Divergence in Non-Equilibrium Molecular Dynamics Simulations of Carbon Nanotube Conductivity and the Effect of System Parameters

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Motivation: Parameterization of Mesoscopic Model for Carbon Nanotubes (CNTs)

Carbon Nanotubes (CNTs) self-assemble into bundles

Tube bundles then form larger, complex networks of bundles

Thess et al., Science 273 (1996)

Hennrich et al., PCCP 4, 2273 (2002)

Experimental imaging of CNT bundles and bundle networks


Resultant system configurations obtained by the mesoscopic model
Carbon Nanotube (CNT) Conductivity

CNT Thermal Conductivity:
- Well over 3,000 W/mK by some accounts
- Wide variation in published results

Simulation Parameters:
Simulation Code: LAMMPS
Atomic Potential: AIREBO (unless otherwise noted)
Chirality: (10,10)
Diameter: ~1.3 nm
Average Temperature: 300 K (unless otherwise noted)
Tube Length Range: 50 nm - 631 nm
(8,240 atoms - 104,440 atoms)
Tube Construction:
40 atom repeatable unit cell
(Two 20 atom rings)
120 atom caps
(half of a C_{240} Fullerene sphere)
Carbon Nanotube Conductivity: Procedure

Direct Non-Equilibrium Molecular Dynamics (NEMD)

- Steady state flux applied through the energy management of bath regions

Energy added to Hot Bath

Energy removed from Cold Bath

$q$
Direct Non-Equilibrium Molecular Dynamics (NEMD)

- Steady state flux applied through the energy management of bath regions
- Temperature is calculated from atomic velocities
Carbon Nanotube Conductivity: Procedure

Direct Non-Equilibrium Molecular Dynamics (NEMD)

- Steady state flux applied through the energy management of bath regions
- Temperature is calculated from atomic velocities
- Conductivity is determined from resulting temperature profile and Fourier's Law

Conductivity in this largely 1D problem can be found with Fourier's Law:

\[ k = \frac{\vec{q}}{\nabla T} \]
**Phonons:** Main energy carrier for CNTs

Phonon transport (and thermal conductivity) can be limited by length of CNT
Carbon Nanotube Conductivity: Comparison

- Lukes and Zhong, JHT 129, 2007
- Padgett and Brenner, Nano Lett. 4, 2004
- Thomas et al., PRB 81, 2010
- Shiomi, private communications (Jpn. J. Appl. Phys. 47, 2007)
Carbon Nanotube Conductivity: Comparison

- Lukes and Zhong (JHT 129, 2007)
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The graph shows the thermal conductivity ($k$ in W/mK) as a function of tube length (nm) for different potential models:

- **AIREBO POTENTIAL**
- **REBO POTENTIAL**
- **BRENNER-STYLE POTENTIAL**
Simulation Parameters: Atomic Potential

**AIREBO**: REBO pair potential with the addition of Lennard-Jones potential for non-bonded Van der Waals interactions


**ALT-Tersoff**: L. Lindsay and D.A. Broido, Phys. Rev. B. 81, 205441 (2010)
Simulation Parameters: Bath Length

C = Central Tube Length
B = Bath Length

It is known that $k$ increased with increasing bath length.

**Common Explanation:**
When $B \ll C$, dissimilarities in the allowable phonon states yields an additional Thermal Boundary Resistance (TBR) at the bath boundary, that affects $k$ measurements.

**Common Approach:**
Bath Length ($B$) should be large enough to reduce TBR (ex: $B \approx 0.5 \ C$)
Tube length is defined as the Central Tube Length ($C$)
Simulation Parameters: Bath Length

- Constant 50 nm central tube length (C)
- Increasing bath tube length (B)
- Constant 96 nm central tube length (C)
- Increasing bath tube length (B)
Simulation Parameters: Bath Length

- Constant 50 nm central tube length (C) Increasing bath tube length (B)
- Constant 96 nm central tube length (C) Increasing bath tube length (B)
- Constant 0.5 nm bath length (B) Increasing central tube length (C)
Simulation Parameters: Bath Length

- Constant 96 nm central tube length (C)
- Increasing bath tube length (B)

Graph showing:
- $k$ (W/mK) on the y-axis
- $B$ (nm) on the x-axis
- $C = 96$ nm tube
- $B \approx C$ and $B > C$ marked with red squares
Simulation Parameters: CNT Length Definition

- Constant 50 nm central tube length (C) Increasing bath tube length (B)
- Constant 96 nm central tube length (C) Increasing bath tube length (B)
- Constant 0.5 nm bath length (B) Increasing central tube length (C)
Simulation Parameters: CNT Length Definition

Length dependence appears nearly independent of bath length.
### Simulation Parameters: CNT Length Definition

<table>
<thead>
<tr>
<th>Central Length</th>
<th>End to End Length</th>
<th>k (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>202.8 nm</td>
<td>206 nm</td>
<td>228</td>
</tr>
<tr>
<td>96 nm</td>
<td>198 nm</td>
<td>225</td>
</tr>
<tr>
<td>50 nm</td>
<td>202 nm</td>
<td>225</td>
</tr>
</tbody>
</table>
Simulation Parameters: Physical Configuration

Uni-directional

Conventional Length Definition:
length between baths
Simulation Parameters: Physical Configuration

Uni-directional

Conventional Length Definition:
length between baths

Bi-directional

Conventional Length Definition:
length of repeated computational cell
Simulation Parameters: Physical Configuration

Uni-directional

Conventional Length Definition:
length between baths

Bi-directional

Conventional Length Definition:
length of repeated computational cell
Simulation Parameters: Physical Configuration

Bi-directional, Periodic Boundary Conditions

\[ k = 160 \text{ W/mK} \]

Bi-directional, Free Boundary Conditions

\[ k = 154 \text{ W/mK} \]
Simulation Parameters: Physical Configuration

Bi-directional, Periodic Boundary Conditions

\[ k = 160 \text{ W/mK} \]

Bi-directional, Free Boundary Conditions

\[ k = 154 \text{ W/mK} \]

Compare To: Uni-directional, Free Boundary Conditions

\[ k = 196 \text{ W/mK} \]
**Simulation Parameters: Physical Configuration**

**Bi-directional, Periodic Boundary Conditions**

![Diagram of bi-directional, periodic boundary conditions](image)

$k = 160 \text{ W/mK}$

51 nm

**Bi-directional, Free Boundary Conditions**

![Diagram of bi-directional, free boundary conditions](image)

$k = 154 \text{ W/mK}$

51 nm
Simulation Parameters: Physical Configuration

Bi-directional, Periodic Boundary Conditions

\[ k = 160 \text{ W/mK} \]

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Bi-directional, Free Boundary Conditions

\[ k = 154 \text{ W/mK} \]

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Compare To: Uni-directional, Free Boundary Conditions

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50 nm
## Simulation Parameters: Physical Configuration

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<th>Length Between Baths plus Bath Lengths</th>
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Conventional length definition for bi-directional works

Inconsistent
## Simulation Parameters: Physical Configuration

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Proposed definition of CNT length

Consistent
There exists wide discrepancies in published calculations of CNT conductivity by molecular dynamics simulation.

Much of these discrepancies can be attributed to inconsistent or flawed definitions of system parameters, such as:
- Interatomic potential
- Physical configuration of simulation
- Definition of CNT length

A consistent convention for defining CNT length is proposed:
- CNT length is defined as the length between opposing bath regions, plus the length of the bath regions themselves.

The simulation configuration should best match the true physical system whenever possible:
- Bath regions should be small relative to overall CNT length
- Uni-directional flux should be implemented
- Free boundary conditions should be employed
Agradecimientos:

Computational Materials Group - University or Virginia
Charlottesville VA, USA

Prof. Leonid Zhigilei - Advisor

Pontifica Universidad Católica de Chile

PASI Organizers!