



Interdependence of length, diameter and strain states on the thermal transport property of nanostructure

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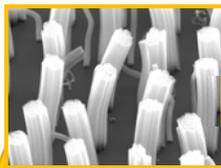
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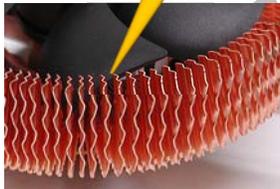
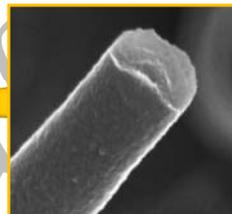
Motivation



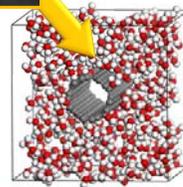
Carbon nanostructures are highly conductive, and can act as excellent materials as nanofins for heat dissipation. MD simulations are performed to study the effect of interfacial resistance on the performance of the CNTs as nanofins.



Carbon nanotube turfs



Cooling Fin



Computational Model



Molecular Dynamics Simulations



- MD simulations involve the determination of classical trajectories of atomic nuclei by integrating the Newton's second law of motion of a system.
- Simulations are carried out on an N particle system

Components of the Interatomic Interactions

A common molecular dynamics force field has a form where the total potential energy is given by the sum of the following contributions:

$$E = \underbrace{U_{vdW}}_{\text{NonBonded potential}} + \underbrace{(U_{\text{Bond}} + U_{\text{Angle}} + U_{\text{Torsion}})}_{\text{Valence interactions}}$$

Periodic Boundary Conditions with

NVE (constant Number of atoms, Volume and Energy)

NVT (constant Number of atoms, Volume and Temperature)

Thermostat algorithm: the instantaneous temperature is pushed towards the desired temperature by scaling the velocities at each step

$$\begin{aligned} \chi &\leftarrow \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_{\text{inst}}}{T} - 1 \right) \right]^{1/2} \\ \underline{v}(t + \frac{1}{2}\Delta t) &\leftarrow \left[\underline{v}(t - \frac{1}{2}\Delta t) + \Delta t \frac{\underline{F}(t)}{m} \right] \chi \\ \underline{v}(t) &\leftarrow \frac{1}{2} \left[\underline{v}(t - \frac{1}{2}\Delta t) + \underline{v}(t + \frac{1}{2}\Delta t) \right] \\ \underline{r}(t + \Delta t) &\leftarrow \underline{r}(t) + \Delta t \underline{v}(t + \frac{1}{2}\Delta t) \end{aligned}$$

System is coupled to a heat bath to ensure the average system temperature maintained close to the desired temperature T_{inst}



Thermal Conductivity (k)



Determination of k based on Molecular Dynamics (MD) Simulations

Equilibrium Molecular Dynamics (EMD)

- Uses Green-Kubo formulation to calculate k

$$k = \frac{1}{3Vk_B T^2} \int_0^{\infty} \langle \underline{J}_z(t) \cdot \underline{J}_z(0) \rangle dt$$

V = volume,
 k_B = Boltzmann constant
 T = Sample Temperature
 J = Heat Current

- EMD based simulation are computationally expensive than NEMD simulation due to the complex calculation involved.

Non-Equilibrium Molecular Dynamics (NEMD)

- Uses Fourier's law

$$q = kA \frac{\Delta T}{\Delta x}$$

q = heat flow rate,
 A = Cross section Area (Assuming $\frac{\Delta T}{\Delta x}$ 3.4 Å nanotube thickness)
 = Temperature Gradient

- Thermal Conductivity can be calculated either by imposing temperature difference ΔT and measuring the heat flow rate q or by indicating the heat flow rate and measuring the temperature gradient.

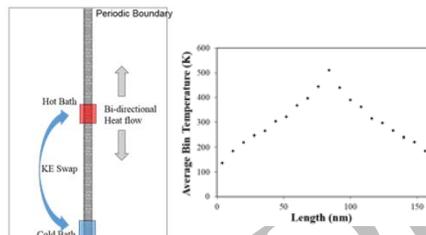


Thermal Conductivity (k)



Non-Equilibrium Molecular Dynamics (NEMD) Simulation Techniques

Muller-Plathe Method



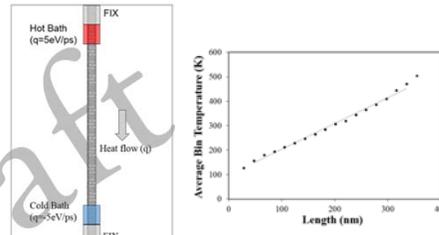
- The cold and hot junctions are created by swapping the velocity of the hottest atom in the cold region with the velocity of the coldest atom in the hot region. This creates the heat flux J given by

$$J = \frac{\sum_{i=1}^n \frac{1}{2} m_i (v_{hot,i}^2 - v_{cold,i}^2)}{2At}$$

- The thermal conductivity is calculated by using following equation:

$$k = - \frac{\langle J \rangle}{\langle \partial T / \partial x \rangle}$$

Heat-Bath Method



- Constant amount (say 5eV/ps) of heat is added to and removed from hot region and cold region respectively. This will create a temperature gradient along the axial direction. After the system reaches equilibrium, the statistical average of the temperature gradient is measured and thermal conductivity of nanotube is calculated using Fourier's Law.



Thermal Conductivity (k)



Procedure of Calculating Thermal conductivity in LAMMPS

SWCNTs of bond length 1.42Å are generated using in-house nanotube generator. AIREBO potential is used for C-C interactions and the time-step for the simulation is taken as 0.001 ps. The following steps summarizes the detail procedure for calculating thermal conductivity in LAMMPS.

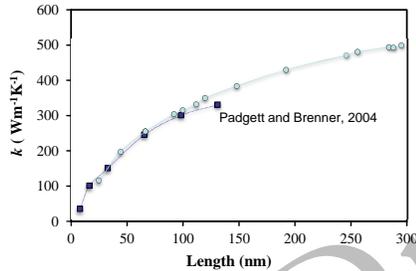
- Minimization of potential energy using Conjugate gradient (CG) method.
- Nanotube is divided into 20 divisions called bins or chunks. The end bins are fixed such that no perturbation occurs in these regions.
- The temperature of atoms in the remaining bins are raised to 300K and equilibrated for up to 200 ps with fixed NVT.
- Constant amount of heat (q=5eV/ps) is added to and removed from 2nd bin and 19th bin respectively for the next 500 ps.
- The time dependent moving average of the temperature gradient is measured for the next 500 ps monitoring the stability of the system
- Finally, the thermal conductivity is calculate using Fourier Law.



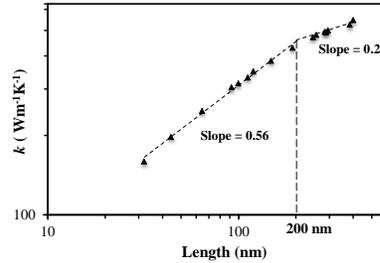
Effect of Length



Increase in length has shown increase in thermal conductivity



Length dependence of the thermal conductivity



Thermal conductivity plotted in Log-scale

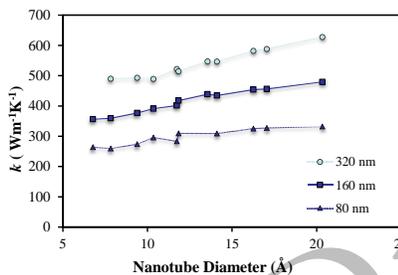
- The thermal conductivity of (10,10) nanotube is calculated at varying length and compared with the value predicted by Padgett and Brenner, 2004. Here, the length of nanotube is the length between hot and cold region.
- Sharp increase in the thermal conductivity with increase in the nanotube length for smaller nanotube. This increase is primarily due to the ballistic dominant thermal transport where the system length is less than phonon mean free path.
- As the length increases beyond the mean free path, the transport phenomenon changes from ballistic to diffusive-ballistic where length of nanotube has lesser effect on the thermal conductivity.
- The transition between the ballistic to diffusive-ballistic regime is indicated by the change of slope of the log-scale plot. The mean free path is found to be close to 200 nm.



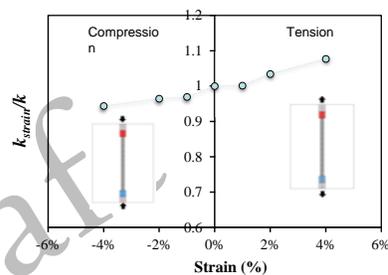
Effect of Diameter and Strain



Effect of diameter and application of strain on the value of k



Diameter dependence of the thermal conductivity



Effect of mechanical strain on thermal conductivity

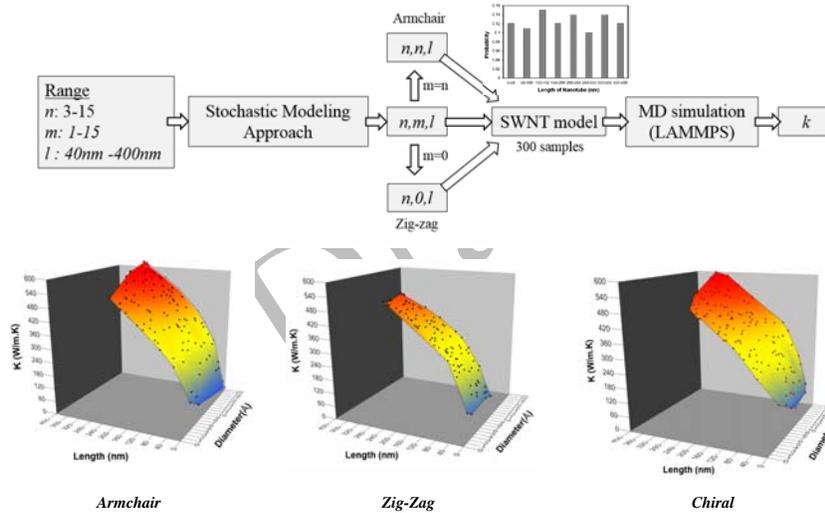
- The results are plotted for varying diameter nanotubes but constant length (80 nm, 160 nm and 320 nm).
- The increase in the diameter of nanotube also enhances the thermal conductivity. However, the enhancement seems very low due to low range of diameter considered in the analysis.
- The thermal conductivity is also calculated for 119.78 nm long (10,10) nanotube applying strain (tension and compression).
- Compressive strain reduces the thermal conductivity while tensile strain increases the thermal conductivity.



Stochastic Modeling Approach



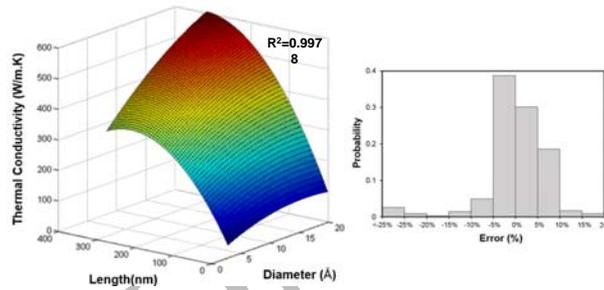
Predicting k of nanotubes generated based on Stochastic Modeling Approach



Stochastic Modeling Approach



Regression based mathematical model for k



Regression model for predicting thermal conductivity

- The results from all 300 samples subjected to multi-variable regression analysis of second order polynomial with length and diameter as independent variable and k as dependent variable.
- For the given range of diameter and length, the polynomial relation was found to be:

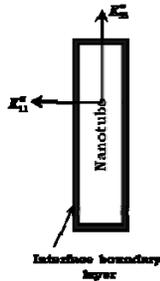
$$k \approx 11.877d + 2.3625l - 0.3712d^2 - 0.00485l^2 + 0.04ld$$
- The model is highly accurate for predicting the thermal conductivity for longer nanotubes ($R^2=0.9978$). 91.73% data has error of prediction less than 10%.



Size Effect - Interfacial Thermal Resistance



- Nanoribbon was heated to a prescribed temperature, followed by the relaxation of the entire ensemble.
-
- In the equilibration simulations, the atoms in the nanotube are heated instantaneously to 500K, 750 and 1000K by rescaling the velocities of carbon atoms in the nanotube.
- The system is allowed to relax without any thermostating effects.



Unit cell of nanotube coated with a very thin interfacial thermal barrier layer

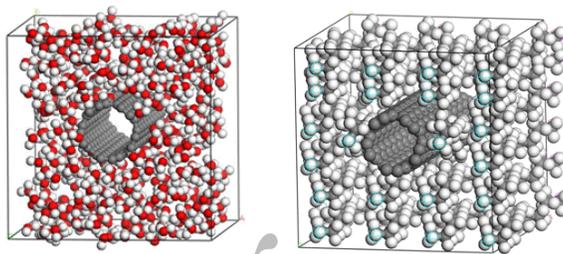
$$\tau = \frac{R_k C_T}{A_T}$$

- τ Time constant of the decay
- C_T Nanotube heat capacity,
- R_k Thermal resistance of nanotube-matrix interface
- A_T Area of the nanotube

The decay of the temperature from the nanotube to the surrounding matrix molecules is limited by the interfacial thermal resistance and is of an exponential order.

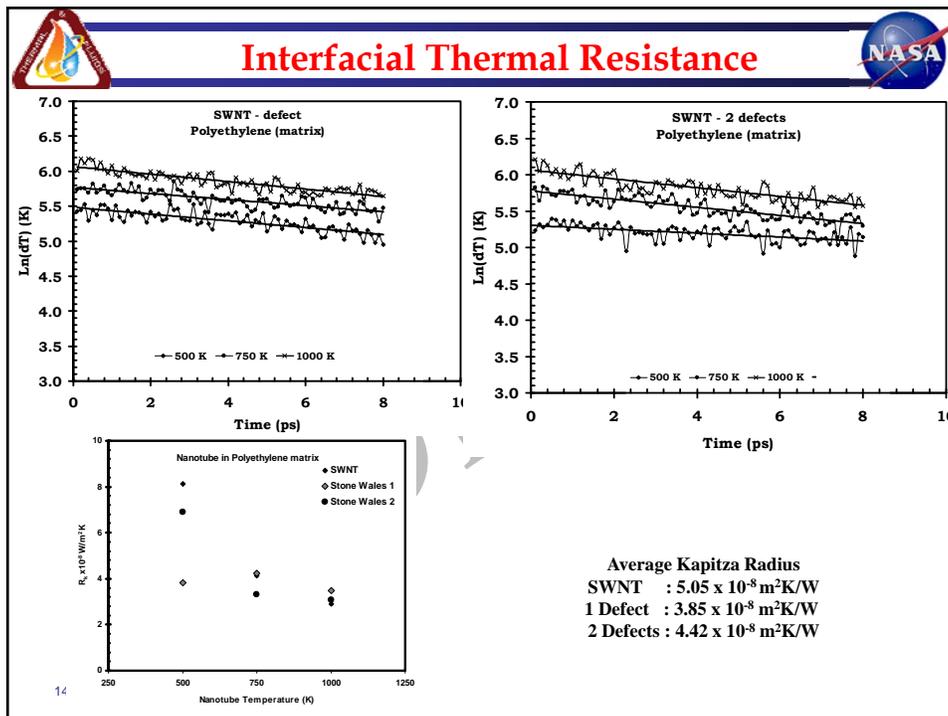
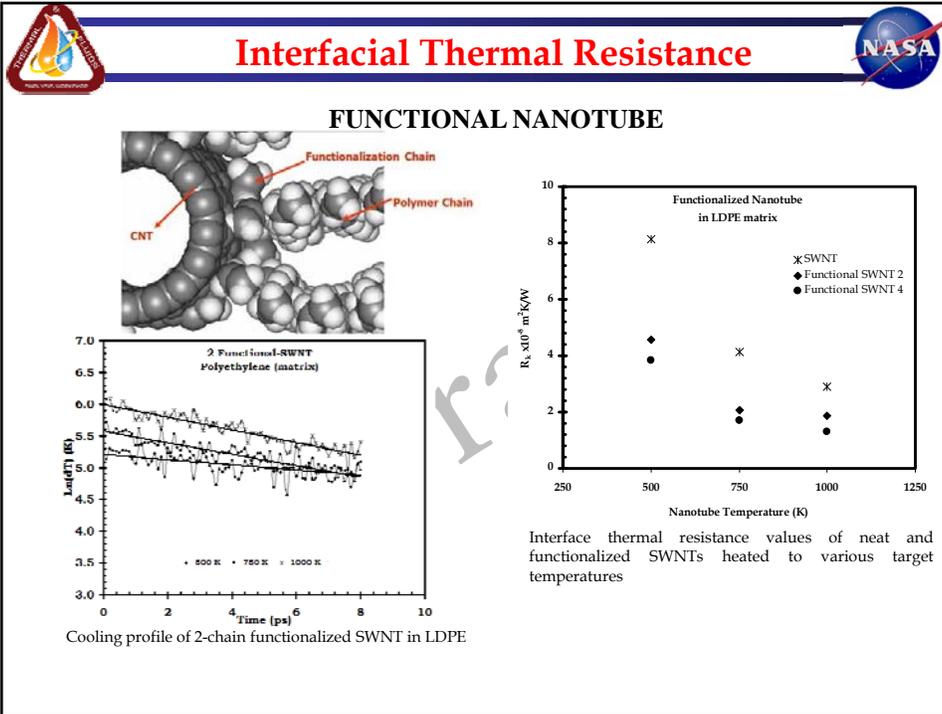


Simulation Procedure



Unit cell with CNT in water and Polyethylene matrix

- The entire systems were minimized and later equilibrated for 1ps (1000steps).
- The temperature scaling was carried out in 10ps as an NVT ensemble (10,000 steps).
- During the minimization and NVT processes, the atoms in the periodic unit cell are allowed to equilibrate within the fixed MD cell.





Conclusions



- The thermal conductivity of single walled carbon nanotubes is calculated using Heat-Bath method- a NEMD based simulation technique.
- For smaller nanotube, the length change in length of nanotube has high effect on the thermal conductivity due to the ballistic dominant thermal transport phenomenon. As the length increases beyond phonon mean free path, the transport phenomenon changes to diffusive-ballistic where length have less effect on k .
- The transition between ballistic to diffusive ballistic regime is 200 nm.
- Increase in diameter of nanotube increases the thermal conductivity.
- Application of compressive strain (tensile strain) decreases (increases) thermal conductivity of 119.78 nm long nanotube (Range of strain: -4% to 4%)
- The interfacial thermal resistance which is attributed to the size of the nanoparticle is considered