal properties are consequences of anharmonicity in solids. Many experimental techniques and theoretical methods have been successfully developed in the study of the anharmonicity and our understanding of the anharmonicity of vibrational modes in materials is emerging nicely.

A new theoretical approach that is based on moments of the Liouvillian has been developed by Dr. Murray Daw’s group. The new approach is expected to be much faster than other theoretical methods. Furthermore, the new approach does not involve perturbation theory and is able to overcome specific difficulties and limitations of other methods.

My work presented in the thesis mainly involves two aspects: 1, I have helped with the implementation based on semi-empirical potentials; 2, I have studied various kinds of nano-materials using the new approach.

For graphene, we study how the anharmonicity (measured by temperature) affects the flexural modes. We find that the dispersion relation of the flexural modes of free-standing graphene is renormalized by anharmonic coupling to other modes. It has been argued in the literature that such anharmonic coupling keeps the graphene sheet stable and relatively flat. Our results agree with anharmonic continuum theory at low temperatures and for small wave vectors, where the continuum theory is supposed to be correct. Not limited to perturbative treatment, our work extends the results to higher temperature and larger wave vector. Our results are not accessible by experiments because the experiments on graphene is too difficult for current equipments.

In the method we assume that the average of the amplitude of any vibrational mode equals zero. The assumption holds for all modes except some specific modes. To account for this special

\[ \text{\footnotesize \cite{1}} \]

\[ \text{The implementation based on the 1st-principle electronic structures is currently being completed.} \]
case, we have had to make modifications to the theory, as explained in Chapter 5, then to the codes for the calculations for carbon nanotubes and fullerenes.

For carbon nanotubes, we study the anharmonic frequencies of all vibrational modes including the radial breathing mode. We demonstrate that the anharmonicity (defined in terms of normalized frequency) is a linear function of temperature. We show that the vibrational modes can be categorized into 3 groups in terms of their temperature dependence and the radial breathing mode is the most anharmonic among all modes. We have treated various nanotubes with different chiralities, lengths and diameters and have found the tubes with larger diameters show more anharmonicity. Our results agree with more limited calculations based on molecular dynamics and available experiments.

For fullerenes, we find that the frequencies of all vibrational modes drop systematically with temperature. As far as we know, there are no previous calculations and our results fill in a two-decade gap in the theoretical treatment of the anharmonicity of fullerenes. Our results agree with the experimental results (for limited number of modes present in the experiments).

Our results provide clearer pictures on the anharmonicity of vibrational modes in the carbon nano-materials.
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$^3$Most of this section is from [1] and is not my work.
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6.3 Plot of the ratio $\omega_N \equiv \omega/\omega_0$ vs. temperature $T$ for the RBMs of three fullerenes.
Chapter 1

Anharmonicity in Solids

1.1 Introduction

Thermal properties of solids are among the most important features studied in condensed matter physics. Many of these thermal properties, such as thermal expansion, finite thermal conductivity, etc., are consequences of anharmonicity in solids. In this chapter, we briefly discuss what anharmonicity is and how anharmonicity affects the frequency and lifetime of vibrational modes.

1.2 Impact of anharmonicity on vibrational modes

Any lattice motion can be considered as a superposition of all vibrations with their own natural frequency. These vibrations are called vibrational modes, a.k.a. normal modes (or phonons in quantum mechanics). The mode lifetime of a vibrational mode is defined as the measurement of the entire duration while the mode vibrates until the vibration dies out. In harmonic systems, a vibrational mode vibrates forever once it starts due to the fact that there is no interaction between them, thus the lifetime is “infinity”. However, if anharmonicity is elicited in the system, the interactions between vibrational modes leads to finite lifetimes. Mode lifetimes microscopically describe vibrational behavior of systems. So they are very important in investigating thermal properties of materials, such as thermal conductivity. [10]
1.2.1 Harmonic lattice dynamics

In the model of lattice dynamics, the interatomic potential $V$ is assumed to be a function of atom distance $r$. It can be expressed as a Taylor expansion as:

$$V(r) = a + b(r - r_0)^2 + c(r - r_0)^3 + d(r - r_0)^4 + ... \quad \text{(1.1)}$$

The expression has no linear term because the system is assumed to be stable when the distance equals the lattice constant $r_0$.

Under harmonic approximation, the expression of potential has the quadratic term as the highest order, which leads to a force that is proportional to displacement. There is no interaction between each vibrational mode so one vibrational mode vibrates at a specific frequency forever once it starts. Harmonic approximation is able to give rise to the number of vibrational modes excited, but is inadequate to explain thermal expansion, thermal conductivity and etc.

1.2.2 Anharmonic lattice dynamics

The anharmonic parts of the potential energy are those involving the terms higher than second-order in Eq. 1.1. When the anharmonicity is not large, for example at very low temperature, the lattice dynamics at elevated temperature can be approximated as harmonic vibrational modes with frequencies that depend on volume. Such a state of the system is called being quasi-harmonic. It is expected that at low temperatures, where harmonic potential dominates the system behavior, the quasi-harmonic frequency will converge to the harmonic frequency. However, when the anharmonicity gets larger, for example at high temperature, the harmonic approximation breaks down. The vibrational modes can not be uncoupled thus energy and motion of a vibrational mode dissipates and transfers to other vibrational modes while the mode gradually dies out, which leads to a finite mode lifetime. In general, the longer the mode lifetime a vibrational mode has, the less interaction it has with other vibrational modes. In the next chapters most of the calculations are of the temperature-dependent frequencies of the vibrational modes.
1.3 Approaches to study anharmonicity of vibrational modes

1.3.1 Experimental methods

Raman spectroscopy [11, 12], Fourier-Transform Infrared (IR) spectroscopy [13] and inelastic neutron scattering [14] are the most prevalent experimental methods to study the frequencies and lifetimes of the vibrational modes in solids.

By utilizing the interaction between electromagnetic wave and solid matter, both Raman spectroscopy and IR spectroscopy give reliable information about the vibrational modes. However, not all modes are Raman-active, nor IR-active. A vibration mode being Raman-active requires a change in polarizability and being IR-active requires a change in dipole moment.
1.3.2 Computational methodologies

The calculation of anharmonic frequencies and lifetimes of vibrational modes must include two steps: Step 1 is to calculate forces; Step 2 is to extract dynamics within an ensemble using those forces. The first step can be achieved by using electronic structure calculations [15] or semi-empirical potentials [16]. For the second step the three common methods are Molecular Dynamics [17], Kinetic Theory (Boltzmann Transport Eq.) [18] and Moments method [3, 4].

Many examples in mode frequencies and lifetimes calculation can be found in the literature, and they can be categorized with the criterion above. However, they all show some downsides: For example, Ladd et al. [19] calculated mode lifetimes of a monatomic fcc lattice at low temperature using molecular dynamics with Green-Kubo (MD-GK) and anharmonic perturbation theory. But it is hard to apply this method to new materials or materials with no appropriate potential to describe. Also, lots of work have been done with the method of Boltzmann Transportation Equation (BTE) with first-principles [20, 21]. The drawback of this method is that the calculations are very expensive to perform and generalize. Another option is to use the BTE with empirical potentials. For example, Broido et al. [22] investigated the lattice thermal conductivity (LTC) of silicon using this approach. However, both the BTE and empirical potentials involve approximations to a considerable degree. Thus each model within the approach might only give a partial description or disagree with other models. The method of Molecular Dynamics and first principles are also widely used ([23], for example), but again, calculations involving first principles are usually very expensive, especially when the system gets large.

Gao, Dickel, Wang and Daw have developed a new computational technique of calculating mode frequencies and lifetimes which is based on moments approximations. They have demonstrated that the results from the moments approximations method is consistent with certain other methods. And it is significantly faster than the method of MD with Green-Kubo, as it only involves Monte Carlo (MC). Besides, the method provides a very general paradigm to calculate mode frequencies and lifetimes of a wide variety of materials. In the next chapter we will discuss more details about this new approach.
The remainder of this dissertation is organized as follows:

- Chapter 2: overview of the background of the moments method.
- Chapter 3: introduction to the Python package called JAZZ.
- Chapter 4: study of the flexural modes in graphene.
- Chapter 5: study of the vibrational modes in single-walled carbon nanotube.
- Chapter 6: study of the vibrational modes in fullerene.
- Chapter 7: summary
Chapter 2

Moments Method\textsuperscript{1}

2.1 Introduction

A new method (second and fourth moments approximation method) of calculating the anharmonicity of modes of materials has been proposed by Dickel, Gao and Daw (DGD) [1, 2, 3, 4]. The approach is based on a recursion method analysis of the Liouvillian and from that they have derived the lifetime of a vibrational mode in terms of moments of the power spectrum of the Liouvillian as projected onto the relevant subspace of phase space. The method utilizes second and fourth moments approximation to calculate anharmonic frequencies and lifetimes of vibrational modes in insulating solids, where lattice vibrations dominate the thermal behavior. The method has been tested on various materials from 1D anharmonic chain to 3D clathrate compounds. Calculations showed that the approximation method provides a fast and reliable scheme to calculate mode frequencies and lifetimes at wide range of temperatures.

In this chapter, we review the theory background of the approximation method.

\textsuperscript{1}Most of the chapter can be found in [1, 2, 3, 4] and is not my work.
2.2 Mode lifetimes and the Green-Kubo Formula

In DGD’s work, they chose the fluctuation of the occupancy factor to describe the system’s behavior and to calculate mode lifetime:

\[ \delta n_k = n_k - \langle n_k \rangle \] (2.1)

According to the Green-Kubo (GK) approach, the mode lifetime is defined as:

\[ \tau_k = \int_{-\infty}^{\infty} dx \chi_k(t) \] (2.2)

where \( \chi_k(t) \) represents the autocorrelation function:

\[ \chi_k(t) = \frac{\langle \delta n_k(0) \delta n_k(t) \rangle}{\langle \delta n_k(0)^2 \rangle} \] (2.3)

In the equation above, \( k \) is the mode index, angular brackets indicate ensemble average over the equilibrium distribution in phase-space:

\[ \langle A \rangle = Z^{-1} \int d\Gamma e^{-\beta H(p, q)} A(p, q) \] (2.4)

\[ Z = \int d\Gamma e^{-\beta H(p, q)} = \prod_i dp_i dq_i \] (2.5)

in which \( d\Gamma \) is the volume of the classical phase space. The autocorrelation function is a function of time that can be explained in phase-space: the system starts from the initial state and then proceeds for a period of time, and the autocorrelation function is the normalized value of the ensemble averages over the equilibrium distribution of the product of one dynamic variable at later time \( t \) and at time 0. If the interaction in the system is simply harmonic, the auto-correlation will show no decay. However, if the interactions involves anharmonicity, after a certain period of time, the autocorrelation will decay to 0. Mode lifetime defined by the GK approach is the integral of the autocorrelation function, so it captures the decaying aspect of the dynamic of the system.
2.3 Canonical Transformation

The expression of $\delta n_k$ for vibrating solids in terms of particle coordinates and momenta $(p_i, q_i)$ is accomplished via a series of two canonical coordinate transformations:

- Normal mode transformation: it transforms from coordinates $(p_i, q_i)$ to normal modes.
- Hamilton-Jacobi transformation: it transforms from normal modes to action-angle variables.

Consider, for example, a 1D anharmonic chain whose Hamiltonian is

$$H(p, q) = \frac{1}{2} \sum_n p_n^2 + \sum_n V(u_{n,n+1})$$  \hspace{1cm} (2.6)

where

$$V(d) = d^2/2 + d^4/24$$  \hspace{1cm} (2.7)

The transformation to normal mode variables $q$ and $\pi$ gives:

$$q_k = \frac{1}{N} \sum_n u_n e^{-i kn}$$  \hspace{1cm} (2.8)

$$\pi_k = \frac{1}{N} \sum_n p_n e^{i kn}$$  \hspace{1cm} (2.9)

The normal modes variables can be transformed to action-angle variables $(S, a)$ by a transformation involving an arbitrary frequency $\omega^X$

$$S_k = \frac{N}{2\omega^X_k} |\pi_k + i\omega^X_k q_k|^2 = \hbar n_k$$  \hspace{1cm} (2.10)

$$\alpha_k = \text{arg}(\pi_k + i\omega^X_k q_k)$$  \hspace{1cm} (2.11)

Now we can find the quasi-harmonic frequency (which depends on both temperature and wave-vector) from:

$$\langle \dot{\alpha}_k \rangle = \omega^Q_k(\beta)$$  \hspace{1cm} (2.12)
Generally it is expected that at low temperatures, the quasi-harmonic frequency will become the harmonic frequency of the lattice and deviate from it as the temperature increases.

We find that the most convenient value of the transformation frequency is \( \omega_k = \omega^Q_k(\beta) \). This choice is made by considering the structure of the auto-correlation function and the resulting lifetime (area under the auto-correlation function).

### 2.4 The Liouvillian and mode lifetime

The evolution of dynamical variables, such as the occupation factor \( \delta n_k \) as defined in the previous section, are governed by Hamilton’s equations, which are, for anharmonic systems, naturally non-linear and correspondingly difficult to treat. However, the lifetime of the mode in a solid in equilibrium is expressed as an ensemble property, as defined in the auto-correlation in Eq. 2.3. The lifetime is therefore an ensemble property, and reflects the dynamical behavior of different parts of the distribution function. That is, any function \( f \) on phase space evolves according to

\[
\frac{df(p,q)}{dt} = -i \hat{L} f
\]  

(2.13)

where the (hermitian) Liouvillian operator

\[
\hat{L} = i\{H, \} = i \sum_l (\frac{\partial H}{\partial q_l} \frac{\partial}{\partial p_l} - \frac{\partial H}{\partial p_l} \frac{\partial}{\partial q_l}) 
\]  

(2.14)

provides the time evolution, so that

\[
f(p,q,t) = e^{-i\hat{L}t} f(p,q,0)
\]  

(2.15)

The time-evolution of macroscopic variables can then computed formally from the microscopic processes captured by the Hamiltonian, by considering the analytical properties of the Liouvillian. In particular, we can express the auto-correlation explicitly in terms of \( \hat{L} \):

\[
\chi_k(t) = \frac{\langle \delta n_k(0) \rangle e^{-it\hat{L}} \delta n_k(0)}{\langle \delta n_k(0)^2 \rangle}
\]  

(2.16)

Extracting the mode-lifetime then becomes the challenge of understanding how the Liouvillian couples the phase-space function \( \delta n_k \) to other modes.
2.5 Brief review of Moments approximation

In Eq. 2.3 the dynamics are expressed primarily in terms of the positions and momenta of the atoms \( q_i, p_i \). The normal mode amplitudes \( \{A_k\} \) are related to the atomic coordinates via the normal mode transformation. The equation of motion can be integrated formally, so that

\[
A_k(t) = e^{-it\hat{L}}A_k(0)
\]  

(2.17)

Thereby we can express the mode auto-correlation explicitly in terms of \( \hat{L} \):

\[
\chi_k(t) = \frac{\langle A_k e^{-it\hat{L}} A_k \rangle}{\langle A_k^2 \rangle}
\]  

(2.18)

The Taylor Series of \( \chi(t) \)

\[
\chi_k(t) = 1 - \mu_{k,2} \frac{t^2}{2!} + \mu_{k,4} \frac{t^4}{4!} - \mu_{k,6} \frac{t^6}{6!} + ...
\]  

(2.19)

relates the derivatives of \( \chi_k(t) \) at \( t = 0 \) to the moments of the Liouvillian acting on the mode amplitude:

\[
\mu_{k,n} = \frac{\langle A_k \hat{L}^n A_k \rangle}{\langle A_k^2 \rangle}
\]  

(2.20)

Specifically, the two lowest moments are related to averages involving forces:

\[
\mu_{k,2} = \frac{\langle A_k^2 \rangle}{\langle A_k^2 \rangle} = \frac{\langle \dot{A}_k A_k \rangle}{\langle A_k^2 \rangle}
\]  

(2.21)

and

\[
\mu_{k,4} = \frac{\langle A_k^2 \rangle}{\langle A_k^2 \rangle}
\]  

(2.22)

where the \( \dot{A}_k \) is the mode-resolved acceleration, which can be calculated via the normal mode transformation from the atomic accelerations.

If some semblance of harmonic-like behavior holds, the second moment will generally reflect the quasiharmonic, temperature-dependent frequency (squared) of the mode. Gao et al. [2] proposed

\footnote{Most of this section is from [1] and is not my work.}
to use the area under the square of the AACF as a measure of the lifetime

$$\tau_k = \int_{-\infty}^{\infty} dx \chi_k(t)^2$$  \hfill (2.23)

This lifetime is not intended to correspond to any particular physical measurement that might be performed, but rather is suggested as a simple generic measure of the rate of the decay of the correlation. Such a measure also lends itself easily to analysis.

DGD observed that the lifetime can be expressed as a function of the moments

$$\tau_k = F(\mu_{k,2}, \mu_{k,4}, \mu_{k,6}, \ldots),$$  \hfill (2.24)

where a determination of the function $F$ involves knowledge of the dynamics of the system. Using dimensional analysis, this form can be re-expressed as

$$\tau_k / \tau_{k,2} = G(\gamma_{k,4}, \gamma_{k,6}, \ldots),$$  \hfill (2.25)

where $\tau_{k,2} = \mu_{k,2}^{-1/2}$, $G$ is yet to be determined, and the $\gamma$ s are dimensionless parameters

$$\gamma_{k,n} = \frac{\mu_{k,n}}{(\mu_{k,2})^{n/2}}$$  \hfill (2.26)

(Note that $\gamma_n \geq 1$.) While it is not generally possible to know all of the moments, DGD proposed that in certain circumstances the lifetime might be practically approximated from a knowledge of only the lowest moments. This suggests a series of approximations, starting with only the second moment

$$\tau = c\tau_2$$  \hfill (2.27)

where $c$ is some dimensionless constant to be determined by more knowledge of the dynamics of the system. The fourth-moment approximation would then be

$$\tau = \tau_2 \tilde{G}(\gamma_4)$$  \hfill (2.28)

where $\tilde{G}$ is some function yet to be determined. The higher moments correspond to ensemble averages of higher powers of the Liouvillian, and so each higher moment involves higher time derivatives of
the dynamical variables.

They further demonstrated how the deviation $\gamma_4 - 1$ is directly related to the temperature-dependent anharmonicity of the system. This derivation helps determining the $\tilde{G}$ function:

$$\tau = \tau_2 G(\gamma_4 - 1)$$  \hfill (2.29)

### 2.6 Determine the $G$ function

Gao et al. [1] then performed Molecular Dynamics calculation in fcc lattice with Lennard-Jonesium potential [24] at various temperatures up to the melting point, constant $V$ and constant $P$ conditions, and for cells ranging from 4 to 32 atoms.

They find that the mode lifetime can be represented by the same relation as shown in Eq. 2.29, more detailedly, in the form of

$$\frac{\tau}{\tau_2} = C \frac{1}{\sqrt{\gamma_4 - 1}}$$  \hfill (2.30)

A value of $C = 1.35$ fits the accumulated data for the modes in the 4-atom cell for both constant $V$ and constant $P$. A value of $C = 1.41$ fits the accumulated data for the modes in the 8-atom, 16-atom, and 32-atom cells at constant $V$. For constant $P$, the best value of $C = 1.55$.

They conclude that the fourth-moment approximation captures the basic trends, though some scatter is observed that could be attributed to deviations at higher moment. The success of the fourth-moment scaling is understood to be due to the simple nature of the mode-resolved densities of states, which are single peaks that are shifted and broadened with increasing temperature.

---

3 My later work establishes a value of 8.33 by fitting to results with Tersoff potential [25], [26]
Chapter 3

Implementation of moments approximation: the Jazz Package

3.1 Introduction

A new method of calculating vibrational mode lifetimes has been developed and reported in a series of papers [1, 2, 3, 4]. The method uses Monte Carlo (MC) sampling of forces. In this chapter reported is a program implemented by Gao, Wang and Daw to carry out these calculations that has been made available to other investigators.

The lifetime of each vibrational mode lifetime is obtained as a MC average of specific products of mode-resolved displacements and forces. The displacements and forces are calculated using a molecular dynamics simulator named LAMMPS [27]. LAMMPS now includes a python interface that makes it possible to control LAMMPS and extract its internal variables from a python script. Using that interface, Jazz treats LAMMPS as a blackbox source of energies and forces. The Jazz wrapper manages the Metropolis Monte Carlo process, displacing the atoms in a controlled way, querying LAMMPS for energies in order to make the accept/reject decision. The forces are extracted from LAMMPS and the appropriate averages obtained, to form the moment-based approximation to the vibrational lifetime of each mode.

\footnote{Most of the chapter has been published in [5].}
3.2 Mode of Implementation

We describe in this section some generalities of the technical details of the implementation. (Full details are available in the documentation provided with the package.)

The three primary python modules provided in this package are

- genvecs0 (determines normal modes from dynamical matrix)
- calcavgs (does the MC averaging, producing the averages in Eq. 3.7)
- calcmoments (combines MC averages to calculate moments and lifetimes, Eqs. 3.8-3.8)

Their functions are explained in general in the following.

The first two modules interface with LAMMPS. The changes in energy required for the MC are computed brute-force, in that the total energy is computed before and after an attempted alteration of atomic positions; no attempt is made to economize based on possible locality of the interactions. This is both advantageous and disadvantageous. The disadvantage is one of speed. It is possible in local interactions to speed up significantly the calculation of the change in energy. However, this requires a different program for each type of interaction. The advantage of our blackbox approach is that it will work for any potential available in LAMMPS. At this stage of our research, this flexibility was desired over whatever speed advantage might be gained for specific potentials.

3.2.1 Normal Modes

The vibrational lifetimes are calculated for each mode, so the normal mode analysis is a necessary first step. At low temperatures, the normal modes are given by the dynamical matrix. These are obtained from the Hessian of the potential energy via numerical derivatives of the forces. Let $u_{i\alpha}$ be the displacement of atom $i$ (mass $m_i$) from its equilibrium position along the cartesian direction $\alpha$. The dynamical matrix [28] is formed from the Hessian (matrix of second derivatives of 

---

2For some simple crystal structures (see Maradudin [28]) symmetry restricts the normal modes to be effectively independent of temperature. However, more complex structures will have normal modes that are temperature-dependent. It is possible in these cases to construct an effective, temperature-dependent dynamical matrix from the ensemble average of the displacement-displacement correlation matrix. This extension of Jazz is planned.
the potential) evaluated at equilibrium:

\[ D_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial u_{i\alpha} \partial u_{j\beta}} |_{0} \]  

(3.1)

The eigenvectors of \( D \) can be labelled by index \( \kappa \) and correspond to normal modes with frequency \( \omega_\kappa \)

\[ \omega_\kappa^2 \eta_{\kappa \alpha} = \sum_{j\beta} D_{i\alpha,j\beta} \eta_{\kappa \beta} \]  

(3.2)

The matrix \( Y \) formed from the eigenvectors

\[ Y_{i\alpha,\kappa} = \frac{1}{\sqrt{m_i}} \eta_{\kappa \alpha} \]  

(3.3)

transforms from the normal mode amplitudes to the atomic displacements

\[ u = Y . A \]  

(3.4)

where \( A \) is the column vector formed from the normal mode amplitudes and the \( u \) is the vector of atomic displacements. Likewise, the mode accelerations can be obtained from the atomic forces by

\[ \ddot{A} = F . Y \]  

(3.5)

### 3.2.2 Ensemble Averages

The ensemble averages in \textit{Jazz} are over positions alone, and are based on the canonical distribution function \( \exp (-V/T) \), where \( V \) is the potential energy of the system and \( T \) is the temperature (expressed in energy units, same as \( V \)). An additional constraint is imposed beyond the usual canonical ensemble, which is that the center-of-mass remains fixed. This constraint makes it easier to deal with averages involving displacements, because of the existence of free modes.

Three free modes involve, for example, sliding of the system in each of three directions. Periodic boundary conditions alone do not limit this sliding. Also, in some cases, such as a cylinder that is periodic along its length but effectively free to rotate, the system will in fact end up rotated during the process of MC sampling unless something is done to avoid it. In \textit{Jazz} we have avoided this problem by identifying certain normal modes as “free modes” and the remaining as “oscillators”. Free
modes are modes for which there is no resistance to displacement, and which therefore correspond to (effectively) zero frequency. Oscillators are modes for which there is at least linear resistance to displacement. Therefore, we can freeze out the free modes by carrying out the MC search only in the subspace of oscillators.

The calculation proceeds by carrying out the MC sampling in the subspace of normal mode amplitudes excluding free modes. Then the displacements, from Eq. 3.4, are added to the equilibrium positions and are transmitted to LAMMPS, which computes the energy and forces of the modified configuration. Three averages are computed (for each mode):

\[
\begin{align*}
S_{1,\kappa} &= \langle A^2 \rangle_{\kappa} \\
S_{2,\kappa} &= \langle A_{\kappa} \dot{A}_{\kappa} \rangle \\
S_{3,\kappa} &= \langle \dot{A}^2 \rangle_{\kappa}
\end{align*}
\] (3.6)

From which the moments for each mode are computed:

\[
\begin{align*}
\mu_{2,\kappa} &= \frac{S_{2,\kappa}}{S_{1,\kappa}} \\
\mu_{4,\kappa} &= \frac{S_{3,\kappa}}{S_{1,\kappa}} \\
\gamma_{4,\kappa} &= \frac{S_{3,\kappa} S_{1,\kappa}}{(S_{2,\kappa})^2}
\end{align*}
\] (3.7)

It is possible to obtain \(S_2\) exactly, by using the virial theorem, as proportional to \(T\). However, we have found that the value of \(\gamma_4\) converges more quickly with sampling size if we use the same sampling for all three sums in Eq. 3.7, rather than using the exact value for one sum and the sampled values for the other two. In particular, calculating all three \(S\) values the same way guarantees that \(\gamma_4 \geq 1\) even for low temperatures where \(\gamma_4\) is approaching 1.

Finally, the mode lifetimes are obtained from [1]

\[
\tau_\kappa = \frac{1.41}{\sqrt{\mu_{2,\kappa}(\gamma_{4,\kappa} - 1)}}
\] (3.8)

\(^3\)Limiting the MC steps to the subspace of oscillators guarantees that the system will not slide — or rotate if the configuration has that freedom — which motion can contaminate averages based on displacements.
3.2.3 Parallelization

The first versions of Jazz are implemented strictly in serial mode, in that LAMMPS calculates the energy changes and forces in serial mode, and also the Monte Carlo calculations managed by Jazz are done serially. Because Monte Carlo is easily run in parallel processes, it is an easy matter to run multiple instances of Jazz, each using a different pseudo-random number seed, and then to combine the results. Based on this, we have implemented a parallel version of Jazz. A measure of statistical error can also be obtained this way by sub-averaging.

3.3 Example: FCC-LJ

As an example of the both the utility of the approach in general and of LAMMPS in particular, we examine the effect of disorder on the vibrational modes of an anharmonic system. This is part of a larger study that we plan to publish in the future.

Generally we understand well how disorder (such as mass disorder in an isotopic mixture) affects vibrational modes in harmonic solids, often through a perturbative approach. Disorder generally is expected to reduce thermal conductivity by modifying the normal modes so that they become localized, all of which is understood as a harmonic effect.

However, there is noticeably less in the literature on a general understanding of how those differences can affect mode lifetimes, which intrinsically requires a nonlinear treatment.

Computer studies in the 60s by workers at Los Alamos [29] obtained surprising results in model calculations on systems with both disorder and anharmonicity, results that contradict the expectations based on perturbation theory. For example, in some range of parameters, disordered anharmonic systems can be seen to have higher lattice thermal conductivity than would be expected from perturbation theory. This rather surprising effect seems to have been noticed mostly by those working in low-dimensional systems, but as far as we can determine, has not received the same attention from those working in bulk systems. One general import of the work has been to question the additivity of relaxation times that does hold in many cases but is not generally true. We are studying then at a generic level the interplay of disorder and anharmonicity, with the well-known Lennard-Jonesium (LJ). In the LJ potential, for example, we can study binary alloys where the constituents differ based on mass, on bond strength, and/or bond length. In doing this calculation, we set up the usual input for LAMMPS, by preparing files to specify atomic positions and types,
with the LJ parameters for the binary alloy being specified as well. *Jazz* was then run (at a specified temperature) to analyze the vibrational mode frequencies and lifetimes. The imposition of periodic boundary conditions selects vibrational modes whose wavevectors are consonant with the periodicity. For that set of normal modes, the code calculates the normal mode eigenvectors, as well as temperature-dependent frequency and lifetime of each.

For example, we have set up cubic cells of 256 atoms in an FCC structure, in both ordered and disordered structures at various compositions, and examined the normal modes in these cells. For 256 atoms, there are 765 non-sliding modes, and for each we have the eigenvector, the frequency, and lifetime. One quick method of examining the characteristic of oscillators is through the Q-factor, where Q is the product of oscillator frequency and lifetime. We can examine the ensemble of modes in this cell then through a plot of the distribution of quality factors, as can be seen in Fig. 3.1. As is seen in this particular case, disorder causes the oscillators to shift to a longer lifetime. This is consistent with Payton *et al.* [29], who found that in a disordered lattice, increasing anharmonicity can lead to higher thermal conductivity, which contradicts the usual thinking about such systems. They reasoned that while disorder can cause localization of vibrational modes, anharmonicity causes a decay of those localized modes that effectively restores a delocalized nature.
Figure 3.1: Disorder in a 3:1 binary alloy with significant bond-length difference causes the full set of normal modes to move to a higher quality factor.
Chapter 4

Anharmonic Renormalization of the Dispersion of Flexural Vibrational Modes in Graphene

4.1 Introduction

In chapters 2-3, Gao and Daw have developed a formalism to calculate lifetimes and frequencies of normal modes in anharmonic systems [1, 2], and Gao, Daw and I have implemented a package called Jazz using the formalism [5]. Now we are trying to apply the package onto some problems of interest. In this chapter we are using Jazz to study the anharmonic renormalization of the dispersion relation of flexural modes.

This chapter is organized as follows. First, we introduce the background of the renormalization of the flexural modes of graphene. Then we report our results and analyses. Finally we compare our results with others and show how our results would contribute to the community.

1Most of the chapter has been published in [6].
4.2 Background

Graphene, like any membrane, is expected to have long-wavelength, out-of-plane (so-called “flexural”) modes. If the membrane is stress-free, the dispersion of those modes should be quadratic in wavenumber (that is, \( \omega \propto k^2 \)) when the harmonic approximation holds \([30, 31, 32]\). The derivation of a more general case can be found in the following subsection. Anharmonicity may modify the dispersion relation, which would affect the transport of heat in the material. Some authors suggest that the flexural modes may in fact dominate the lattice thermal conductivity of graphene \([33, 34]\). Anharmonic coupling of the flexural modes to in-plane modes have been shown to stabilize the sheet with respect to rippling \([35, 36, 37]\). The coupling of the flexural modes to electrons also has significant effect on the electrical conductivity \([38]\).

The effect of anharmonicity on the dispersion relation of the long-wavelength flexural modes was considered in the continuum limit by Mariani and von Oppen (MvO) \([9]\). Their results show that \( \omega \sim k^2 \) at low temperatures as expected, while \( \omega \sim k^{3/2} \) at high temperature. Details about their results can be found in the illustration section below.

As has been observed experimentally \([39, 40, 41]\) and analyzed theoretically \([35]\), free-standing graphene sheets are unstable to rippling of characteristic length on the order of 50-200 Å at room temperature. Atomistic simulations using bond order potentials \([42]\) have confirmed rippling when the simulation cell sizes were sufficiently large; for cells smaller than the Ginzburg length \([36]\) the ripples are suppressed and the sheet remained relatively flat. The analysis of MvO is based on perturbation around flat graphene.

We apply here the “moments method” implemented for inter-atomic potentials, for calculating the temperature-dependent frequency. Our simulations are performed on cells smaller than the Ginzburg length which would inhibit rippling, and therefore should be compared directly to the results of MvO. Our results confirm that the dispersion relations are renormalized and that the form of MvO holds in the region of low \( k \) and \( T \). We also note deviation from their form outside of that region, determining then the range of validity of their approach.

4.2.1 Illustration using a 1-D atom chain

We demonstrate below it is not hard to derive that flexural modes have quadratic dispersion in free-standing, stress-free graphene within harmonic theory. To better illustrate this problem and
simplify the derivation while not losing the generality, we consider an ideal one-dimensional atom
chain.

4.2.1.1 Dispersion relation of flexural modes in stress-free harmonic systems

Consider for the atom chain all the masses for the $n$ atoms are $m$ and the lattice constant is $a$. $n$ is large enough so that the length of the chain can be treated as infinity. Under the stress-free assumption, $a$ is also the preferred bond length at equilibrium. Flexural modes are modes in which the atoms displace perpendicularly to the chain, thus we only consider atom displacements $h_i$ as such.

The distance between the $i$th and the $(i + 1)$th atoms (first-nearest neighbors) is expressed as:

$$l^{(1)}_i = \sqrt{a^2 + (h_{i+1} - h_i)^2}^{1/2} \quad (4.1)$$

and for the distance between the $i$th and the $(i + 2)$th atoms (second-nearest neighbors):

$$l^{(2)}_i = \sqrt{4a^2 + (h_{i+2} - h_i)^2}^{1/2} \quad (4.2)$$

If we take up to the second nearest neighbor into consideration, the total energy of the system can be expressed as:

$$E_{total} = \sum_{i} \kappa_1 (a - l^{(1)}_i)^2 + \kappa_2 (2a - l^{(2)}_i)^2 \quad (4.3)$$

$$E_{total} = n[\kappa_1(a - l^{(1)})^2 + \kappa_2(2a - l^{(2)})^2] \quad (4.4)$$

in which $\kappa_1$ and $\kappa_2$ are constant factors. We minimize the total energy regarding the lattice constant $a$ using

$$\frac{\partial E_{total}}{\partial a} = 0 \quad (4.5)$$

Then solve for $a$:

$$a = \frac{\kappa_1 l^{(1)} + 2\kappa_2 l^{(2)}}{\kappa_1 + 4\kappa_2} \quad (4.6)$$
The equation of motion can be written as:

$$m \frac{\partial^2 h_n}{\partial t^2} = \kappa_1 (1 - \frac{l^{(1)}}{\sqrt{(h_{n+1} - h_n)^2 + a^2}})(h_{n+1} - h_n + h_{n-1} - h_n) + \kappa_2 (1 - \frac{l^{(2)}}{\sqrt{(h_{n+2} - h_n)^2 + 4a^2}})(h_{n+2} - h_n + h_{n-2} - h_n) \quad (4.7)$$

Only consider the first term in the Taylor expansion under harmonic assumption, the equation of motion can be written as:

$$m \frac{\partial^2 h_n}{\partial t^2} = \kappa_1 (1 - \frac{l^{(1)}}{a})(h_{n+1} - h_n + h_{n-1} - h_n) + \kappa_2 (1 - \frac{l^{(2)}}{2a})(h_{n+2} - h_n + h_{n-2} - h_n) \quad (4.8)$$

Substituting Equation 4.9 into the equation above, we have:

$$m \frac{\partial^2 h_n}{\partial t^2} = \kappa_1 \frac{2\kappa_2 l^{(2)} - 4\kappa_2 l^{(1)}}{\kappa_2 l^{(1)} + 2\kappa_2 l^{(2)}}(h_{n+1} + h_{n-1} - 2h_n) + \kappa_2 \frac{2\kappa_1 l^{(1)} - \kappa_1 l^{(2)}}{2(\kappa_1 l^{(1)} + 2\kappa_2 l^{(2)})}(h_{n+2} + h_{n-2} - 2h_n) \quad (4.9)$$

To simplify the expression, we use \(\kappa'_1\) and \(\kappa'_2\) to replace \(\kappa_1 \frac{2\kappa_2 l^{(2)} - 4\kappa_2 l^{(1)}}{\kappa_2 l^{(1)} + 2\kappa_2 l^{(2)}}\) and \(\kappa_2 \frac{2\kappa_1 l^{(1)} - \kappa_1 l^{(2)}}{2(\kappa_1 l^{(1)} + 2\kappa_2 l^{(2)})}\), respectively. Note that:

$$\kappa'_1 = -4\kappa'_2 \quad (4.10)$$

which will be useful later. Thus,

$$m \frac{\partial^2 h_n}{\partial t^2} = \kappa'_1 (h_{n+1} + h_{n-1} - 2h_n) + \kappa'_2 (h_{n+2} + h_{n-2} - 2h_n) \quad (4.11)$$

The general solution of the differential equation is:

$$h = h_0 e^{-i\omega t + ikx} \quad (4.12)$$

Substituting into equation 4.11, we have:

$$-m\omega^2 = \kappa'_1 (e^{ika} + e^{-ika} - 2) + \kappa'_2 (e^{2ika} + e^{-2ika} - 2) \quad (4.13)$$

$$m\omega^2 = 2\kappa'_1 (1 - \cos ka) + 2\kappa'_2 (1 - \cos 2ka) \quad (4.14)$$
\[ m\omega^2 = 4\kappa'_1 \sin^2 \frac{ka}{2} + 4\kappa'_2 \sin^2 ka \] \hspace{2cm} (4.15)

\[ m\omega^2 = 4\kappa'_2 (\sin^2 ka - 4 \sin^2 \frac{ka}{2}) \] \hspace{2cm} (4.16)

\[ m\omega^2 = \kappa'_1 \sin^4 \frac{ka}{2} \] \hspace{2cm} (4.17)

As we proved above, when \( ka \to 0 \), we have the dispersion relation: \( \omega \sim k^2 \). That is to say, the dispersion of transverse modes is indeed quadratic near the zone center.

Expanding the system from 1-D chain to 2-D sheet does not affect any of the terms in the derivation as long as only the purely transverse modes are what we are considering. To sum up, the transverse dispersion is quadratic in either a chain or a plane.

### 4.2.1.2 Dispersion relation of flexural modes in harmonic systems under stress

Now what if stress is introduced into the system? Does stress stiffen the dispersion curve?

First let us go back to the 1-D atom chain problem and imagine the chain is not stress-free. Use \( b \) to denote the new preferred bond lengths at equilibrium, which is not equal to lattice constant \( a \) any more. The distance between the nearest neighbors becomes

\[ l_i^{(1)} = [b^2 + (h_{i+1} - h_i)^2]^{1/2} \] \hspace{2cm} (4.18)

and the distance between the second nearest neighbors becomes

\[ l_i^{(2)} = [4b^2 + (h_{i+2} - h_i)^2]^{1/2} \] \hspace{2cm} (4.19)

By following similar steps shown in the stress-free case, we take derivatives of the total energy regarding the lattice constant \( a \) by using:

\[ \frac{\partial E_{\text{total}}}{\partial a} = 2n\lambda \] \hspace{2cm} (4.20)
in which \( \lambda \), which measures the stress force acting on an atom, \( \neq 0 \). Then solve for \( a \):

\[
a = \frac{\kappa_1 l^{(1)} + 2\kappa_2 l^{(2)} + \lambda}{\kappa_1 + 4\kappa_2} \quad (4.21)
\]

Then follow the same steps shown in the stress-free case above, instead of Equation 4.9, we get the following expression:

\[
m \frac{\partial^2 h_n}{\partial t^2} = \kappa_1 \frac{2\kappa_2 l^{(2)} - 4\kappa_2 l^{(1)} + \lambda}{\kappa_1 l^{(1)} + 2\kappa_2 l^{(2)} + \lambda} (h_{n+1} + h_{n-1} - 2h_n) + \kappa_2 \frac{2\kappa_1 l^{(1)} - \kappa_1 l^{(2)} + 2\lambda}{2(\kappa_1 l^{(1)} + 2\kappa_2 l^{(2)} + \lambda)} (h_{n+2} + h_{n-2} - 2h_n)
\]

(4.22)

Note that in this case,

\[
\kappa' \neq -4\kappa' \quad (4.23)
\]

unless \( \kappa_1 = -4\kappa_2 \), which is a very rare case that we do not take into consideration here.

Contrary to Equation 4.24, we get,

\[
m\omega^2 = 4\kappa' \sin^2 ka - 4\sin^2 \frac{ka}{2} + \lambda_1 \sin^2 \frac{ka}{2}
\]

(4.24)

in which, \( \lambda_1 \neq 0 \).

\[
m\omega^2 = \lambda_1 \sin^2 \frac{ka}{2} + \kappa'_1 \sin^4 \frac{ka}{2}
\]

(4.25)

As we can see, when \( ka \to 0 \), we have the dispersion relation: \( \omega \sim k \). In other words, under the not stress-free condition, the dispersion of transverse modes becomes linear near the zone center in the 1-D atom chain.

Again, the derivation also holds in a 2-D atom sheet as long as only transverse modes are considered.

### 4.2.1.3 Dispersion relation of flexural modes in graphene

In MvO’s paper [43], they also claim that flexural modes have quadratic dispersion relation under harmonic and stress-free assumption by solving the the elastic Lagrangian density [30, 44]:

\[
L = \frac{\rho_0}{2}(\ddot{u} + \ddot{h}^2) - \frac{1}{2}\kappa_0(\nabla^2 h)^2 - \mu u_{ij}^2 - \frac{1}{2}\lambda u_{kk}^2,
\]

in terms of the mass density \( \rho_0 \), the out-of-plane
distortions $h(\mathbf{r})$, the in-plane distortions $\mathbf{u}(\mathbf{r})$ and the strain tensor $u_{ij} = \frac{1}{2} \times [\partial_i u_j + \partial_j u_i + (\partial_i h)(\partial_j h)]$. Since the graphene system obeys the rotational symmetry of the membrane in the space [45, 43], in other words, rotating the free-standing free-stress graphene sheet require no energy, there is no $(\nabla h)^2$ term in the Lagrangian density. Then solving the Lagrangian density gives the quadratic dispersion.

The effect of anharmonicity on the dispersion relation of the long-wavelength flexural modes was considered in the continuum limit by Mariani and von Oppen (MvO) [9]. Following Nelson and Peliti [36], they began with the potential energy of nearly flat graphene, including corrections to the harmonic potential that are lowest-order in wavevector and amplitude, which then couple the flexural modes to in-plane modes. Assuming classical dynamics, the in-plane modes were integrated out, leaving an effective, temperature-dependent interaction among the flexural modes. They then applied a one-loop renormalization group analysis to this effective Hamiltonian to demonstrate that the coupling of flexural modes to the in-plane modes renormalizes the dispersion of the flexural modes. They found that the frequency $\omega$ of a flexural mode with wavevector $k$ at temperature $T$ is given by

$$\omega = \alpha(T, k) k^2$$

in which

$$\alpha(T, k) = \alpha_0 [1 + \frac{k^2}{k_c^2}]^{1/4}$$

where the temperature dependence is carried by wavevector scale $k_c$, which varies as $T^{1/2}$. These results show that $\omega \sim k^2$ at low temperatures as expected, while $\omega \sim k^{3/2}$ at high temperature. Their analysis is expected to hold for low $k$ and $T$, but they do not determine the range of $k$ and $T$ for which the analysis is expected to hold.

### 4.3 Setting up our calculations

The method we are using to calculate temperature-dependent frequency of anharmonic flexural modes in this work is the combination of moments and Monte Carlo calculations. It is an atomistic calculation that does not use continuum approximation.

\footnote{Note that the 6-fold rotational symmetry of graphene insures that the dispersion relation for small $k$ will be isotropic (that is, independent of the direction of $k$). Further out in the Brillouin zone, the dispersion relation depends as well on direction of $k$.}
Unlike constant volume calculation, in which the lattice constant is unchanged throughout the temperature range, the lattice constant is dependent on temperature in constant pressure calculation. To justify the lattice parameter at each temperature, we have run molecular dynamics within isothermal-isobaric ensemble (“npt” in LAMMPS) with constant (zero) pressure. Thus we have incorporated thermal expansion or contraction into the *Jazz* calculation.

All calculations were performed using *Jazz* in parallel on the Palmetto Cluster of Clemson University.

- The 3098-square-angstrom graphene sheet consists of 1152 atoms in the simulation box, as is shown in Fig. 4.1, and triclinic periodic boundary conditions are consistent with the six-fold rotational symmetry of graphene. The periodic boundary conditions are only to limit the modes included in the calculation to those whose wavevector are commensurate with the supercell.

- The atomistic potentials we have used are Original Tersoff Potential [46, 47] for carbon and also the modified Tersoff potential specially tailored for graphene [25].
• The temperatures we have used are about $5K$, $9K$, $19K$, $38K$, $75K$, $150K$, $300K$, $600K$ and $1200K$.

• The Monte Carlo calculation includes $4.6 \times 10^7$ steps, and spreads over 100 independent processor cores.

Besides, the flexural modes have been visualized using the configurations (the configuration data file) and eigenvectors, and then the visualizations are used not only to identify the flexural modes but also to determine the wave-vectors for each flexural mode.

### 4.4 Our results with Jazz and analyses

We have extracted the frequency for each flexural mode under each temperature. Plotted have been the dispersion relation of the flexural modes calculated by this method at different temperatures, as is shown in Fig. 4.2. The points are the atomistic results from Jazz and the curves are simple power law fits to the points. At $T = 0K$, the best fit to the curve is to a quadratic dispersion. At the highest temperature ($1200K$), the best fit is to $k^{1.8}$ (for the original Tersoff, $k^{1.7}$), which is inside of the range of behavior of the continuum calculations. We have calculated the dispersion at several other temperatures between 0 and 1200 $K$, and the dispersion curves fall in between those of the two extreme temperatures. The results shown here at $T = 0K$ are actually from the harmonic force constants determined from the current cell, but they differ negligibly from what we obtain by the moments method at very low temperature. At $T = 0K$, the best power-law fit is to a quadratic dispersion. The value of $\alpha_0$ is determined to be $62.8\,\text{Å}^2 - \text{THz}$ by this quadratic fit \(^4\), compared with the value of $62\,\text{Å}^2 - \text{THz}$ obtained via first-principles calculations by Mingo and Broido [31].

As is obvious from Fig. 4.2, the change in dispersion relation with temperature is subtle. To make a precise comparison between the atomistic and continuum results, we note that Eqs. 4.26-4.27 establish a peculiar relation between $\omega$, $k$, and $T$. In particular, a little rearrangement gives:

$$\frac{\omega^4}{k^6} = \alpha_0^4(k_c^2 + k^2)$$ \hspace{1cm} (4.28)

\(^3\)Near the Brillouin zone center the dispersion for graphene is isotropic (depends only on the magnitude of $k$). The $k$-vectors used in Fig. 4.2 have various directions, but — as the figure shows implicitly — they are close enough to the center that the dependence of the frequency on direction is very weak, so we are able to plot the dependence that way.

\(^4\)Our value of $\alpha_0$ determined this way for the original Tersoff is $44.9\,\text{Å}^2 - \text{THz}$.  

28
where all of the wavevector dependence on the right hand side is in the \(k^2\) term and all of the temperature dependence enters into \(k_c^2 = \beta T\), where \(\beta\) is a constant. Plotting \((\omega^4/\hbar^6)\) vs. \(k^2\) should then reveal a series of parallel straight lines at low temperatures, shifted by temperature. The vertical intercepts are a measure of the anharmonicity and should scale linearly with temperature.

This replotting of the calculated, temperature-dependent dispersion curves is done according to Eq. 4.28 in Fig. 4.3, where now we include all of our calculated temperatures. The points are atomistic results and the solid lines simple linear fits to the points, such that the slope of each is fixed by the harmonic (\(T=0\)K) calculations. This leaves one parameter used for the fit at each temperature above \(T=0\)K, which is the vertical offset. In this plot, we do the fit only for modes with \(k\) below 0.4 Å\(^{-1}\), above which there is some deviation.

By subtracting off the \(k\)-dependent part of Eq. 4.28 we can isolate the temperature-dependence:

\[
\frac{\omega^4 - \omega_0^4}{\hbar^6} = \alpha_0 \beta T
\]  

(4.29)

where \(\omega_0\) is the frequency of the mode at \(T=0\)K. We again replot the calculated results for \(T\) below 200K according to this form in Fig. 4.4, where the lines are simple horizontal fits (for the first 5 \(k\)-vectors), and they illustrate in a clearer way the quality of the the fits in Fig. 4.3 at low temperatures.

(A word about the error bars in Figs. 4.3 and 4.4 is in order. The rotational symmetry of graphene determines that there are sets of symmetry-equivalent \(k\) vectors. Because our Monte Carlo sampling does not enforce the rotational symmetry of the graphene, the variation we find among each set is a measure of the statistical quality of the sampling in this calculation. The calculated results plotted in these figures are determined by examining the statistical variation among those symmetry-equivalent \(k\)-vectors: the points are the averages, and the error bars are the rms deviation.)

The intercepts in Fig. 4.3 give the values of \(k_c^2\). We then plot \(k_c^2\) vs. temperature in Fig. 4.5 to test the prediction that \(k_c^2\) should be linear in \(T\). The points are atomistic results and the line is a linear fit to the low-temperature calculations below 200 K, showing that the relation \(k_c^2 \propto T\) is followed at low temperatures, where the approach of Mariani and von Oppen is expected to have the best success.

In Fig. 4.6, we replot the calculations from Fig. 4.5, now in log-log form, to demonstrate that the slope in Fig. 4.6 for temperatures below \(T = 200K\) is close to 1, confirming that \(k_c^2\) is linear.
in $T$ at low $T$ but deviates at higher $T$.

Finally, considering our results altogether, we are able to get a good fit to all of our calculated points up to $k=0.4$ Å$^{-1}$ and $T=200K$ to the form of Mariani and von Oppen using just two parameters ($\alpha_0$ and $\beta$). The value of $\beta$ determined overall is $2.0 \times 10^{-4} \text{Å}^{-2}\text{K}^{-1}$, which is a little higher than the value calculated from MvO ($6.1 \times 10^{-5} \text{Å}^{-2}\text{K}^{-1}$). For larger values of $k$ or higher $T$, there is some deviation as noted.

The results shown here are for the modified Tersoff potential. We have also performed the same calculations using the original Tersoff potential [46, 47], and find that the agreement with the form predicted by Mariani and von Oppen is the same for low $T$ and $k$, and that the deviation outside of that range is similar. The original Tersoff matches the continuum results over a larger range of $k$, agreeing out to $k = 0.5$ Å$^{-1}$. The value of $\beta$ is smaller for the original Tersoff than the modified Tersoff by an order of magnitude ($3.3 \times 10^{-5} \text{Å}^{-2}\text{K}^{-1}$). This difference in $\beta$ is consistent with the stronger anharmonicity of the original Tersoff. (The modified Tersoff potential was the result of an attempt to tone down the anharmonicity, to bring the calculated value of lattice thermal conductivity closer to experiment [25].)

### 4.5 Conclusions

We have presented results obtained for the temperature-dependent dispersion relation of flexural modes in graphene. These results have been obtained using a new method based on Monte Carlo averages of displacements and forces. In the present calculation the energies and forces required for the MC calculation were obtained using two versions of the semi-empirical Tersoff potential — the original version for diamond and another modified for graphene.

We then analyzed the dispersion relation to show that our results confirm the non-linear continuum results of Mariani and von Oppen. Mariani and von Oppen’s approach is based on a perturbative expansion of the potential energy and is therefore expected to be good at low $T$ and $k$. Our results (based on a semi-empirical potential) represent a more robust potential energy surface, and should hold out to higher $k$ and $T$. It is encouraging to see that the two very different approaches (continuum vs. atomistic) yield the same behavior in the low $k$ and low $T$ region. Furthermore, the continuum calculations did not establish the range of temperatures or wave vectors for which the expansion is expected to hold. Our calculation shows that their approximation works well
Figure 4.2: The dispersion of the flexural modes, calculated using the moments method at two temperatures ($T = 0$ K and 1200 K). The points are the results of our calculations, and the lines are simple power-law fits. These results are for the modified Tersoff potential. The dispersion curves for several intermediate temperatures have been calculated and are smooth intermediates to these curves, so they have been omitted from this plot for the sake of presentation.

up to temperature and wavevector noted, and that even outside of that range the form is not an unreasonable approximation to our results. The agreement also serves as a test of the new, atomistic method, showing that it is able to handle a rather subtle anharmonic feature of the vibrational modes.
Figure 4.3: Plot of $(\omega^4/k^6)$ vs. $k^2$ at various temperatures. Points are the results of the present calculation. The lines are simple, one-parameter fits to the values for the lowest five $k$-vectors. The single parameter for each temperature is the vertical offset, the slope for all being determined by the $T=0\text{K}$ calculations. Error bars are statistical, as discussed in the text.
Figure 4.4: Plot of $(\omega^4 - \omega_0^4)/k^6$ vs. $k^2$ at low temperatures. This is a replotting of the calculations from Fig. 4.3 to emphasize the temperature dependence. Points are the results of the present calculations, and the horizontal lines are simple fits to the values of the lowest five $k$-vectors. Error bars are statistical, as discussed in the text.
Figure 4.5: Plot of $k_c^2$ vs. $T$, showing the linear behavior at low temperatures predicted by Mariani and von Oppen [9]. The points are our calculations, and the line is a one-parameter linear fit to the lower temperature calculations.
Figure 4.6: Plot of $\ln(k_c^2)$ vs. $\ln(T)$, along with a linear fit to the lower temperature calculations. The continuum theory predicts a slope of 1. [9].
Chapter 5

Anharmonicity of Radial Breathing Modes in Carbon Nanotubes

5.1 Introduction

In the last chapter we studied the renormalization of flexural modes in graphene using Jazz. In this chapter we use the similar technique to study the radial breathing mode in carbon nanotube and their dependence on temperature, diameter, length, etc.

5.2 Background

Carbon nanotubes (CNT) are allotropes of carbon with a cylindrical nanostructure. They have unusual properties, which are valuable for nanotechnology, optics, electronics and other fields of science and technology. The diameter \( d \) of a nanotube with chirality of \((n_1, n_2)\) is determined by:

\[
d = \frac{a_0}{\pi} \sqrt{n_1^2 + n_1 n_2 + n_2^2}
\]

(5.1)

with \( a_0 = 2.46 \, \text{Å} \), which is the in-plane lattice constant of graphene.

The Radial breathing mode (RBM) corresponds to radial expansion-contraction of the nanotube. According to the literature \([48]\), the RBM’s frequency \( \omega_{RBM} \) depends on the nanotube

\footnote{Most of the chapter has been published in \([7]\).}
diameter $d$ as:

$$\omega_{RBM} = \frac{c_1}{d} + c_2$$  \hspace{1cm} (5.2)$$

In which $c_1$ and $c_2$ are empirically derived parameters.

Vibrational modes of single-wall carbon nanotubes (SWNTs) are accessible experimentally via Raman spectroscopy[11, 49, 50]. A typical Raman spectrum of a SWNT reveals two prominent peaks associated with intrinsic (not defect-related) modes: the Radial Breathing Mode (RBM) and the so-called “G-band”, a group of high-frequency modes that have an analog in graphene. Extensive theoretical investigations of the vibrational modes of SWNTs have been carried out, most commonly using the harmonic approximation.[51, 52]

By examining the temperature-dependence of the Raman spectra, it is possible to explore the anharmonicity of the RBM and G-band in particular. Raman spectra of the RBM and G-band in SWNT bundles have revealed that their frequency drops with temperature between 300$K$ and 800$K$.[53, 54]. Molecular dynamics calculations on individual SWNTs agree with these observations.[54]

In this work, we apply the “moments method”[5, 2] to investigate the temperature-dependence of the frequency of all of the modes of a SWNT. We also study how the chirality, diameter and length of the tube affect the anharmonicity. We find that generally all of the vibrational modes shift to lower frequency with increasing temperature. Within that generality, we find that, with respect to anharmonicity, there are three basic groups of modes. Vibrational modes with largely longitudinal character (that is, displacements parallel to the length of the tube) as well as modes with largely azimuthal displacements (transverse to the length but tangential to the tube) are more anharmonic than the large majority of radial modes. The exception are the azimuthally symmetric radial modes, which are the most anharmonic of all modes. The RBM itself is the most anharmonic of all modes, and the G-band is nearly as much.

In the next section, we discuss the method, and in the following sections we discuss our results, ending with the conclusions that that the RBM is the most anharmonic of the vibrational modes of the SWNT as revealed by its shift with temperature. We also find that the anharmonicity of these modes is not sensitive to chirality or length but does depend on diameter. We discuss our results in relation to experiments and previous calculations.
5.3 Setting up our calculations

The calculation involves ensemble averaging of products of normal mode amplitudes $A_{kb}$ and accelerations $\ddot{A}_{kb}$, which are obtained by projecting the atomic displacements and forces onto the normal modes. Using the harmonic modes as a basis is justified by the weakly anharmonic character of this system. The lowest, non-trivial moment of the power spectrum of the displacement-displacement autocorrelation

$$\mu_2(kb) = -\frac{\langle A_{kb}\ddot{A}_{kb} \rangle}{\langle A_{kb}^2 \rangle - \langle A_{kb} \rangle^2} (5.3)$$

(where the angle brackets indicate ensemble averages) gives a simple measure of the temperature-dependent dynamics of the system.

The previous expression includes the possibility that $\langle A_{kb} \rangle$ is non-zero, which was not included in our previous chapters because the systems considered previously had sufficiently high symmetry that the average displacement vanished. However, in the present case, the average displacement of the RBM deviates significantly from zero as the temperature increases, and so we have extended the expressions derived in previous work to include non-zero first moments.

The quasi-harmonic (temperature-dependent) frequency $\omega(k)$ is given by

$$\omega(kb) = \sqrt{\mu_2(kb)} (5.4)$$

The moment is calculated by standard Monte Carlo integration. This method was used recently to study the anharmonic renormalization of flexural modes in graphene. [6]

In this study, the interatomic interaction is described by a Tersoff potential tailored somewhat for graphene [55, 46, 25]. The normal modes are identified from the eigenvectors of the harmonic force constant matrix. We generated various tubes of different chirality, diameter and length. (The diameter is related to the chirality by $d = \sqrt{n_1^2 + n_1n_2 + n_2^2} a_0/\pi$ in which $(n_1, n_2)$ are the usual chiral indices and $a_0 = 2.46$ Å, the in-plane lattice constant of graphene. [56]) We studied tubes with lengths ranging from 1.3 nm to 13 nm and diameters from 0.78 nm to 2.35 nm, with various chiralities. All computational cells are under periodic boundary condition along the length of the tube. The Monte Carlo calculation includes 400 steps per atom, and spreads over 100 independent processor cores on Palmetto Cluster of the University. The lattice parameter of the cells is determined at each temperature by molecular dynamics with adjustable cell size at constant
(zero) pressure, thus incorporating thermal expansion or contraction. In some parts of the analysis, we focus on particular modes, but all have been included in the calculation.

As noted above, the RBM is highly symmetrical; the displacements are dominantly radial and are uniform along the length of the tube. Other modes displacing along the radial direction — we refer to simply and more generally as “radial modes” — are related to the RBM by a dispersion along the tube axis — as in \( \cos (kz) \) where \( k \) is the wavevector and \( z \) is the distance along the axis of the tube — and/or a phase related to the azimuth angle \( \phi \) — as in \( \cos (m\phi) \) with integer \( m \). The \( k = 0 \) modes are at the \( \Gamma \)-point in the one-dimensional Brillouin zone. The RBM is then a special radial mode with \( m = 0 \) and \( k = 0 \). Figs. 5.1 and 5.2 illustrate the RBM and a typical radial mode. Most of the radial modes are not visible in Raman spectra, but as we have noted before the RBM appears prominently.

### 5.4 Our results and analyses

We begin by presenting the results for a typical nanotube. The anharmonicity is easily displayed by comparing the frequency \( \omega \) at some temperature as compared to the zero-temperature frequency \( (\omega_0) \). Figure 5.3 is a scatterplot of the ratio \( \omega_N \equiv \omega/\omega_0 \) vs. \( \omega_0 \) for all modes of a SWNT(15,0) nanotube with periodic length 6.5 nm (so it has 900 atoms in the unit cell) at \( T = 1200K \). As can be seen from the figure, closer analysis shows that the modes fall into three basic groups according to anharmonicity. The least anharmonic modes (those that show the least drop in frequency with increasing temperature) are the radial modes (except for a small group which will be discussed in a moment). The modes with largely longitudinal and azimuthal displacements are more anharmonic. The modes with displacements mostly in-plane would seem to be more anharmonic because displacements in the plane will have a more direct effect on the bond length than out-of-plane displacements.

Finally, in Fig. 5.3 there is a stand-out set at a frequency of about \( 35 \times 10^{12} \) rad/s, which are radial modes that are azimuthally symmetric (that is, have \( m = 0 \)). These modes include the RBM and related modes with \( k \neq 0 \). Among this set, we find that the RBM is the most anharmonic of all the modes of the nanotube. This is consistent with the experimental Raman results reported in Ref. [54], where both the RBM feature and the G-band are seen to shift with temperature but in fractional terms the RBM is more anharmonic. These azimuthally symmetric radial modes differ
(a) Side view (the \(yz\) plane) of the radial breathing mode given that the tube is along the \(z\) axis.
(b) Side view (the \(yz\) plane) of the radial breathing mode given that the tube is along the \(z\) axis.
(c) Top view of the radial breathing mode.

Figure 5.1: Visualization of the breathing mode in carbon nanotube. The blue dots are positions of atoms and the black arrows correspond with the direction of atoms' oscillations for the mode. The magnitudes of the arrows have been adjusted artificially for better figure quality. (The unit for the sidebars is \(\text{Å}\).)
Figure 5.2: Visualization of a radial mode with wave vector of $0.097 \text{ Å}^{-1}$ along the nanotube. Again, the blue dots are positions of atoms and the black arrows correspond with the direction of atoms’ oscillations for the mode. The magnitudes of the arrows have been adjusted artificially for better figure quality. (The unit for the sidebars is Å.)
Figure 5.3: Scatterplot of the ratio $\omega_N \equiv \omega/\omega_0$ vs. $\omega_0$ for all of the modes of a SWNT(15,0) tube. $\omega$ is the frequency at temperature ($T = 1200K$) and $\omega_0$ is the corresponding harmonic frequency (at $T = 0K$). For a perfectly harmonic system, all points would be at the top (at a value of 1); due to anharmonicity, all of the modes of this system drop to lower frequency with increasing temperature. The more anharmonic modes exhibit lower values of $\omega_N$. Lines are drawn in this figure as guides to the eye to indicate the different groupings of modes described in the text.
Figure 5.4: The dispersion relations of the azimuthally symmetric (that is, \( m = 0 \)), radial modes of SWNT(15,0) at various temperatures calculated using the moments method. The periodic length is 6.5 nm, so there are 900 atoms in the unit cell. A fit to Eq. 5.5 is shown. The results for several other intermediate temperatures have been calculated and are intermediate to these results, so they have been omitted from this plot for the sake of presentation.

From the RBM by the longitudinal wavenumber \( k \). So we focus on these modes by showing the temperature-dependent dispersion curves in Fig. 5.4. At \( T = 0 K \) the frequencies (purely harmonic) follow a quartic dispersion

\[
\omega(k) = c_0 + c_1 k^4
\]  

(5.5)

The value of \( c_0 \) (at \( k = 0 \)) then corresponds to the frequency of the RBM. The temperature dependence is made clearer in Fig. 5.5 by replotting the same data in terms of the ratio to the harmonic frequency vs. temperature. In both figures, it is clear that the RBM has stronger temperature dependence than the other azimuthally symmetric radial modes. The frequency of the RBM is roughly
Figure 5.5: The ratio of anharmonic frequency to harmonic frequency ($\omega_N(T) = \omega(T)/\omega_0$) vs temperature for radial modes of various wavevector $k$. 
linear with temperature, and the temperature coefficient $p$ in

$$\omega_N(T) = 1 + pT$$  \hspace{1cm} (5.6)$$

is determined for this tube to be $-6 \times 10^{-5} K^{-1}$. Fig. 5.5 also shows that $p$ decreases with increasing wavevector $k$. The RBM is the most anharmonic of the set (indeed, of all modes).

Two different experimental observations using Raman spectra of nanotube powders [53, 54] of similar diameter (both estimated to be 1.3 to 1.4 nm) determine a slope in the range of 300-800 $K$ of $-7 \times 10^{-5} K^{-1}$ and $-2 \times 10^{-5} K^{-1}$, which span our value. We note that it is not clear how to compare calculations of isolated nanotubes with the experimental Raman spectra of nanotube powders; it is expected that in such powders the tubes touch and interactions with neighboring tubes would affect their vibrational characteristics. This could be studied theoretically by bringing tubes in contact with each other, which is beyond the scope of the present calculation, but could be done in the future with the same methods.

A Molecular Dynamics (MD) simulation [54] using one of the original Tersoff potentials for carbon [55] for a (10,10) tube (1.4 nm) reported a value of $p$ of $-5 \times 10^{-5} K^{-1}$, very close to our calculation and also within the range reported in the two experiments. The minor difference between the present calculations and those previously reported might be attributed in part to the different chiralities and diameters considered, in part to the interatomic potential (we used a potential with Tersoff form that was somewhat optimized to graphene [25]), or possibly in part to the difference in technique (MD vs. moments). At any rate, the differences are not large.

One might hypothesize that the RBM is more anharmonic than other modes because it is radial — that is, maybe displacements in the radial direction are more anharmonic than displacements in other directions — but that is disproved by our results that demonstrate that the large majority of radial modes are not as anharmonic as the RBM. The strong temperature dependence of the RBM frequency, especially in contrast to the other radial modes with $k \neq 0$ can be understood rather in terms of the high symmetry of the RBM (with $k = 0$ and $m = 0$). The RBM has the same symmetry as the nanotube itself (in that any operation that returns the atomic structure of the nanotube to itself also returns the RBM to itself) and can therefore couple easily with other modes. In terms of the usual 3rd order and 4th order force constant matrices (see, for example, Madelung [57]), the high symmetry of the RBM allows it to couple with many other modes of the
Figure 5.6: The slope $p$ of the temperature dependence of the frequency (Eq. 5.6) of the RBM is plotted vs. the diameter $d$ of the tube. For this plot, we chose a series of tubes with chirality from $(10,0)$ to $(30,0)$. Other corresponding sequences of tubes show similar behavior.

tube. This ubiquitous coupling would mean that the frequency shift of the RBM may depend on the number of other modes present in the tube. The number of such modes will vary with tube diameter and length, so we investigate that here.

In Fig. 5.6, we show that the value of $p$ for the RBM (from Eq. 5.6, Fig. 5.5) depends on the diameter of the tube. That is, the anharmonicity of the RBM is stronger for tubes with larger diameter. This is consistent with the observation in the previous paragraph, because as the diameter of the tube increases the number of modes that are available to couple with the RBM increases, thereby resulting in a stronger anharmonicity.

However, by contrast, we show in Fig. 5.7 that the temperature dependence of the modes is not very dependent on the periodic length of our calculation. Periodicity restricts the calculation so that only vibrational modes with wavelength commensurate with the periodic length are allowed.
Figure 5.7: The slope $p$ of the temperature dependence of the frequency (Eq. 5.6) of the RBM of the (15,0) SWNT is plotted vs. the periodic length $l$ of the supercell.
Increasing the length of the periodic cell allows more modes to be present, and also to couple with the RBM which is present always. However, our results indicate only a weak dependence of the anharmonicity on the periodic length.

5.5 Conclusions

We have presented the results of a study of anharmonicity of vibrational modes of SWNTs obtained by the “moments method”, which is based on Monte Carlo averages of products among displacements and forces. The forces and energies required for the MC calculation were obtained from a semi-empirical Tersoff potential, somewhat optimized for graphene.

Generally all modes shift down in frequency with increasing temperature. Modes with largely in-plane character (longitudinal and azimuthal modes) are more strongly anharmonic than most modes with radial character, with the exception of azimuthally symmetric radial modes (which includes the RBM). In terms of the fractional shift in frequency, the RBM is the most anharmonic of all modes of the nanotube. The temperature dependence of the frequency of the RBM increases with the diameter of the tube. This is attributed to an increase in the number of azimuthal modes eligible to couple with the RBM. As far as we can determine from searching the literature, this is the first time that the effect of diameter on the anharmonicity has been appreciated. The pronounced anharmonicity of the RBM is attributed to its ubiquitous coupling to other azimuthal modes, which is allowed by its high symmetry. The results provide a clearer picture of the anharmonicity of the vibrational modes of a SWNT.
6.1 Introduction

This chapter is a continuation of our study of anharmonicity of the structures formed from a single sheet of carbon atoms — first graphene, then SWNTs, and finally fullerenes — using the “moments method”.

During the history of the discovery and understanding of structures formed from a single layer of carbon atoms, vibrational modes have been one of the fundamental characteristics most studied [51, 58]. The usual experimental tools for studying vibrational modes are Raman spectroscopy, IR scattering, and inelastic neutron scattering, and these have been variously applied to these structures. The low-temperature frequencies of these modes determined by experiment have been compared, usually favorably, to those predicted on the basis of the harmonic approximation. However, in some cases, the modes shift with temperature, which is a sign of anharmonicity. Though the temperature dependence is often available experimentally, and though a full understanding of vibrational modes is fundamental to the understanding of these structures, there have been much fewer theoretical treatments of their anharmonic character. Recently, for example, the anharmonic character of the flexural modes of graphene has been of central focus to the understanding of thermal

\[1\] Most of the chapter has been published in [8].
conductivity and even the stability of these sheets [45, 6].

By comparing our results directly to experiment, we are using this work not only to test the new theoretical method, but also we are filling in a two-decade gap in the theoretical treatment of the anharmonicity of fullerenes, in that the experiments that were reported 21 years ago have not been answered by corresponding theoretical analysis. Furthermore, by testing our new method on materials that have been well-studied experimentally, we are preparing for work in the near future on materials that have not been so well studied.

Vibrational modes of fullerenes have been studied by Raman spectroscopy [59, 60], IR scattering [61] and inelastic neutron scattering [62]. The complete assignment of the vibrational modes of C\textsubscript{60}, the most-studied fullerene, has been made experimentally by these three approaches and also theoretically (in the harmonic approximation) using, for example, the DFT method [62, 63].

By examining the temperature dependence of the Raman spectra, it is possible to explore the anharmonicity of the Raman-active modes. Raman spectra of C\textsubscript{60} have revealed that the frequency of all the peaks drops with temperature. [64] In the present work, we apply the “moments method”[2, 5] to investigate theoretically for the first time the temperature-dependence of the frequency of all of the modes of individual fullerenes. We also study how the size of the individual fullerene affects the anharmonicity of the modes. We find that the value of the anharmonicity (measured by \( \omega'(T)/\omega(0) \)) of all the modes for the fullerenes is about \(-3 \times 10^{-5} K^{-1}\), largely independent of the mode or the size of the fullerene.

6.2 Setting up our calculations

In this study, the interatomic interaction is described by a Tersoff potential tailored somewhat for graphene [46, 25, 55]. The normal modes are identified from the eigenvectors of the harmonic force constant matrix. We accumulated \(10^6\) Monte Carlo steps on each individual fullerene. In some parts of the analysis, we focus on the RBM, but all modes have been included in the calculation. We studied \(C_{20-Ih}, C_{30-D6h}, C_{60-Ih}, C_{70-D5h}, C_{84-D6h}, C_{100-D5h}, C_{180}, C_{240}\). For those fullerenes that have isomers, we chose the most symmetrical structures. (The notation following the hyphen in the expression of a specific fullerene indicates the symmetry group that the fullerene has.) For the ellipsoid-shaped fullerenes, the mode in which the fullerene contracts or expands uniformly is treated as the RBM, although its symmetry is not \(A_g(1)\). For example, for the \(C_{70}\) fullerene we call
the $A'^1_1(2)$ mode the RBM.

6.3 Our results and analyses

We begin by presenting the results of the harmonic frequencies of the RBMs for the individual fullerenes. Fig. 6.1 shows that the harmonic frequency of the RBM has an inverse relationship with the size of the fullerene (measured by the number of the atoms in the molecule.) This behavior is similar to that seen for the RBM of SWCNTs. [48] Our harmonic results resemble and serve as a calibration against earlier experimental results and other calculational results that use different methods or different empirical potentials. [65, 66, 67] However, the main focus of this study is on the anharmonicity of the modes, as we will discuss next.

In terms of the anharmonicity of the vibrational modes, we find that the frequencies of
Figure 6.2: Scatterplot of the ratio $\omega_N \equiv \omega/\omega_0$ vs. $\omega_0$ for all modes of the $C_{60}$ fullerene at $T = 1200K$. For a perfectly harmonic system, all points would be at the top (at a value of 1); due to anharmonicity, all of the modes of this system drop to lower frequency with increasing temperature. The more anharmonic modes exhibit lower values of $\omega_N$. 
Figure 6.3: Plot of the ratio $\omega_N \equiv \omega/\omega_0$ vs. temperature $T$ for the RBMs of three fullerenes.
all the modes for all the fullerenes drop roughly linearly with temperature, and in proportion to frequency as well. We therefore define as a measure of the anharmonicity

\[ p = \frac{1}{\omega_0} \frac{d\omega}{dT} \]

so that a perfectly harmonic system would have \( p = 0 \). Our calculated value of \( p \) for all the modes falls between \(-2 \times 10^{-5} K^{-1}\) and \(-4 \times 10^{-5} K^{-1}\) for all the fullerenes we studied here. As an example, Fig. 6.2 is a scatterplot of the ratio \( \omega_N \equiv \omega/\omega_0 \) vs. \( \omega_0 \) for all modes of the \( C_{60} \) fullerene at \( T = 1200K \). All modes show similar temperature dependence. In comparison, slopes between \(-0.8 \times 10^{-5} K^{-1}\) and \(-2 \times 10^{-5} K^{-1}\) are observed experimentally [64] for the shifts of the peaks in Raman spectra of solid \( C_{60} \) up to \( 840K \), and slopes between \(-0.8 \times 10^{-5} K^{-1}\) and \(-1.3 \times 10^{-5} K^{-1}\) are observed experimentally [68] for the shifts of the peaks in IR spectra of \( C_{60} \) embedded in KBr pellets. The comparison between our calculations and the experiment is reasonably good; the differences could be attributed to many aspects, such as individual \( C_{60} \) vs. solid \( C_{60} \) and also the quality of the empirical potentials, which are usually not determined by reference to anharmonic properties.

Motivated by the high anharmonicity of the RBM in SWCNTs [7], we pick out the RBMs in fullerenes and study their anharmonicity in particular. Fig. 6.3 shows the temperature dependence of the frequency of RBMs of three fullerenes \((C_{20-\text{Ih}}, C_{60-\text{Ih}}, \text{and } C_{180})\) that were typical of the rest in this regard. The results for the other fullerenes we considered \((C_{36-\text{D6h}}, C_{70-\text{D5h}}, C_{84-\text{D6h}}, C_{100-\text{D5h}}, \text{and } C_{240})\) are very similar and were not included in the plot because they overlap significantly with the three shown. The value of \( p \) does not appear to vary much with the size of the fullerene. In contrast, we have observed in SWCNTs that the value of \( p \) of the RBMs increases in magnitude with diameter of the tube. [7]

### 6.4 Conclusions

We have presented the results of a study of anharmonicity of vibrational modes of fullerenes obtained by the “moments method”, which is based on Monte Carlo averages of products among displacements and forces. The forces and energies required for the MC calculation were obtained from a semi-empirical Tersoff potential, somewhat optimized for graphene-like structures.

Our results for the harmonic part resemble earlier works, showing that the harmonic fre-
quency of the RBM of the fullerene is inversely related to the size of the fullerene. With regards to anharmonicity, generally all modes, including the RBMs, shift down in frequency with increasing temperature at a roughly similar fractional slope for all fullerenes we have studied. The size of the fullerene does not affect strongly the anharmonicity of the modes. The results fill in a two-decade gap in the theoretical treatment of the anharmonicity of fullerenes and provide a clearer picture of the anharmonicity of the vibrational modes of fullerenes.
Chapter 7

Summary

Thermal properties have been one of the most fundamental characteristics to study about materials. Many of these thermal properties, such as thermal expansion, thermal conductivity and etc, are consequences of anharmonicity of vibrational modes in solids.

The anharmonicity of vibrational modes in structures formed from a single layer of carbon atoms is one of the fields that are poorly understood due to the limitations of available techniques. In this dissertation, I study and aim to better understand the vibrational modes in these structures.

The common experimental tools for studying vibrational modes are Raman spectroscopy, IR scattering and inelastic neutron scattering, and these have been variously applied nowadays. Whereas calculations of frequencies and lifetimes of vibrational modes involves two steps: 1, to gain forces, which can be done with either semi-empirical potentials or electron structure calculations; 2, to extract modes frequencies and lifetimes using those forces, which can be done with Molecular Dynamics or Boltzmann Transport equation. Practically, many of the vibrational modes are not detectable using current experimental techniques, and so far there is no clear way of conducting mode frequencies and lifetimes calculation on wide variety of materials. Dickel and Daw proposed a general and practical approach to calculate the frequencies and intrinsic mode lifetimes of solids based on the Moments approximation.

In chapter 1, backgrounds on anharmonicy in solids were reviewed. How anharmonicity affects the frequencies and lifetimes of vibrational modes was explained. Current experimental and computational approaches to study the anharmonicity of vibrational modes were discussed.

In chapter 2, a new approximation method to calculated mode frequencies and lifetimes of
vibrational modes was discussed, upon which most of work presented in the thesis is based. This method is based on ensemble averages of displacements and forces and it utilizes the Green-Kubo Formula, Canonical Transformation, and the Liouvillian operator.

In chapter 3, a Python package called *Jazz* was introduced. The package is based on the Moments method discussed in Chapter 2. *Jazz* is a Python wrapper for *LAMMPS*, implemented to calculate the lifetimes of vibrational normal modes based on forces as calculated for any interatomic potential available in that package. The anharmonic character of the normal modes is analyzed via the Monte Carlo-based moments approximation.

In chapter 4, I studied the effects of anharmonicity on the dispersion of the flexural modes in free-standing stress-free graphene. I find that the dispersion relation of the flexural modes of graphene is renormalized by anharmonic coupling to other modes. My calculations confirm that the anharmonic continuum results of Mariani and von Oppen hold in detail for small wave number and at low temperatures, which is very encouraging to see. I also examine the deviation from the continuum result outside of that range.

In chapter 5, I studied the anharmonicity of the vibrational modes of single-walled carbon nanotube. I find that modes with displacements largely within the wall are more anharmonic than modes with dominantly radial character, except for a set of modes that are related to the radial breathing mode which are the most anharmonic of all. I also find that periodicity of the calculation along the tube length does not strongly affect the anharmonicity of the modes, but that the tubes with larger diameter show more anharmonicity. Comparison is made with available experiments and other calculations.

In chapter 6, I studied the anharmonicity of the vibrational modes of fullerenes. I find that the frequencies of all vibrational modes drop systematically with temperature and that the size of the fullerene does not strongly determine the anharmonicity of its modes. My results fill in a two-decade gap in the theoretical treatment of the anharmonicity of fullerenes. Favorable comparison is made with experiments.

The above work serves to provide clearer pictures of anharmonicity of vibrational modes in carbon nano-materials.
Bibliography


