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An investigation of the size effect and molecular orientation on the values of thermal conductivity of long-chain n-alkanes by molecular dynamics simulation

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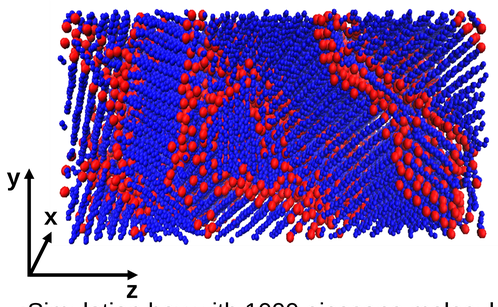
Abstract

In this study, the thermal conductivity of long chain n-alkanes ($C_{20}H_{42}$) is studied by utilizing equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) simulations. In order to remove the possible size effect from the results for solid n-alkanes, a new method is used to determine the thermal conductivity of the solid systems. A new approach is conducted, where the length of the system increases by raising the number of molecules in the base structure and macroscopic thermal conductivity can be determined by fitting the results from the simulations. Besides, a parameter based on the distribution of the molecular orientation is determined to show the connection between molecular orientation and thermal conductivity. All simulations were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) molecular dynamics package.

Background and Objectives

- Phase change materials (PCM) such as n-alkanes are widely used in thermal energy storage (TES) applications for the merits of high latent heat, chemical stability and negligible supercooling. However, the low thermal conductivity of PCM constrains the thermal performance in TES system. Therefore, understanding the thermal transport phenomena of n-alkanes such as n- eicosane ($C_{20}H_{42}$) is crucial for enhancing the heat transfer efficiency of TES.



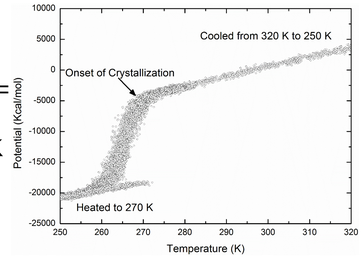
- Simulation box with 1000 eicosane molecules

(Red balls are CH_3- group and Blue balls are CH_2- group)

Methodology

Initialization and Equilibration:

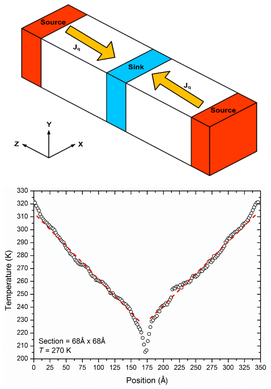
- Time step = 0.5 fs
- NPT at T = 320 K (Liquid)
- Cooled down to T = 250 K (Solid)
- Heated to T=270 K (Solid)
- Average rate of cooling: 1 K/ns

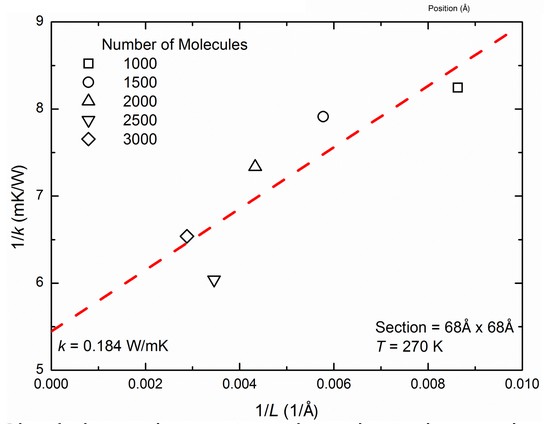


Thermal conductivity measurement by Non-Equilibrium Molecular Dynamics (NEMD):

- Heat flux was imposed by exchanging the kinetic energy between the sink and source.
- Associated temperature profile was extracted after enough time (2.5 ns) for the system to reach steady state.
- The Fourier's law :

$$q_z = -k_z \frac{dT}{dz}.$$

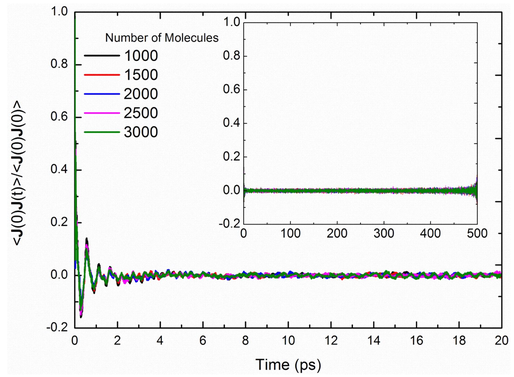




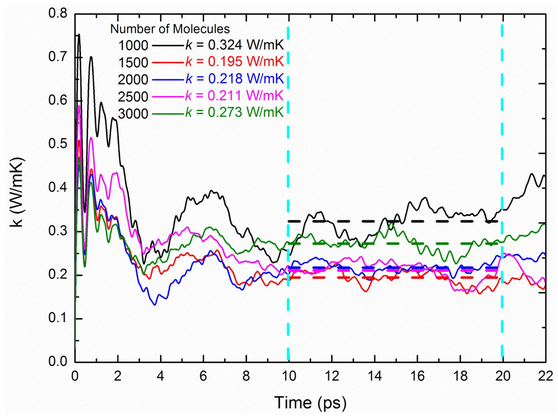
- Simulation box Length dependent thermal conductivities for molecules at temperatures of 270 K predicted from the NEMD method

Thermal conductivity measurement by Equilibrium Molecular Dynamics (EMD):

- Green-Kubo formula:
- $k_z = \frac{V}{k_B T^2} \int_0^\infty < \boldsymbol{J}(t)\boldsymbol{J}(0) > dt$
- Integration of heat current auto-correlation function (HCACF) contains information about thermal boundary conductance.
- Correlation time: 1,000,000 timesteps (500 ps).
- Determining k_z by calculating the integration of HCACF.
- k_z values from EMD simulations are plotted.



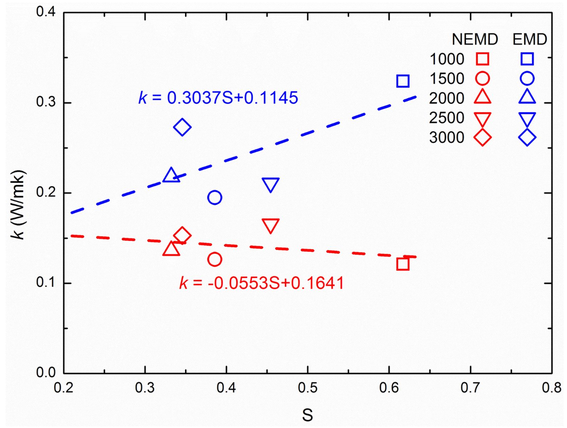
Normalized HCACF for different number of molecules (1000, 1500, 2000, 2500 and 3000)



- Thermal conductivities for molecules at temperatures of 270 K predicted from the EMD method

Orientation Factor

- S = 0.5(3<$cos^2(\theta)$> -1)
- <> indicating the average obtained over all molecules;
- θ is the angle between the end-to-end vector of individual molecules and z axis.



Correlation of local thermal conductivity with orientation factor

Conclusions

- Solid molecules of eicosane exhibits a strong length-depend for thermal conductivity by using NEMD.
- The converged value of the HCACF is difficult to get for EMD method, more data need to be added.
- Thermal conductivity and orientation factor are correlated.

Acknowledgement

This material is based upon work supported by the US Department of Energy under Award Number DE-SC0002470.

Disclaimer

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