Solving Nanotube Puzzles on a Supercomputer

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Outline

- **Introduction**
  - What to expect from computer modeling
  - Computational tools

- **Curious Morphologies: Function Follows Form**
  - High thermal conductivity of nanotubes
  - Thermal contraction of nanotubes
  - Magnetism in carbon foam

- **Structural Transformations in Fullerenes and Nanotubes**
  - Fusion of fullerenes in peapods
  - Fusion of nanotubes
  - Field-induced disintegration of nanotube electron emitters
  - Resilience of sputtered nanotubes

- **Behavior of Defective Nanotubes**
  - Defect tolerance of nanotubes
  - Detection of Stone-Wales defects
  - Deoxidation of defective nanotubes

- **Summary and Conclusions**

- **Review:**
  *David Tománek, Carbon-based nanotechnology on a supercomputer, Topical Review in J. Phys.: Condens. Matter 17, R413-R459 (2005).*
What to expect from computer modeling

Zooming in beyond observation

- C$_{60}$ "buckyball"
- Bucky shuttle
- Carbon foam
- Fullerene encapsulation
- Peapod packing
Computational tools

- Electronic structure calculations based on the *ab initio* Density Functional formalism
- Time evolution of electronic wave functions: Time-Dependent Density Functional formalism
- Atomic motion: Molecular dynamics simulations with electrons in the ground and excited state
- Forces from total energy expressions:
  \[ E_{\text{tot}} = E_{\text{tot}}(\{R_i\}) = E_{\text{tot}}\{\rho(r)\} \]
  *ab initio* Density Functional formalism
  \[ E_{\text{tot}} = \sum_i E_{\text{coh}}(i) = \sum_i [E_{bs}(i) + E_{\text{rep}}(i)] \]
  parametrized LCAO formalism (CRT)
- Massively parallel computer architectures and suitable algorithms distribute load over processors for speed-up
San Francisco, April 19 — A Japanese laboratory has built the world’s fastest computer, a machine so powerful that it matches the raw processing power of the 20 fastest American computers combined and far outstrips the previous leader, an IBM-built machine.
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Review:
Curious Morphologies: Function Follows Form

High Thermal Conductivity of Nanotubes

- Nanotubes may help solve the heat problem:
  Efficient conductors of electrons and heat
- Record Heat Conductivity:
  * Diamond (isotopically pure): 3320 W/m/K
  * Nanotubes: 6,600 W/m/K (theory, SWNT)
    >3,000 W/m/K (experiment, MWNT)

(room temperature values)
(combination of large phonon mean free path, speed of sound, hard optical phonon modes)

Nanotubes contract rather than expand

Physical origin: length contraction due to a gain in configurational and vibrational entropy

Challenge: Large unit cells with >100,000 atoms required


Thermal contraction of nanotubes
Magnetism in carbon foam


- Synthesis by Laser Ablation of Amorphous Carbon

Scanning Electron Microscopy Image and possible structure of Nanostructured Carbon Foam

Ferromagnetic behavior (all known carbons are diamagnetic!)
Das fünfte Element

Leicht, luftig, locker: Physiker entwickeln einen magnetischen, halbleitenden Nanoschaum aus Kohlenstoff

Fifth form of carbon?
Fifth element?

Scientists create fifth form of carbon

Jim Giles

Magnetic carbon 'nanofoam' could find medical applications.

Researchers have created a new form of carbon: a spongy solid that is extremely lightweight and, unusually, attracted to magnets. The foam could one day help treat cancer and enhance brain scans, say the inventors.

The new structure was created when physicists at the Australian National University in Canberra bombarded a carbon target with a laser capable of firing 10,000 pulses a second. As the carbon reached temperatures of around 10,000 °C, it formed an intersecting web of carbon tubes, each just a few billionths of a metre long. The researchers have called the solid a 'nanofoam'.

John Giapintzakis of the University of Crete has used an electron microscope to study the structure of the nanofoam. He says it is the fifth form of carbon known after graphite, diamond and two recently discovered types: hollow spheres, known as buckminsterfullerenes or buckyballs, and nanotubes.

It could help treat tumours, says David Tománek of Michigan State University, who has also worked with the foam. He points out that the new structure is very bad at transferring heat. So Tománek proposes that the foam could be injected into tumours, and the tumours exposed to infrared radiations. The foam would absorb the radiation and kill the tumour as it heated up, he suggests, without heating the surrounding tissue.
Why should carbon foam be magnetic?

Physical origin:
Sterically protected carbon radicals are stabilized in surfaces with a negative Gaussian curvature

Spin polarized electrons are delocalized across entire structure

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Structural Transformations in Fullerenes and Nanotubes

Fusion of fullerenes in peapods

Fig. 1. Transmission electron microscopy images. (A) is for \((C_{60})_n@SWNTs\), (B) for \((C_{60})_n@SWNTs\) heated in \((<10^{-6}\ \text{Torr})\) at 800°C for 14 h (HT800), (C) for HT100 (D) for HT1200. A and B indicate similar electron microimages, but in B we can occasionally find that some adjacent \(C_{60}\) molecules are linked together as indicated by arrowheads. In C, some of the \(C_{60}\) molecules coalesce together and transform to a tubular structure. In D, no \(C_{60}\) molecules can be observed but we easily find DWNTs; in some of their inside-tubes are terminated by caps and the lengths are of order of \(~10\ \text{nm}~\).


\(T=1,100°C\)
Stone-Wales rearrangement pathway for fusion of fullerenes

[Hiroshi Ueno, Shuichi Osawa, Eiji Osawa, and Kazuo Takeuchi, Fullerene Science And Technology 6, 319-338 (1998)]

Do we understand the energetics?
Do we understand the Stone-Wales process?

Search in 360-dimensional configuration space using string method:

Stone-Wales is a multi-step process

- Activation barriers do not exceed \( \approx 5 \text{eV} \)
Minimum energy path for the $2\text{C}_60 \rightarrow \text{C}_{120}$ fusion

**Conclusions:**
- Fusion is exothermic.
  Energy gain $\Delta E \approx 1\text{Ry}$.
- Essential initial step: (2+2) cycloaddition

Fusion of nanotubes

The zipper mechanism

Minimum energy path for the \((5,5)+(5,5)\rightarrow(10,10)\) fusion

Sequence of Stone-Wales transformations

\[\begin{align*}
0 & \rightarrow 1 \quad \cdots \rightarrow 9 \\
\end{align*}\]

\[\Delta E[eV] \]

\[\begin{align*}
0 & \quad 1 & \quad 2 & \quad 3 & \quad 4 & \quad 5 & \quad 6 & \quad 7 & \quad 8 & \quad 9 \\
\end{align*}\]

\[\text{Conclusion: Fusion is exothermic}\]
Geometry of fusing Nanopants

**Type A:**
6 heptagons in junction area

**Type B:**
1 octagon, 4 heptagons in junction area
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Review:
Behavior of Defective Nanotubes

Defect tolerance of nanotubes

- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?

Will atomic vacancies trigger failure under
- high temperatures?
- illumination?
Equilibrium structure near a monovacancy in $sp^2$ carbon

Strain too large

Barely stable
Stability of defective tubes at high temperatures

♦ Danger of pre-melting near vacancies?

- Nanotube remains intact until 4,000 K
- **Self-healing** behavior:
  - Formation of new bond helps recover
    - structural stiffness
    - conductance
Reconstructed geometry

Stability increase due to reconstruction (bond formation across vacancy)

Does reconstruction affect favorably transport in defective tubes?
Quantum conductance of a (10,10) nanotube with a single vacancy

Good news for applications: Self-healing by reconstruction may remove one of the sharp dips

Stability of defective tubes during electronic excitations

Challenges:

♦ Perform Molecular Dynamics simulations on the adiabatic surface of an electronically excited state

♦ Solve the time-dependent Schrödinger equation for electrons during ionic motion
First-principles Molecular Dynamics simulation on the adiabatic surface of an electronically excited state

To follow the correct adiabatic surface of an excited state is quite difficult

First-principles Simulation tool for Electron-Ion Dynamics

Details: Sugino & Miyamoto PRB 59, 2579 (1999); PRB 66, 89901 (2002).

Optical excitation ($\Delta E=0.9$ eV)
Time evolution of the electronic states

- Very long-lived excitation
- Correct PES is followed in case of level alternation

\[ \Psi_n(t+\Delta t) = \exp(-i/\hbar H\Delta t) \Psi_n(t) \]
Structural changes under illumination

- **Self-healing** due to new bond formation
Detection of Stone-Wales defects

$\pi^*$ state (electron)

$\sigma-\pi$ hybridized state (hole)

$\uparrow$ 6 eV

$\Rightarrow$ Can Stone-Wales defects be removed by photo-excitations?
Stone-Wales defects cannot be removed, but can be identified using photo-excitations.
STM characterization of Stone-Wales defects

Y. Miyamoto, A. Rubio, S. Berber, M. Yoon, and D. Tománek, 
Deoxidation of defective nanotubes

How to deoxidize?

- By heat treatment?
  ⇒ No: Larger damage to nanotube

- By chemical treatment with H?
Alternative to thermal and chemical treatment

*Electronic excitations!*

O2s $\rightarrow$ O2p excitation (33 eV)

hopeless
Auger decay following the O1s → 2p excitation (~520 eV)

Deoxidation by photo-surgery
Summary and Conclusions

- Carbon nanotubes are Nature’s best thermal conductors.
- Carbon nanotubes contract thermally.
- Nanostructured carbon may become magnetic.
- Fusion of fullerenes inside a nanotube starts with a cycloaddition and continues exclusively with Stone-Wales transformations.
- Fusion of nanotubes occurs efficiently via a zipper mechanism.
- Nanotube field electron emitters decay by thermally assisted Coulomb explosion at the tip.
- Carbon nanotubes are unusually stable when sputtered.
- Heat and photo-excitations may induce self-healing behavior in defective nanotubes.
- Photo-excitations may be used to detect specific defects by their vibrational signature.
- Photo-excitations can be used to selectively remove oxygen impurities.
The End