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Computational Nanotechnology of Materials, Devices and Machines: Carbon Nanotubes

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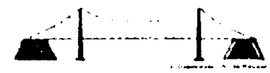
K. Cho --- Stanford University
D. Brenner -- NC State University
R. Ruoff --- University of Washington, St. Louis

IPT Integrated Product Team on Devices and Nanotechnology

The IPT vision is:



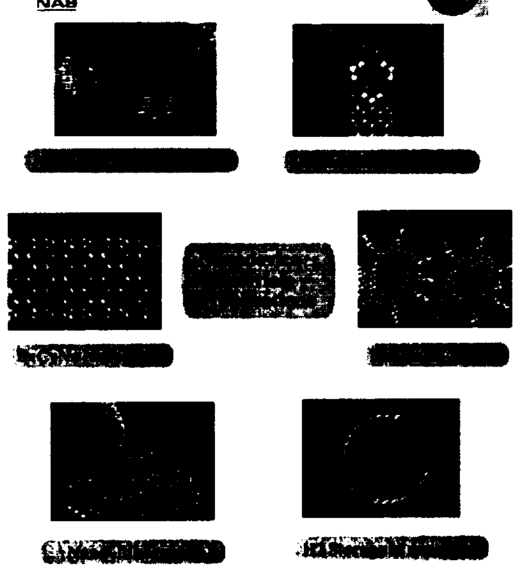
NASA Mission Needs

- Onboard computing systems for future autonomous intelligent vehicles
  - powerful
  - compact
  - low power consumption
  - radiation hard

- High performance computing (Tera- and Peta-flops)
  - processing satellite data
  - integrated space vehicle engineering
  - climate modeling
- Smart, compact sensors
- Light weight displays for space vehicles
- Advanced instrumentation for space astronomy

http://www.ipt.arc.nasa.gov/index.html

Research Focus



Techniques

- **Large Scale Classical Molecular Dynamics on a Shared Memory Architecture Machine**

  Tersoff-Brenner reactive many-body potential for hydrocarbons
  Long Range (6-12) Van der Walls interactions

  Parallel implementation on a shared memory Origin2000 machine

Srivastava and Barnard - **IEEE SuperComputing '97**

- **Quantum Molecular Dynamics Methodology**

  Tight-binding molecular dynamics in an non-orthogonal atomic basis (GTBMD) method.

  Previous Parametrization : Silicon and carbon
  M. Menon and K. R. Subbaswamy, **Phys. Rev. B (1993-94)**

  Extended to heteroatomic systems including: C, B, N
  M. Menon and D. Srivastava
  Chem. Phys. Lett. Vol. 307, 407 (1999)

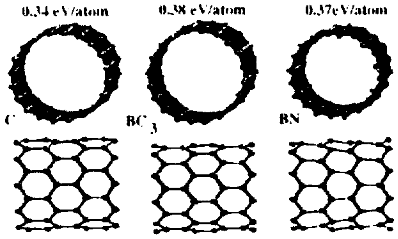
CxByNz Nanotubes

- **Band gap engineering over a larger range should be possible:**

BN	~ 5.5 eV
BC_2N	~ 2.0 eV
C	~ 0 – 1 eV
BC_3	~ 0.5 eV

  - a variety of junctions, quantum dots and superlattices should be possible
  - should be more robust

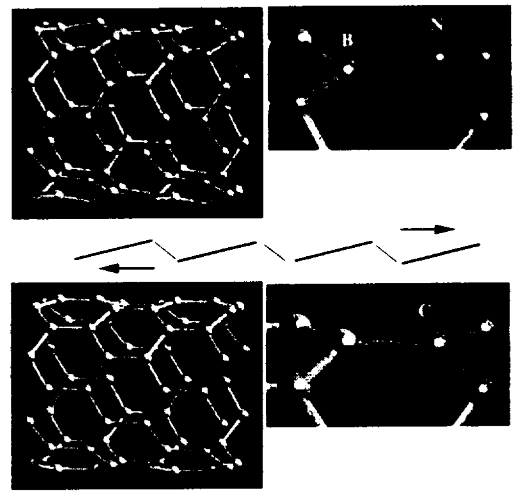
- **Example: Composite (10,0) nanotube**



reconstruction due to polar BN bond

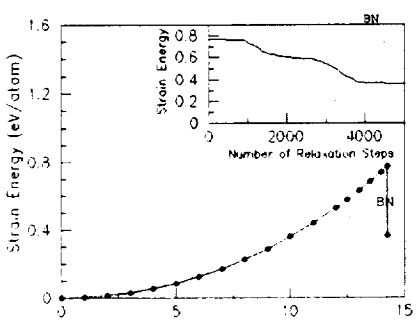
BN Nanotubes - Structure Simulations

- BN bond buckling effect



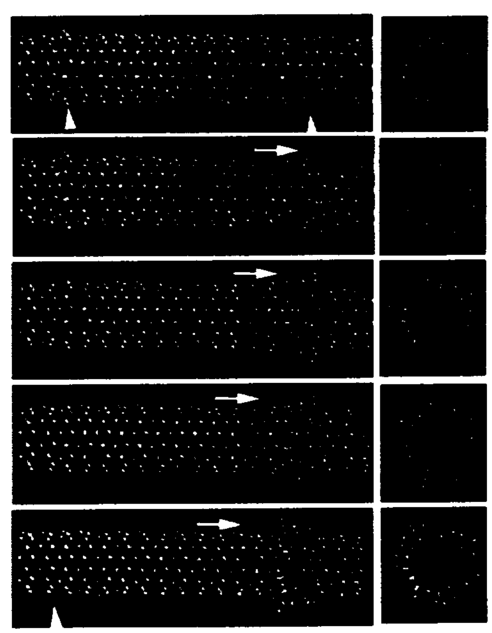
BN Nanotubes – Nanomechanics

- **Young's modulus and plasticity of a compressed BN nanotube.**



- **Y (BN) = 1.2 TPa — BN is 92% as strong as CNT !**
  Y (C) = 1.3 TPa
- **BN nanotube plastically collapses at even higher strain than C nanotube.**

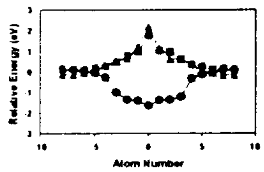
Anisotropic Plasticity/Strain Release in Compressed BN

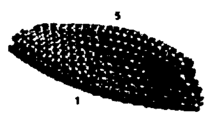


Functionalization of Nanotubes
Nano-Mechano-chemistry

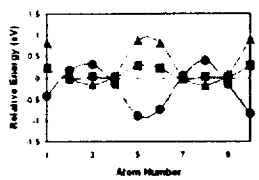
- Predictions of enhanced chemical reactivity in regions of local conformational strains: Kinky Chemistry

Kink on a bent tubule



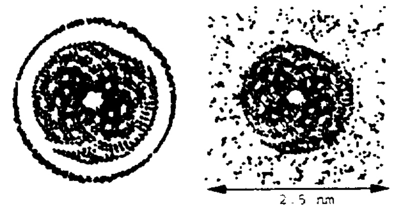


Ridge on a twisted tubule



Binding Energy
Cohesive Energy
Electronic Energy

Functionalization of Nanotubes
Nano-Mechano-Chemistry

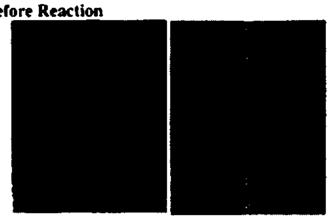


Torsionally twisted SWNT equilibrated in an H bath

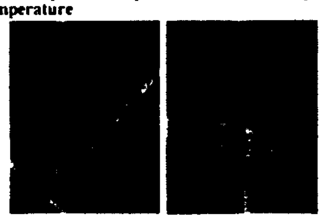
Nano Mechano-Chemistry

SEM images of MWNTs dispersed on a V-ridge substrate

(a) Before Reaction



(b) Same sample after exposure to nitric acid vapor at room temperature

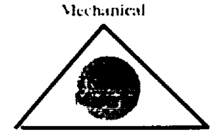


"Predictions of enhanced chemical reactivity in regions of local conformational strains: kinky chemistry," D. Srivastava, J. D. Schall, D. W. Brenner, K. D. Ausman M. Feng, and R. Ruoff, J. Phys. Chem. Vol. 103, 4330 (99)

Comments:

Nanotechnology Materials and Applications.

- compressed C nanotubes in composites
- Nanostructured skin effect
  Functionality of a smart material
- Nano Electromechanical Sensors (NEMS)
- Components of Molecular Electronics
- mechanical kink catalyzed chemistry
  - kinky chemistry
- hydrogen storage in nanotubes



Research Focus III
BxCyNz Composite Nanotubes and Junctions

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BC_2N	**~ 2.0 eV**
C	**~ 0 – 1 eV**
BC_3	**~ 0.5 eV**

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  – should be more robust

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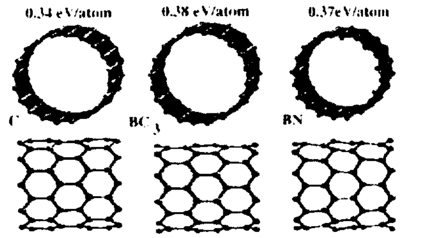
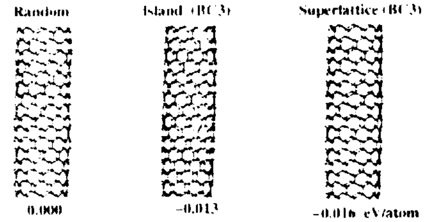


reconstruction due to polar BN bond

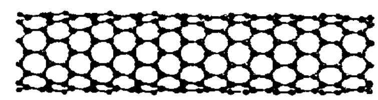
Composite Nanotubes and Junctions

- **B doping of Carbon Nanotube**



phase separation of doped and undoped regions is thermodynamically stable !

- **BN/C Junctions**

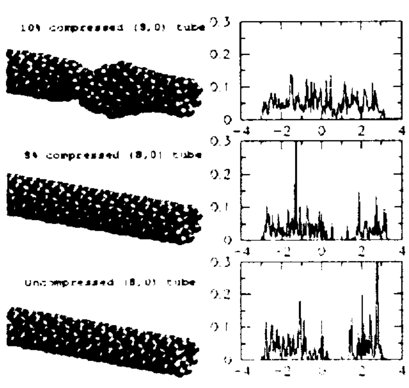


Interface Energy = 2*BN/C – BN – C
Interface Energy = 0.33eV/CB bond

Stable interfaces should be possible !

Nano Mechano–Electronics I

- Mechanical deformations alter the Electronic Characteristics of Nanotubes

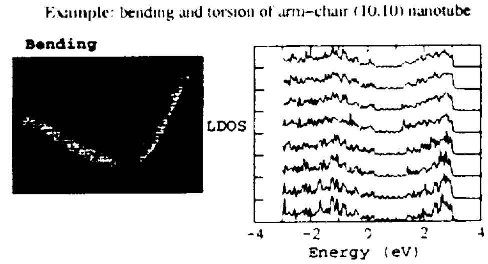


Nano mechano–electronics effects are [illegible] dependent on tube [illegible]

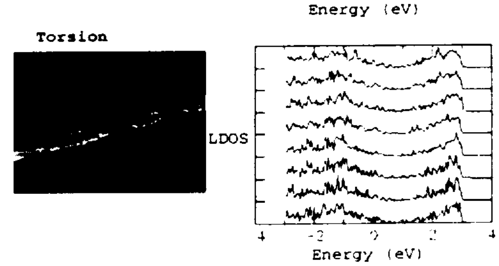
Nano Mechano–Electronics II

Example: bending and torsion of arm–chair (10,10) nanotube

Bending



Torsion



Technique Development Focus I

Large Scale Classical Molecular Dynamics on a Shared Memory Architecture Machine

- Brenner's reactive many-body potential for hydrocarbons
  Long Range (6–12) Van der Walls interactions
- Parallel implementation on a shared memory Origin2000 machine
  - Cell method
  - Spatial Decomposition for Neighborlist
  - Lexical Decomposition for Force Calculations

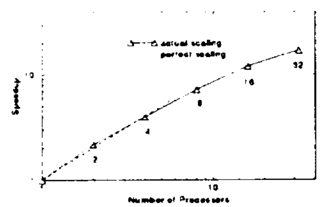


Figure 7: Scaling of the parallel Brenner's potential code on the SGI Origin2000, simulating compression of a four-wall carbon nanotube with 84400 atoms.

Srivastava and Barnard – IEEE SuperComputing '97

Technique Development Focus II

Quantum Molecular Dynamics Methodology:

$$U = U_{el} + U_{rep} + U_0$$

U_{el} = **Sum [one electron energies]**

U_{rep} = **Sum [repulsive pair potential]** occupied

- Non-orthogonal atomic basis GTBMD method

Secular Eq. $\det(h_{ij} - E\, s_{ij}) = 0$

The forces on an atomic coordinates are given by

$$F_x = - dU/dx$$

Molecular Dynamics : system is dynamically evolved at each time step

Previous Parametrization : Silicon and carbon
M. Menon and K. R. subbaswamy, Phys. Rev. B (1993-94)

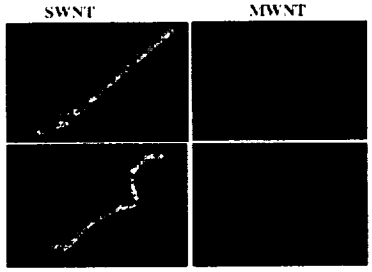
Extended to heteroatomic systems including: Si, C, B, N
M. Menon and D. Srivastava, Phys. Rev. Lett. submitted (98)

Research Focus I
Nanotube – Nanomechanics/materials

- **Nanotubes are extremely strong highly elastic nanofibers**
  - high value of Young modulus
    steel – 0.2 TPa
    swnt – 1.2 TPa
- **Dynamic response of nanotubes to ballistic deformation**
  - axial compression, bending and torsion
  - comparison between SWNT and MWNT behavior

(Axial Compression)

SWNT **MWNT**



- redistribution of strain
  sharp buckling leading to bond rupture
- SWNT is stiffer than the MWNT

Nanomechanics of Carbon Tubes: Instabilities beyond Linear Response

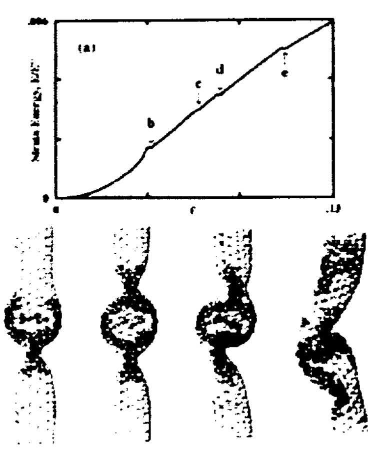
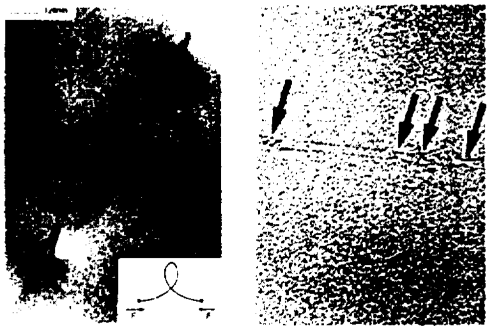


FIG. 1. MD-simulated nanotube of length L = 6 nm, diameter d = 1 nm, and armchair helicity (7,7) under axial compression. The strain energy (a) displays four singularities

Nanotubes in Composites

- Experiment : Buckling and Collapse of Embedded Carbon Nanotubes

O. Lourie et. al. Phys. Rev. Lett. Vol. 81, 1638 (1998).



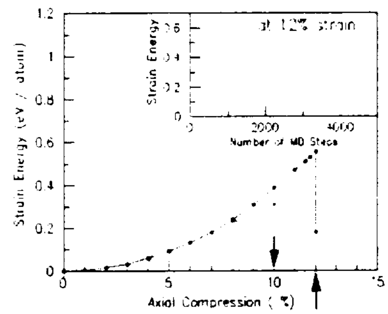
(a) (b)

Under Compressional strain two modes are observed

- (a) - long multi-wall nanotubes behave as elastic rods that buckle, bend and loop
- (b) - thin walled nanotubes locally collapse or fracture rather than buckle

Compressed Nanotubes in Composites

- Energetics of collapse-plasticity of (8,0) CNT at 12% compression strain.

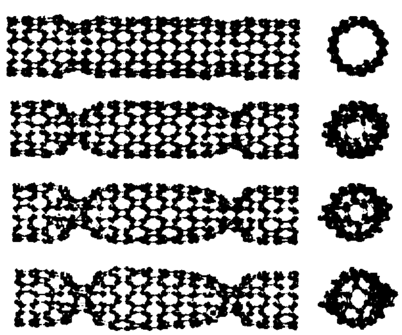


Quantum GTBMD Method
classical atomistic (with Tersoff-Brenner potential)

- Linear response regime (Y = 1.3 TPa) followed by pinching/buckling (classical MD) or collapse/plasticity (quantum MD).

Compressed Nanotubes in Composites

- Spontaneous collapse-plasticity of (8,0) CNT through graphitic (sp2) to diamond like (sp3) type transition.

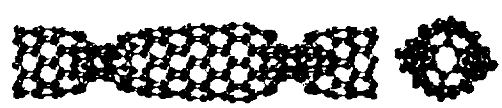


(a) side view (b) top view

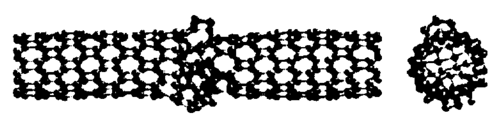
D. Srivastava, M. Menon and K. Cho, Phys. Rev. Lett. Vol. 83, 2973 (1999)

Compressed Nanotubes in Composites

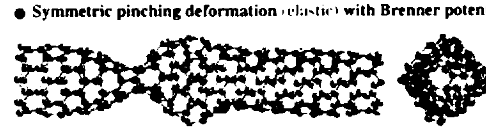
- Comparison with classical atomistic simulation, and a CNT with B point defect.



- With a single B point defect



- Symmetric pinching deformation (elastic) with Brenner potential



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hp8 / HP LaserJet 8000 Series

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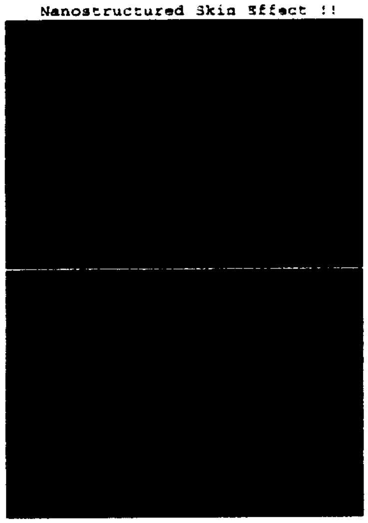
BN Nanotubes - Nanomechanics

Applications !!

- **BN reinforce composites with anisotropic plasticity**

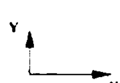
Nanostructured Skin Effect !!



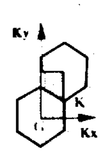
Carbon–based Electronics

- molecular wires
- topological defect mediated hetero–junctions – switching
  transisting
  tunneling devices
- C nanotubes doped with B and N
  BN nanotubes (insulator ~ 5eV gap)
  heterojunctions
  superlattices
- Combination of the above two – to taylor the probable device characteristics
- **interconnects – Carbon/metal junctions**

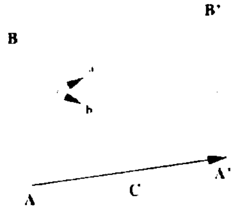
Carbon Nanotube Electronics Band Structure (basics)



Hexagonal Lattice of a Graphene Sheet – (2xunit cell)

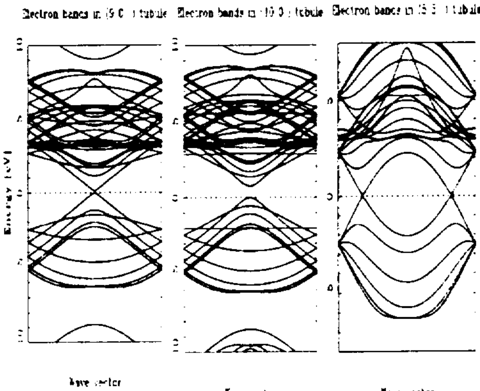


First Brillouin zone for an arm–chair tube



$C_h = n\,a + m\,b$ (chiral vector)

Carbon Nanotube Electronics Band Structure



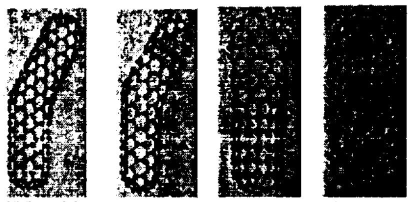
(9,0) tube **(10,0) tube** **(5,5) tube**

Armchair [illegible] metal[illegible]

Otherwise [illegible]

Carbon based Electronics I

2- point Nanotube Heterojunctions
Molecular Electronic Switches



(10,0) – (6,6)   (9,0) – (5,5)   (8,0) – (7,1)   (12,0) – (11,0)

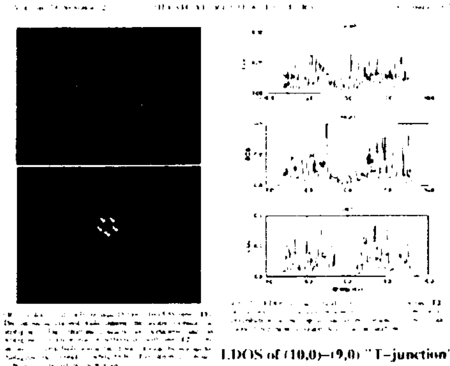
Bent Junctions   Straight Junctions

Chico et. al. Phys. Rev. Lett., 96
Charlier et. al. Phys. Rev. B, 96
Lambine et. al. Chem. Phys. Lett., 96
Saito et. al. Phys. Rev. B, 96

Semiconductor-Metal
Semimetal-Metal

We studied the effect of capping the tubes and relaxing the junctions with a quantum GTBMD method.

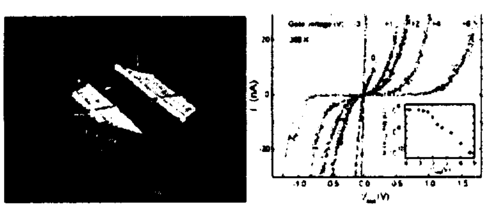
Carbon based Electronics II



LDOS of (10,0)–(9,0) "T–junction"

3–terminal "T–tunnel" Junctions of Nanotubes

Room Temperature Nanotube Transistor (expt)



S. J. Tans et. al., Nature (1998) – Delft Group, – C. Dekker

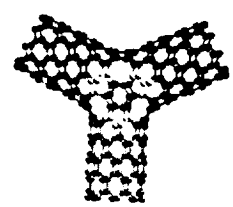
- Similar measurements and configuration for both SWNT and MWNT have been studied by Ph. Avouris and his co-workers at IBM Yorktown Heights.

Hybrid nanotube - silicon electronics

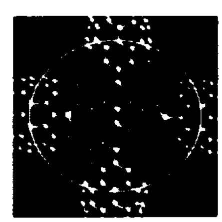
[illegible] metal electrode-nanotube contact

Carbon based Electronics III

Pathways to Two Dimensional Molecular "Networks"



Metal–Semiconductor–Metal "Y" Tunnel Junction



A four–terminal nanotube heterojunction

"It turns out that all of our proposed junctions satisfy – Generalized Euler's Rule about the global topology of connected networks"

V. Crespi, Phys. Rev. Lett. (98)