Phonon Spectra Prediction in Carbon Nanotubes Using a Manifold-Based Continuum Finite Element Approach

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Phonon Spectra Prediction in Carbon Nanotubes Using a Manifold-Based Continuum Finite Element Approach
Overview

CNT Background
Motivation
Phonon Behavior
FEA Development
Results
Concluding Remarks

http://www.sciencedirect.com
Introduction

Phonons are quantized lattice vibrations
Important for understanding thermal, elastic, and electrical properties
In CNTs, excitation of phonons leads to electron scatter and hence resistance to ballistic electron transport
This study seeks to quantify phonon spectrum present in CNTs
CNT Background


Length Scale
- Human hair $\phi \sim 80,000$ nm
- CNT $\phi \sim 1$ nm

Synthesis
- Arc discharge
- Laser ablation
- Chemical Vapor Deposition

Carbon nanotube - Wikipedia
## Motivation – Unique Material Properties!

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>SINGLE-WALLED NANOTUBES</th>
<th>BY COMPARISON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>0.6 to 1.8 nanometer in diameter</td>
<td>Electron beam lithography can create lines 50 nm wide, a few nm thick</td>
</tr>
<tr>
<td>Density</td>
<td>1.33 to 1.40 grams per cubic centimeter</td>
<td>Aluminum has a density of 2.7 g/cm³</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>45 billion pascals</td>
<td>High-strength steel alloys break at about 2 billion Pa</td>
</tr>
<tr>
<td>Resilience</td>
<td>Can be bent at large angles and restraightened without damage</td>
<td>Metals and carbon fibers fracture at grain boundaries</td>
</tr>
<tr>
<td>Current Carrying Capacity</td>
<td>Estimated at 1 billion amps per square centimeter</td>
<td>Copper wires burn out at about 1 million A/cm²</td>
</tr>
<tr>
<td>Field Emission</td>
<td>Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart</td>
<td>Molybdenum tips require fields of 50 to 100 V/µm and have very limited lifetimes</td>
</tr>
<tr>
<td>Heat Transmission</td>
<td>Predicted to be as high as 6,000 watts per meter per kelvin at room temperature</td>
<td>Nearly pure diamond transmits 3,320 W/m-K</td>
</tr>
<tr>
<td>Temperature Stability</td>
<td>Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air</td>
<td>Metal wires in microchips melt at 600 to 1,000 degrees C</td>
</tr>
<tr>
<td>Cost</td>
<td>$1.500 per gram from BuckyUSA in Houston</td>
<td>Gold was selling for about $10/g in October</td>
</tr>
</tbody>
</table>

P.G. Collis and P. Avouris, “Nanotubes for Electronics,”
Scientific American, Dec. 2000
Discovery Channel – 10 Uses for Carbon Nanotubes

1. Space elevator
2. Faster computer chips
3. Enhanced solar cells
4. Cancer treatment
5. Improved, thinner TVs
6. Better capacitors that replace batteries
7. Flexible displays
8. Bone healing
9. Body armor “Theoretically 100 times stronger than steel and six times lighter.”
10. Faster flywheels

Phonon Behavior

Phonon: A phonon is a quantized mode of vibration occurring in a rigid crystal lattice, such as the atomic lattice of a solid.

Classical Approach: modal analysis

\[ M_{IJ}^{\rho} \ddot{U}_{J}^{\rho} + K_{IJ}^{\rho} U_{J}^{\rho} = 0 \]
Modeling Approach

Derive shell-like equations of motion referencing basis vectors in the undeformed tangent space
Equate strain energy to interatomic potential energy
Discretize EOMs using finite elements $T_X \Omega_0$
Solve for normal modes of vibration
Model - Kinematics

Mappings from parametric body

Vectors referencing tangent spaces and their basis vectors

$$G_{\alpha} = \frac{\partial X}{\partial \xi^\alpha} = \frac{\partial Z^a}{\partial \xi^\alpha} I_a$$

$$g_{\alpha} = \frac{\partial x}{\partial \xi^\alpha} = \frac{\partial z^a}{\partial \xi^\alpha} i_a$$

$$\Phi = \varphi \circ \varphi_0^{-1} : X \in \Omega_0 \mapsto x = \Phi(X) = \varphi(\varphi_0^{-1}(X)) \in \Omega$$

$$\Phi : X \mapsto x = \Phi(X) = X + U(X) - O$$

$$g_{\alpha} = G_{\alpha} + \frac{\partial U}{\partial \xi^\alpha} = G_{\alpha} + \frac{\partial U^\beta}{\partial \xi^\alpha} G_{\beta} + U^\beta \frac{\partial G_{\beta}}{\partial \xi^\alpha}$$
Model - Kinematics

Deformation gradient maps line segments in tangent spaces

\[
F \equiv \frac{\partial x}{\partial X} \in \mathbb{R}^{3 \times 3} : T\Omega_0 \to T\Omega \\
dx = F \cdot dX
\]

Gradient

\[
F \equiv \frac{\partial x}{\partial X} = \frac{\partial x}{\partial \xi^\alpha} \frac{\partial \xi^\alpha}{\partial X} = g_\alpha \otimes G^\alpha = \delta^\alpha_\beta g_\alpha \otimes G^\beta
\]

\[
\nabla_x \equiv \frac{\partial}{\partial X} = \frac{\partial}{\partial \xi^\alpha} \frac{\partial \xi^\alpha}{\partial X} = G^\alpha \frac{\partial}{\partial \xi^\alpha} = G^{\alpha\beta} G_\beta \frac{\partial}{\partial \xi^\alpha}
\]
Toroidal Parameterization

\[ Z^1 = (R + \xi^3 \cos \xi^1) \sin \xi^2 \]
\[ Z^2 = (R + \xi^3 \cos \xi^1) \cos \xi^2 \]
\[ Z^3 = \xi^3 \sin \xi^1 \]
\[ r = \xi^3 \]

Yields \( G_\alpha \) and Christoffel Symbols

\[ \Gamma^\eta_{\rho\beta} \]

\[ F \equiv \frac{\partial x}{\partial X} = \left[ \delta^\eta_\beta + \frac{\partial U_\eta}{\partial \xi^\beta} + U^\rho \Gamma^\eta_{\rho\beta} \right] G_\eta \otimes G^\beta \]
Energy Connection

\[ W_0 \equiv \frac{E^{\text{rae}}}{A_{\text{Hex}}} = \frac{E^{\text{stretch}} + 2E^{\text{angle}}}{A_{\text{Hex}}} \]

\[ P = \frac{\partial W_0}{\partial F} \]

- Bond vectors
  \[ r_{ij} = F \cdot R_{ij} \]

- Modified Morse Potential
  \[ E_{\text{stretch}} = D_e \left( \left[ 1 - e^{-\beta(r-r_0)} \right]^2 - 1 \right) \]
  \[ E_{\text{angle}} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \left[ 1 + k_{\text{sextic}} (\theta - \theta_0)^4 \right] \]
Equations of Motion

Hamilton’s Principle

\[ P = \frac{\partial W_0}{\partial F} \]

\[ \delta E^{\text{tot}} = \delta \int_{\Omega_0} W_0(F) \, d\Omega_0 + \delta E^{\text{ext}} = \int_{\Omega_0} \frac{\partial W_0}{\partial F} : \delta F \, d\Omega_0 + \delta E^{\text{ext}} = 0 \]

where

\[ \delta E^{\text{ext}} = - \int_{\Omega_0} \delta U \cdot t_0 \, d\Omega_0 + \int_{\Omega_0} \rho_0 \ddot{U} \cdot \delta U \, d\Omega_0 \]

Interpolate \( U \)

\[ U = N^I(\xi_1, \xi_2) \hat{U}_i t_i^\beta G_\beta \]

Taylor expand \( P \)

\[ P_\alpha^\beta = P_\alpha^{\beta 0} + \frac{\partial^2 W_0}{\partial F_\beta \partial F_\mu} \frac{\partial F_\sigma}{\partial \hat{U}_J^\rho} \bigg|_{U=0} \hat{U}_J^\rho + O(\hat{U}_J^{\rho 2}) \]

Expressions found in closed form
Equations of Motion

Stiffness matrix from interatomic energy

\[ K_{ij}^{\sigma \rho} = \int_{\Omega_0} \left( \frac{\partial^2 W_0}{\partial F_\alpha^\rho} \frac{\partial F^\mu_\sigma}{\partial \hat{U}_j^\rho} \frac{\partial F^\alpha_\beta}{\partial \hat{U}_i^\sigma} \right) d\Omega_0 \]

Mass matrix from inertial work

\[ M_{ij}^{\sigma \rho} = \int_{\Omega_0} \rho_0 N^i N^j t^i_\sigma t^j_\rho G_{ij} d\Omega_0 \]

Completed form of EOMs

\[ M_{ij}^{\sigma \rho} \ddot{U}_j^\rho + K_{ij}^{\sigma \rho} \dot{U}_j^\rho = 0 \]

4-noded shell element
used in all results presented
Results - RBM Validation

Experimentally Determined Values\[1\]

\[(10,10) : 4.86 \text{ THz} \]
\[(13,0) : 6.33 \text{ THz} \]

Quantum Calculations\[1\]

\[(10,10) : 4.7 - 5.85 \text{ THz} \]
\[(13,0) : 7.41 \text{ THz} \]

Radii: 6.765 Angs. 5.08 Angs.

Results – (10,10) Bending

Radii: 6.765 Angs.      5.08 Angs.

40.9262 GHz          41.2959 GHz

45.438 GHz          45.7258 GHz          95.3129 GHz

Other methods\(^2\) yield 41.2 GHz as fundamental bending mode

Results – (13,0) Bending

Radii: 6.765 Angs.  5.08 Angs.

14.9898 GHz

17.3485 GHz

81.872 GHz

78.3678 GHz

79.2083 GHz

82.7701 GHz
Results – (10,10) Toroidal Bending

60.1693 GHz

62.3895 GHz

65.5137 GHz

65.6843 GHz

158.0734 GHz

158.1115 GHz
Concluding Remarks

CNT have many outstanding properties
Finite element formulations have been developed for predicting phonon spectra
The method compares favorably with experimental results and computationally intensive algorithms
Models generalize well to imperfect tubes and non-ideal geometries (wavy, etc.)
Elements are re-usable
ACKNOWLEDGEMENTS

This work was motivated and supported by technical staff at the MITRE Corporation involved in an ongoing effort to develop a small antenna matching network using toroidal and straight carbon nanotubes. Dr. Lucien Teig originally suggested this study as part of an effort to quantify electron scatter. Ms. Sarah O’Donnell and Ms. Janet Worth, the project leaders, generously supported the effort with internal research funding. Ideas and insights were provided to authors by other group members, including Dr. David Lamensdorf, Mr. Jim Marshall, and Dr. Aleksandra Markina-Khusid.
Top 5 Uses

1. **Space elevator**
   Sending a payload into space by rocket is expensive ($10,000 per pound) and dangerous. Some are proposing a very tall elevator that would stretch from the ground to beyond Earth's atmosphere. Making this a reality requires a long, strong cable tethered to a counterweight in geosynchronous orbit maintained at a fixed position about 22,000 miles above the earth. CNTs are the only known material up to the task. Among other things, a successful space elevator could be a means for safe disposal of nuclear waste and give life to a space tourism industry.

2. **Faster computer chips**
   The processing speed of a computer chip depends on the number of transistors it has. Today, typical desktop processors using silicon transistors have less than half a billion. Computer chips using CNTs could blow that number away. Their small size - just one nanometer wide - means many billions of CNT transistors could be packed onto a single processing chip making for smaller, faster computers and electronics.

3. **Better solar cells**
   Semiconducting materials altered with certain impurities are used in solar cells. When struck by light, these materials release electrons, creating usable electricity. Most of today's solar cells use silicon semiconductors, but that could change. Because they're so tiny, billions of CNTs could be tightly packed onto solar cells and release far more electricity per square inch than silicon. In addition, carbon nanotubes absorb light so well that a professor at Rice University used them to create the darkest ever man-made material.

4. **Cancer treatment**
   CNTs are so small they might one day be used to target and destroy individual cancer cells. By treating CNTs with certain proteins, scientists are developing a method to bind them specifically to cancerous cells. Once attached, the CNTs, which are excellent conductors of heat, could be exposed to infrared light shone through the patient's skin. The light would heat the CNTs to a temperature high enough to destroy the cancer cells while leaving surrounding tissue undamaged. While more research must be done, this method could offer a way to treat certain cancers without harming healthy tissue, a current drawback of treatments like chemotherapy.

5. **Better, thinner TVs**
   Traditional tube TVs essentially work by firing electrons at substances called phosphors to make them glow, creating the colored light of a television picture. This process requires an electron gun in a relatively big picture tube. But new displays, called field emission displays miniaturize the process by using tiny electron emitters positioned behind individual (microscopic) phosphorus dots. An array of CNTs, which are excellent electron emitters, could be used in field emission displays to excite the phosphorus dots, creating bright, high resolution displays that are only millimeters thick and consume less power than plasma and liquid crystal displays.
6. Better capacitors that replace batteries
Instead of storing electricity chemically like a battery, capacitors hold it physically by building a charge on a material called a dielectric. The dielectric's surface area determines how much charge it can hold. CNTs have extraordinarily high surface areas, and using them as the dielectric could increase the storage ability of capacitors to be on par with modern batteries. But if we already have batteries what's the use? Batteries take hours to charge and lose their capacity with time. Capacitors don't have these problems. CNT capacitors might one day be used in instantly rechargeable laptops and electric cars.

7. Flexible displays
The dream of fold-up TVs and computer screens that can fit inside people's pockets has, up until now, been stifled by rigid silicon semiconductors. While some organic semiconductors have used in bendable plastic displays, their performance has been fairly poor. But CNTs, in addition to being very flexible, compare favorably to silicon in terms of performance. Researchers at Purdue and the University of Illinois-Urbana-Champaign are developing carbon nanotube flexible displays which one day could be used for things like electronic newspapers and roll-up handheld devices.

8. Bone healing
Researchers at the University of California-Riverside have discovered that CNTs can act as scaffolds around which bone cells will grow by attracting hydroxyapatites, calcium crystals in the body that are critical for bone formation. The technology might one day help individuals with bone diseases or particularly catastrophic injuries regrow bones.

9. Body armor
Researchers at Cambridge University have figured out how to spin many tiny carbon nanotubes together to create fibers that have the strength of Kevlar, a composite material used in bullet-proof vests. With new techniques rapidly emerging to make longer CNTs, spun fibers using the longer CNTs will soon surpass Kevlar in strength, and weigh less. As CNT prices drop, spun CNT fibers could be the material of choice for better, lighter body armor.

10. Faster flywheels
A flywheel is like a battery in that it stores energy. But unlike a battery, this energy is mechanical and stored via a wheel rotating at high speed (the faster the spin, the more energy it stores). Flywheels offer certain advantages over batteries. But a flywheel, if spun too fast, can shatter because of the strength limits of its material. Because of their strength, CNTs could be used to make faster flywheels that store more energy without shattering. While Flywheels have seen only limited use in amusement rides, race cars and backup power supplies, using CNTs could allow flywheels to become more prevalent in areas like public transportation and hybrid cars.