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CALCULATING THE PHONON MODES OF GRAPHENE USING THE 4<sup>th</sup> NEAREST  
NEIGHBOR FORCE CONSTANT METHOD**Mikiyas S. Tsegaye**Department of Electrical Engineering  
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pmn3d@virginia.edu**ABSTRACT**

Graphite has always been a very important material both industrially and academically due to its physical structure. But ever since the isolation of Graphene (a single sheet of Graphite) a few years ago, it's been one of the most widely studied molecular systems for its potential applications in nano-electronics and other break-through areas. Some of the desirable traits of Graphene are its high thermal and electronic mobility, and its low noise properties. This paper outlines a standard method for calculating phonon dispersion curves in Graphene by making use of force constant measurements. This information is usually obtained from approximations of inter-atomic potentials, which involve derivatives of simplified potential approximations between every atom in Graphene to get the force constant tensors. In this paper, the measured values for the force constants are used in a mathematically rigorous way to calculate the Graphene phonon dispersion curves.

**NOMENCLATURE**

$D$	dynamical matrix	[N/m]
$w$	frequency	[cm <sup>-1</sup> ]

**INTRODUCTION**

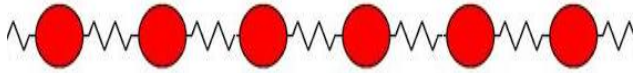
one of the prominent issues that the microelectronics industry is struggling with today is heat

generation and dissipation in solid state devices. Therefore, while the industry makes the transition to nanoscale transistors, there is an opportunity to incorporate new materials that possess not only excellent electrical properties, but also desirable thermal properties that will lend themselves to efficient heat extraction and dissipation. Graphene, along with Carbon Nanotubes, has recently been hailed as such a material. A considerable amount of research is currently going into the use of graphene in integrated circuits. Some of this research focuses on the use of graphene nano-ribbons as semi-conducting channels in graphene-based transistors, and a portion of the research focuses on the potential use of graphene and CNT's as interconnects. Regardless of the final application of graphene in IC chips, there is a consensus that its thermal properties are just as important as its electrical properties, if not more so.

**BACKGROUND**

Heat is mainly carried by lattice vibrations in non-metallic materials. Electrons also contribute to heat transport. Lattice vibrations, when quantized, are known as phonons. At low temperatures, atoms are frozen in place and the inter-atomic potential that exists in the motionless structure is used to calculate how the atoms influence each other. The force that is exerted is in fact the derivative of this potential. This potential is parabolic in shape around the equilibrium distance between atoms, and

therefore can be approximated by a harmonic oscillator's potential profile. For this reason, we can model atoms as masses connected by springs, as depicted in figure 1. The stiffness of the springs corresponds to the strength of the bonds between adjacent atoms. Within this harmonic approximation, we can write down the equations of motion for all atoms, and solve them together to find out how kinetic energy is transferred among them.



**Figure 1. Chain of masses connected by springs**

It was classically believed that the energies of these oscillations were continuous, but we now know that all harmonic waves actually have quantized energies. For this reason, phonons are understood as discrete vibrational 'packets' or 'particles' with energies that are integer multiples of  $h\nu$  (*Planck's constant times frequency*). This is why we treat vibrations as particles with certain energies depending on their frequencies.

The vibrational properties of a structure can be described by its phonon dispersion relation. This relation describes the relationship between the phonon frequencies and the reciprocal-space wave vectors,  $k$ , associated with those frequencies.

## METHOD

The method that we will focus on for this paper is known as the 4<sup>th</sup> nearest neighbor force constant method (4NNFC). We show how this method is implemented based on how it is described in the book "Physical Properties of Carbon Nanotubes" by M. S. Dresselhaus and co. [1]. As was pointed out above, we start with a set of equations of motion for as many atoms as we like in the structure.

In general, the equation of motion for a system of atoms is written as:

$$M \cdot \ddot{u}_i = \sum_j K^{(ij)} \cdot (u_j - u_i) \quad (1)$$

Where " $i$ " is the central atom, " $j$ " represents neighboring atoms, " $M$ " is the mass, and " $u$ " is the atomic displacement, and  $K$  is the 3X3 force constant matrix between " $i$ " and " $j$ ".

What this means is that the Oscillations of atom " $i$ " are transferred to atom " $j$ " through the  $K$  force constant matrix.

After Fourier transforming equation 1, we can show that the equation can be rewritten formally as equation (2) by introducing a *Dynamical Matrix* " $D$ " with dimensions of 3x3 for every atom in the unit cell:

$$D(k) \cdot u_j = 0 \quad (3)$$

all we have to do to find the frequencies  $\omega^2(k)$  is solve the equation:

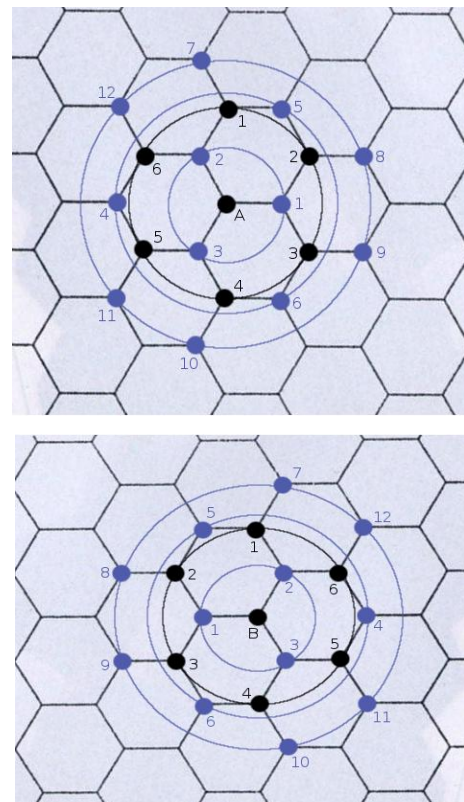
$$\det(D(k)) = 0 \quad (4)$$

for periodic systems such as graphene, the elements of the dynamical matrix are actually given by the product of the force constant matrix  $K(ij)$  and the phase factors  $e^{i \cdot k \cdot R_{ij}}$ .

$$D^{(ij)} = K^{(ij)} \cdot e^{(i \cdot k \cdot R_{ij})} \quad (5)$$

## APPLICATION TO GRAPHENE

Graphene has a honeycomb structure made entirely of carbon atoms. Therefore it has a hexagonal structure with a basis of two. In this paper we will consider interactions with up to the four nearest neighbor atoms. This is depicted in the following two figures.



**Figure 2. Two atoms in the graphene unit cell, A and B, and their nearest neighbors connected by rings**

There are two atoms in the unit cell, therefore the dynamical matrix is going to be 6X6. For convenience, it is common to break up the dynamical matrix into four separate matrices, each of which are 3X3 in size. The following equation demonstrates this fact:

$$D(k) = \begin{pmatrix} D^{AA} & D^{AB} \\ D^{BA} & D^{BB} \end{pmatrix} \quad (6)$$

where  $D^{AA}$  describes the effects of A type neighboring atoms on atom A,  $D^{AB}$  describes the effects of B type neighboring atoms on atom A,  $D^{BA}$  describes the effects of A type atoms on atom B, and so on and so forth. In the first picture of fig 2, while considering atom A, the matrix  $D^{AA}$  is calculated by adding all the contributions from A type atoms up to the fourth nearest neighbors. These contributions are calculated by multiplying the appropriate force constant tensors K by the corresponding phase factors, as shown in equation 5. All the other matrices are calculated in the same fashion.

But where do we get the appropriate force constant tensors? In this implementation of the 4NNFC model, we construct the tensors from force parameters that that are given in reference 1. These parameters are reproduced below. The parameters represent force constants in Newtons per meter in the radial (bond stretching), tangential in-plane (bond bending), and tangential out-of-plane (bond bending out-of-plane) directions.

	radial	Tangential	
		in-plane	out of plane
Ring 1	$\Phi_r = 365.0$	$\Phi_i = 245.0$	$\Phi_o = 98.2$
Ring 2	$\Phi_r = 88.0$	$\Phi_i = -32.3$	$\Phi_o = -4.0$
Ring 3	$\Phi_r = 30.0$	$\Phi_i = -52.2$	$\Phi_o = 1.5$
Ring 4	$\Phi_r = -19.2$	$\Phi_i = 22.9$	$\Phi_o = -5.8$

**Table 1. force constants in unit of N/m**

As an example, we will construct the first two force constant tensors that couple atom A to atoms B1 and B2.

$$K^{(A, B1)} = \begin{pmatrix} \Phi_r^1 & 0 & 0 \\ 0 & \Phi_i^1 & 0 \\ 0 & 0 & \Phi_o^1 \end{pmatrix}$$

The only difference between B1 and B2 is their angles in reference to atom A. Therefore to calculate the force constant tensor for atom B2, we must take the B1 tensor and apply tensor rotation rules to it. This simply involves

the following operation:

$$K^{(A, B2)} = U^{-1} \cdot K^{(A, B1)} \cdot U \quad (7)$$

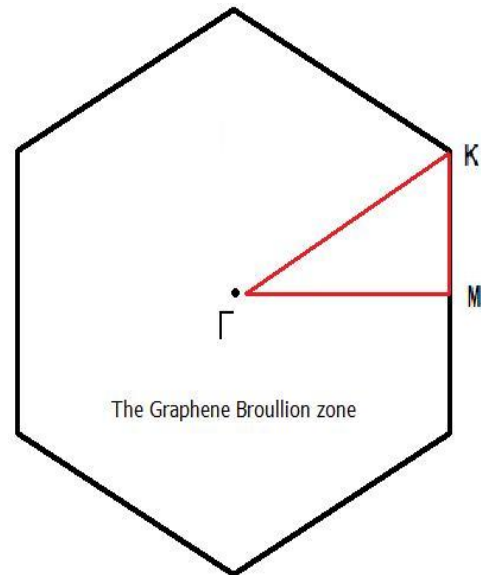
where U is a rotation tensor defined as follows:

$$U = \begin{pmatrix} \cos(\theta) & \sin(\theta) & 0 \\ -\sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (8)$$

and  $\theta$  is the angle that corresponds to B2, which in this case happens to be  $2\pi/3$ .

Using this method, we can now calculate all the force constant tensors that couple atoms A and B to all their nearest neighbors. The next step is to construct the 6X6 dynamical matrix according to equation (6), and solve for its eigenvalues. The eigenvalues are actually squares of the frequencies that we want, so we must be careful to take square roots after solving for these eigenvalues. The last step is to plot the frequencies versus the reciprocal wave vector within the Brillouin zone. This plot will be our dispersion relation. The above procedure is straightforward to implement in a mathematical simulation package such as Matlab, as done here.

Technically, frequency relations can be plotted for any specific direction in reciprocal space, but it is often useful to plot them along directions that have high symmetry. This simply means that the dispersion shows continuity as we traverse several different segments of wave vectors. The following figure shows the most symmetric path within the Brillouin zone (BZ).



**Figure 3. The Brillouin zone for graphene, with high-symmetry lines shown**

## RESULTS

The following plot shows the dispersion relation along the wave vector that goes from the  $\Gamma$ -point (center of Brillouin Zone) to the M-point (edge center of Brillouin Zone).

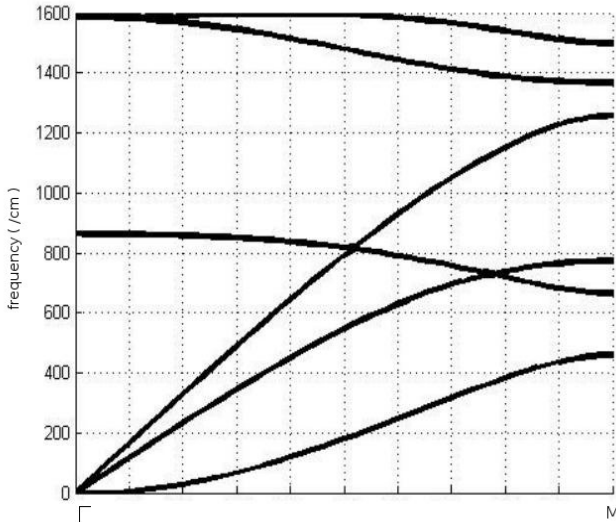


Figure 4. Dispersion relation, Gamma to M

The second high-symmetry direction to plot is from the M-point (edge center of BZ) to the K-point (edge corner of BZ). The following relation is obtained:

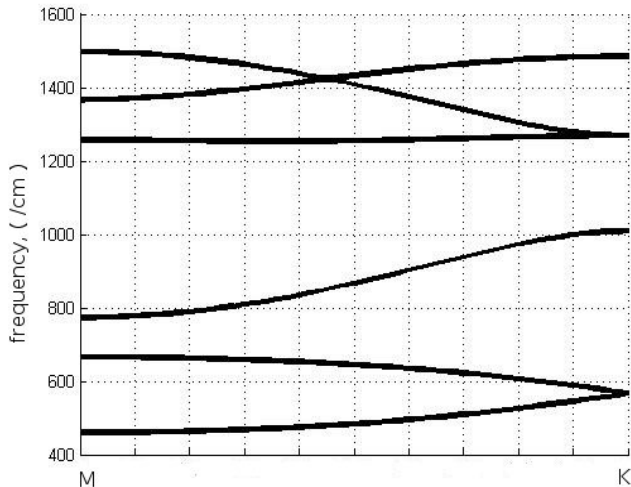


Figure 5. Dispersion relation, M to K

The last dispersion plot will be along the line that goes from K back to  $\Gamma$ . This part of the dispersion looks as follows:

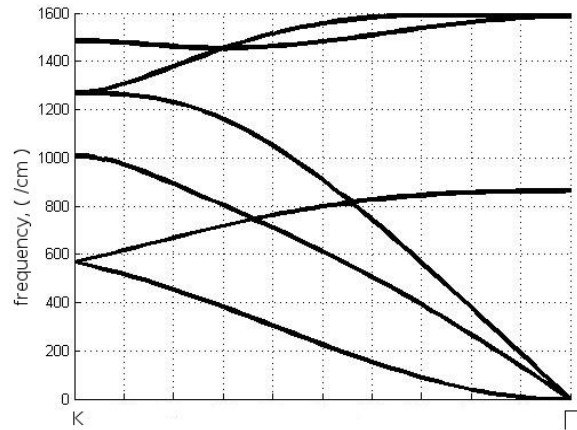


Figure 6. Dispersion relation, K to  $\Gamma$

## DISCUSSION

It is well worth noting that the inclusion of fourth nearest neighbors in this model is necessary in order to account for twisting motions that contribute to the vibrational properties of graphene. It is clear to see from our results that we can reproduce experimentally measured dispersion relations very well [2].

We get six branches in the dispersion, which is expected since our dynamical matrix was  $6 \times 6$ , and each atom in the unit cell has three degrees of freedom. Of the six branches, the three that originate at the  $\Gamma$ -point are known as acoustic branches, while the remaining three are known optical branches. Acoustic phonons have much higher group velocities (generally associated with the speed of sound in the material), and are therefore responsible for the majority of heat conducted by the material. Optical branches, on the other hand, are a result of atoms vibrating out of phase from each other, and can be sparked into action by interactions with photons. They do not contribute heavily to heat conduction. Each of these branch types can also be associated with three distinct directions of atomic vibration: Longitudinal (L), Transverse (T), and Out-of-plane (Z).

## CONCLUSIONS

We have seen that it is important to understand the vibrational properties of materials in order to maximize their full potential in technological applications, and to also avoid pitfalls and unintended consequences. A very powerful way of analyzing thermal properties of materials is to study their phonon dispersion relations. We have seen in this paper how to construct one of the models (4NNFC) used to calculate the phonon band structure of materials,

and we have seen a specific application with graphene. This information is useful in the calculation of thermal properties like heat capacity, heat conductivity and several other transport phenomena.

## **ACKNOWLEDGEMENTS**

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- [2] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, P. Ordejón, *Physical Review Letters* 92, 075501.