Thermal Conductivity of Graphene and Its Applications on Heat Spreading Materials

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Abstract. Graphene consists of a single layer of carbon atoms arranged in two-dimensional hexagonal lattice. This research set up model of graphene with heat source and sinks to visualize the movement of carbon atoms. Moreover, molecular dynamics simulations were tools to study the thermal conductivity of graphene and other properties of a material. The result shows that the thermal conductivity of graphene in the room temperature is relatively high among the existing materials. Various possibilities for its application will be briefly discussed, mainly focused on heat spreading materials. At last, there will be a discussion about graphene’s future development.

1. Introduction
As one layer of graphite, graphene is an allotrope of carbon that organized into honeycomb structure [1]. Graphene has lots of beneficial properties that derived from their extraordinary physical and mechanical properties [2]. Graphene is one of the thinnest materials in the world—the dimension of one carbon atom (0.34 nm) [3]. But graphene is regarded as the strongest material, outperforming steel and diamond, and it is lighter than paper[4]. The thinness, high tensile strength and lightness make graphene a highly potential material, attracting much researchers to analyze its further properties and applications beyond those data. So far, some of the discovered properties that may directly benefit people include high electrical conductivity and high thermal conductivity [5-6].

Thermal conductivity measures a material’s ability to transfer heat. In the room temperature, the thermal conductivity values in the range of 3080-5150 W/mK, significantly higher than any other materials from the same size [6]. However, the thermal conductivity of graphene decreases significantly as analyzing it in a micrometer scale, which contradicts the Fourier’s Law [7]. In this research, method of Molecular Dynamic Simulation will help calculating the thermal conductivity of graphene in a relatively small size. While other materials have a relatively constant value of thermal conductivity in room temperature, the thermal conductivity of graphene varies as its sample size changes. This could mean that theoretically, graphene can absorb unlimited amount of heat, which will in turn, have potential advantages in heat conducting and spreading in various field. Based on the data, there are some practical use of graphene discovered recently and its potential use in the future.

2. The general applications of graphene
Because of graphene’s superb performance in the thermal conductivity, it would be a priority as making thermal interface material, heat spreader, and thermal greases[8-10]. Its high quality as a heat reservoir and a heat transferrer makes it a popular scientific field for researchers. A heat spreading material, especially when using as electronics packaging, has its job to lead a uniform heat dissipation[11]. However, in recent years, as pursuing higher speed and smaller size of electronics,
heat flux of electronics increased dramatically, causing a low efficiency of heat dissipation and resulting in a shorter lifetime of transistor[12-14]. Therefore, developing a high efficiency heat spreading materials is one of the best ways to solve the problem of heat dissipation in electronics packaging. Graphene, with high performance of heat spreading, is a promising material for electronics packaging.

3. Method of calculating thermal conductivity: MD simulation
Molecular Dynamics simulation (MD simulation) is one of the most popular tools on calculating thermal conductivity and analyzing a material’s data of other properties. MD simulation is able to create a condition that is harder or couldn’t do in the laboratory, such as high pressure or high temperature. For example, when analyzing materials deep in earth, using MD simulation would be a much better choice than sending people directly down to earth. Therefore, MD simulation is a better choice when the experimental environment is hard to find. Even though MD simulation is powerful and effective, it has certain limits. There is a restriction on atom’s length scale (around nanometer) and time scale (around nanosecond to picosecond), because the key idea of MD simulation is to monitor atom’s movements and draw conclusions from data[15].

In MD simulation, there are three elements that we need to find based on Newton’s second law, which is \( F = ma \). This theory leads to three elements of MD simulation: interatomic potential, species of atoms, and their initial condition. Interatomic potential comes from Lennard-Jones Model, which is two atom’s potential when they are in a distance that neither attract nor repulse each other[16]. For the species of atoms, the relative mass of the atom is necessary. At last, the initial condition we need to know includes initial position, velocity and temperature. All of those data are needed as computing input file.

3.1. Setup of input file
In the general setup, I set the units as metal, which has standard unit as length in Angstrom, time in picosecond, and energy in eV. The units are small and convenient enough for molecular scale simulation. Atom style is atomic, so each of atoms represents a solid. Then, I set boundary as periodic in all three directions, so I can define their dimensions later.

For the system setup, I set lattice as custom with value of 2.53, so everything I list below should be the ratio of values, and the actual length needs to multiply the ratio by 2.53. Since the graphene is a 2-D shape, value in the direction of \( z \) should remain constant, and I set that in the middle of the depth, which is 0.5. Then, I notice that the graphene is abundant of trapezoid setting next to each other, forming collateral hexagons. Therefore, from basis 1 to basis 4 are four points of trapezoid. Then, lattice spacing for \( x \), \( y \), and \( z \) direction comes from \( a_1 \), \( a_2 \), and \( a_3 \). After multiplying them by 2.53, we get 2.53, 4.38, and 3.45 Angstrom, which are the dimensions of lattice box. Then, I set the entire graphene in the ratio of 37:3:1, which appears to be a rectangle with thin layer. After that, I create 1 region box, because the graphene consists of the duplication of the shape setting up in the lattice. Then, I searched the relative mass of the carbon, and got a value of 12.0107[17].

Next category is potential. The pair style is 3.0 and pair coefficient is \( C \), representing carbon atom. For initialization, I set velocity as 300.0 which correspond to the temperature. Then, timestep is 0.001, which is low enough for me to visualize its movement later. The neighbor list in the next part determines how often lists are built as a simulation runs. Here I add heat source and sink in order to calculate its thermal conductivity. I put the heat source in the middle of the graphene and make it flow to the two ends of graphene. From 42.0 and 52.0 scale mark is the heat source, and two heat sinks are in 0.0-4.0 scale mark to 88.0-92.5 scale mark. So, it allows same amount of heat to flow in and out.

Then, I set its output frequency as 100, which means I can get data in every 100 steps. Trajectory, which shows visualization, is another output file I will get when I run this file.

Next part is equilibration in NVT and NVE. NVT represents number of atoms, volume and constant temperature respectively. Then, I set both initial and final temperature as 300 kelvins, which is close to the room temperature. NVE represents number of atoms, volume and constant energy. This
is also in equilibrium. I will run this program in equilibrium for 10,000 times to get the data and to compare those values with nonequilibrium ones. When setting up temperature nonequilibrium, I choose the range from 280K to 320K, fluctuating around the room temperature. The temperature of 320K will be emitted from the heat source, and heat sinks will receive a temperature of 280K. I set the temperature change as 40K in order to see more clearly of the effect of heat change over time. Finally, in the frequency of 1000, it runs 1,000,000 times.

Figure 1. Programmer of Input File

3.2. Analyze the data

From the first output file, I get four categories of data, including timestep, temperature, pressure and volume. Even though I didn’t deliberately change the pressure in the input file, it fluctuates as the temperature changes. However, the graphene is stable and solid, and its volume stabilizes at 4239.89 bars.

As shown in Figure 2, in the Temperature vs. Timesteps graph, the temperature is around 300 K overall. But in the first 10,000 timesteps, it varies in a larger scale, almost reaching 250 K and 350 K. But from 10,000 to 20,000 timesteps, it concentrated more and it’s obvious that the mean value is a little lower than 300 K. This might be the result of losing energy in an equal and constant rate. From the Pressure vs. Timesteps graph in the right side of Figure 2, pressure is relatively high in the first half and becomes lower and more concentrated in the second half, which is corresponding to the temperature changes.

Figure 2 Timestep vs. Temperature and Pressure plot

This is the other output file with energy input and output. As presenting in the two graphs, we could see from their tendency and scale mark and their magnitude of slope are about the same. They both start from 20,000 timestep and end at 270,000 timestep. As reaching the end, both of them get very close to 240 in their own direction. Therefore, it tells that there are negligible energy loss in the entire process of conducting heat, which in turn proves that it has a relatively high thermal conductivity.
3.3. VMD visualization: visualize the movement of graphene
Figure 4 shows the atoms’ movement when transferring heat. As shown in the figure, it is relatively stable and maintaining hexagonal shape as viewing from the top. However, since I set the region box as periodic in z direction with a relatively large range, atoms are able to move freely in the vertical direction. When start running the first hundred steps, atoms oscillate a little, but never divert from the hexagon. However, when the temperature is at nonequilibrium, atoms start to move up and down drastically and shift to next layer when looking at the side views.

3.4. Result of simulation: calculate thermal conductivity of graphene
Based on the Fourier’s Law \( q = -k \nabla T \), \( q \) (heat rate per unit area) and \( \nabla T \) (temperature gradient) needs to be find out through data in output files. In order to find the heat rate, we need to find out the magnitude of slope of energy output. We get a value of 0.0011 eV/step. Then, the unit area in this situation is depth multiply by height (3.14×13.15) Å². After unit conversion, we get the result of \( q=4.26\times10^{11} \) W/m². Temperature gradient is to divide distance from heat source to heat sinks by their change in temperature, which is \(-0.3\times10^{10} \) K/m. Finally, when putting those values in the equation, we get \( k=q/\nabla T =142 \) W/mK.

4. Heat spreading materials
The self-heating chips on various devices we currently use are a large part that can be upgraded. Since the designers and customers are tended to decrease the size of electronic devices and increase the speed, improved thermal management could be a way to solve those issues[18]. Graphene, as a 2-D material with 10 times higher thermal conductivity than copper, attracts much attention on development of graphene-based heat spreading materials[19]. Those materials include graphene-based film (GBF) and graphene-based electrically conductive adhesive (G-CA). Guangjie Yuan et al
conducted the simulation for the thermal performance of GBF and G-CA and tested their effectiveness[20]. They made four separate experiments to find the best heat spreading material for 3D electronic packaging: without GBF and G-CA, only GBF, only G-CA, and with both GBF and G-CA. After the experiment, they got the result that as using the combination of GBF and G-CA, the temperature of hotspot was the lowest and the temperature was more evenly distributed on the surface of chip. This result reassures the superior thermal conductivity of graphene and the fact that it is a great material for electronic packaging.

A study that evaluated the cooling effect as the thickness of two different graphene-based heat spreaders increases was done by Y. Zhang et al[21]. The two methods they compared are graphene-based films produced by vacuum filtration and graphene-based films fabricated by drop coating. The best cooling effect (6°C) of the heat spreader made by vacuum filtration was obtained with the thickness of only 30 nm. But for the thick drop coated films, the thickness doesn’t seem to play a major role on the cooling effect, decreasing 4°C with all three sample thicknesses. The comparison of those two methods provides a conclusion that as the graphene-based film goes further away from the hotspot with increasing film thickness, the cooling effect decreases. This result proves the effectiveness of graphene-based heat spreader with closer distance to the hotspot and smaller thickness of the film.

5. Conclusion
In summary, the thermal performance of graphene shows its promising applications on the electronic devices as heat spreader. The result of MD Simulation shows that the input and output energy are nearly identical. Moreover, the thermal conductivity shows a 142 W/Km result. So far, from the practical perspective, graphene-based materials exceed any other materials. But the issue is that the graphene is so expensive, costing $100 per gram, because it is hard to produce and easy to be oxidized. Once the graphene is oxidized, it doesn’t have much use. Therefore, to grow the graphene might be a faster and more cost-effective way of multiplying the output of graphene. Right now, the researchers are developing ways to grow the graphene. Once the cost of graphene is bringing down, all the theories developed by researchers will be applied in the real life and benefit people.

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