Computational Studies of Confined and Externally Flowing Gases on the Mechanical Properties of Carbon Nanotubes

Susan B. Sinnott

University of Florida

Department of Materials Science & Engineering

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- Dr. Boris Ni
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Outline

- Computational details
- Transport of small molecules through carbon nanotubes
- Deflection of carbon nanotubes and effects of filling

Computational Details

- Numerical integration of Newton's equation of motion:

  F = ma

$$E = \sum_i \sum_{j(>i)} [\underbrace{V_R(r_{ij}) - b_{ij} V_A(r_{ij})}_{\text{Reactive Empirical Bond Order (REBO) potential}} + \underbrace{V_{vdw}(r_{ij})}_{\text{Lennard-Jones (LJ) potential}}]$$

  - Constant *N, V, and T*
  - Langevin thermostats applied to maintain T

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Brenner et al., *J. Phys: Condens. Matt.* **14**, 783 (2002)

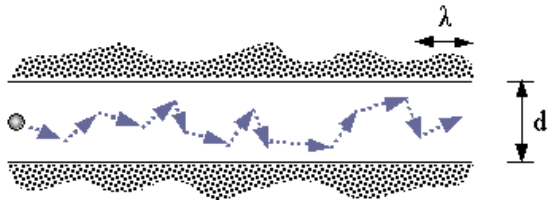
Molecular Transport in Nanopores: Motivation

- Carbon nanotube bundles might be ideal for use in tailored ultrafiltration membranes with fewer blocked ends and more uniform pore sizes
- Molecules confined to nanometer–scale pores behave in a manner that is fundamentally different from the behavior of fluids in macroscopic porous systems
  - Motion dominated by diffusion
  - Some transport mechanisms unique to nanometer–scale pore systems

Diffusion Modes in Small (μm and nm-Scale) Pores

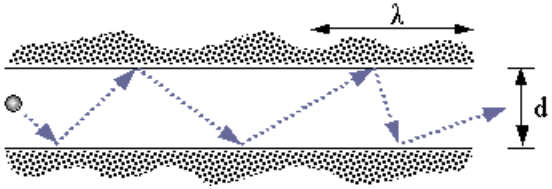
Molecular (transport) diffusion

- Mean free path (λ) is relatively short compared to pore size (d)



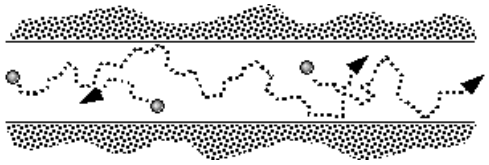
Knudsen diffusion

- λ is relatively long compared to d



Normal-mode or bulk fluid diffusion

- Molecules can pass each other within pore



$$\langle z^2 \rangle = 2Dt$$

where z is displacement, t is time, D is normal diffusion coefficient

Diffusion Modes in Small (μm and nm-Scale) Pores

Transition-mode diffusion

$$\langle z^2 \rangle = 2Ct^{\alpha}$$ where 0.5 (single file) $< \alpha < 1$ (normal mode)

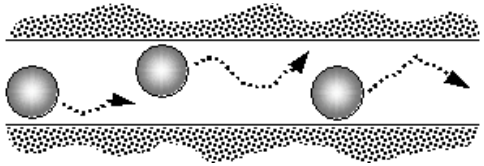
Anomalous diffusion (superdiffusion)

$$\langle z^2 \rangle \sim t^{\alpha}$$ where $1 < \alpha < 2$

Ballistic motion

$$\langle z^2 \rangle \sim t^2$$

Single-file diffusion

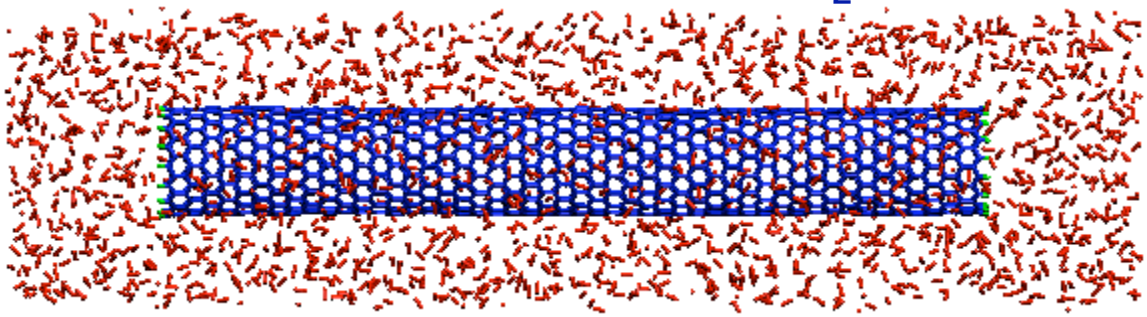


- Molecules cannot pass each other because of their large size relative to *d*

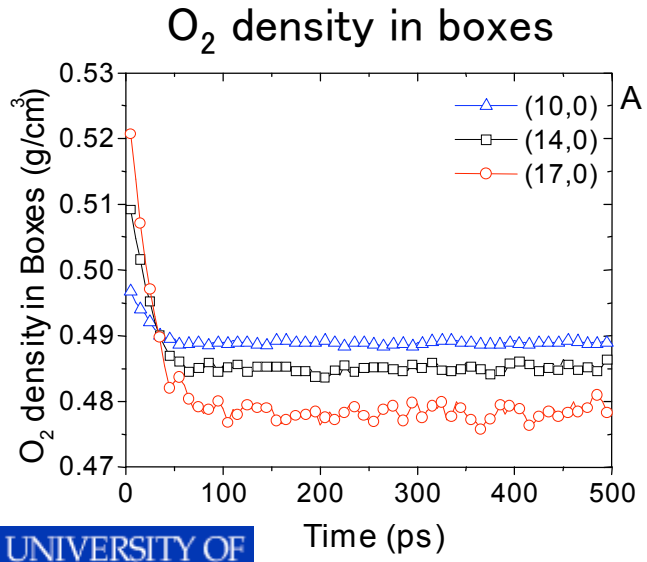
$$\langle z^2 \rangle = 2F\sqrt{t}$$ where *F* is single-file mobility

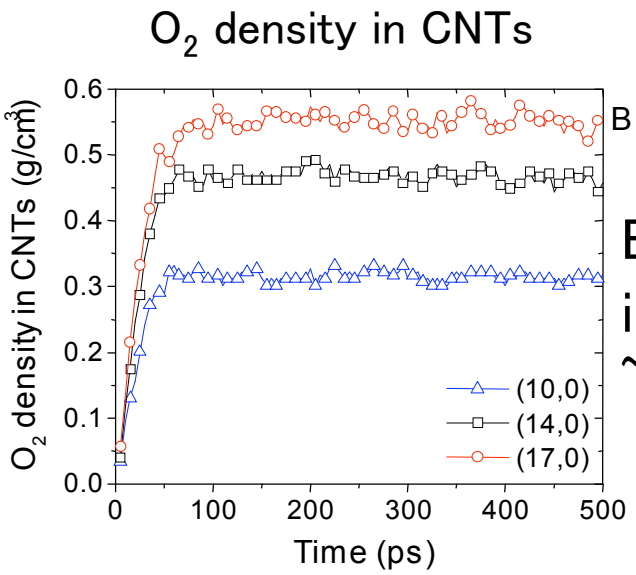
Equilibrium Transport

System: CNTs in a box full of O_2



Initially empty, H–terminated CNT





Equilibrium state is reached at ~100 ps

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Equilibrium Transport Results

Commutation of molecules across the CNT opening

– Increases with increasing CNT diameter

CNT	Number of O_2 at 500 ps		Number of O_2 at 100 ps	
	Total	Entered before 100 ps	Total	Left before 500 ps
(10,0)	32	28 (87.5 %)	31	3 (9.7 %)
(14,0)	89	64 (71.9 %)	90	26 (28.9 %)
(17,0)	158	101 (63.9 %)	155	59 (38.1 %)

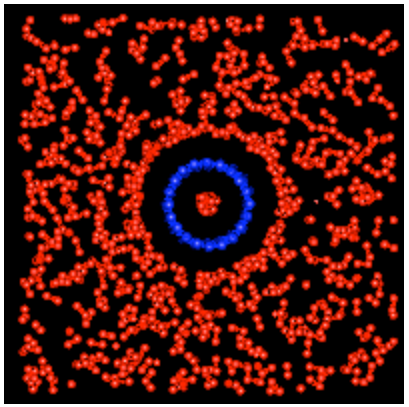
As the diameter of CNT ↓, the amount of commuting O_2 ↓

because the O_2–CNT interaction ↑

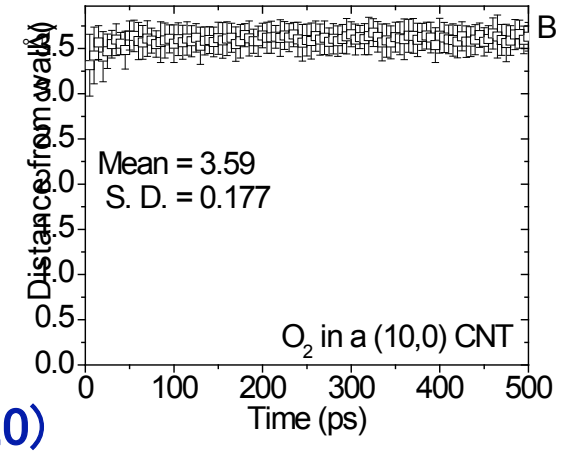
Equilibrium Transport Results

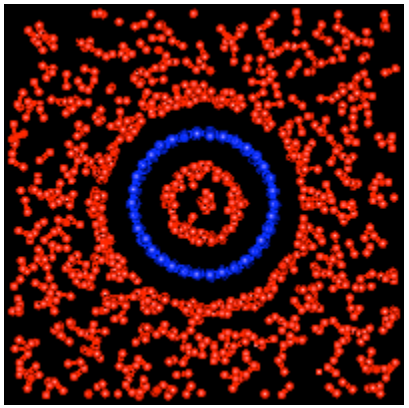
Location of O_2 in CNTs

- Prefer to stay at the van der Waals bond distance from the CNT wall
- Formation of O_2 layered (ring) structures
- Increase in CNT wall–O_2 distance, and broadening in the distribution, as CNT diameter increases

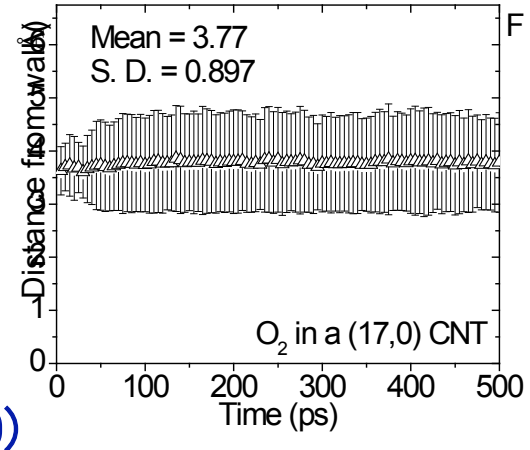


(10,0)





(17,0)



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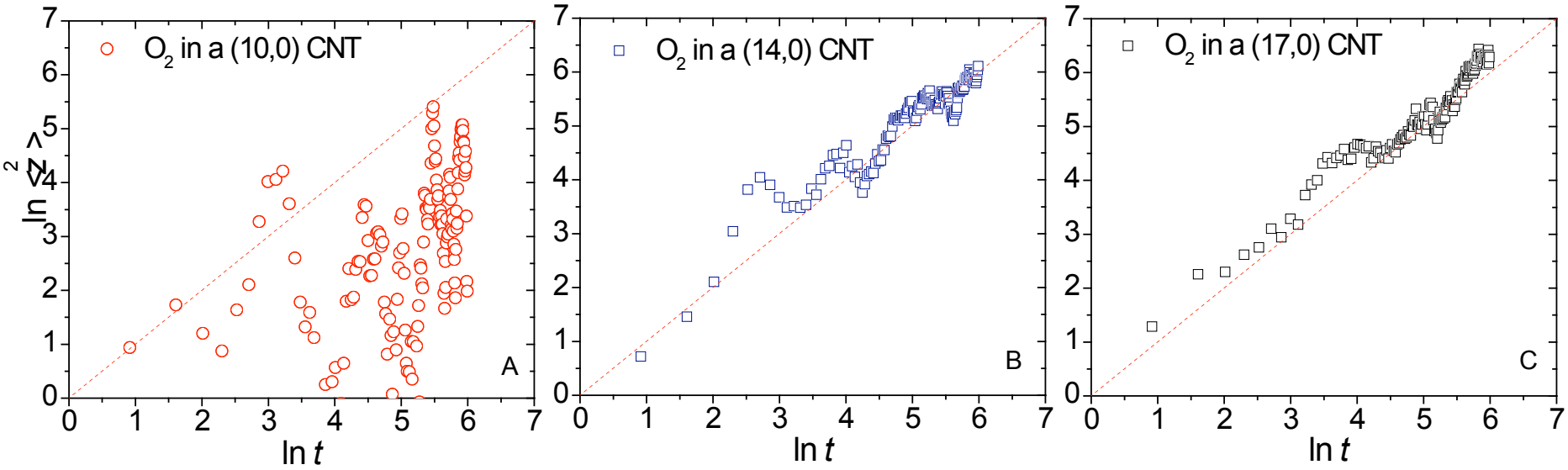
Equilibrium Transport Results

Anomalous transport in smaller diameter CNTs is predicted
- Deviates from normal mode diffusion



Diffusion Modes: Log–log plots of $\langle z^2 \rangle$ vs. t

As CNT diameter increases, molecular transport approaches normal–mode diffusion

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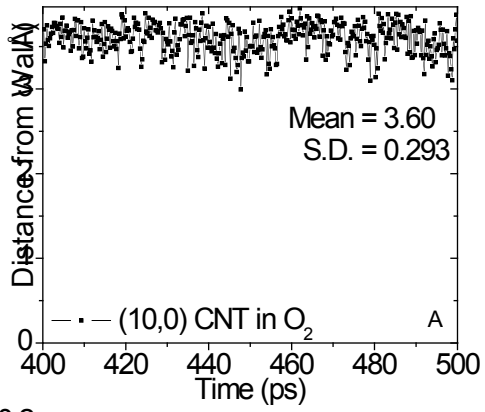
Equilibrium Transport Results

CNT–O_2 Interaction:

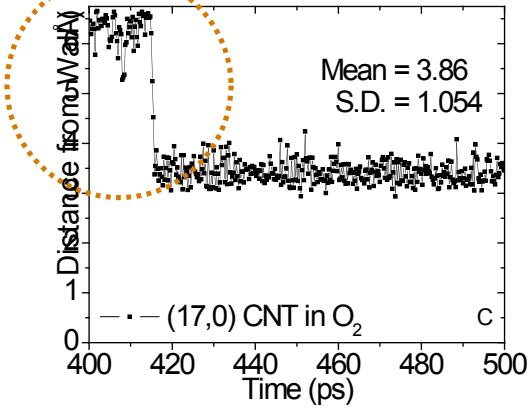
- Fluctuation in wall–O_2 distance, and PEs
- Difference between wall–O_2 PE and O_2–O_2 PE increases as the CNT diameter decreases
- Transfer of O_2 between layer structures in the (17,0) CNT → inversion of the PEs

O_2–CNT Distance

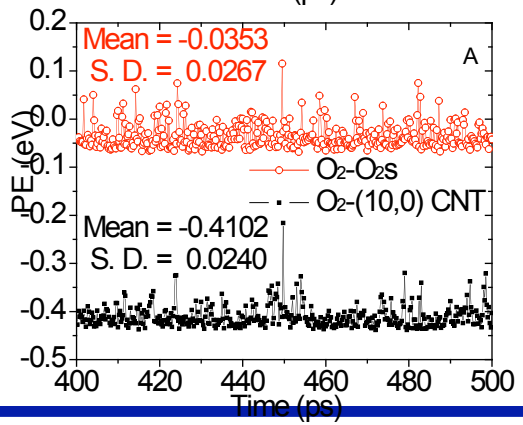
(10,0)

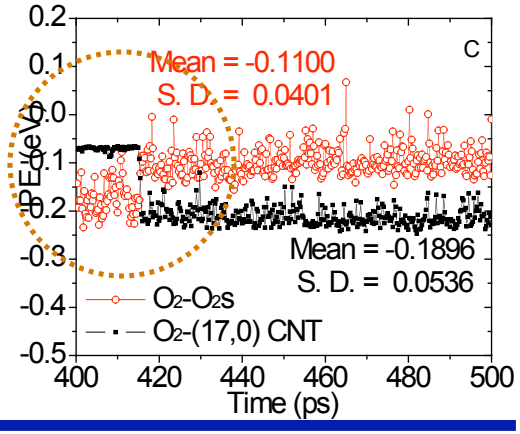


(17,0)



PE





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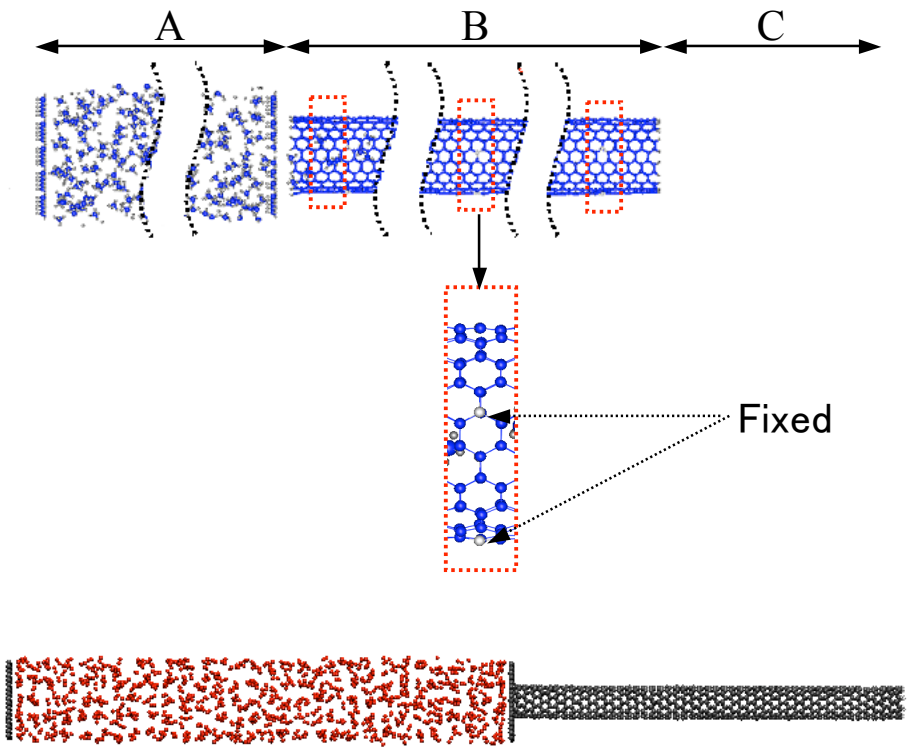
Non-Equilibrium Transport

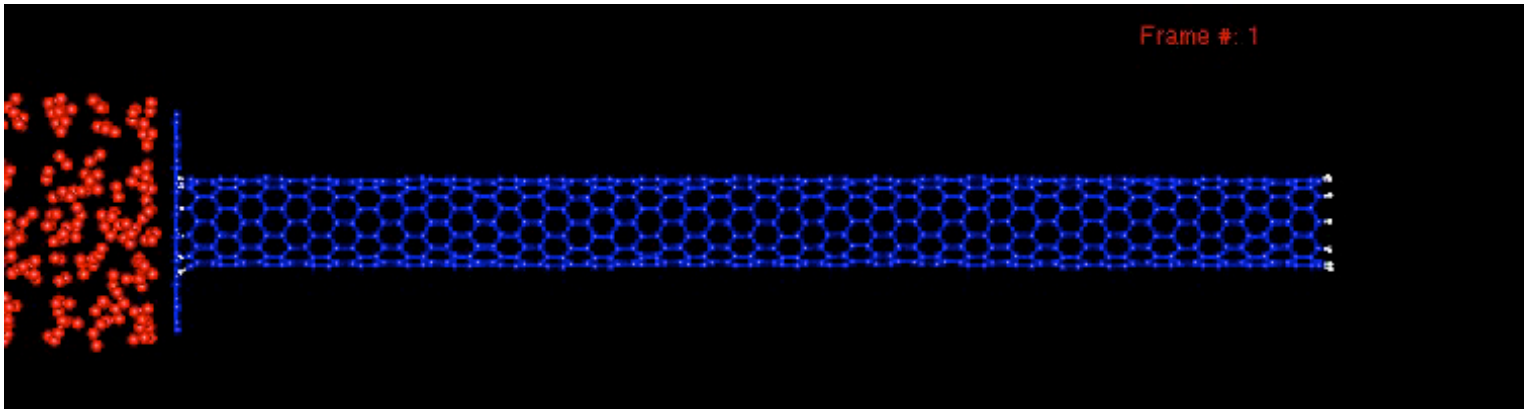
Region A: Gas Reservoir
- CH_4, O_2

Region B: Tube region
- Hydrogen-terminated
- Armchair & zigzag
- Diameter = 8.0 – 13.8 Å
- Length = 100 Å

Region C: region at the other end of the tube



Non-Equilibrium Transport Results



Stage I

- Forward gas flow

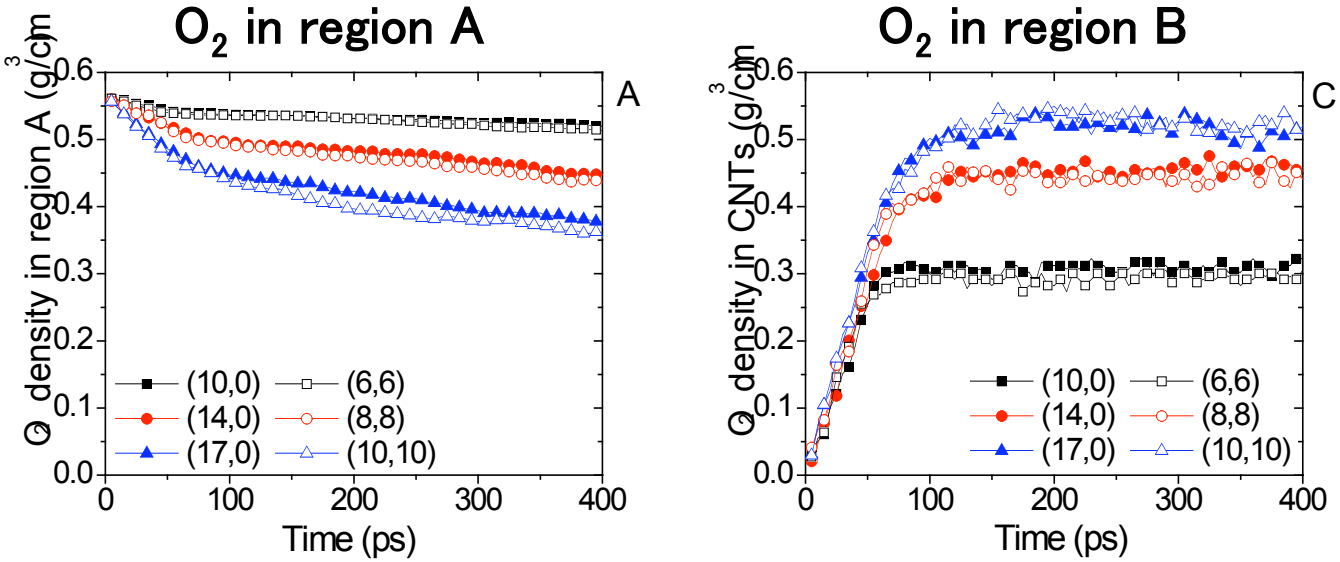
Stage II

- "Bouncing" motion of gas molecules
- Increase of gas density in Region B

Stage III

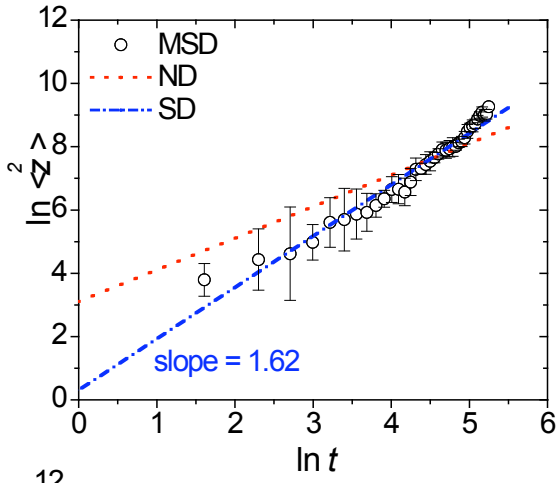
- Equilibrium or near-equilibrium
- Level-off of gas density in Region B

Molecular Densities

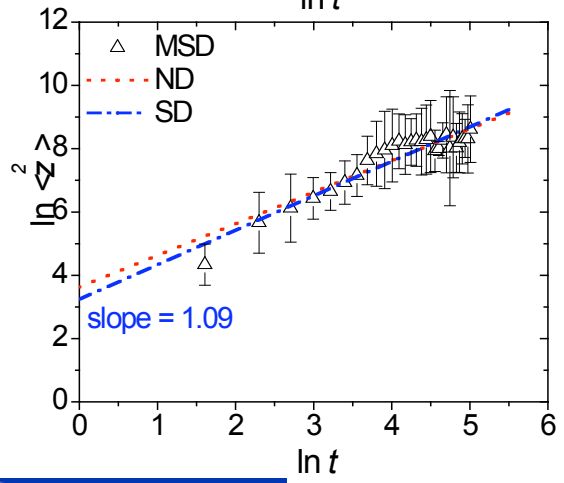


The rate of transport of the O_2 molecules entering CNTs from the gas reservoir does not depend on the helical symmetry of the nanotube, but does strongly depend on nanotube diameter.

Diffusion Modes: Log–log plots of $\langle z^2 \rangle$ vs. t



CH_4@(10,0)



CH_4@(17,0)

Exponents of t for CH_4

CNT	Stage III
(10,0)	1.62
(14,0)	1.22
(17,0)	1.09
(6,6)	1.62
(8,8)	1.17
(10,10)	1.20

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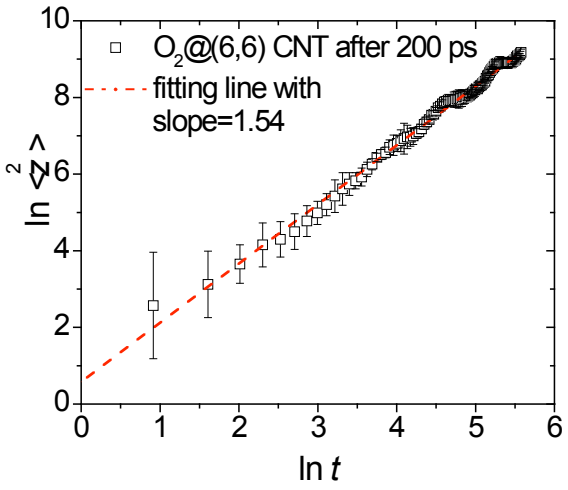
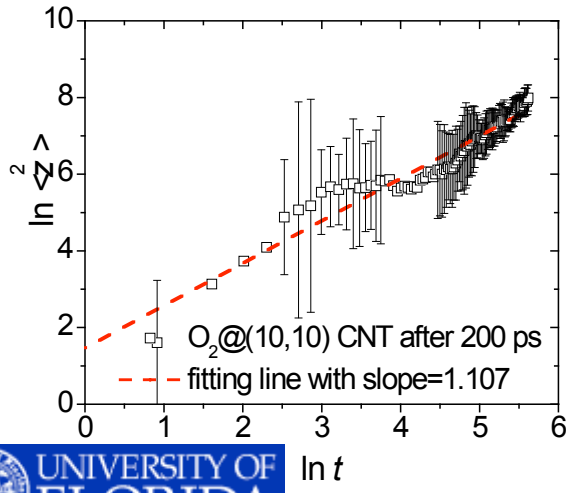
Diffusion Modes: Log–log plots of $\langle z^2 \rangle$ vs. t



O_2@(10,0)



O_2@(17,0)

Exponents of t for O_2

CNT	Stage III
(10,0)	1.52
(14,0)	1.60
(17,0)	1.18
(6,6)	1.54
(8,8)	1.80
(10,10)	1.11

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Why does anomalous diffusion occur?

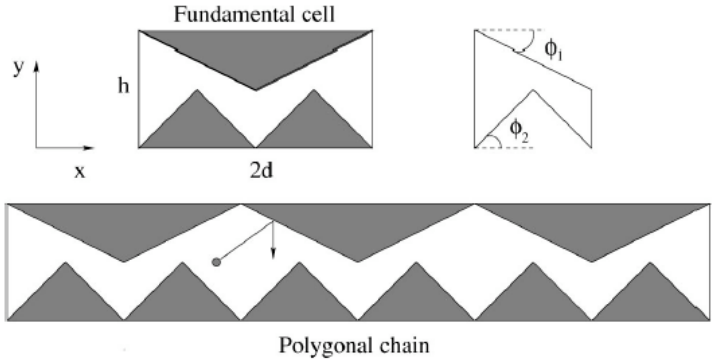


FIG. 1. Schematic representation of the polygonal billiard chain and its parameters. The fundamental cell $\mathcal{D}$ is also shown.

$$\left\langle (\Delta x)^2 \right\rangle = At^B$$

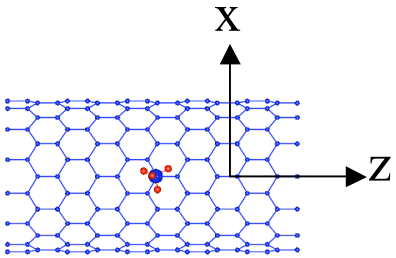
When $\phi_2 = \pi/4$, subdiffusion

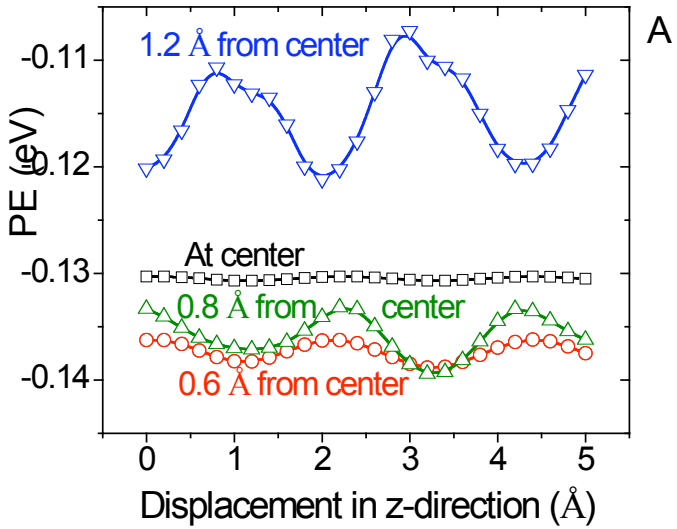
When $\phi_2 = \pi/3$, superdiffusion

D. Alonso, *Physical Review E* **66**, 066131 (2002)

Example: Polygonal billiards

Fluctuations in potential between a fluid molecule and the nanotube wall





Conclusions

- Molecular transport through carbon nanotube interiors changes with time due to changes in the nanotube–molecule and molecule–molecule interactions
- Molecules prefer to maximize their van der Waals interactions with the CNT wall during transport
- The transport of molecules can be accelerated in CNTs where periodic potential peaks act as physical obstacles

K.-H. Lee and S.B. Sinnott, *J. Phys. Chem. B* (2004)
K.-H. Lee and S.B. Sinnott, *Nano Letters* (in press)

Deflection and Mechanical Properties o f Carbon Nanotubes: Motivation

- Outstanding mechanical properties

  high Young's modulus, strength, and flexibility

- Desire to explore use in nanoelectromechanical systems (NEMS)

  e.g., nano-switches, nano-tweezers, etc.

- Hydrodynamics of nanotubes in fluids

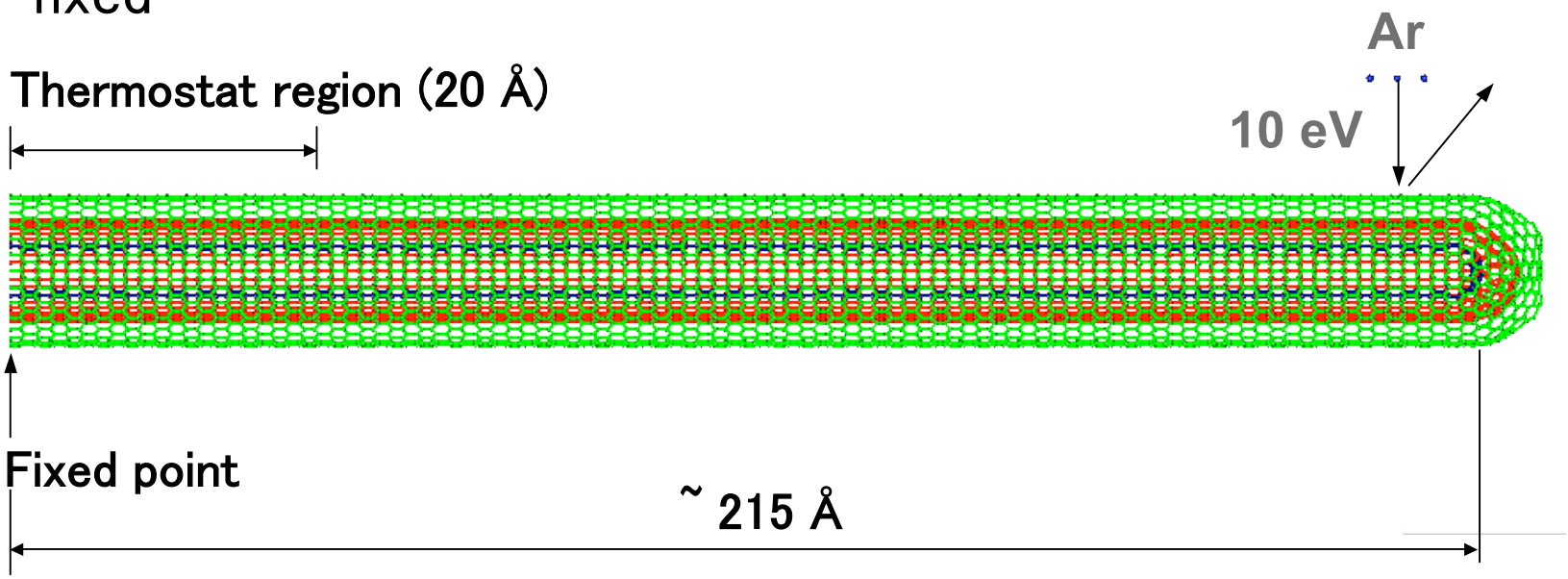
  e.g., nano-sensors, nano-valves in gas channels, etc.

- Study of the mechanical response to collision events and recovery of the nanotubes after release

- Examine the effect of filling nanotubes on their mechanical responses

System Setup

Bending motion of nanotubes by external impacts from incident Ar atoms while one end of the nanotube is firmly fixed



Ar collision on (28,0) SWNT, (19,0)@(28,0) DWNT, and (10,0)@(19,0)@(28,0) TWNT

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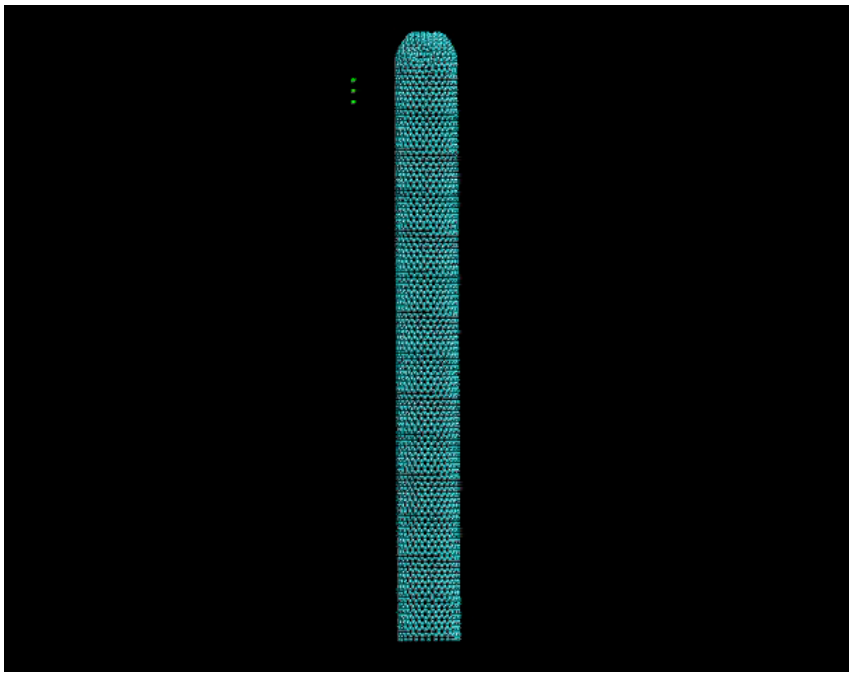
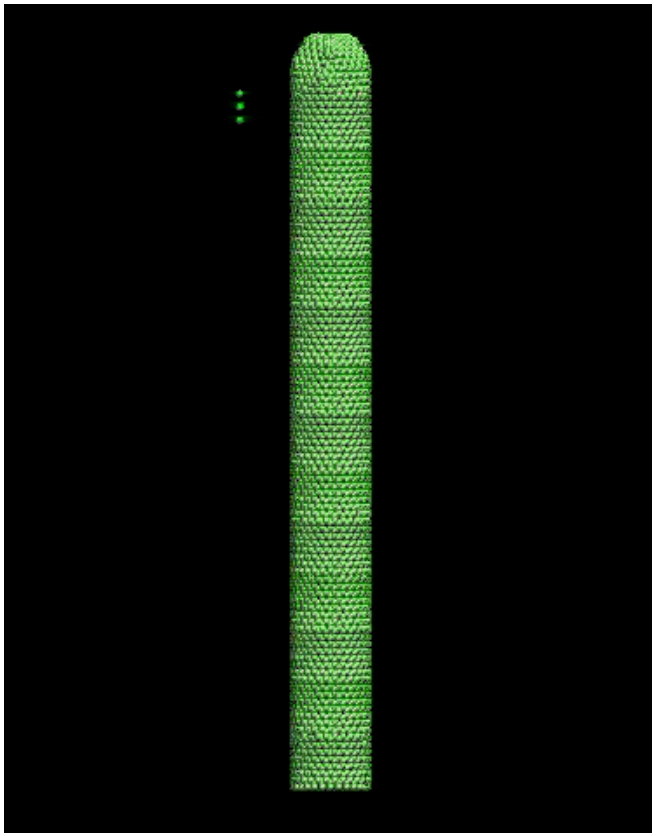
Motion of Nanotubes in Response to Collisions

20 ps: 9 Ar atoms colliding each collision event, repeated 10 times

120 ps: relaxation





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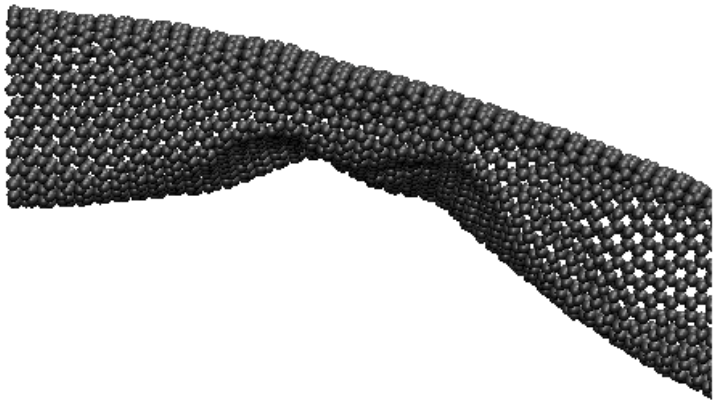
(28,0) SWNT

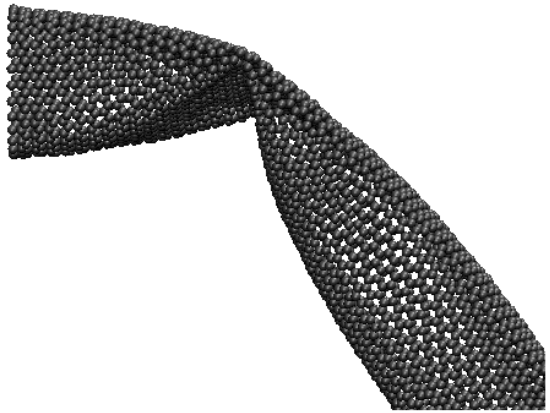
(10,0)@(19,0)@(28,0) TWNT

Description of Response

Deformation

1) After first collision
   - Confined to the nanotube tip
   - Energy absorption and delayed response
2) After multiple collisions
   - The nanotube bends, “rumples” form in the wall structure
3) After relaxation
   - SWNTs fold over following 10 collision events





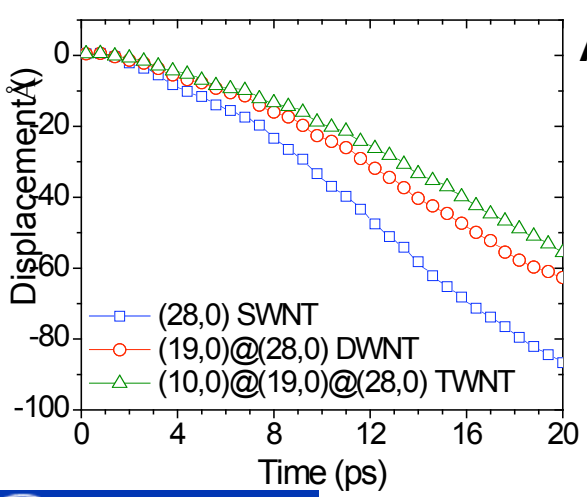
Description of Response

Displacement

1) After first collision
   - No displacement and delayed response
2) After multiple collisions
   - SWNT moves down faster than DWNT and TWNT

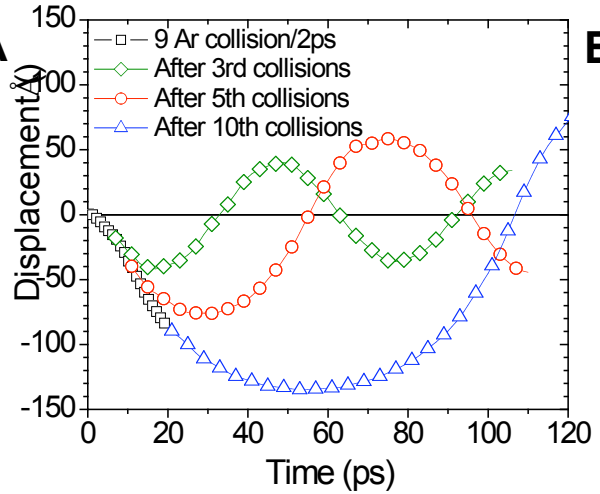
After relaxation

- Further displacement
- Displacement increases as the number of collision events increase
- Nanotube flexes in an oscillatory manner



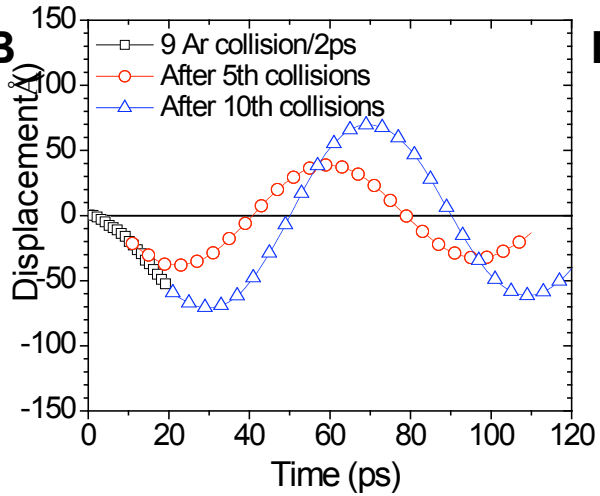
(28,0) SWNT

A



B

(10,0)@(19,0)@(28,0) TWNT



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Dependence of Oscillation on System Conditions

As the length of CNTs ↑, A_0 ↑, ϕ ↑, τ ↑, f ↓, and Q ↑
As the number of CNT walls ↑, A_0 ↓, and ϕ ↓
As the number of collision events ↑, A_0 ↑

$$A = -A_0 \cos(2\pi f t - \varphi) e^{-t/\tau}$$

A_0 = estimated amplitude at the initial state of the relaxation process
f = frequency
t = time in ps
ϕ = angular phase shift
t = relaxation time

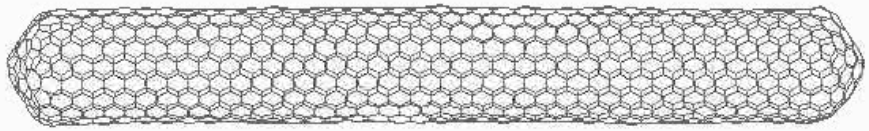
Conclusions

The frequency and amplitude of the oscillation of nanotubes in response to external fluid flow can be modulated by the number of impact events (momentum), the number of walls in the nanotube target, CNT aspect ratio, and amplitude damping by energy dissipation.

The simulation results agree well with continuum calculations except when the CNTs are relatively short or the momentum of the Ar is high.

Lee, Keblinski and Sinnott, *Nano Letters* (2005)

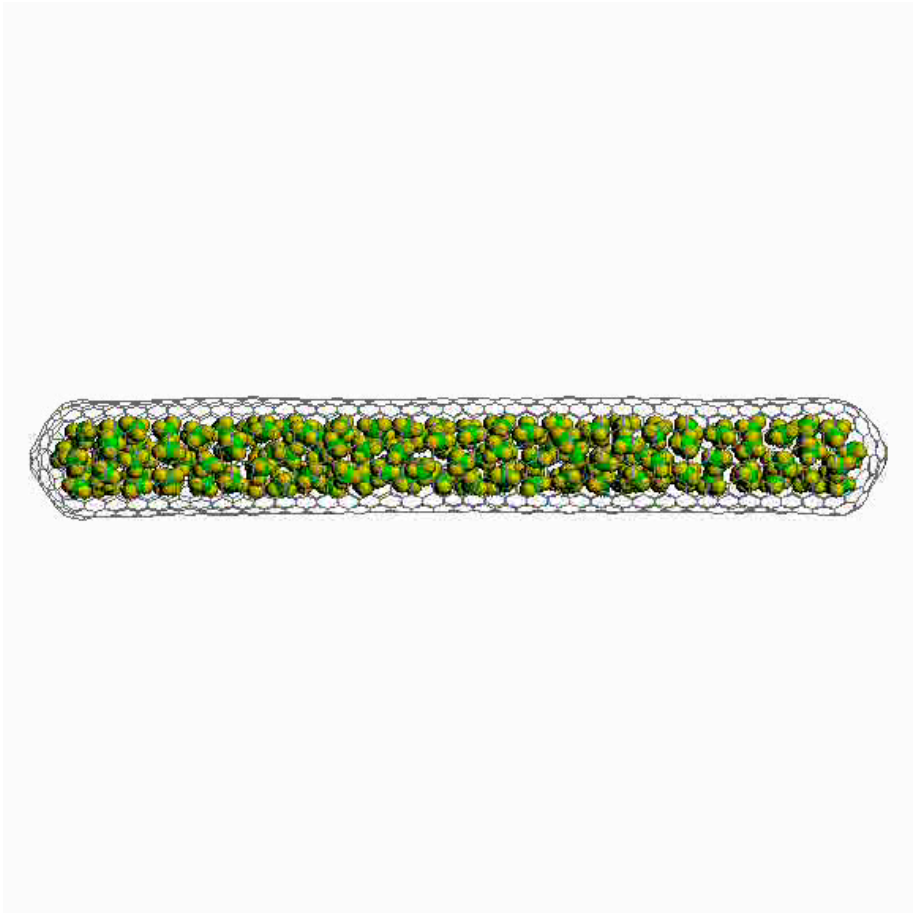
Compression of Empty Nanotubes



100 Å (10,10) single-walled nanotube

- Caps held rigid, thermostat applied to section of the nanotube near the ends, rest of the nanotube evolves with no additional constrains.
- Move one rigid end of the nanotube toward the other rigid end at a constant rate of 41 m/s and record forces
- Repeat trajectory 5 times
- Simulation performed at 300K

Compression of Methane Filled Nanotubes



- Same procedure for compression
- 100 Å (10,10) single-walled nanotube
- Simulation performed at 300 K
- Methane density is 0.292 g/cm^3

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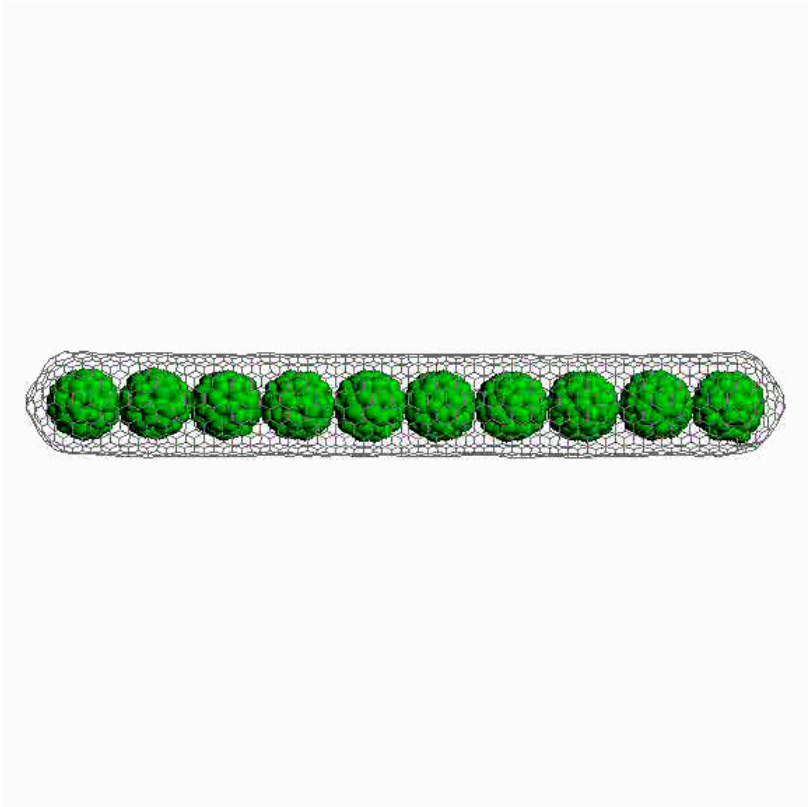
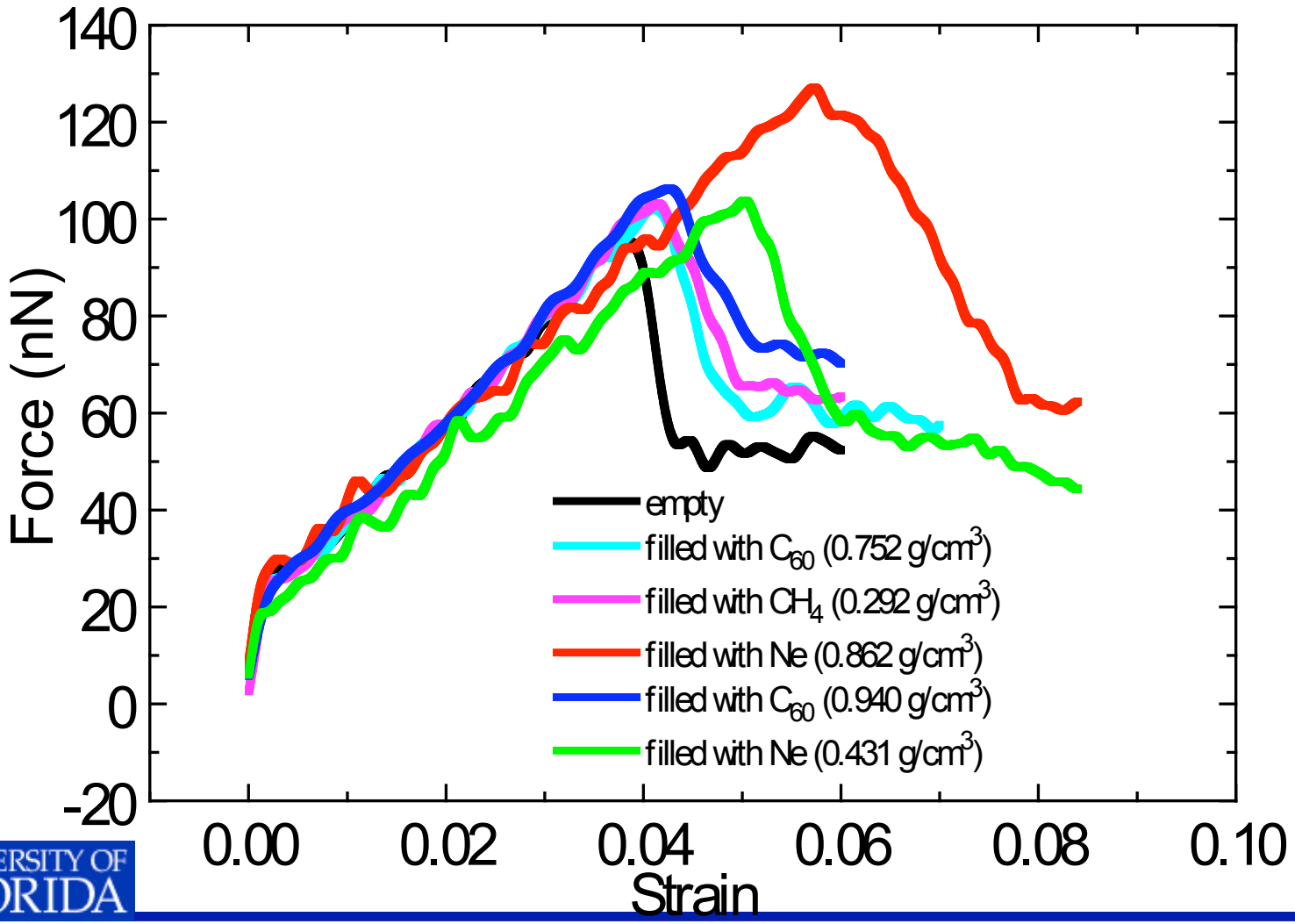
Compression of Fullerene Filled Nanotube - High Density



- Same procedure for compression
- 100 Å (10,10) single-walled nanotube
- Simulation performed at 300 K
- 10 C_{60} molecules (density is is 0.940 g/cm^3)

Force Curves for 100 Å Tubes



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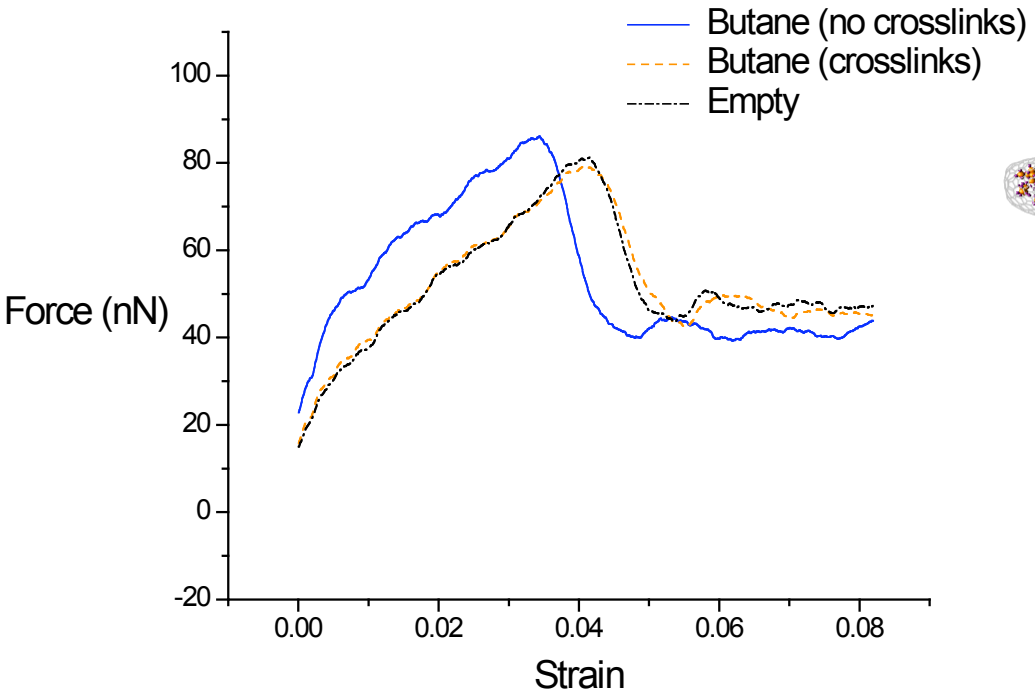
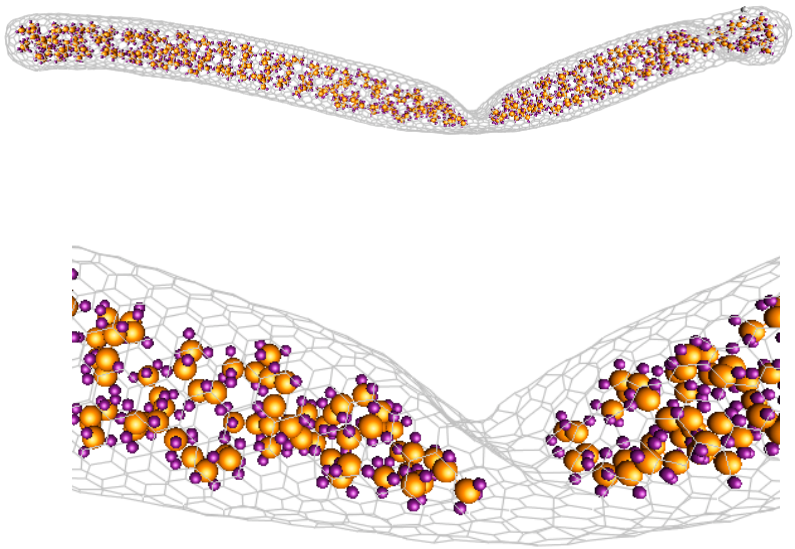
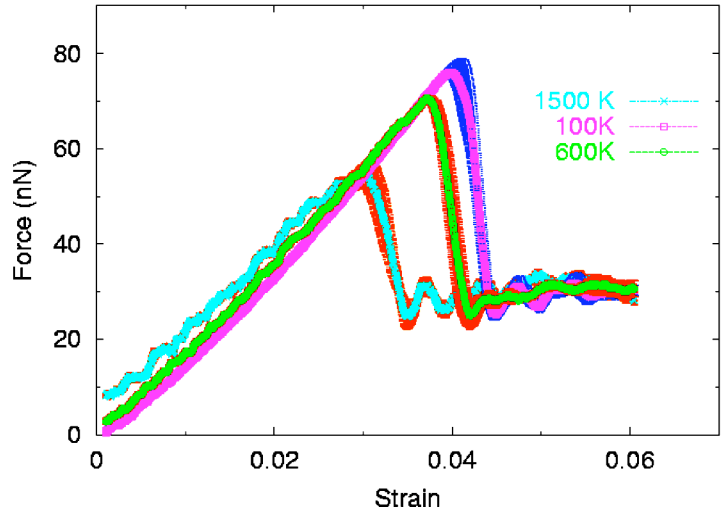
Force Curves for 200 Å Tubes Filled with n-Butane

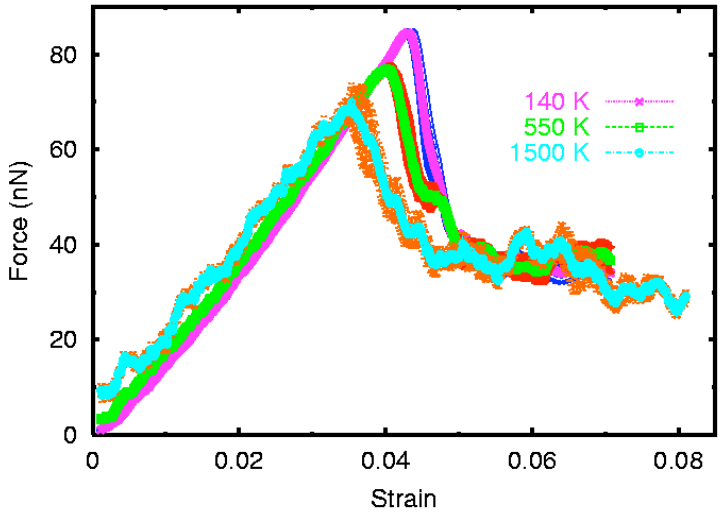




Effect of Temperature on Compression



Empty



Filled with C_{60}

Density = 0.752 g/cm^3

Conclusions

- The simulations predict that filled nanotubes have a slightly higher buckling force than empty nanotubes but have the same stiffness (Young's modulus) if the molecules are spherical. If the molecules are flexible, some yielding behavior is predicted.
- Filling the nanotubes decreases the dependence of the buckling force on temperature

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Trotter et al., *J. Nanosci. Nanotechnol.* (in press)
Ni, Sinnott, Mikulski, Harrison, *Phys. Rev. Lett.* (2002)