Are interfaces good or bad for thermal management?

Mediocre carbon nanotube composites and ultra-low thermal conductivity solids

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Work Supported by NSF under DMR 134725 and U.S. Department of Energy, Office of Science under Contract W-31-109-Eng-38

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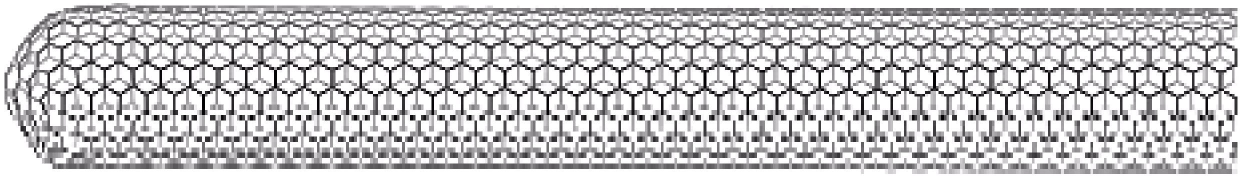
Carbon Nanotube Composites

The best fiber spoiled by the interface

Carbon Nanotube Composites and Transport

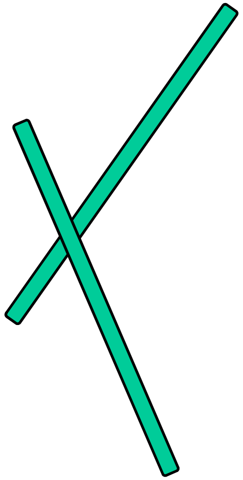


- Carbon Nanotubes
  - ➔ Pure (defect free) are excellent heat conductors (3000 W/mK) and depending on the tube chirality may be electrically conductive or semiconductive
  - ➔ Very high aspect ratio fibers (~1000) should lead to a great enhancement of composite thermal and electrical conductivity at low volume fraction, due to low percolation threshold
  - ➔ Experimental results do not confirm all of these these predictions. For example, thermal conductivity increase is significant, but not as high as expected.

Fibers and Percolation

- When a continuous path along the carbon nanotubes is created, i.e. the percolation threshold is exceeded, a sharp increase in transport characteristics is expected

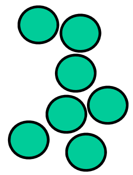
- To percolate each fiber has to be, on average, in contact with ~ 2+ other fibers.



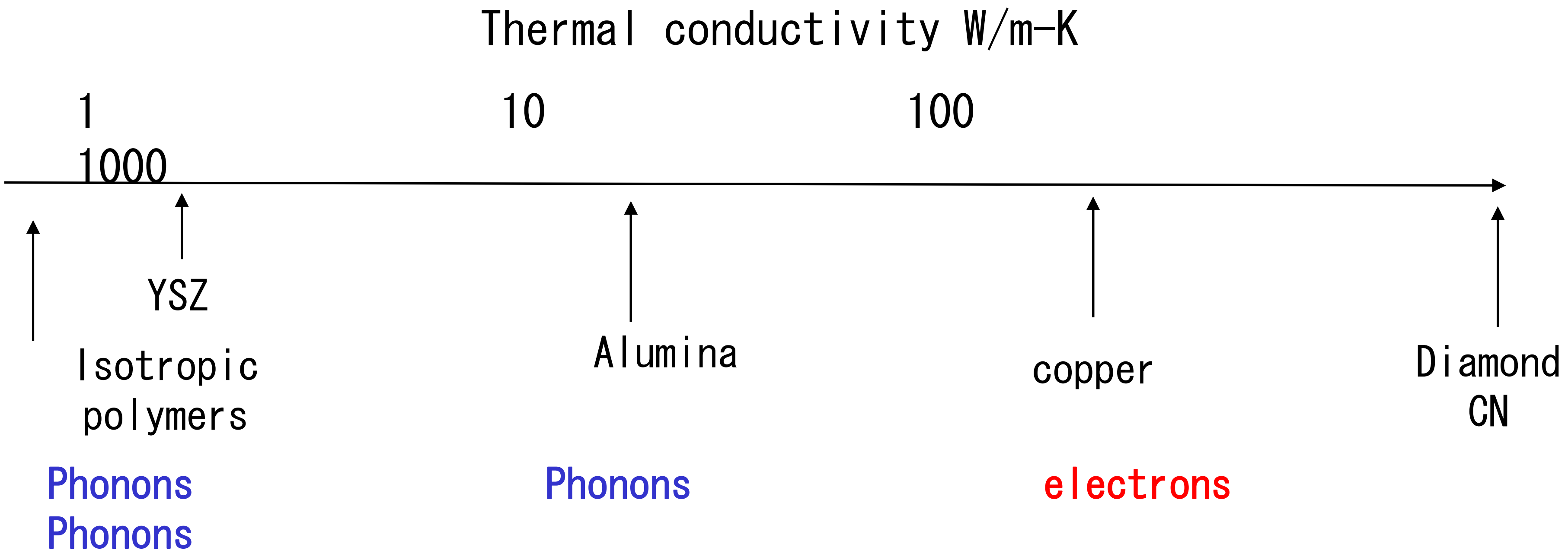
➔ At the percolation threshold: Number of contacts/fiber ~ L V_{fiber} ~ constant

➔ **V_c ~ 1 / L** - the percolation threshold proportional to the inverse of the aspect ratio

➔ For spheres V_c ~ 30% volume, for carbon nanotube composites V_c can be of the order of 0.1%



Conductivity Matrix vs. Fiber



Electrical conductivity

Cu – σ= 5 10^5 $(\Omega cm)^{-1}$

diamond – σ=10^{-10} $(\Omega cm)^{-1}$

$$\frac{\sigma_{conductor}}{\sigma_{insulator}} =$$

10^{15} – electrical conductivity

10^4 – thermal conductivity

Electrical Transport - Puzzle # 1

- Percolation threshold, V_c, is 0.3% - indeed very low

- Above the percolation threshold conductivity, σ, exhibit universal scaling

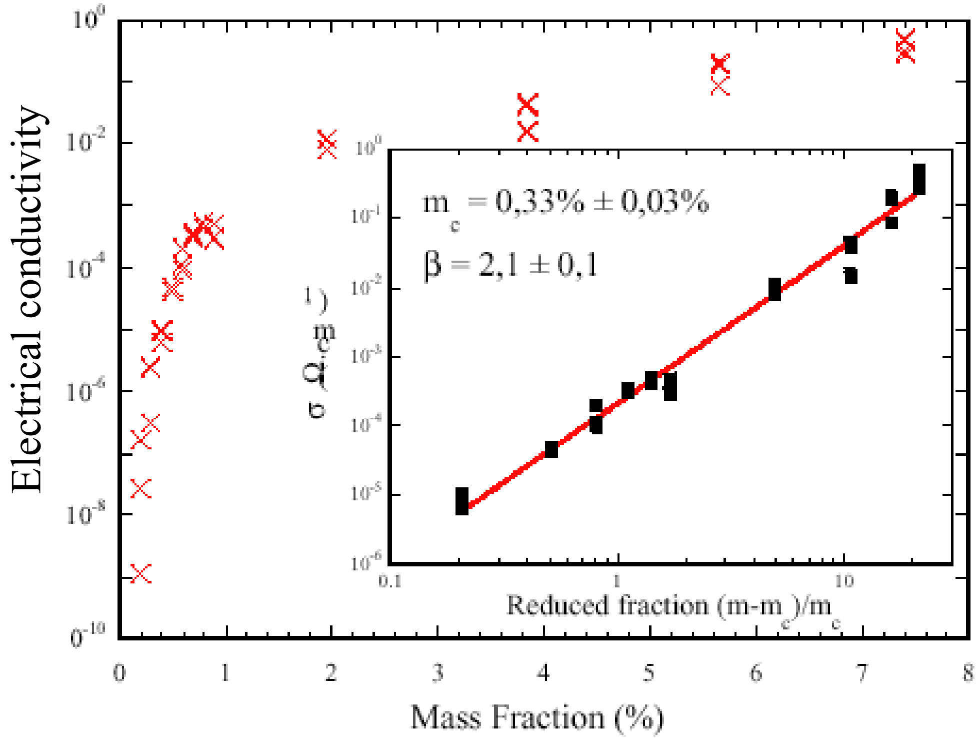
$$\sigma \sim (V - V_c)^{\alpha}$$

with $\alpha \approx 2$ - just percolation in 3 dimensions

- But why the percolation threshold scaling law holds up to

$$\frac{V}{V_c} = 100 \text{ ?!}$$

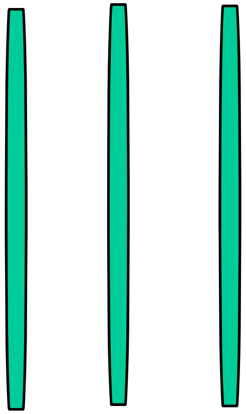
Electric transport properties and percolation in carbon nanotubes / PMMA composites



J-M Benoit, at. al. Mat. Res. Soc. Symp. Proc. Vol. 706 (2002)

Simple Rule of Mixtures for Thermal Conductivity

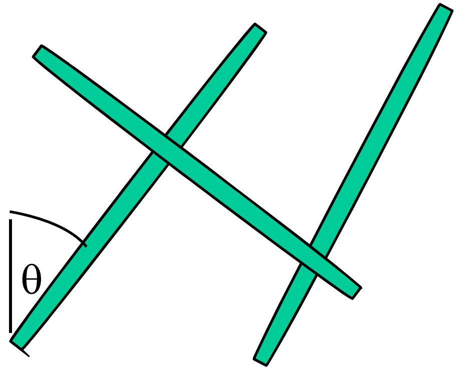
Highly conductive fibers in a low conductivity matrix well above the percolation threshold



$$k_{comp} = V_{tube} k_{tube} \langle \cos^2 \theta \rangle$$

k_{comp} – composite conductivity

V_{tube} – volume fraction of tubes



$$k_{comp} = V_{tube} k_{tube}$$

$$k_{comp} = V_{tube} k_{tube} \frac{1}{3}$$

for k_{tube} = 3000 W/m-K, k_{matrix} = 0.2 W/m-K and V_{tube} = 0.01

k_{comp} = 30 W/m-K

k_{comp} = 10 W/m-K

fifty-fold increase!!

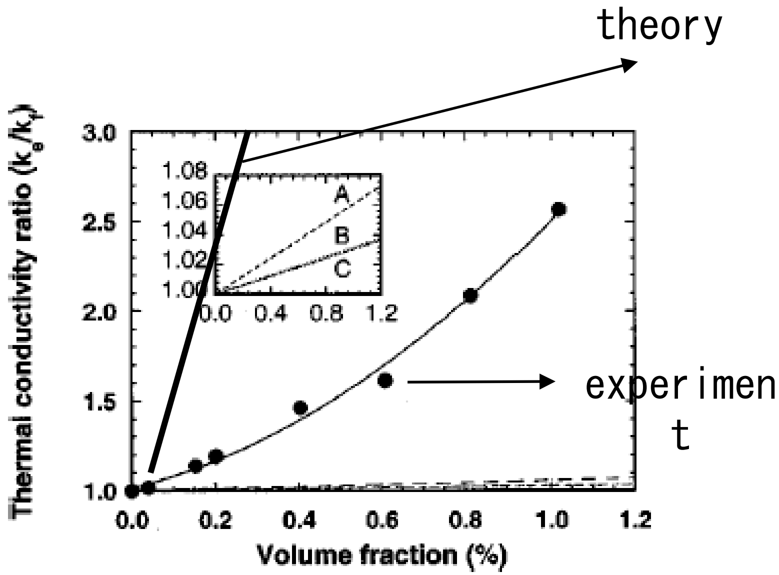
Thermal Transport Puzzle # 2

- Actual increase at 1% volume fraction is only 2-3 fold rather than 50 fold

- Nothing special happens at the percolation threshold

- Thermal conductivity increases are non-linear in fiber volume fraction

- Possible explanations
  - ➔ Intrinsic tube conductivity compromised by defects
  - ➔ Interfacial resistance of the tube-matrix interface. → $J_Q = \sigma_K \Delta T$



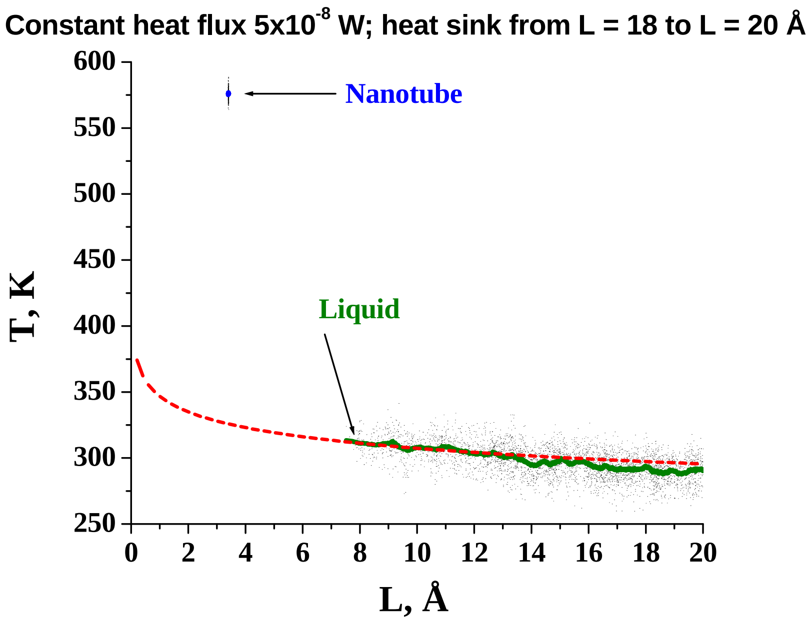
S-U. Choi, *at al.*, Appl. Phys. Lett. **79**, 2252–2254 (2001).

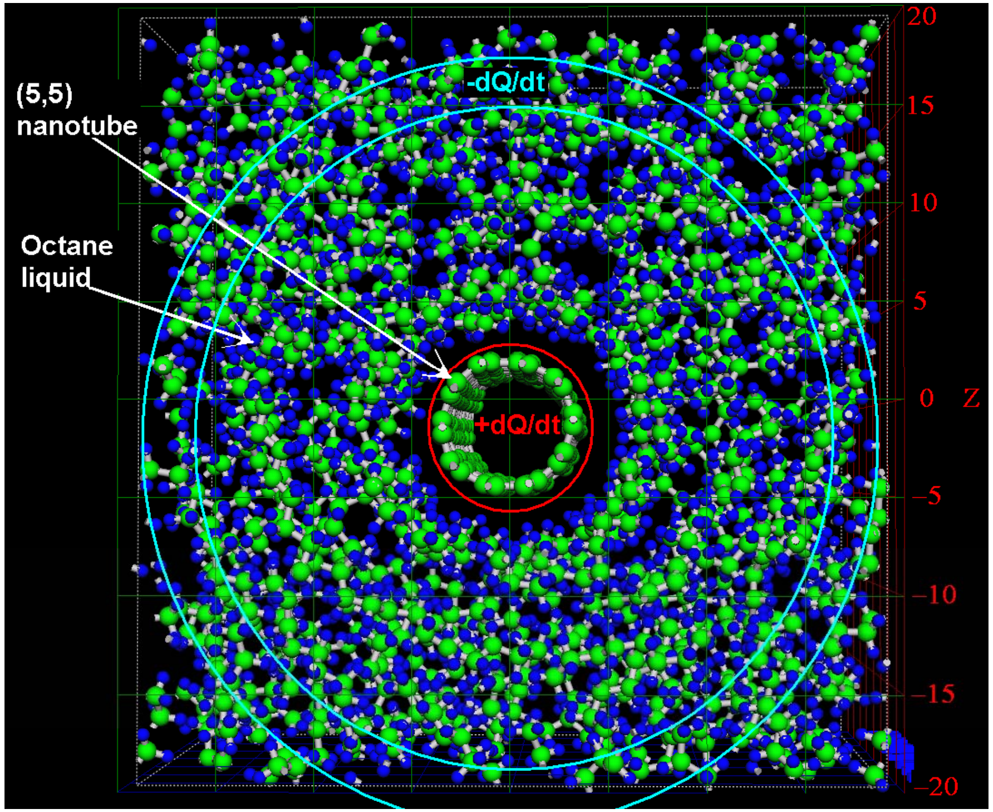
Nanotube – Matrix Heat Transfer: Simulation

Constant flux simulations

1. Pour the heat to the tube and remove from the liquid

2. Monitor the temperature profile





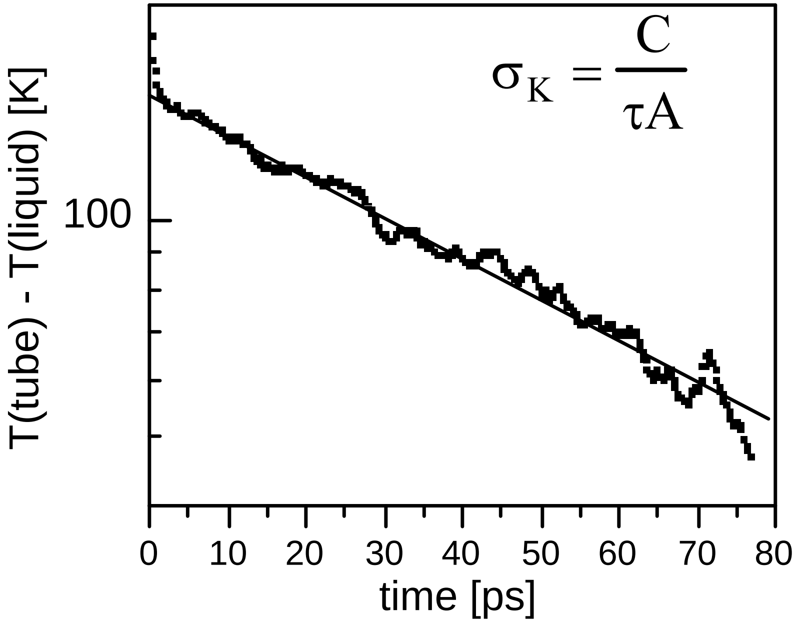
$$\sigma_K = \frac{J_Q}{\Delta T} = \frac{dQ/dt}{A\Delta T}$$

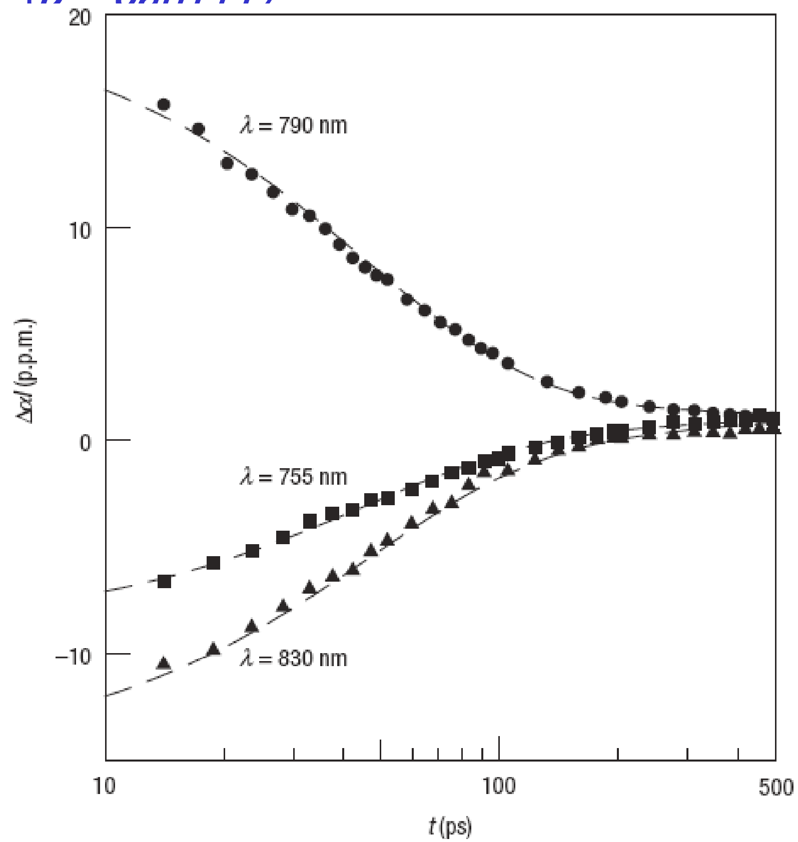
- Most of the temperature drop at the interface
- Interfacial conductance, $\sigma_K \sim 25$ M W/K-m^2

Relaxation Simulations and Experiment

MD Simulations

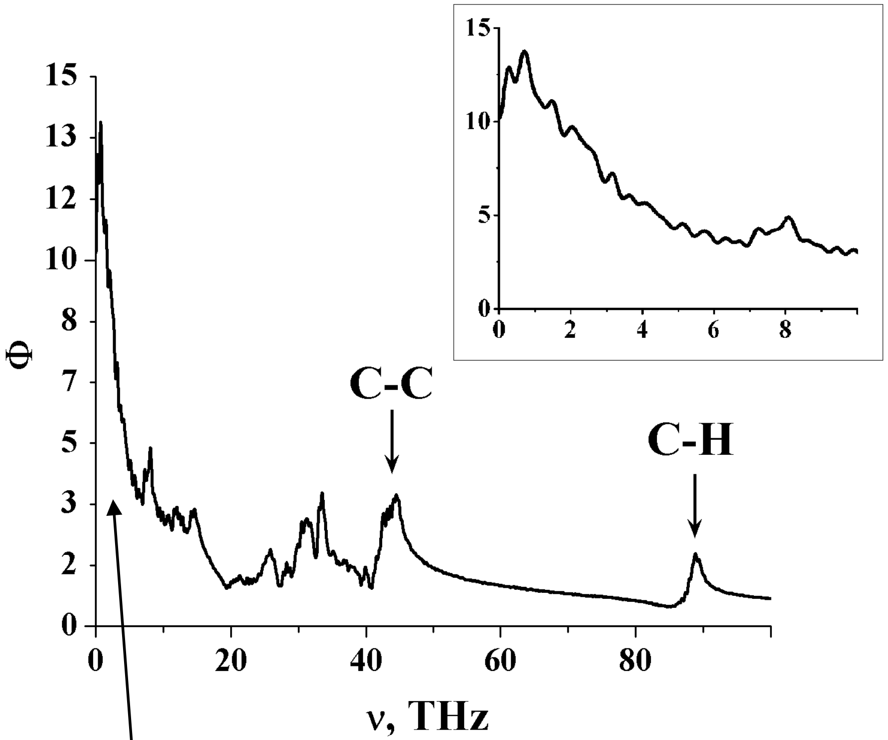
Laser pump and probe experiment (D. Cahill)

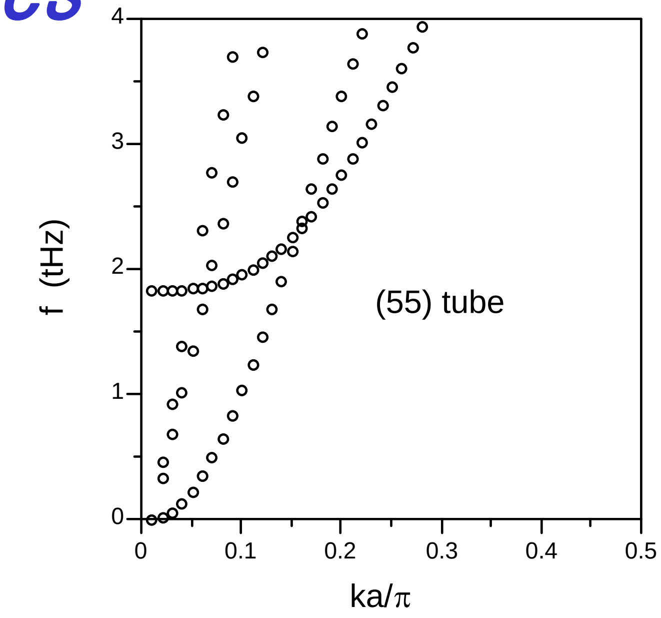




- Exponential decay
- Relaxation time ~ 40-70 ps
- Interfacial conductance, σ_K ~ 10-20 M W/K-m^2

Vibrational Modes in Liquid and Nanotubes



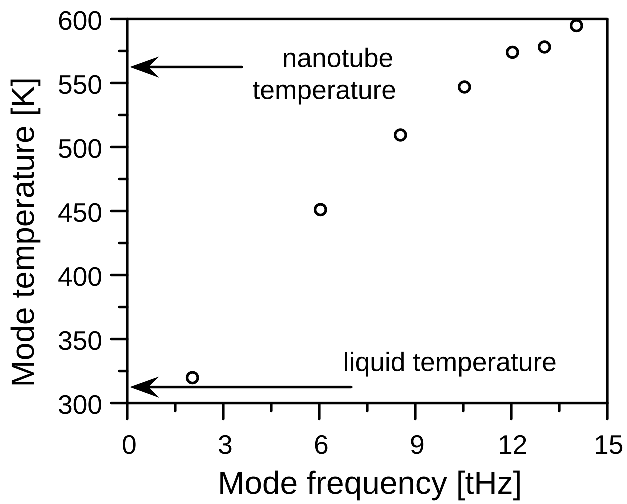


- Liquid has low frequency modes associated with weak dispersion forces between liquid molecules. The same forces act between liquid and nanotube walls
- Carbon nanotubes have a small number of low frequency modes associated with bending and squeezing. Only these modes can couple strongly with liquid.

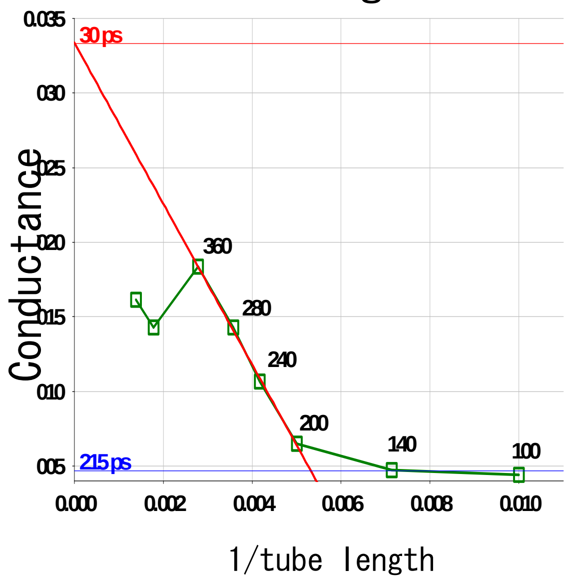
Weak harmonic coupling between liquid and carbon nanotubes leads to large thermal interfacial resistance - the same for nanotube-polymer composites

Mechanism of the Heat Flow

"Temperature of bending modes"



Conductivity dependence on length



Lowest frequency bending mode

$$\omega = \frac{(4.73)^2}{L^2}\sqrt{\frac{IE}{\rho A}}$$

- Only few low frequency bending modes are effective in coupling with liquid

So What About Nanotube Based Composites?

- Equivalent matrix thickness interfacial resistance, h_M, is defined as the thickness of the matrix over which the temperature drop is the same as the temperature drop at the interface.

$$h = \frac{\text{matrix conductivity}}{\text{int erfacial conductivity}} = \frac{k}{\sigma_K}$$

- For interfacial conductance, σ_k = ~1.0 x 10^7 W/K-m^2 and low conductivity matrix, k= 0.2 W/K-m

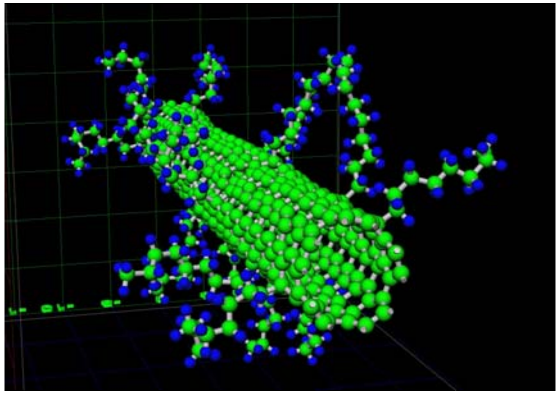
$$h_M = 20\ \text{nm}$$

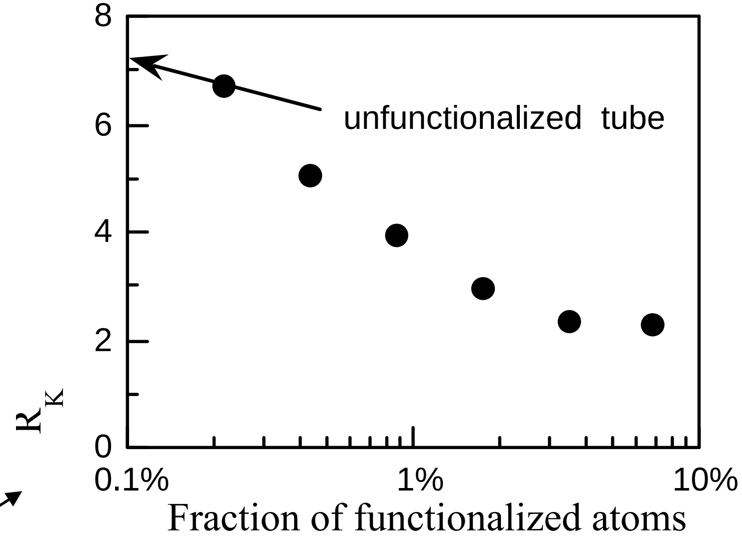
- Equivalent tube length, h_{CNT}, (k= 3000 W/K-m)

$$h_{CNT} \sim 0.3\ \text{mm}$$

In CN composites, interfacial resistance plays a major role in determining effective heat flow

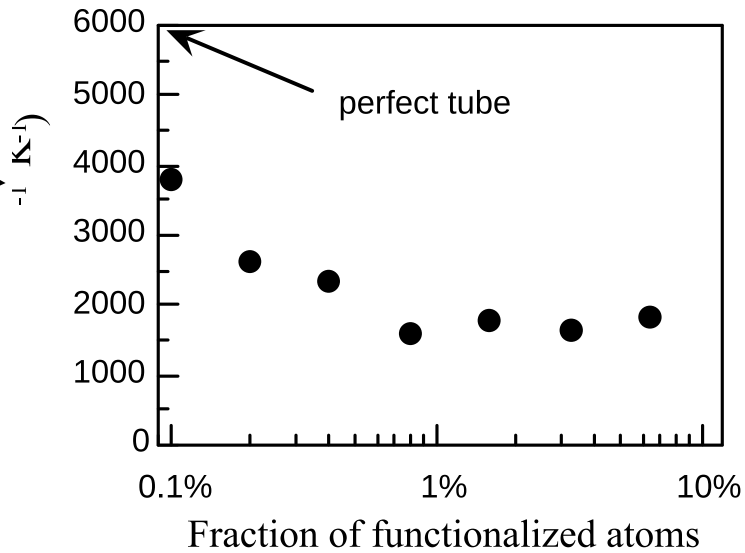
Chemical Functionalization





- Functionalization reduces interfacial resistance

- But, the points of chain molecule attachments act as scattering centers for heat carrying phonons thus reduce tube axial conductivity

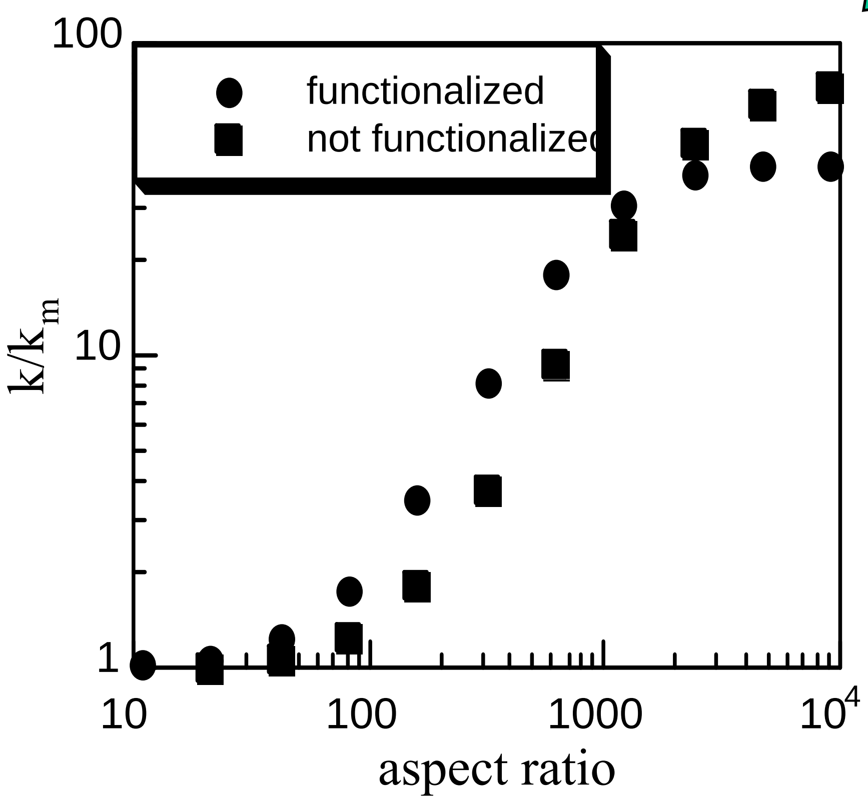


Net Effect on Composite Conductivity

$$L_c \approx \sqrt{r_{tube} k_{tube} R_K}$$

L_c/r = 100 for functionalized tubes

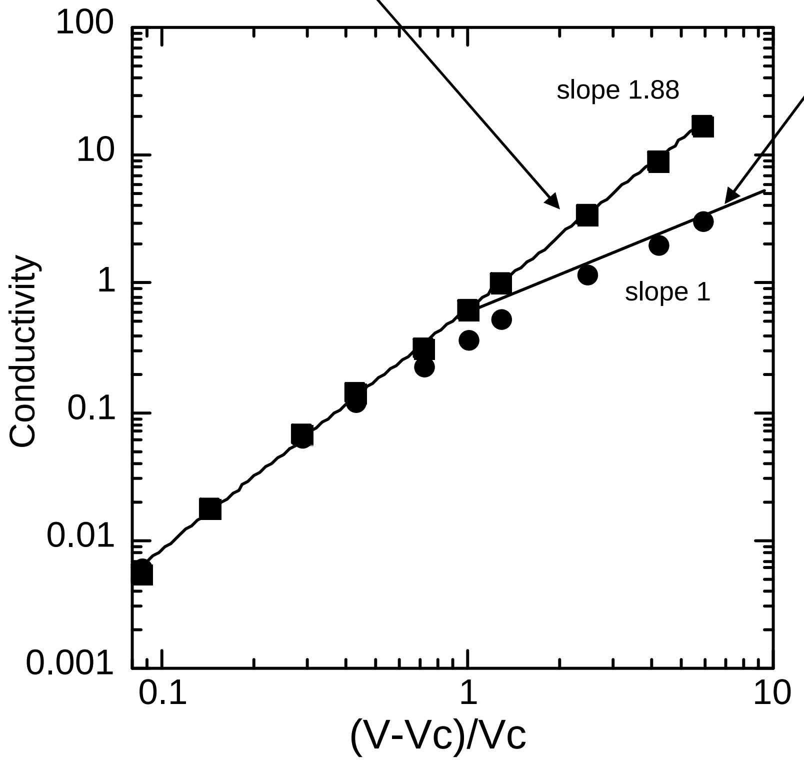
L_c/r = 200 for unfunctionalized tubes



- L_c gives the typical distance over which the heat can be carried by one tube
- Tubes much shorter than L_c do not contribute much to the composite conductivity due to surface resistance and relatively small surface area
- Tubes much longer then L_c are always strongly coupled to the matrix and composite conductivity is not sensitive to boundary resistance
- For tube length comparable with L_c, composite conductivity can be improved by chemical functionalization

Conductivity on Percolating Tube Networks

Contact resistance　　　No contact resistance



- Monte-Carlo (MC) simulations of diffusion of "carriers" on a network of tubes
- MC move rules mimic either contact resistance or bulk resistance
- Carrier mobility, μ, proportional to the carrier diffusion constant. The conductivity, σ, is given by

$$\sigma \sim \mu V \sim (V-V_c)^2$$

- Near the percolation threshold for both mechanisms
- For bulk resistance above ~ $V = 2V_c$, $\sigma \sim V$
- For contact resistance percolation threshold power law appears to persist

Electrical vs. Thermal Percolation

- At macroscopic level thermal and electrical transport are described by the same equations.
- For example in the steady state temperature satisfied the Laplace Equation

$$\Delta T = 0$$

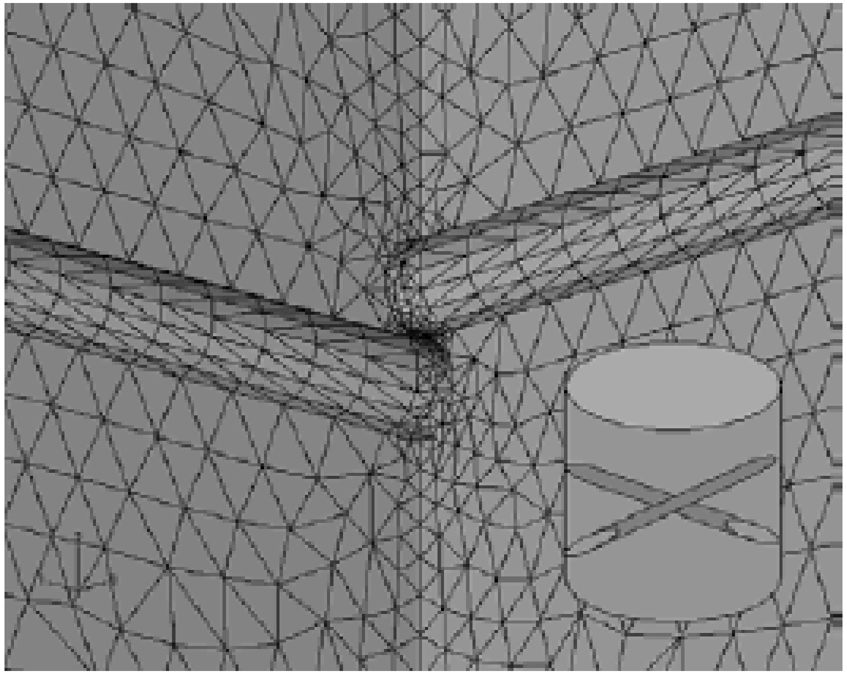
- The flux continuity condition at the matrix-fiber interface

$$-J_Q = k_m \frac{\partial T_m}{\partial \mathbf{n}} = k_f \frac{\partial T_f}{\partial \mathbf{n}}$$

- The electrical transport is described by the same equations, T is replaced with potential and thermal conductivity with electrical conductivity

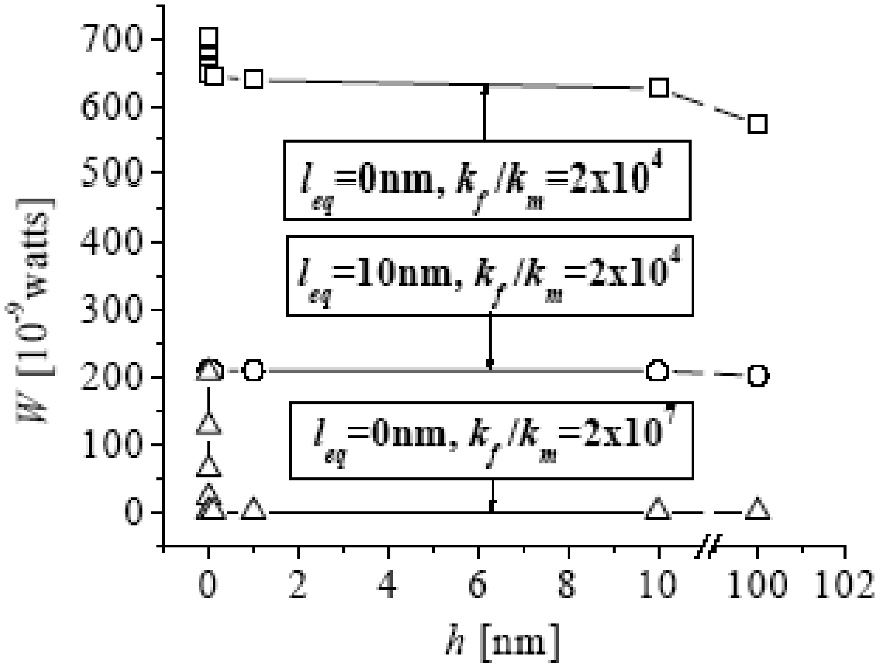
Finite Element Calculations

- *Heat flow between two fibers*



- *Ends of one fiber kept at higher temperature than the other – the rest of boundaries are adiabatic (no heat flux across the interface)*

Heat Flow Rate vs. Tube separation

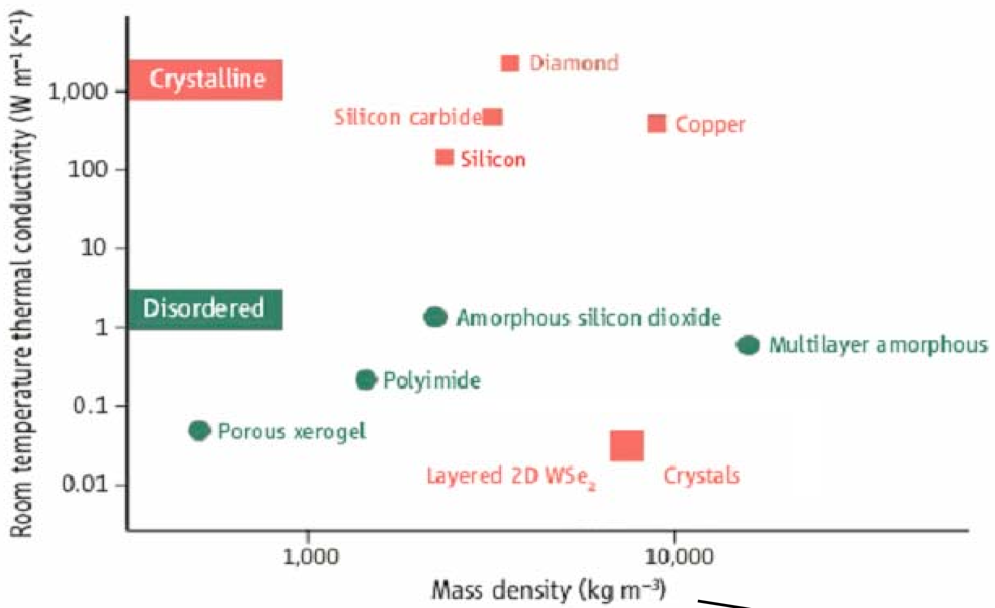


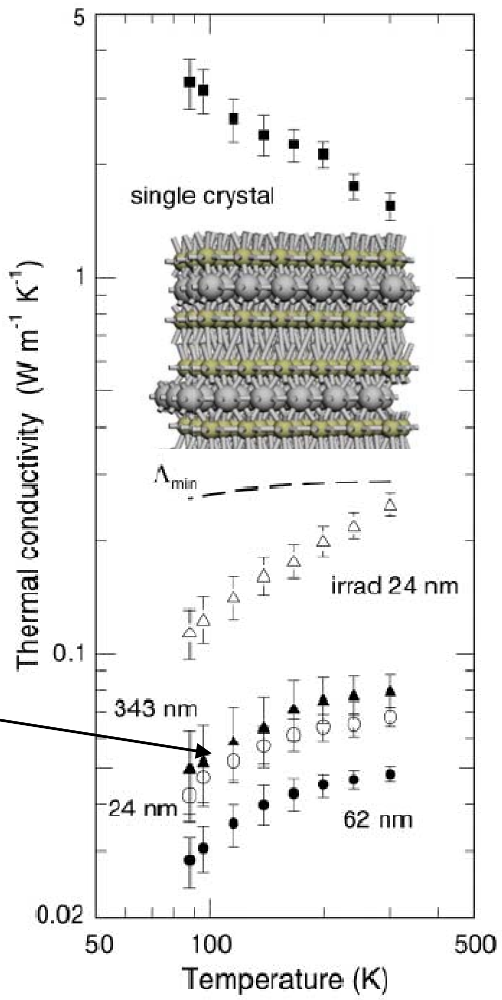
- Relatively small fiber to matrix conductivity ratio and interfacial thermal resistance completely eliminates the effect of fiber-fiber contacts

- For the electrical conductivity problem larger ratio of fiber to matrix conductivity leads to electrical percolation

Ultra-low Thermal Conductivity of Layered Materials

Below the amorphous material limit





Thermal conductivity below Einstein limit

Why it is so low?

- Stacking disorder ?

- Grain boundaries ?

C. Chiritescu, D. G. Cahill, et al., *Science. 315, 353(2007)*.

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Model structures

A B A B A B A B A B

QuickTime™ and a
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Perfect crystal

A C A B C B A B A B

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Stacking disorder

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Grain boundaries

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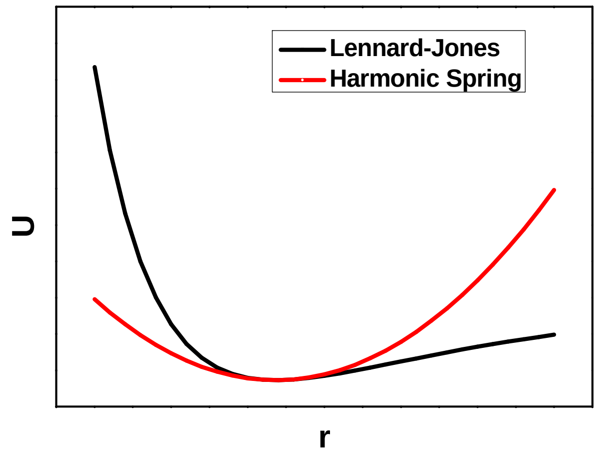
Mass disorder

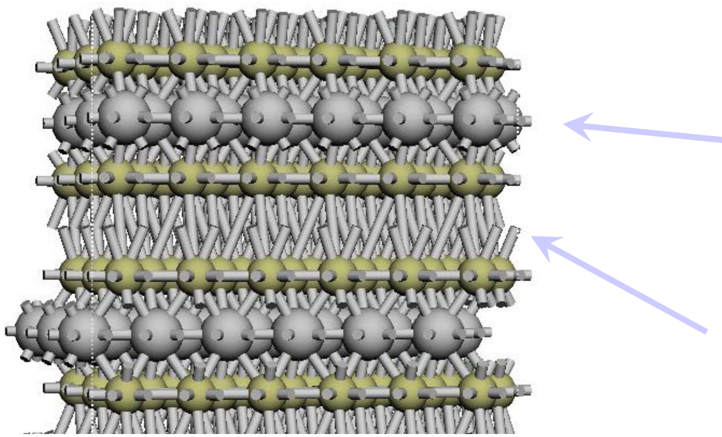
Model interactions

Lennard-Jones potential

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Harmonic springs





Two sets of ε and σ parameters are used

- Within WSe_2 sheet: ε = 0.455 eV and σ = 2.31 Å

- Between layers: ε = 0.04 eV and σ = 3.4 Å

Molecular dynamics results

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Perfect crystal and stacking disordered structures show strong film thickness dependence not observed in experiment

Structures with grain boundaries show lower conductivity and weaker size dependence

Phonon Localization and Polarization

Perfect crystal

Low frequency phonons are delocalized and polarized

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Higher frequency phonons are delocalized but not well polarized

Phonon Localization and Polarization

Stacking disorder

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Low frequency phonons are delocalized and polarized, same way as in perfect crystal

Higher frequency phonons can be localized or delocalized but they do not matter much for thermal transport

Phonon Localization and Polarization

Grain boundary

Low frequency phonons are weakly localized and weakly polarized

Conductivity reduction and weak size dependence

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Higher frequency phonons can be localized or not and are not polarized

Phonon Localization and Polarization

Mass disorder

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Even low frequency modes are localized

↓

Ultimate conductivity reduction and essentially no size dependence

Thermal conductivity of a dense solid below that of still air

Interfacial Perspective

Interfacial conductance from relaxation and equilibrium simulations

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$G \approx 25\ MW/m^2\text{-}K$

↓

Effective conductivity

$\kappa = Gxd$

d=1nm - grain boundary size

$\kappa \approx 0.025\ W/m\text{-}K$

Actual conductivity

$\kappa \approx 0.05\ W/m\text{-}K$

Collective aspect of the vibrational heat transfer is responsible for the difference

Layered Crystals - Conclusions

Stacking disordered is insufficient to lead to ultra-low thermal conductivity which is due to the fact that low frequency phonons are still polarized and carry heat over large distances

Nanostructuring (introduction of grain boundaries) depolarize and partially localize phonons leading to amorphous-like thermal transport and ultra-low thermal conductivity which can be also understood in terms of the interfacial thermal resistance.

Introducing mass disorder leads to complete localization of phonons and further reduction of thermal conductivity to level below that of conductivity of still air.