Structural rigidity and thermal conductance of nanostructured carbon: nanotubes and foams

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14. ABSTRACT
Structural rigidity, phonon modes, and thermal conductivity of carbon nanostructures: nanotubes and graphitic foam.

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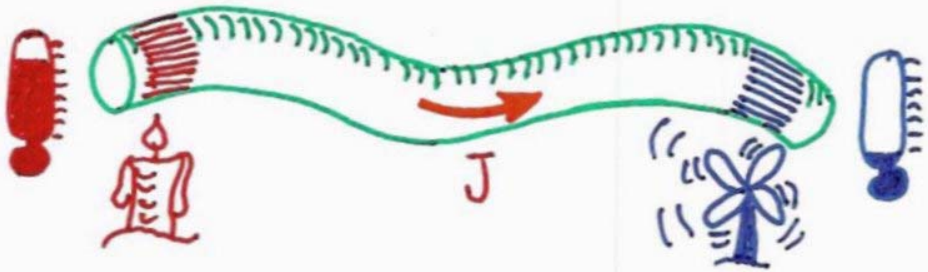
Outline

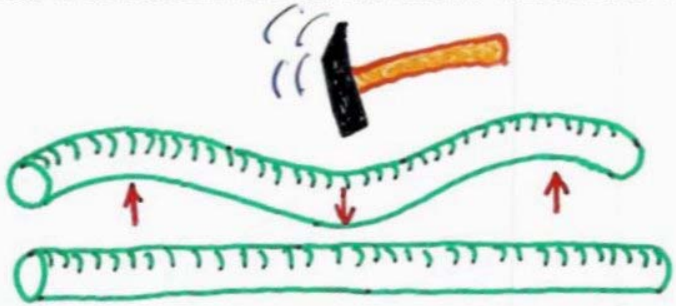
- **Motivation**
- **Computational Techniques**
- **Thermal Conductivity in Nanotubes**
  - Approaches and Pitfalls
  - Temperature Dependent Thermal Conductivity
  - Effect of Inter-Wall Interactions on Thermal Conductivity
  - Effect of Isotope Mixture on Thermal Conductivity
- **Low-Frequency Phonon Modes of Nanotubes**
  - Equilibrium Structure of Multi-Wall Tubes and Ropes
  - Soft Phonon Modes of Single-Wall Tubes
  - Libration and Rotation Dynamics of Interacting Tubes
  - Dynamics of Twistons and Orientational Melting
- **Hybrid Graphitic Foam**
  - Equilibrium Structure
  - Elastic Properties
  - Electronic Structure
- **Summary and Conclusions**

Motivation

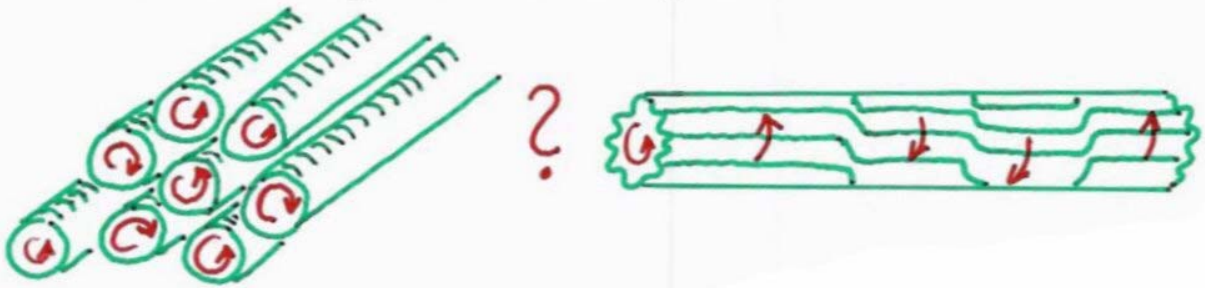
- Can Nanotubes **conduct heat** well?



- Which **Phonon Modes** limit Thermal Conduction?



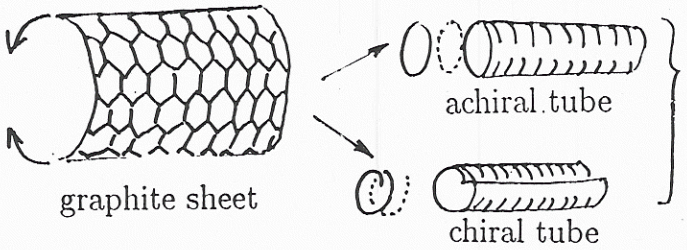
- Can interacting **Nanotubes Spin and Twist**?

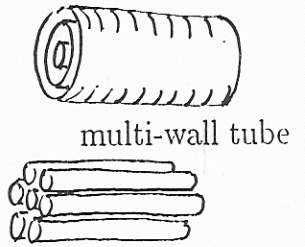


- Is nanostructured carbon foam the ultimate structural and thermal material?

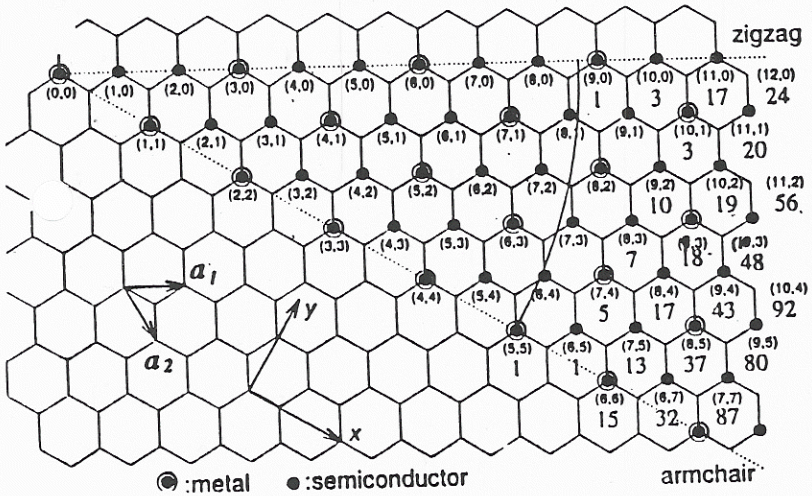
Morphology of carbon nanotubes

- **Structure of carbon nanotubes:**





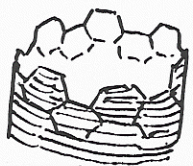
- **Classification of carbon nanotubes:**



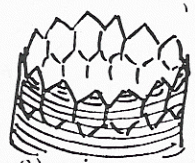
$\vec{R} = m\vec{a}_1 + n\vec{a}_2$

defines uniquely the (m, n) nanotube

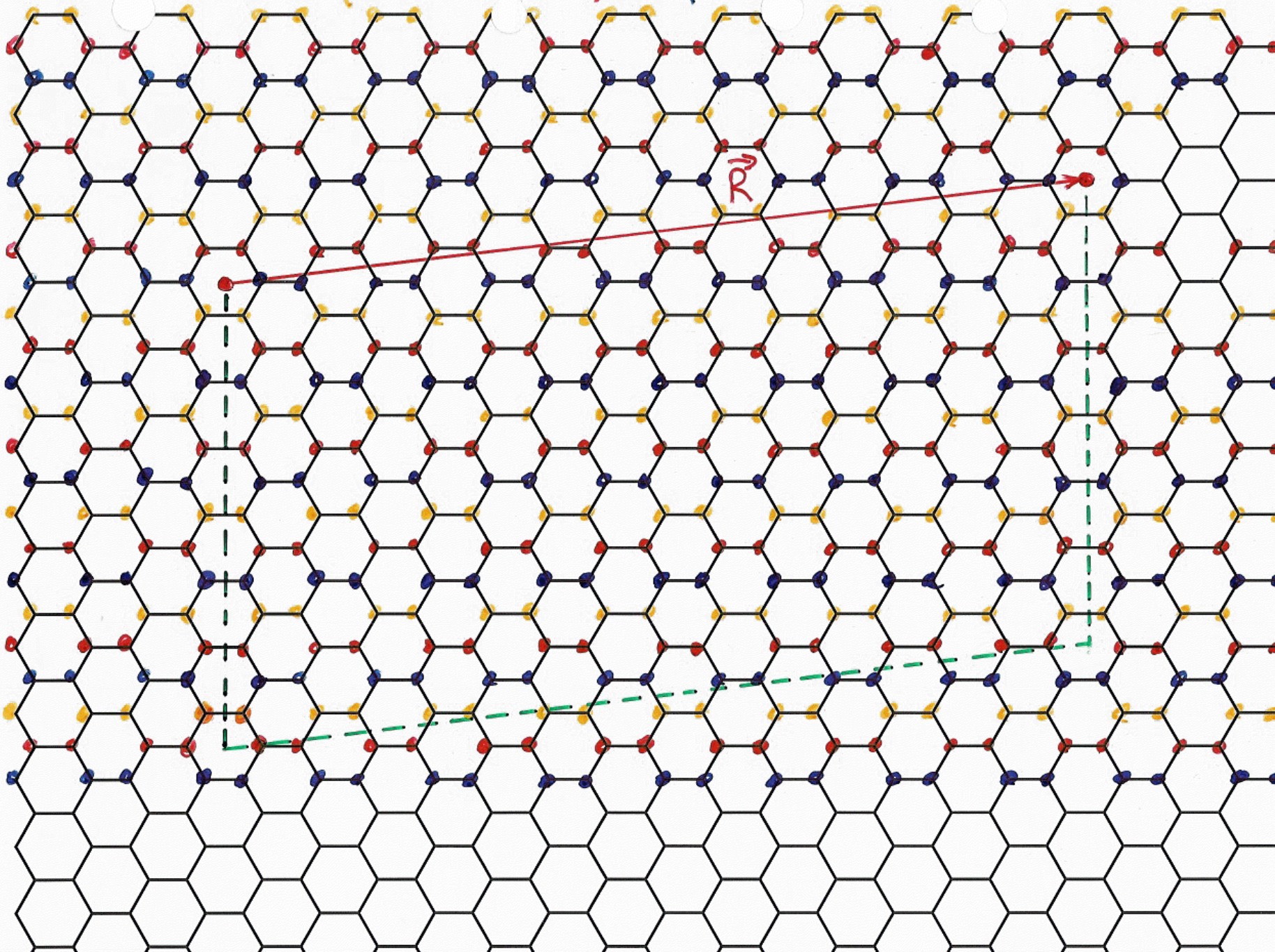
- **Types of achiral nanotubes:**



(n, n): armchair nanotubes



$(n, 0)$: zig-zag nanotubes


φ=0
φ=+2π/3
φ=−2π/3
R

Computational Techniques

- **Total Energy Calculations**
  - *Ab initio* Density Functional Formalism
    - **Plane-wave code** with energy cutoff of 50 Rydbergs
    - Soft nonlocal pseudopotentials and Ceperley-Alder **exchange-correlation** potential
    - 200,000 plane waves in the basis set
  - Parametrized Linear Combination of Atomic Orbitals (LCAO) Formalism
    - Parametrization based on *ab initio* Density Functional results
    - **Very fine k-points mesh** for the inter-tube interaction
    - $O(N)$ technique for **very large systems**
    - Ideally suitable for **massively parallel computation**
  - Tersoff Potential

- **Thermodynamics: Monte Carlo simulations**

- **Time-dependent processes: Molecular dynamics simulations**

- **Transport: Landauer-Büttiker Formalism**
  - Conductance $G(E)$ evaluated by using

$$G(E) = \frac{2e^2}{h} T(E) = \frac{1}{12.9\ \mathrm{k}\Omega} T(E)$$

Thermal Conductivity in Nanotubes

VOLUME 84, NUMBER 20 PHYSICAL REVIEW LETTERS 15 MAY 2000

Unusually High Thermal Conductivity of Carbon Nanotubes

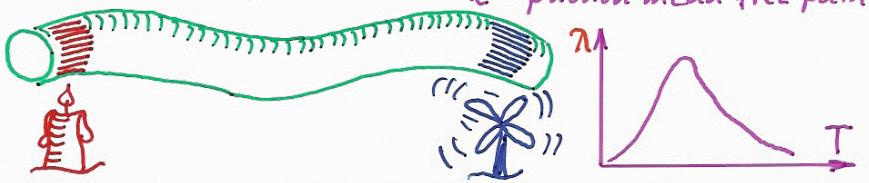
Savas Berber, Young-Kyun Kwon,* and David Tománek
Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116
(Received 23 February 2000)

$$\frac{1}{A}\frac{dQ}{dt} = -\lambda \frac{dT}{dz}$$

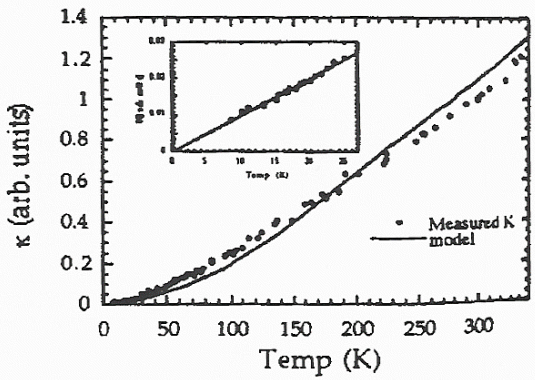
λ = thermal conductivity

$$\lambda \propto C\, v\, l$$

C = heat capacity/volume
v = speed of sound
l = phonon mean free path



- **Experimental Observation for a Nanotube "Mat"**



J. Hone, M. Whitney, A. Zettl, Synthetic Metals **103**, *2498 (1999)*

– Raw data ($T = 300$ K): $\lambda \approx 0.7$ W/m·K

– Extrapolated data ($T = 300$ K): $\lambda \approx 1,800 - 6,000$ W/m·K

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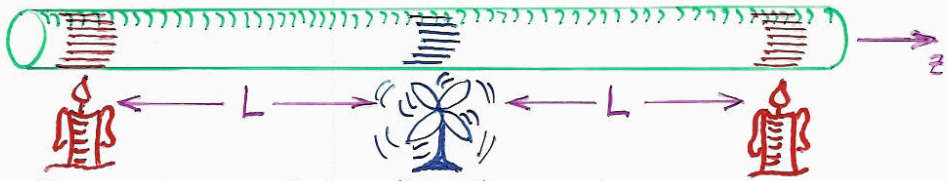
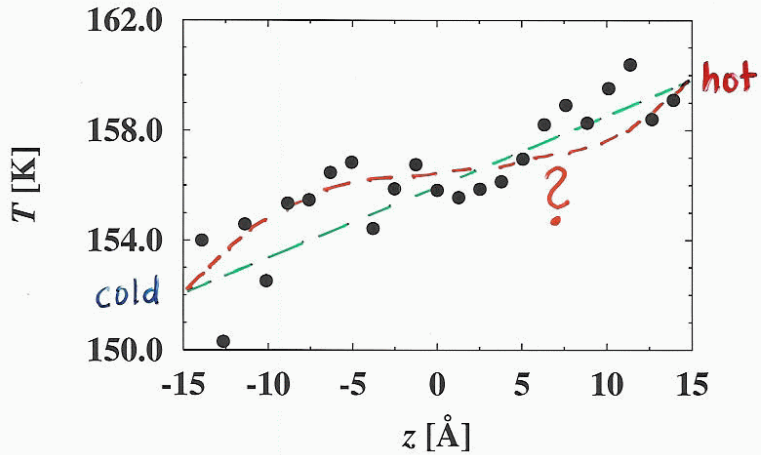
▶ Approaches and Pitfalls

- **Direct Molecular Dynamics Approach**



– Temperature profile in a $(10, 10)$ nanotube



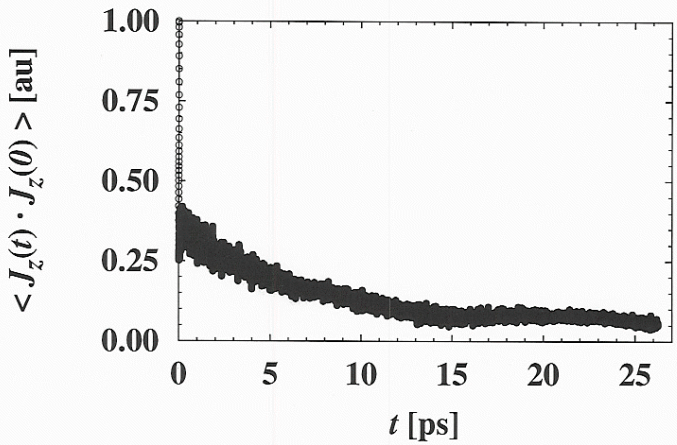
- Pitfalls of Direct Molecular Dynamics:
  - $L << l \approx 100$ nm
    $\Longrightarrow$ velocity rescaling mimics "grain boundary", limits l
  - Large statistical uncertainty
  - $T(z)$ not linear
  - $dT/dz >> 0 \Longrightarrow$ spatial variation of thermal conductivity

- **Equilibrium Molecular Dynamics Approach**
  - Green-Kubo formula for the Navier-Stokes thermal conductivity:

$$\lambda = \frac{1}{3Vk_BT^2}\int_0^\infty < \mathbf{J}(t)\cdot\mathbf{J}(0) > dt$$

$$\mathbf{J}(t) = \frac{d}{dt}\sum_i \mathbf{r}_i\Delta e_i = \sum_i \mathbf{v}_i\Delta e_i - \sum_i \sum_{j(\neq i)} \mathbf{r}_{ij}(\mathbf{f}_{ij}\cdot\mathbf{v}_i)$$

  - Heat flux autocorreltation function in a $(10, 10)$ nanotube



- Pitfalls of Equilibrium Molecular Dynamics:
  - Slow convergence
  - Extensive ensemble averaging crucial
  - Autocorrelation function requires large data storage

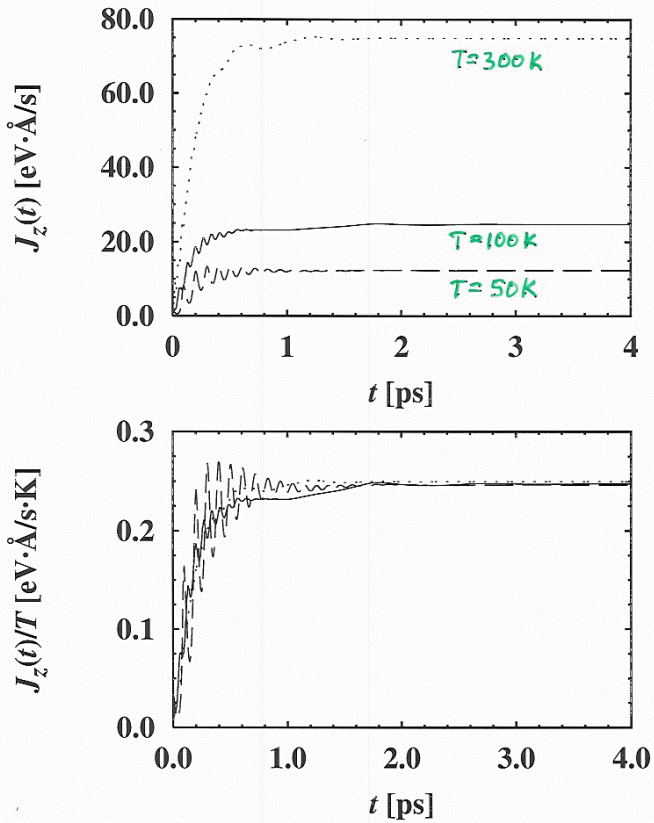
- **Non-Equilibrium Molecular Dynamics Approach**

$$\lambda = \lim_{\mathbf{F}_e \to 0} \tilde{\lambda}(\mathbf{F}_e) \ , \quad \tilde{\lambda}(\mathbf{F}_e) \equiv \lim_{t \to \infty} \frac{< J_z(\mathbf{F}_e, t) >}{F_e T V}$$

F_e = thermal force, α = Nosé-Hoover thermostat multiplier

$$\Delta \mathbf{F}_i = \Delta e_i \mathbf{F}_e - \sum_{j(\neq i)} \mathbf{f}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{F}_e) + \frac{1}{N} \sum_j \sum_{k(\neq j)} \mathbf{f}_{jk}(\mathbf{r}_{jk} \cdot \mathbf{F}_e) - \alpha \mathbf{p}_i$$

– Axial heat flux in a $(10, 10)$ nanotube for $F_e = 0.2$ Å^{-1}



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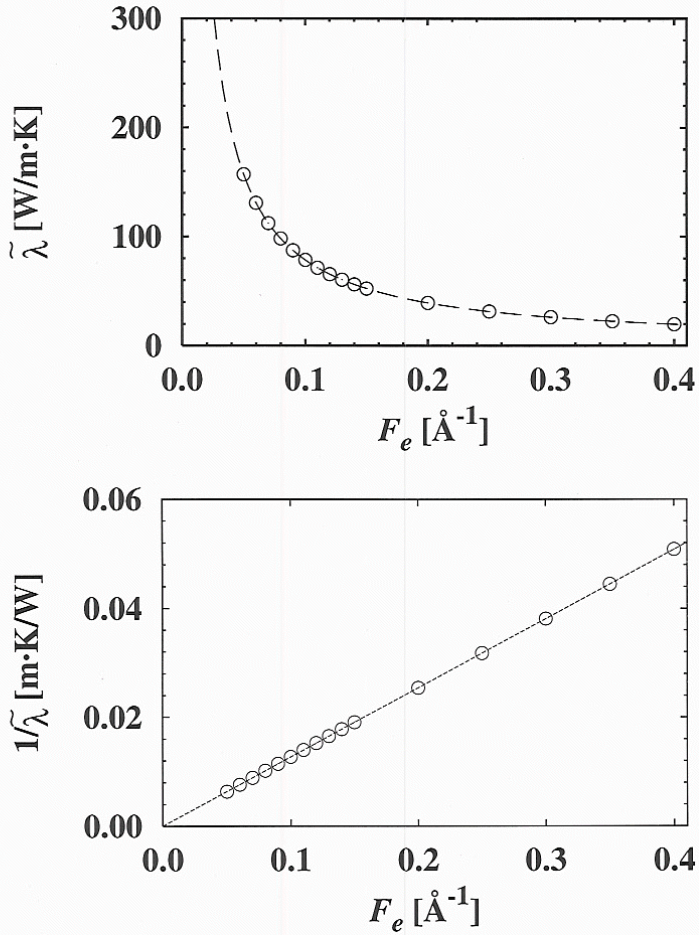
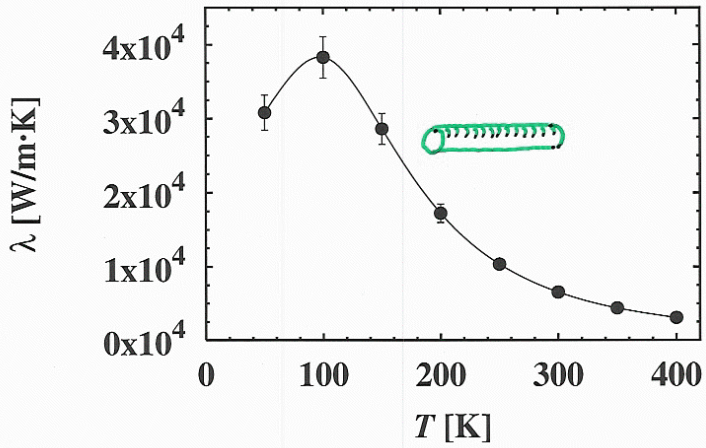
– Heat transport dependence on F_e



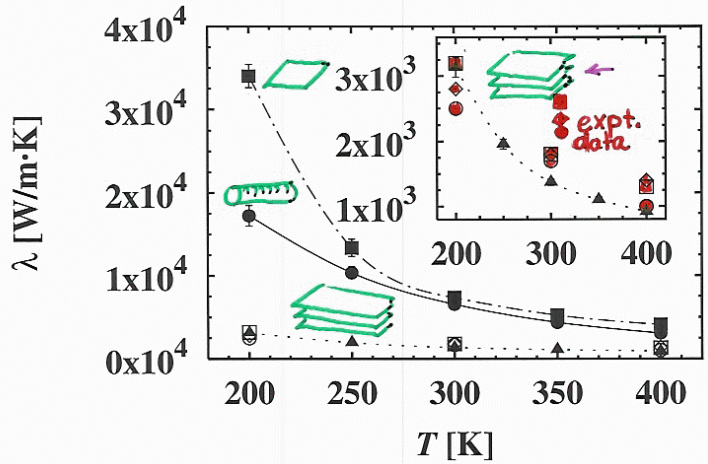
- Pitfalls of Non-Equilibrium Molecular Dynamics:
  - $F_e \to 0$ limit requires careful evaluation
  - Careful coupling to thermostat required

Temperature Dependent Thermal Conductivity

- Thermal conductivity of an isolated (10,10) carbon nanotube

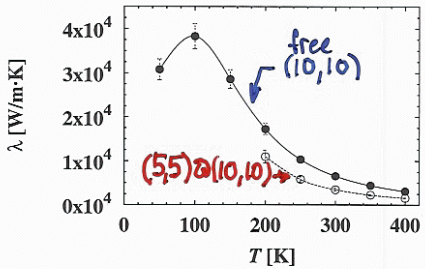


- Thermal conductivity of various carbon allotropes

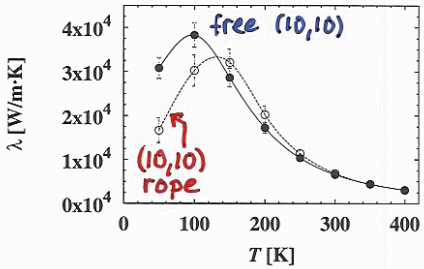


Effect of Inter-Wall Interactions on Thermal Conductivity

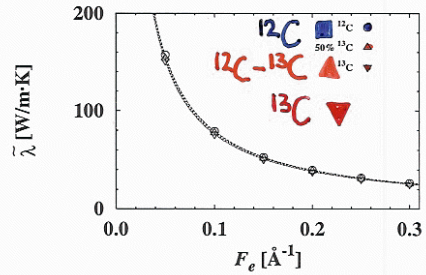
- Thermal conductivity of a (5,5)@(10,10) double-wall carbon nanotube



- Thermal conductivity of bundled (10,10) nanotubes



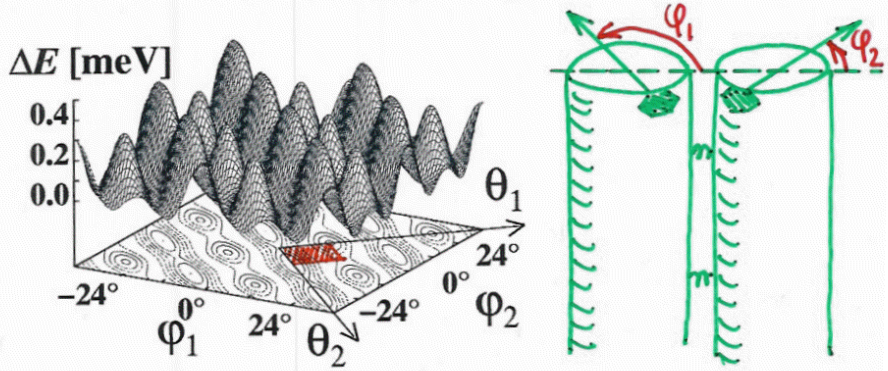
Effect of Isotope Mixture on Thermal Conductivity



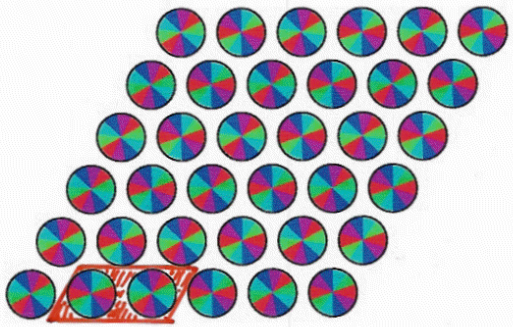
T=300 K
free (10,10)

Low-Frequency Phonon Modes of Nanotubes

- **Equilibrium Structure of Bundled and Multi-Wall Tubes**
  - **Interaction between neighboring (10,10) tubes**



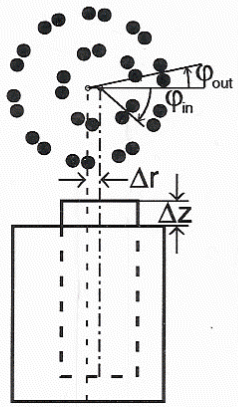
  - **Equilibrium structure of bundled rigid (10,10) tubes**

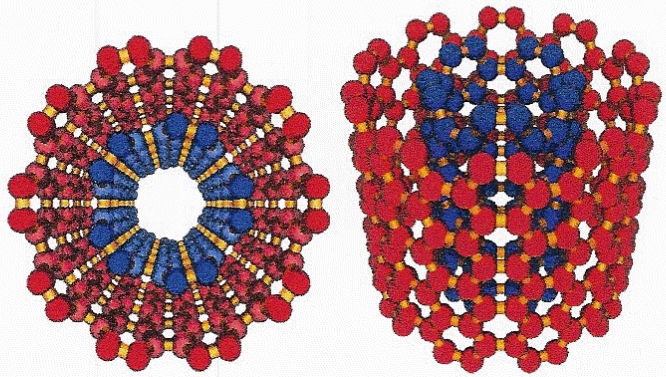


– Two-dimensional oblique lattice.

- **(5,5)@(10,10) Double-Wall Tube Geometry**

[*Electronic and structural properties of multiwall carbon nanotubes*, Young-Kyun Kwon and David Tománek, Phys. Rev. B **58**, R16001 (1998)]



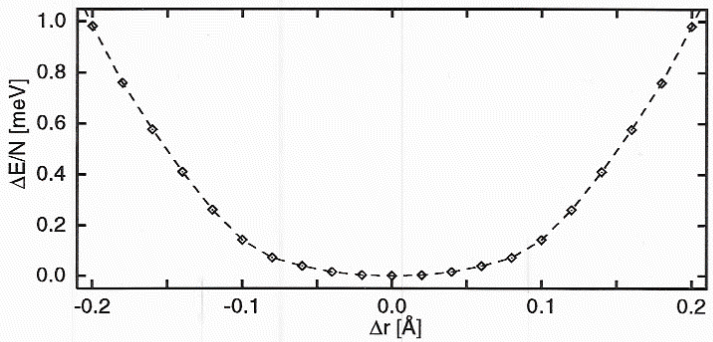


(5,5)@(10,10) Double-Wall Tube

$\Delta r = 0 \qquad \Delta z = 0$

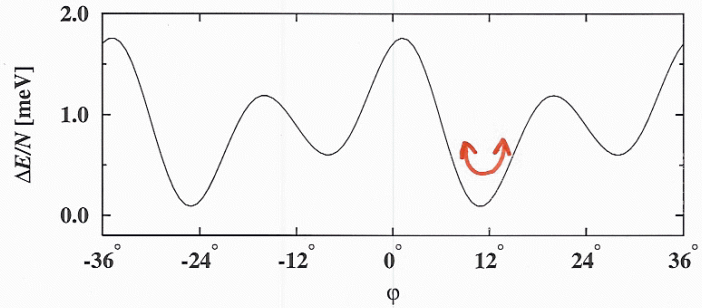
$\varphi_{in} = 0° \qquad \varphi_{out} = 0°$

– Dependence of Energy on Off-Axis Displacement Δr



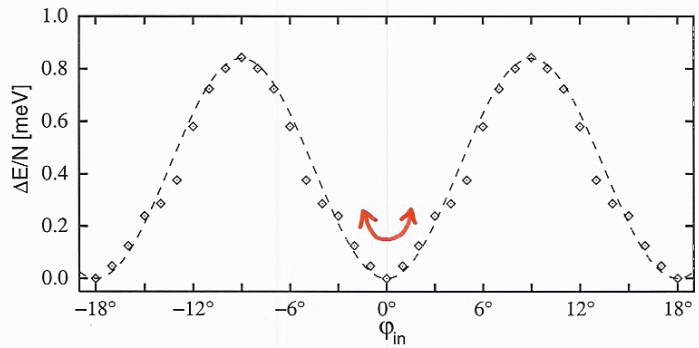
▶ Libration and Rotation Dynamics

- **(10,10) tube "ropes"** [*PRB* **58**, *R13314 (1998)*]



  - Librational motion at $T \leq T_{OM}$
  - Libration frequency $\nu \approx 12 - 60$ cm^{-1}
  - Experimental observation (W. Holmes *et al.*):
    - Infrared modes at $\nu \approx 15, 22, 40$ cm^{-1}
    - These modes disappear at $T \approx 30 - 180$ K

- **(5,5)@(10,10) double-wall tube** [*PRB* **58**, *R16001 (1998)*]



  - Librational motion at $T \leq T_{OM}$
  - Libration frequency $\nu \approx 33$ cm^{-1}

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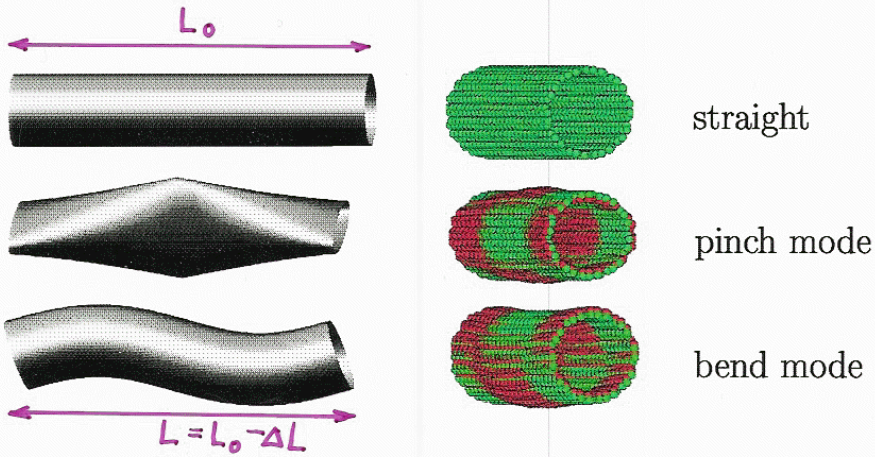
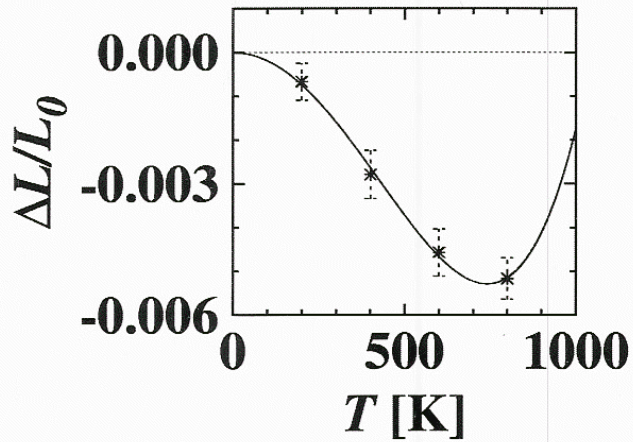
▶ Soft Phonon Modes of Single-Wall Tubes



▶ Thermal Expansion of Single-Wall Tubes



$\Longrightarrow$ Thermal contraction dominates over bond expansion at low temperatures

▶ Thermodynamics of Orientational Melting

VOLUME 84, NUMBER 7 PHYSICAL REVIEW LETTERS 14 FEBRUARY 2000

Orientational Melting in Carbon Nanotube Ropes

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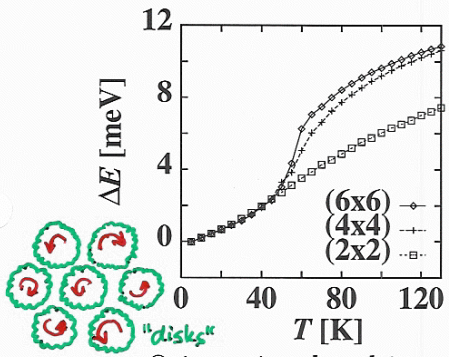
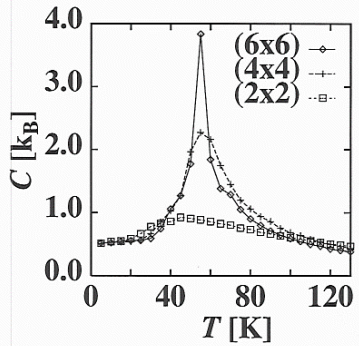
Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116
(Received 24 August 1999)

- **Floppy tubes** – unrealistic model
  (Torsionally decoupled "layers" within tube)

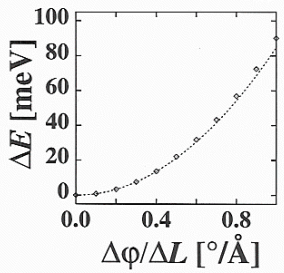




  – Orientational melting at $T_{OM} \approx 55$ K
  – Librational motion for $T \lesssim T_{OM}$
  – Free rotation at $T \gtrsim T_{OM}$

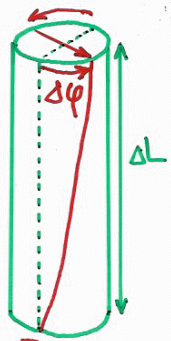
- **Rigid tubes** – realistic model
  (torsional coupling between "layers" within tube)

  – Torsion energy



$$\Delta E_{tor,at}(\Delta\varphi/\Delta L) \approx \kappa \left(\frac{\Delta\varphi}{\Delta L}\right)^2$$

$$\Delta E_{tor,tot}(\Delta\varphi/\Delta L) \sim \frac{1}{\Delta L} \to 0 \quad \text{for } \Delta L \to \infty$$



~25nm orientational dislocation = twiston

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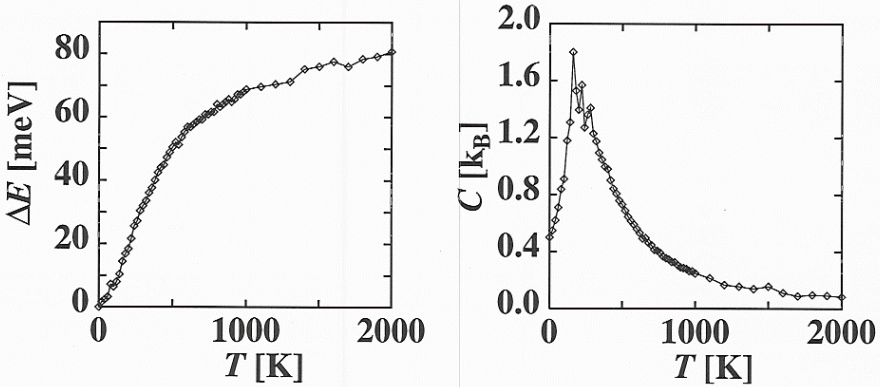
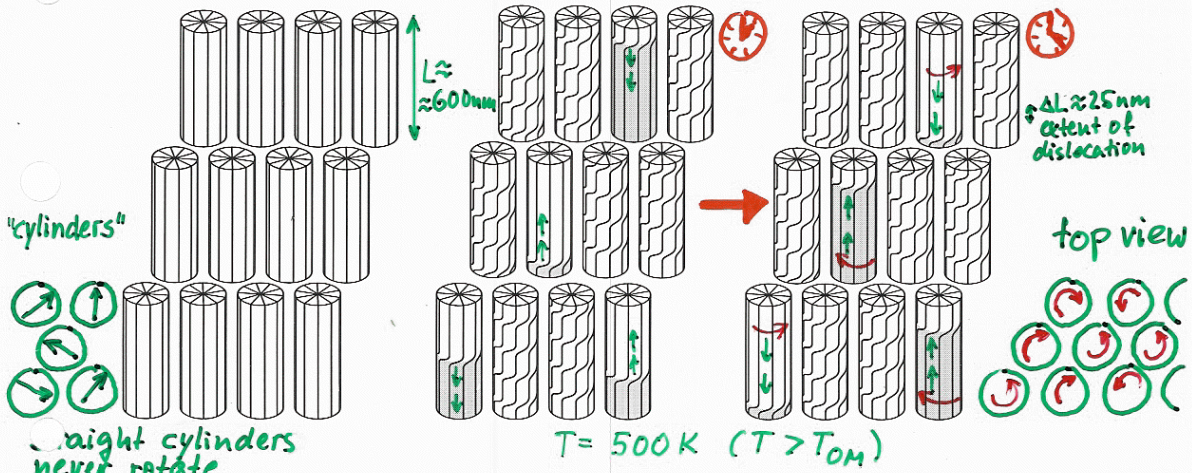
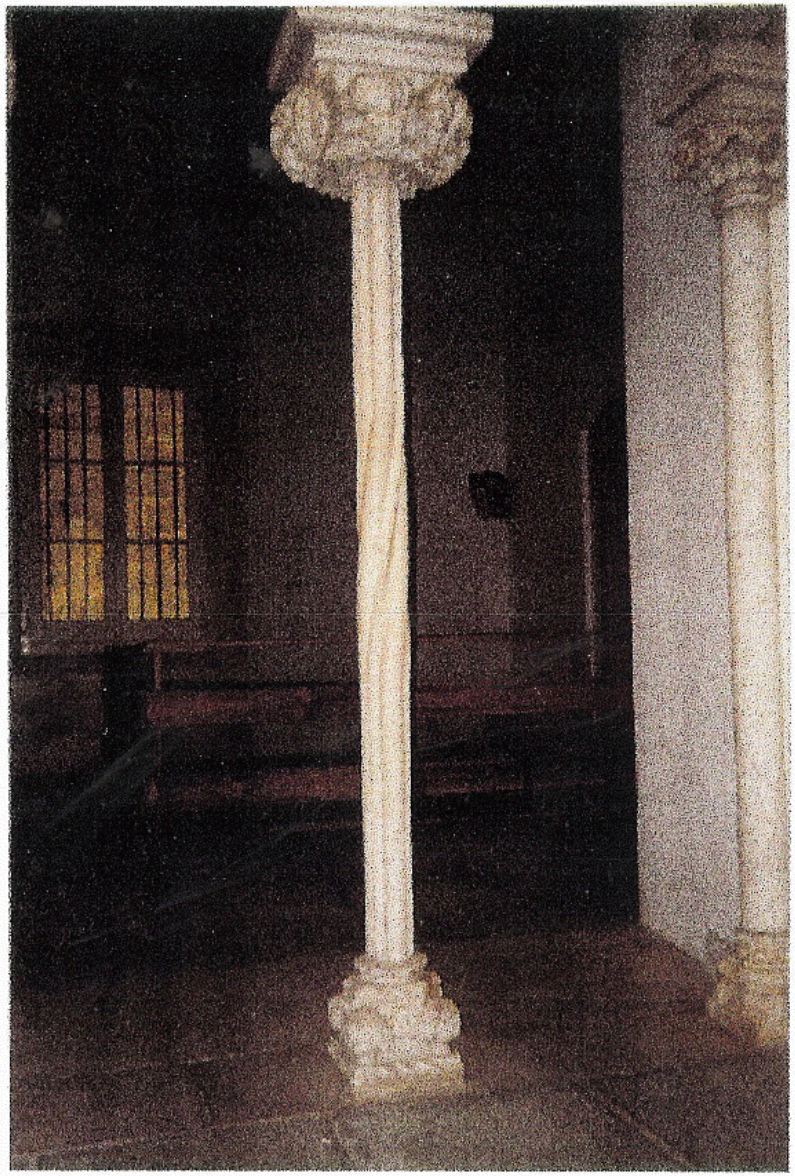
∗ Torsion is thermally activated during synthesis

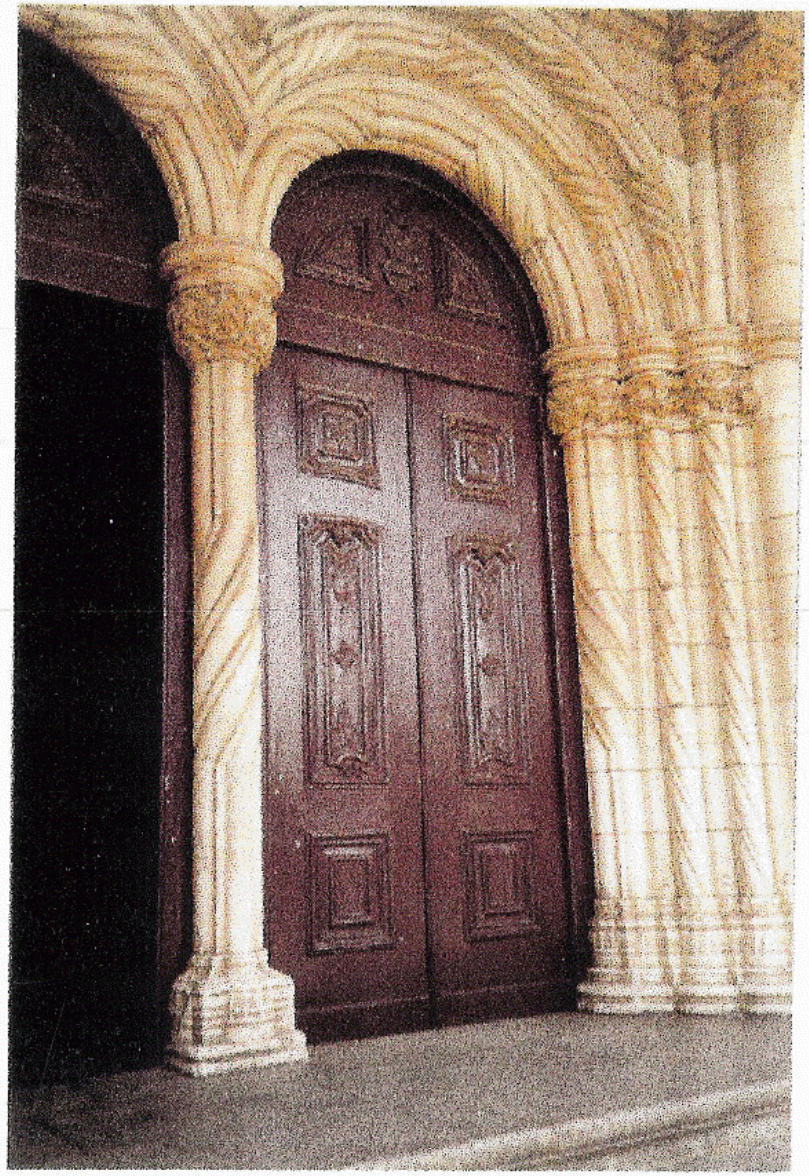
– Orientational melting





* Orientational disclocations, introduced during synthesis, are pinned for $T \lesssim T_{OM}$.
* Axial motion of orientational dislocations corresponds to tube rotation.
* Orientational melting, described by free "diffusion" of orientational dislocations along tubes, occurs for $T \gtrsim T_{OM} \approx 100$ K.
* Orientational dislocations (twistons) are scattering centers for electrons → strong effect on transport (1D system!).

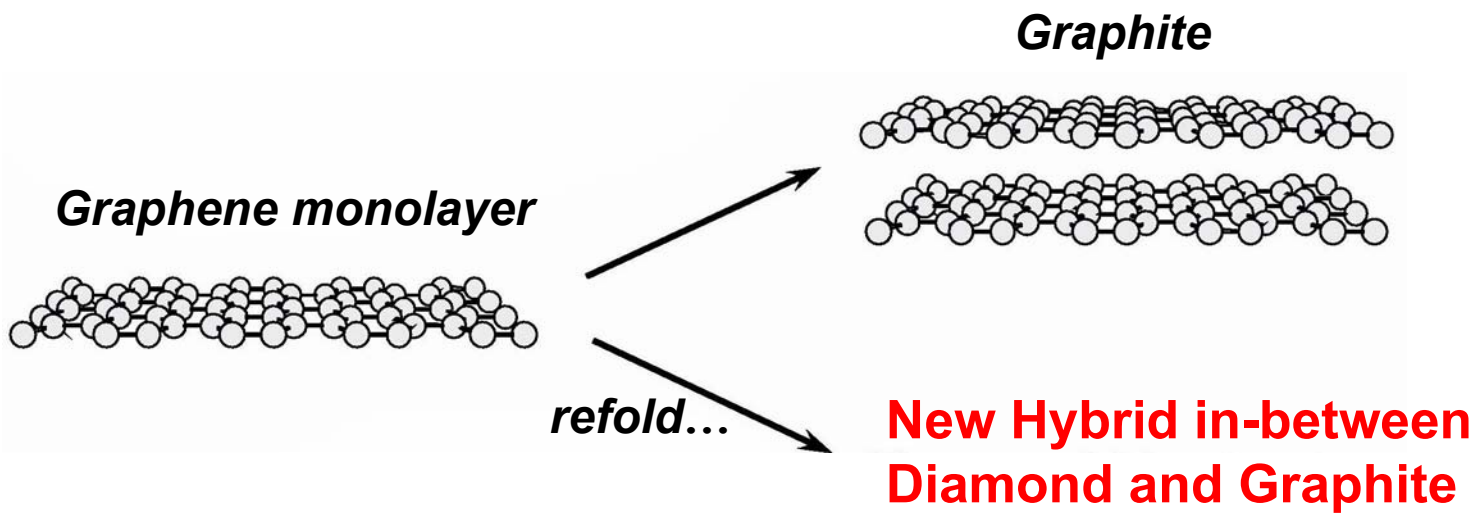




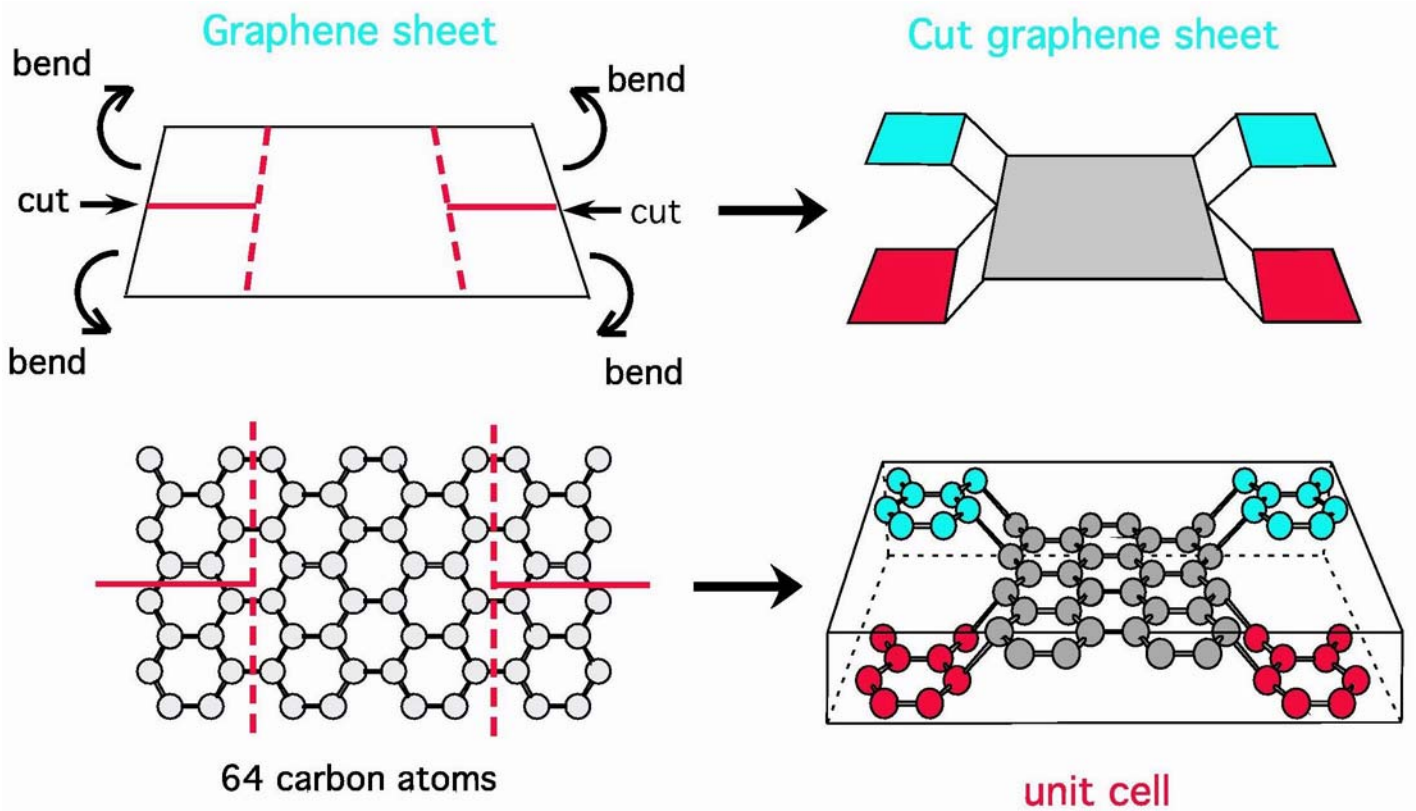
Twistons of Évora (Portugal)

Morphology of Hybrid Graphitic Foam

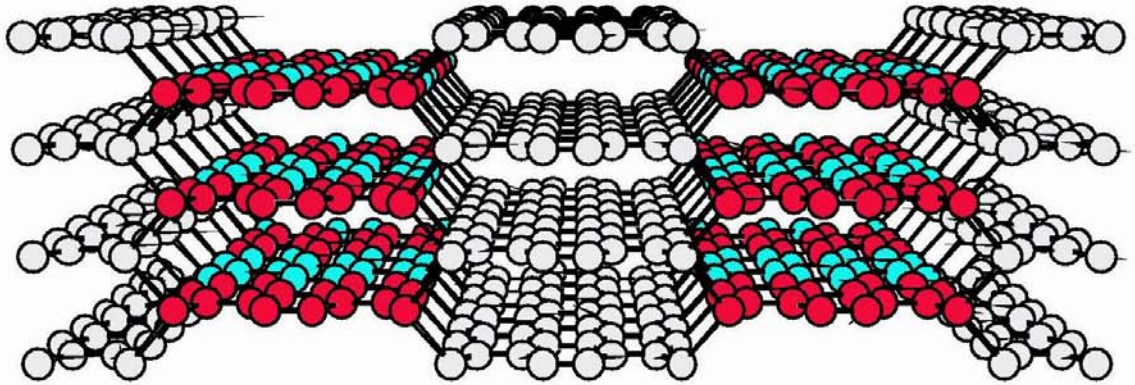
- **Relationship to graphite**

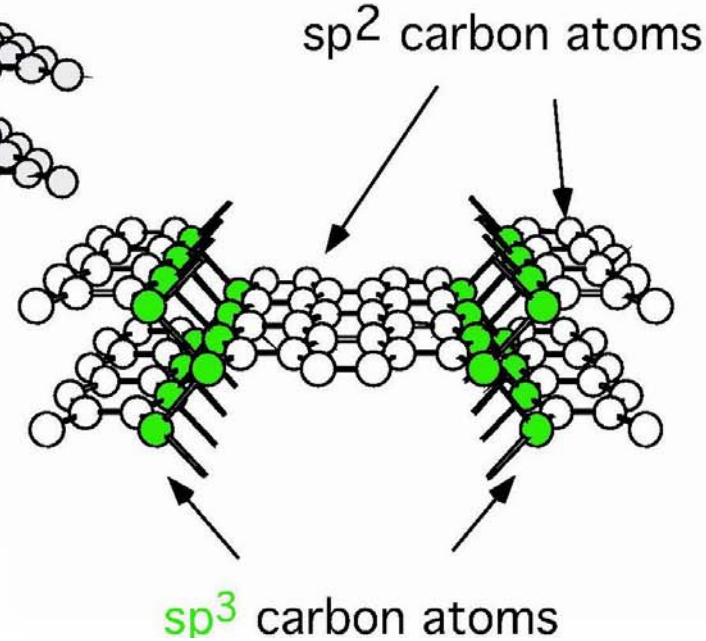


•**Folding Process**



•**Hybrid Graphitic Foam**





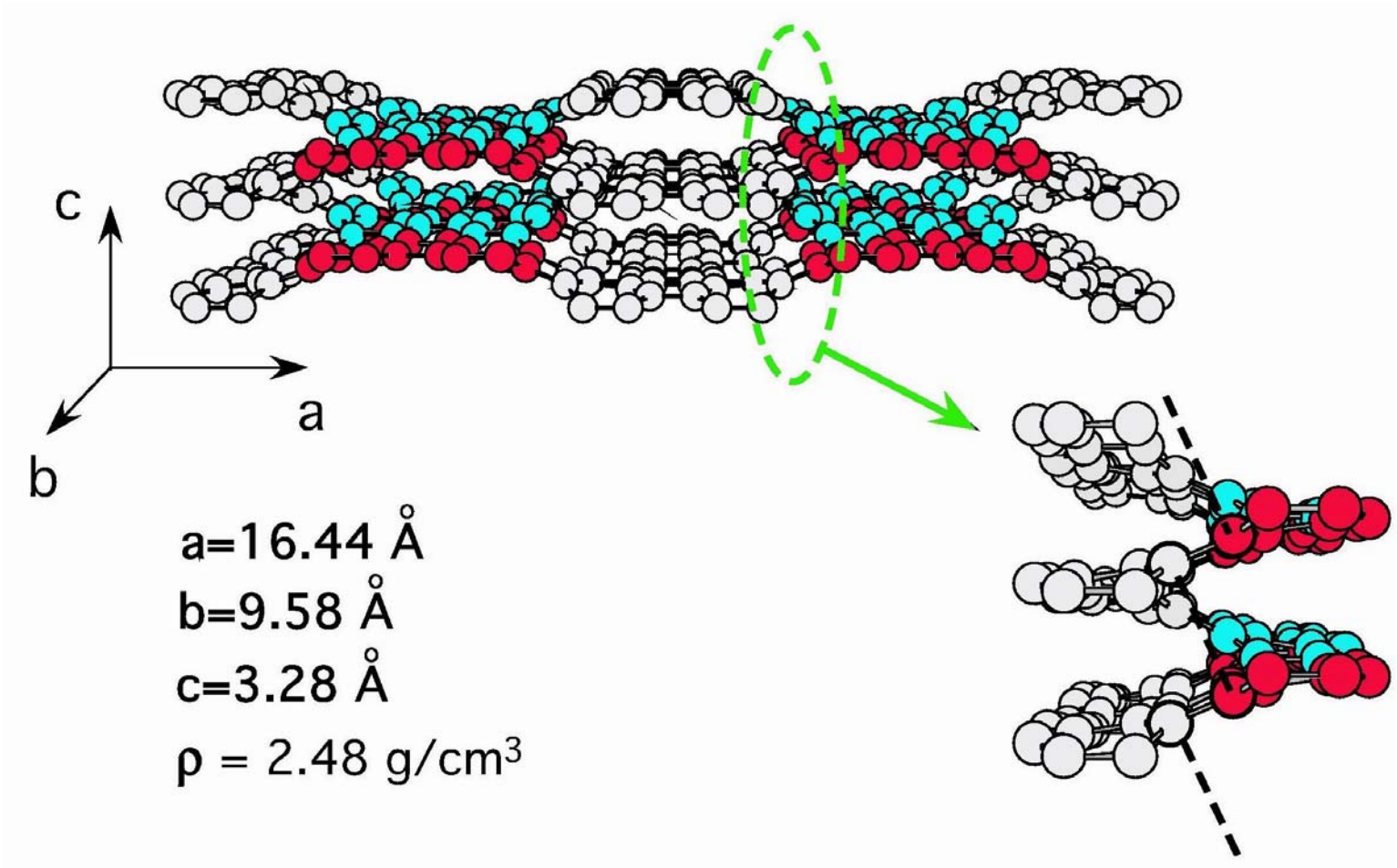
Terrace size $\rightarrow \infty$***: graphite***

Terrace size $\rightarrow 0$***: diamond***

Present study:

- ***Optimized structure***
- ***Elastic properties***
- ***Electronic structure***

Optimized Structure



Elastic Properties

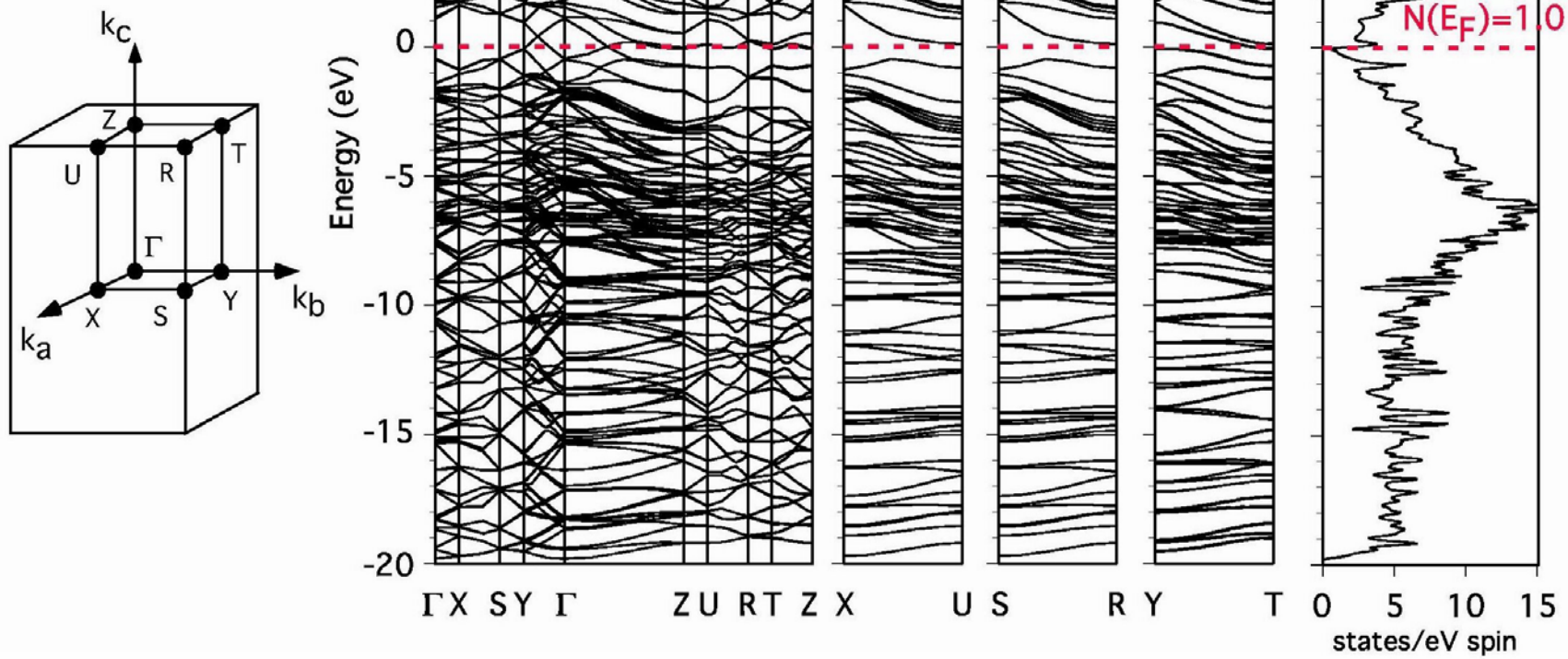
	New graphitic foam	Graphite	Diamond
ρ	2.48 g/cm^3	2.27 g/cm^3	3.51 g/cm^3
C_{11} (along a axis)	9.02 Mbar	12.3 Mbar	11.29 Mbar
C_{22} (along b axis)	9.42 Mbar		
C_{33} (along c axis)	0.816 Mbar	0.34 Mbar	
Bulk modulus	0.792 Mbar	0.326 Mbar	4.69 Mbar

Electronic Structure

Brillouin Zone

Band Structure

Density of States



Graphitic foam is metallic: $N(E_F)$=1.0 states/eV/spin

Summary and Conclusions

- We studied the structural rigidity, phonon modes, and thermal conductivity of **carbon nanostructures**: nanotubes and graphitic foam.

- We found that
  - The unusually **high thermal conductance** of nanotubes results from the large phonon mean free path.
  - Weak inter-tube coupling results in a very **soft librational motion**.
  - **Orientational dislocations** are frozen in during the synthesis of interacting nanotubes. Relatively free diffusion motion of orientational dislocations occurs for $T \gtrsim T_{OM} \approx 160$ K, marking the onset of **orientational melting**.
  - **Hybrid graphitic foam** offers an **unsusual combination of properties**: low mass density, high structural rigidity, possibly high electric and thermal conductivity.