Sliding prevention in super-strong self-collapsed nanotube cables (and graphene nanoscrolls)

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TRIESTE, TRENDS IN NANOTRIBOLOGY 2011
Self-collapsed nanotubes in a bundle

Experimental evidence:
Motta et al., Advanced Materials, 2007

Theory:

The design of self-collapsed super-strong nanotube bundles
Nicola Maria Pugno ab,c,*
Graphene nanoscrolls

Graphene, a promising nanomaterial for future electronics, can be rolled up into “nanoscrolls”, shown here in cross section in yellow. Simulations reported in the journal Small show these scrolls can be controlled using a tiny voltage to direct the flow of water or even drugs across cell membranes.
Buckling pressure of long cylindrical shells

\[ p_C = \frac{3N^\alpha D}{R^3} \]

Buckling pressure of nanotubes in a bundle

\[ p_C = \frac{3N^\alpha D}{R^3} - \frac{\gamma}{R} \]

Pressure around a cylindrical cavity in a “liquid-like” material: interaction between the nanotubes
Buckling pressure: theory vs MD

Theory vs MD (MD by Elliot et al., Physical Review Letters, 2004)
Self-collapse: theory

Self-collapse condition

\[ p_C = 0 \]

Self-collapse radius

\[ R \geq R_C^{(N)} = \sqrt[3]{\frac{3N^\alpha D}{\gamma}} = \sqrt[6]{6} R_0^{(N)} \]

\[ D = 0.11 \text{ nN} \cdot \text{nm} \]
\[ \gamma = 0.18 \text{ N/m} \]
\[ \alpha \approx 2 \]

\[ 2R_C^{(1)} \approx 2.7 \text{ nm} \]
\[ 2R_C^{(2)} \approx 5.4 \text{ nm} \]
\[ 2R_C^{(3)} \approx 8.1 \text{ nm} \]
### Self-collapse: theory vs experiments

<table>
<thead>
<tr>
<th>Nanotube number</th>
<th>Number ( N ) of walls</th>
<th>Diameter of the internal wall [nm]</th>
<th>Collapsed (Y/N) Exp. &amp; Theo.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>4.6</td>
<td>Y</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>4.7</td>
<td>Y</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>4.8</td>
<td>Y</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>5.2</td>
<td>Y</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5.7</td>
<td>Y</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>4.2</td>
<td>N</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>4.6</td>
<td>N</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>4.7</td>
<td>N</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>6.2</td>
<td>Y</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>6.5</td>
<td>Y</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>6.8</td>
<td>Y</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>6.8</td>
<td>Y</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>7.9</td>
<td>Y</td>
</tr>
<tr>
<td>14</td>
<td>2</td>
<td>8.3</td>
<td>Y</td>
</tr>
<tr>
<td>15</td>
<td>2</td>
<td>8.3</td>
<td>Y</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>8.4</td>
<td>Y</td>
</tr>
<tr>
<td>17</td>
<td>3</td>
<td>14.0</td>
<td>Y</td>
</tr>
</tbody>
</table>
Fracture Mechanics

\[ d\Phi - F du - 2\gamma (P_C + P_{vdW}) dz = 0 \]

Predicted bundle strength

\[ \sigma_C = 2 \cos \beta \sqrt{E\gamma \frac{P}{S}} \]

Maximum strength

\[ \sigma_C^{(theo,N)} = 2 \sqrt{E\gamma \frac{N}{t}} \]

\[ \sigma_C^{(max)} = \sigma_C^{(theo,1)} = 48.5 \text{GPa} \]
\[ \sigma_C^{(theo,2)} = 34.3 \text{GPa} \]
\[ \sigma_C^{(theo,3)} = 28.0 \text{GPa} \]
Strength increment due to the self-collapse

\[ \frac{\sigma_C^{(0)}}{\sigma_C^{(0)}} = \sqrt{\frac{2\pi R + P_{vdW}}{2\pi R \left(1 - \frac{1}{R} \sqrt{\frac{N^\alpha D}{2\gamma}} \right) + P_{vdW}}} \]

Strength self-collapsed/strength not self-collapsed

\[ R \geq R_C^{(N)} = \sqrt{\frac{3N^\alpha D}{\gamma}} \]

Self-collapsed radius

\[ \left| \frac{\sigma_C^{(0)}}{\sigma_C^{(0)}} \right|_{\text{max}} = \sqrt{\frac{1}{1 - \frac{1}{\sqrt{6}}} \approx 1.30} \]

Maximum ratio

Strength increment up to 30%
Other related calculations

Dog-bone configurations

Peapods:
fullerens in a nanotube

Critical buckling pressure
vs fullerene (linear fractional) content
Self-rolling of graphene nanoribbons due to the competition between surface (vdW), initially prevailing, and elastic (bending), finally prevailing, energies: formation of nanoscrolls (SEE MOVIE)

Work performed in collaboration with the H. Gao’ group (LAMMPS MD simulations)
**Geometry**

\[ r = r_0 + \frac{t}{2\pi} \theta \]

**Length**

\[ B \approx \int_0^{2\pi N} \left( r_0 + \frac{t}{2\pi} \vartheta \right) d\vartheta = 2\pi r_0 N + \pi t N^2 \]

Constant length: one degree of freedom, e.g. the core radius

\[ B = \frac{\pi}{t} (R^2 - r_0^2) \]

\[ \frac{dN}{dr_0} = -\frac{N}{R}, \]

\[ \frac{dR}{dr_0} = 1 + \frac{dN}{dr_0} t = 1 - \frac{Nt}{R} = \frac{r_0}{R}. \]
Elastic bending energy

\[
\frac{dW}{dA}(r) = \frac{D}{2} \frac{1}{r^2}
\]

Bending energy per unit area

\[
W = \frac{\pi DL}{t} \ln\left(\frac{R}{r_0}\right)
\]

Stored bending energy

\[
dW = \frac{\pi DL}{t} \left( \frac{dR}{R} - \frac{dr_0}{r_0} \right)
\]

Change in bending energy
Energy minimization

Bending energy

\[ dW = -\frac{\pi DL}{t} \frac{R^2 - r_0^2}{R^2} \frac{dr_0}{r_0} \]

Surface energy

\[ d\Gamma = 2\pi \gamma L \left( dr_0 + dR \right) = 2\pi \gamma L \left( 1 + \frac{r_0}{R} \right) dr_0 \]

Total energy

\[ \frac{dE_{tot}}{dr_0} = \frac{dW}{dr_0} + \frac{d\Gamma}{dr_0} \]

Equilibrium can be calculated imposing  \( dE=0 \)
### Equilibrium Core Radius

The equation for the equilibrium core radius is given by:

$$\frac{2\gamma t}{D} = \frac{1}{r_0} - \frac{1}{\sqrt{(Bt/\pi) + r_0^2}}$$

<table>
<thead>
<tr>
<th>Theo/MD comparison</th>
<th>$r_0$ (nm)</th>
<th>$R$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MD</td>
<td>Theo.</td>
</tr>
<tr>
<td>Zigzag$^{(v)}_a$</td>
<td>0.32</td>
<td>0.37</td>
</tr>
<tr>
<td>Armchair$^{(v)}$</td>
<td>0.25</td>
<td>0.36</td>
</tr>
<tr>
<td>Chiral$^{(v)}$</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>Zigzag$^{(w)}$</td>
<td>0.60</td>
<td>0.59</td>
</tr>
<tr>
<td>Armchair$^{(w)}$</td>
<td>0.61</td>
<td>0.56</td>
</tr>
<tr>
<td>Chiral$^{(w)}$</td>
<td>0.68</td>
<td>0.79</td>
</tr>
<tr>
<td>Zigzag$^{(v, \text{halfed} W)}_b$</td>
<td>0.67</td>
<td>0.63</td>
</tr>
</tbody>
</table>

$^a(v)$ means in vacuum and $(w)$ means in water. $^b$50% reduction in van der Waals interaction.

Close agreement with MD simulations.
No best fit

By applying an electrical field we can tune the effective surface energy and the core radius and thus we can control the fluid (here water) flow.
Energy storage: modeling

Pressure inside the nanoscroll: new energy term in the equilibrium equation

Gigapascals are required to open (in an explosive way, i.e. the process is unstable) the nanoscroll.

\[ d\Phi = -p_i 2\pi L r_0 dr_0 + p_e 2\pi L R dR = -2\pi L r_0 dr_0 p, \]

\[ \frac{dE}{dr_0} = \frac{dW}{dr_0} + \frac{d\Gamma}{dr_0} + \frac{d\Phi}{dr_0}. \]

Int J Fract
DOI 10.1007/s10704-010-9545-y
Published online: 12 October 2010
Nano-oscillators: modeling

Lagrange Equation and breathing motion

Natural frequency of the system can be deduced

\[
\frac{\pi DL}{h} \left( 1 - \frac{r_0^2}{Bh/\pi + r_0^2} \right) \frac{1}{r_0} - 2\pi \gamma L \left( 1 + \frac{r_0}{\sqrt{Bh/\pi + r_0^2}} \right)
\]

\[
+ 2\pi r_0 L p - \frac{4\pi^2 M}{h^2} \left( r_0 r_0^2 + r_0^2 \right) - C \dot{r}_0 = 0
\]

\[
\omega_0 = \sqrt{\frac{\pi D}{4\rho B^3 h^2}} \left[ \frac{\alpha^3 (\alpha + 3)}{(1 + \alpha)^2} + 2\frac{\gamma}{D} \sqrt{\frac{Bh^3}{\pi}} \frac{\alpha^2 \sqrt{\alpha}}{(1 + \alpha)^{3/2}} - 2\frac{Bh^2 p}{\pi D \alpha} \right]
\]
Nano-oscillators: Theory vs MD

We can open the nanoscroll under resonance! Smart nanovectors.

APPLIED PHYSICS LETTERS 95, 163113 (2009)
But expansion prevails over rolling: we fixed the core radius inserting a CNT...
Nano-motors: modeling

\[ \frac{f}{L} = -\frac{1}{L} \frac{\delta V}{\delta x} = \gamma_{CS} - \gamma_{CC} + \frac{D}{2[(B-x)h/\pi + r_0^2]} \]

\[ 6\left[\rho(B-x) + M_0/L\right] \ddot{x} - 3\rho \dot{x}^2 + 4(\gamma_{CC} - \gamma_{CS}) - 2D/\left[(B-x)h/\pi + r_0^2\right] = 0. \]

Net (positive or negative) driving force and Lagrange equation
Nanoscroll crystals

Theory and MD (still to be submitted, similar to the previously discussed one for nanotube bundle/crystals)
Gigantic electrostriction

- **Graph 1**: Plot of $V/V_0$ against $\lambda$ with data points labeled "crystalline" and "bundle".
- **Graph 2**: Plot of effective coefficient $\gamma_{\text{eff}}$ against $\lambda$.
- **Graph 3**: Plot of $\gamma_{\text{dipole}}$ against $E$ (v/nm).
- **Graph 4**: Plot of electrostriction coefficient against $E$ (v/nm).
I thank:

the European Research Council (ERC Starting Grant 2011 on “Bio-inspired hierarchical super nanomaterials) for support;

the conference organizers for the invitation;

and you for your attention!

My refs:

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Molecular and Nanostructural Mechanisms of Deformation, Strength and Toughness of Spider Silk Fibrils

Andrea Nova,†,‡ Sinan Keten,§ Nicola M. Pugno,¶,⊥,¥ Alberto Redaelli,‖ and Markus J. Buehler*,†,¶,⊥,¥,‖

Hierarchical simulations for the design of supertough nanofibers inspired by spider silk

Federico Bosia,¶,⊥ Markus J. Buehler,‡,§ and Nicola M. Pugno‡,¶,⊥,¥,‖
Km-long crack front in geckos

Experiments on several insects, spiders and lizards (from S. N. Gorb, M. Varenberg, N. M. Pugno, Soft Matters, 2010) Peeling line proportional to mass supports our model