Term Project of Molecular Simulations in Mechanical Engineering(ME 653)

May 1, 2024

Study of Thermal Conductivity via EMD and NEMD methods

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- **Motivation**: The motivation behind calculating thermal conductivity is rooted in the fundamental need to understand how materials transfer heat, a critical aspect in diverse fields like engineering, physics, materials science, and environmental studies. Engineers rely on thermal conductivity data to design efficient systems, from building insulation to industrial heat exchangers. Energy conservation efforts benefit from insights into thermal conductivity, aiding in the design of energy-efficient systems and structures. Additionally, it plays a significant role in environmental studies, influencing climate models and geothermal processes. From optimizing manufacturing processes to enhancing energy efficiency, calculating thermal conductivity enables precise control and prediction of heat transfer, driving advancements across multiple disciplines.
- **Objective:** The thermal conductivity coefficient is a crucial parameter in various fields. Here are some applications where the calculation of the thermal conductivity coefficient plays a significant role:
  - **Insulation Materials**: When designing a building, architects and engineers must choose insulation materials with appropriate thermal conductivity coefficients. For example, using materials like fiberglass or foam with low thermal conductivity helps maintain a comfortable indoor temperature without excessive heating or cooling requirements.
  - **Electronic Devices**: In smartphones and laptops, thermal conductivity plays a crucial role in managing the heat generated by processors and other components. Heat sinks and thermal paste improve thermal conductivity and dissipate heat efficiently, preventing overheating and ensuring device performance.
  - **Automotive Engineering**: Car manufacturers use thermal conductivity calculations to design efficient cooling systems for engines and exhaust systems. High thermal conductivity materials like aluminum are used in radiators and heat exchangers to transfer heat away from the engine, improving fuel efficiency and engine performance.
  - **Solar Panels**: In solar panel design, understanding the thermal conductivity of materials used in photovoltaic cells and supporting structures is essential. Proper thermal management helps prevent overheating solar panels, improving their efficiency and lifespan

- **Food Industry**: Thermal conductivity calculations optimize heating and cooling processes in food processing and packaging. For example, materials with specific thermal conductivity properties are chosen in microwaveable food packaging to ensure even food heating without overheating the packaging.
- **Medical Devices**: Thermal conductivity is critical in medical devices like MRI machines and laser equipment. Designing components with appropriate thermal properties helps manage heat dissipation, ensuring patient safety and device reliability.

- **Approach:** In this term paper, we are investigating two distinct approaches for calculating thermal conductivity (κ) the Equilibrium Molecular Dynamics (EMD)/Green-Kubo Method and the Non-Equilibrium Molecular Dynamics (NEMD) method based on Fourier's law of conduction. These methods offer different perspectives on how to characterize and quantify thermal conductivity, each with its strengths and limitations.

(1) EMD(Equilibrium Molecular Dynamics)/ Green-Kubo Method: It is most convenient to consider compiling the transport properties as an implicit part of any equilibrium MD simulation. The added computational overhead is relatively small, especially for the self-diffusivity. The main caveat is that longer simulations than normal may be required to achieve reasonable averages. The general formula for computing a transport property via an EMD simulation is given as

$$\gamma = \int_0^\infty dt \langle \dot{\xi}(t)\dot{\xi}(0)\rangle_i \tag{1}$$

Where:

- γ is the transport coefficient (within a multiplicative constant)
- $\langle\dot{\xi}(t)$ is the mechanical variable associated with the particular transport property under consideration
- $\langle\dot{\xi}(t)$ signifies a time derivative.

Integrals of the form given by Equation are known as "Green-Kubo" integrals. It is trivial to show that an integrated form of Equation 1 results in an equivalent expression for γ known as the "Einstein" formula

$$\gamma = \lim_{t\to\infty} \frac{h(\xi(t) - \xi(0))^2}{2t} = \frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}h(\xi(t) - \xi(0))^2 \tag{2}$$

where the derivative form is often preferred.
For thermal conductivity, the integral is over the energy current, and for ionic conductivity, the integral is over the ionic current.
Derivation of Thermal Conductivity (κ):

- **Define the thermal conductivity:** Start with the expression for the thermal conductivity κ in terms of heat flux auto-correlation function $C_q(t)$:

$$\kappa = \frac{k_B T}{2V} \int_0^\infty C_q(t) dt \tag{3}$$

  Where:
  - κ is the thermal conductivity,
  - V is the volume of the system,
  - k_B is the Boltzmann constant,
  - T is the temperature,
- **Relate Heat flux to Temparature Gradient:** Express the heat flux $\mathbf{q}$ in terms of the thermal coefficient α and temperature gradient ∇T

$$\mathbf{q} = -\alpha \nabla T \tag{4}$$

- **Auto-correlation function of Heat flux:** Calculate the auto-correlation function $C_q(t)$ for the heat flux q using molecular dynamics simulations. This involves averaging over time the product of the heat flux at time t and the heat flux at time t + τ where τ is the time lag

$$q(t) = V_1 \langle q(t) q(t+\tau) \rangle \tag{5}$$

- **Integrate the Auto-correlation function:** Perform the integral of $\mathbf{C_q(t)}$ over time from 0 to ∞ obtain the thermal conductivity κ using the Green-Kubo relation.
- **Calculate the Thermal Coefficient:** Once you have the thermal conductivity κ from the Green-Kubo integral, use the relation $\alpha = \frac{\nu \mathbf{k_B}}{\mu}$ to calculate the thermal coefficient, where μ is the mobility of particles obtained from the Einstein relation or other means.

which leads us to the final **Green-Kubo** equation for thermal conductivity calculation given by:

$$\kappa = \frac{V}{k_B T^2} \int_0^\infty \langle J(t) J(0) \rangle dt \tag{6}$$

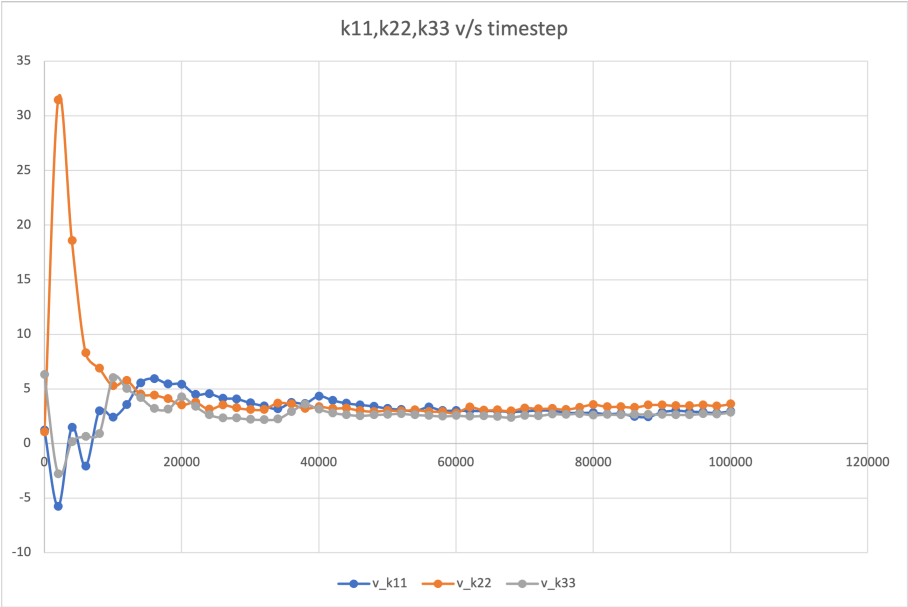
Where:

- κ is the thermal conductivity,
- V is the volume of the system,
- k_B is the Boltzmann constant,
- T is the temperature,
- $J(t)$ is the heat current operator, and
- $\langle J(t)J(0)\rangle$ is the autocorrelation function of the heat current.

Molecular Dynamics Simulation

- For a liquid solution, it is safest to run in the microcanonical (NVE) ensemble, rather than the canonical (NVT) or isothermal–isobaric (NPT) ensembles. This is because thermostats required to maintain constant temperature and barostats required to maintain constant pressure can interfere with the dynamics of the system, and thus the resulting transport properties can be skewed.
- It is important that each step consist of both an equilibration and production period.
- Here we have used NVT ensemble for the equilibration of the system and then applied the NVE ensemble for the calculation of thermal conductivity.
- Steps for equilibration like NPT and NVT ensemble is also can be done but NPT alone for the equilibration is not allowed because barostats (which alter positions through volume changes) greatly affect the dynamics of a system.
- A study by Basconi and Shirts reached a similar conclusion, and provides guidelines for how thermostats should be applied when computing transport properties.
- In practice, several tricks-of-the-trade are employed to reduce fluctuations and, thereby, the standard deviation (σ). For thermal conductivity, it is a standard practice to average the mean squared displacement or heat flux autocorrelation function over all N molecules.
- The conductivity is a tensor, and it is common practice in homogeneous systems to average the diagonal components κ_{xx},κ_{yy},κ_{zz}.
- If system is homogeneous then $\kappa_{xx} = \kappa_{yy} = \kappa_{zz}$.

$$\kappa = \frac{1}{3}(\kappa_{xx} + \kappa_{yy} + \kappa_{zz}) \tag{7}$$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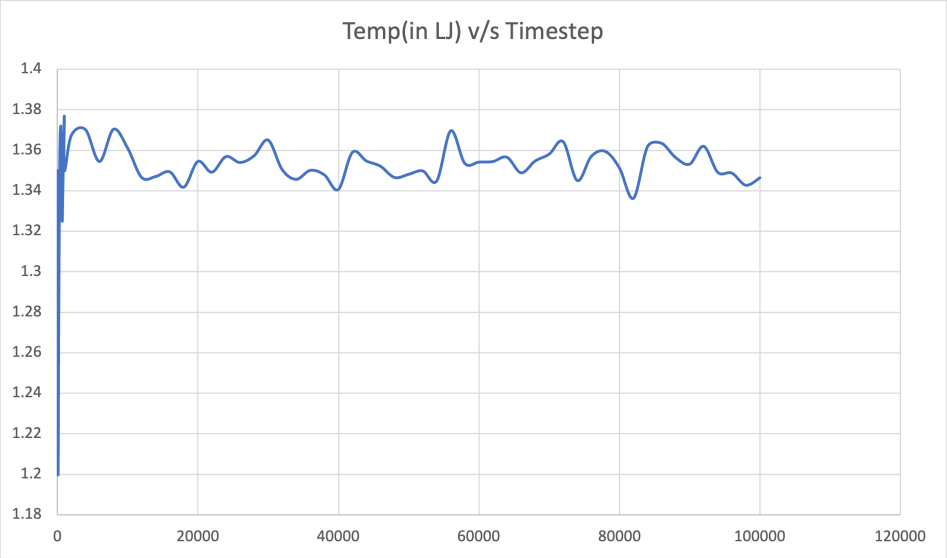
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60000
80000
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120000

(2) NEMD(Non Equilibrium Molecular Dynamics:

Non-Equilibrium Molecular Dynamics (NEMD) is a computational technique used in molecular simulations to study the behavior of systems under non-equilibrium conditions. Unlike Equilibrium Molecular Dynamics (EMD), which focuses on systems at thermal equilibrium, NEMD investigates dynamic processes that occur when a system is subjected to external forces or gradients.

In NEMD simulations, various methods can be employed to induce non-equilibrium conditions, such as applying external forces, imposing temperature or pressure gradients, or introducing constraints on the system. These methods allow researchers to study phenomena like heat conduction, fluid flow, and mechanical properties under realistic conditions that may not be achievable in equilibrium simulations.

NEMD has become a powerful tool in materials science, chemistry, and biophysics for understanding transport phenomena and dynamic processes at the molecular level. Its applications range from studying thermal conductivity and diffusivity in materials to investigating the flow of fluids through nanoscale channels.

Derivation of Thermal Conductivity (κ):

- **Define the Heat Flux:** Heat flux is the rate of heat transfer per unit area. In NEMD, it's typically calculated as the time derivative of the energy (E) flowing across a plane perpendicular to the direction of the imposed temperature gradient (∇T). Mathematically, heat flux is given by:

$$J = -\frac{dE}{dt} \tag{8}$$

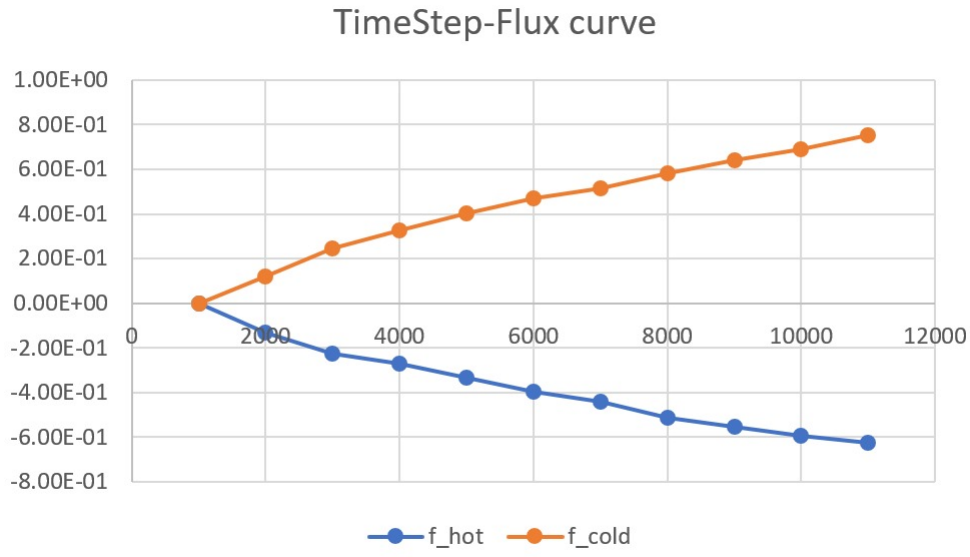
  Where:

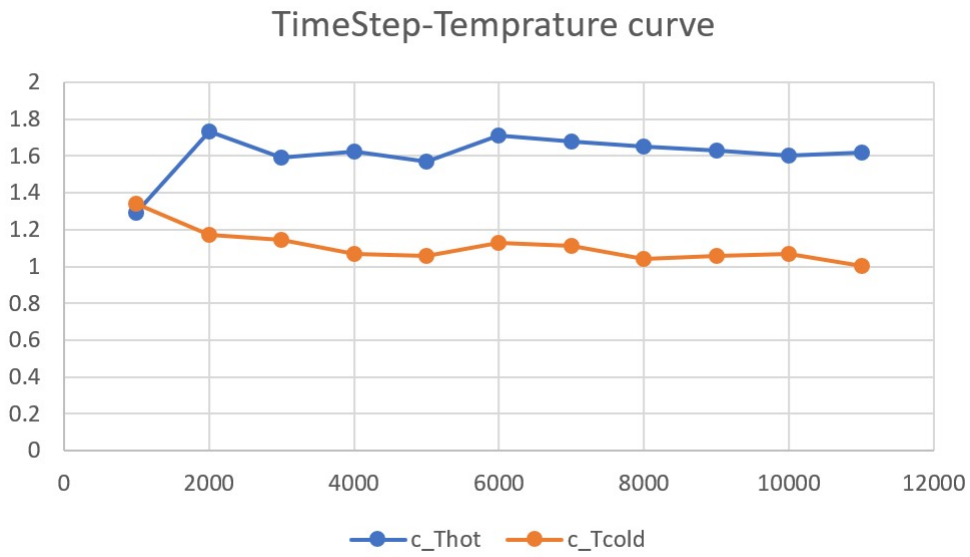
  * **J** is Heat Flux
  * $\frac{dE}{dt}$ is time derivative of energy
  * **A** is cross-sectional Area perpendicular to gradient

- **Fourier's Law of Heat Conduction:** Fourier's law relates heat flux (J) to the temperature gradient (∇T) and thermal conductivity (κ). It's expressed as:

$$J = -\kappa \cdot \nabla T \tag{9}$$

- **Substitute Heat Flux from NEMD:** Substitute the expression





for heat flux ($\mathbf{J}$) from step 1 into Fourier's law:

$$-\frac{dE}{dt} = -\kappa \cdot \nabla T \tag{10}$$

– **Simplify and Rearrange:** Rearrange the equation to solve for thermal conductivity (κ):

$$\kappa = \frac{dE}{dt \cdot \nabla T} \tag{11}$$

- **Merits and Demerits of EMD/ Green Kubo method:**
  - **Merits:**
    * EMD works with systems in equilibrium, where all properties (including temperature) are constant over time. This makes it easier to analyze thermodynamic properties in a steady-state condition.
    * Approach using equilibrium is a relatively easy and computationally efficient method in comparison to non-equilibrium because it samples the equilibrium distribution of molecular configuration.
    * EMD facilitates thermal conductivity prediction in all directions using one simulation, whereas NEMD requires the use of a thermal gradient and therefore only enables the calculation of thermal conductivity in one direction.
  - **Demerits:**
    * EMD simulations typically involve slow relaxation processes, especially in systems with large temperature gradients or significant thermal transport phenomena. This can lead to long simulation times to reach equilibrium.
    * EMD may not be suitable for studying large temperature gradients or highly nonequilibrium systems since it assumes uniform temperature distribution.
    * EMD may not provide insights into transient or dynamic behavior, making it less suitable for studying time-dependent phenomena.
- **Merits and Demerits of NEMD method:**
  - **Merits:**
    * NEMD directly measures the thermal conductivity of materials by imposing a heat flux and measuring the resulting temperature gradient. This makes it a powerful tool for studying thermal transport phenomena.
    * NEMD simulations can capture transient and dynamic behavior, allowing for the study of time-dependent phenomena such as heat conduction and phonon dynamics.
    * NEMD simulations can be used to study systems with large temperature gradients or in highly nonequilibrium conditions, providing insights into extreme thermal transport scenarios.

- **Demerits:**
  - The non-equilibrium methods usually suffer from length effects, especially in the quasi-one-dimensional systems, because of the boundary scattering and hence lead to smaller estimates of κ that depend on L_z.
  - NEMD simulations often involve smaller system sizes and shorter simulation times compared to EMD simulations, leading to reduced statistical accuracy in some cases.

- **Effect of Density on Thermal Conductivity**

  The variation of density with thermal conductivity can be understood by considering how the arrangement of atoms or molecules within a material affects its ability to conduct heat. Here are some additional details on this relationship:

  - **Atomic/Molecular Arrangement:**
    - Denser Packing: In materials with higher density, atoms or molecules are typically more closely packed. This denser packing allows for better phonon (heat-carrying vibrations) transmission through the material, leading to higher thermal conductivity.
    - Crystal Structure: Crystalline materials, where atoms or molecules are arranged in regular, repeating patterns, often exhibit higher thermal conductivities compared to amorphous materials. This is because the ordered arrangement in crystals allows phonons to travel more efficiently.
  - **Effect of Defects:**
    - Impurities and Defects: The presence of impurities, vacancies, or defects in a material can disrupt the regular arrangement of atoms or molecules. This disruption can hinder the propagation of phonons and reduce thermal conductivity, even in materials with high density.
    - Grain Boundaries: In polycrystalline materials, grain boundaries where different crystal grains meet can act as barriers to phonon transport, affecting thermal conductivity. The density of these boundaries and their structure can influence overall thermal conductivity.
  - **Phase Transitions:**

* Density Changes: Some materials undergo phase transitions with changes in temperature. For example, water transitions from ice to liquid to vapor at different temperature ranges, each with its own density. These phase transitions can significantly affect thermal conductivity, as the density and arrangement of molecules change.
* Anomalous Behavior: Certain materials may exhibit anomalous behavior in thermal conductivity near phase transition points. For instance, the thermal conductivity of water near its freezing point increases, contrary to the usual trend where thermal conductivity decreases with decreasing temperature.

– **Material-Specific Considerations:**

* Gases vs. Solids: In gases, increasing density can initially lead to higher thermal conductivity due to increased molecular collisions. However, at very high densities, the mean free path of molecules decreases, limiting heat transfer. In solids, denser materials generally have higher thermal conductivities.
* Composite Materials: The density-thermal conductivity relationship can vary in composite materials, where different phases or components interact. The arrangement and interface between these components can influence overall thermal conductivity.

• **Effect of Temperature on Thermal Conductivity:**

Understanding the temperature dependence of thermal conductivity involves considering the material's intrinsic properties, phase behavior, structural changes, and interactions at different temperature ranges.

– **Phonon Theory:**

* Increasing Vibrational Energy: As temperature rises, the vibrational energy of atoms or molecules increases. In solids, this leads to more frequent and energetic phonon collisions, promoting faster heat transfer and thus increasing thermal conductivity.
* Temperature-Dependent Mean Free Path: The mean free path of phonons, which is the average distance they travel between collisions, is often inversely related to temperature. Higher temperatures lead to shorter mean free paths, facilitating more efficient heat conduction.

– **Material-Specific Effects:**
  * Metals: In metals, thermal conductivity generally increases with temperature within certain ranges. This is due to increased lattice vibrations and electron-phonon interactions, which enhance heat transfer.
  * Semiconductors and Insulators: The relationship between temperature and thermal conductivity in semiconductors and insulators can be more complex. Factors like phonon scattering mechanisms, impurities, and defects play significant roles and can result in non-linear temperature dependencies.
– **Phase Transitions:**
  * Changes in Thermal Conductivity: Materials undergoing phase transitions, such as melting or solidification, can experience abrupt changes in thermal conductivity at specific temperature ranges. For example, the thermal conductivity of water increases significantly upon freezing due to the ordered arrangement of ice crystals.
  * Anomalous Behavior: Near phase transition points, some materials exhibit anomalous changes in thermal conductivity with temperature. This behavior can be influenced by structural changes, density variations, and phase transformations.
– **Temperature Range:**
  * Low Temperatures: At very low temperatures, thermal conductivity in metals can decrease due to reduced lattice vibrations and phonon scattering by defects and impurities.
  * High Temperatures: In some materials, thermal conductivity may plateau or exhibit a slight decrease at very high temperatures due to increased phonon-phonon scattering and electron-phonon interactions.
– **Composite and Heterogeneous Materials:**
  * Temperature Effects on Interfaces: In composite materials or heterogeneous structures, the thermal conductivity can be influenced by temperature-dependent changes in interface properties. For example, thermal barriers or enhancements at interfaces can vary with temperature, affecting overall heat transfer.

– **Experimental Considerations:**

* Transient Effects: When measuring thermal conductivity at different temperatures, transient effects like thermal inertia and thermal relaxation times can influence the observed values.
* Thermal Expansion: Changes in material dimensions with temperature (thermal expansion) can also indirectly affect thermal conductivity, especially in anisotropic materials.

- **Result:** After running the simulations for both EMD/Green Kubo method and NEMD method we got the value of $\kappa = 3.41$ from the EMD method and $\kappa = 3.78$ from the NEMD method.
- **Conclusion:** EMD simulations were used to determine the thermal conductivity in all directions, while the NEMD simulations were used to determine the thermal conductivity in one direction only.