Computational methods for nano-mechanical sensors

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My research interests

- **Development** of fundamental computational methods for structural dynamics and uncertainty quantification
  - A. Dynamics of complex systems
  - B. Inverse problems for linear and non-linear dynamics
  - C. Uncertainty quantification in computational mechanics

- **Applications** of computational mechanics to emerging multidisciplinary research areas
  - D. Vibration energy harvesting / dynamics of wind turbines
  - E. Computational nanomechanics
1. Introduction

2. One-dimensional sensors - classical approach
   - Static deformation approximation
   - Dynamic mode approximation

3. Overview of nonlocal continuum mechanics

4. One-dimensional sensors - nonlocal approach
   - Attached biomolecules as point mass
   - Attached biomolecules as distributed mass

5. Two-dimensional sensors - classical approach

6. Two-dimensional sensors - nonlocal approach

7. Conclusions
Nanoscale systems have length-scale in the order of $O(10^{-9})$ m.

Nanoscale systems, such as those fabricated from simple and complex nanorods, nanobeams and nanoplates have attracted keen interest among scientists and engineers.

Examples of one-dimensional nanoscale objects include (nanorod and nanobeam) carbon nanotubes (Ijima, 1993), zinc oxide (ZnO) nanowires and boron nitride (BN) nanotubes, while two-dimensional nanoscale objects include graphene sheets and BN nanosheets.

These nanostructures are found to have exciting mechanical, chemical, electrical, optical and electronic properties.

Nanostructures are being used in the field of nanoelectronics, nanodevices, nanosensors, nano-oscillators, nano-actuators, nanobearings, and micromechanical resonators, transporter of drugs, hydrogen storage, electrical batteries, solar cells, nanocomposites and nanooptomechanical systems (NOMS).

Understanding the dynamics of nanostructures is crucial for the development of future generation applications in these areas.
Nanoscale systems

(a) DNA

(b) Zinc Oxide (ZnO) nanowire

(c) Boron Nitride nanotube (BNNT)

(d) Protein
General approaches for studying nanostructures
Progress in nanotechnologies has brought about a number of highly sensitive label-free biosensors.

These include electronic biosensors based on nanowires and nanotubes, optical biosensors based on nanoparticles and mechanical biosensors based on resonant micro- and nanomechanical suspended structures.

In these devices, molecular receptors such as antibodies or short DNA molecules are immobilized on the surface of the micro-nanostructures. The operation principle is that molecular recognition between the targeted molecules present in a sample solution and the sensor-anchored receptors gives rise to a change of the optical, electrical or mechanical properties depending on the class of sensor used.

These sensors can be arranged in dense arrays by using established micro- and nanofabrication tools.
Cantilever nano-sensor

Array of cantilever nano sensors (from http://www.bio-nano-consulting.com)
Cantilever nano-sensor

Carbon nanotube with attached molecules
The mechanics behind nano-sensors

A) Static mode

B) Dynamic mode

i) Added mass

ii) Stiffness
Introduction

Mass sensing - an inverse problem

- This talk will focus on the detection of mass based on shift in frequency.
- Mass sensing is an inverse problem.
- The “answer” in general is non-unique. An added mass at a certain point on the sensor will produce an unique frequency shift. However, for a given frequency shift, there can be many possible combinations of mass values and locations.
- Therefore, predicting the frequency shift - the so called “forward problem” is not enough for sensor development.
- Advanced modelling and computation methods are available for the forward problem. However, they may not be always readily suitable for the inverse problem if the formulation is “complex” to start with.
- Often, a carefully formulated simplified computational approach could be more suitable for the inverse problem and consequently for reliable sensing.
The need for “instant” calculation

Sensing calculations must be performed very quickly - almost in real time with very little computational power (fast and cheap devices).
Single-walled carbon nanotube based sensors

Cantilevered nanotube resonator with an attached mass at the tip of nanotube length: (a) Original configuration; (b) Mathematical idealization. Unit deflection under the mass is considered for the calculation of kinetic energy of the nanotube.
Single-walled carbon nanotube based sensors - bridged case

Bridged nanotube resonator with an attached mass at the center of nanotube.
Resonant frequencies of SWCNT with attached mass

- In order to obtain simple analytical expressions of the mass of attached biochemical entities, we model a single walled CNT using a uniform beam based on classical Euler-Bernoulli beam theory:

\[ EI \frac{\partial^4 y(x, t)}{\partial x^4} + \rho A \frac{\partial^2 y(x, t)}{\partial t^2} = 0 \]  \hspace{1cm} (1)

where \( E \) the Youngs modulus, \( I \) the second moment of the cross-sectional area \( A \), and \( \rho \) is the density of the material. Suppose the length of the SWCNT is \( L \).

- Depending on the boundary condition of the SWCNT and the location of the attached mass, the resonant frequency of the combined system can be derived. We only consider the fundamental resonant frequency, which can be expressed as

\[ f_n = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} \]  \hspace{1cm} (2)

Here \( k_{eq} \) and \( m_{eq} \) are respectively equivalent stiffness and mass of SWCNT with attached mass in the first mode of vibration.
Cantilevered SWCNT with mass at the tip

- Suppose the value of the added mass is $M$. We give a virtual force at the location of the mass so that the deflection under the mass becomes unity. For this case $F_{eq} = \frac{3EI}{L^3}$ so that

$$k_{eq} = \frac{3EI}{L^3} \quad (3)$$

- The deflection shape along the length of the SWCNT for this case can be obtained as

$$Y(x) = \frac{x^2 (3L - x)}{2L^3} \quad (4)$$

- Assuming harmonic motion, i.e., $y(x, t) = Y(x) \exp(i\omega t)$, where $\omega$ is the frequency, the kinetic energy of the SWCNT can be obtained as

$$T = \frac{\omega^2}{2} \int_0^L \rho AY^2(x) dx + \frac{\omega^2}{2} MY^2(L)$$

$$= \rho A \frac{\omega^2}{2} \int_0^L Y^2(x) dx + \frac{\omega^2}{2} M 1^2 = \frac{\omega^2}{2} \left( \frac{33}{140} \rho AL + M \right) \quad (5)$$
Therefore

\[ m_{eq} = \frac{33}{140} \rho AL + M \]  \hspace{1cm} (6)

The resonant frequency can be obtained using equation (54) as

\[
\begin{align*}
      f_n &= \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} \\
      &= \frac{1}{2\pi} \sqrt{\frac{3EI/L^3}{\frac{33}{140} \rho AL + M}} \\
      &= \frac{1}{2\pi} \sqrt{\frac{140}{11}} \sqrt{\frac{EI}{\rho AL^4}} \sqrt{\frac{1}{1 + \frac{M}{\rho AL} \frac{140}{33}}} \\
      &= \frac{1}{2\pi} \frac{\alpha^2 \beta}{\sqrt{1 + \Delta M}} \\
\end{align*}
\]  \hspace{1cm} (7)

where

\[
\alpha^2 = \sqrt{\frac{140}{11}} \quad \text{or} \quad \alpha = 1.888 \]  \hspace{1cm} (8)

\[
\beta = \sqrt{\frac{EI}{\rho AL^4}} \]  \hspace{1cm} (9)

and \[ \Delta M = \frac{M}{\rho AL} \mu, \quad \mu = \frac{140}{33} \]  \hspace{1cm} (10)
Clearly the resonant frequency for a cantilevered SWCNT with no added tip mass is obtained by substituting $\Delta M = 0$ in equation (7) as

$$f_{0n} = \frac{1}{2\pi} \alpha^2 \beta$$  \hspace{1cm} (11)

Combining equations (7) and (11) one obtains the relationship between the resonant frequencies as

$$f_n = \frac{f_{0n}}{\sqrt{1 + \Delta M}}$$  \hspace{1cm} (12)
General derivation of the sensor equations

- The frequency-shift can be expressed using equation (41) as

\[ \Delta f = f_{0n} - f_n = f_{0n} - \frac{f_{0n}}{\sqrt{1 + \Delta M}} \]  

(13)

- From this we obtain

\[ \frac{\Delta f}{f_{0n}} = 1 - \frac{1}{\sqrt{1 + \Delta M}} \]  

(14)

- Rearranging gives the expression

\[ \Delta M = \frac{1}{\left(1 - \frac{\Delta f}{f_{0n}}\right)^2} - 1 \]  

(15)

- This equation completely relates the change in mass frequency-shift. Expanding equation (80) in Taylor series one obtains

\[ \Delta M = \sum_{j=1}^{\infty} (j + 1) \left(\frac{\Delta f}{f_{0n}}\right)^j, \quad j = 1, 2, 3, \ldots \]  

(16)
General derivation of the sensor equations

Therefore, keeping upto first and third order terms one obtains the linear and cubic approximations as

\[ \Delta M \approx 2 \left( \frac{\Delta f}{f_0} \right) \]  \hspace{1cm} (17)

and

\[ \Delta M \approx 2 \left( \frac{\Delta f}{f_0} \right) + 3 \left( \frac{\Delta f}{f_0} \right)^2 + 4 \left( \frac{\Delta f}{f_0} \right)^3 \]  \hspace{1cm} (18)

The actual value of the added mass can be obtained from (15) as

\[ M = \frac{\rho AL}{\mu} \frac{\left( \alpha^2 \beta \right)^2}{\left( \alpha^2 \beta - 2\pi \Delta f \right)^2} - \frac{\rho AL}{\mu} \]  \hspace{1cm} (19)

Mass detection from frequency shift

Using the linear approximation, the value of the added mass can be obtained as

\[ M = \frac{\rho AL}{\mu} \frac{2\pi \Delta f}{\alpha^2 \beta} \]  \hspace{1cm} (20)
The general relationship between the normalized frequency-shift and normalized added mass of the bio-particles in a SWCNT with effective density $\rho$, cross-section area $A$ and length $L$. Here $\beta = \sqrt{\frac{EI}{\rho AL^4}}$ s$^{-1}$, the nondimensional constant $\alpha$ depends on the boundary conditions and $\mu$ depends on the location of the mass. For a cantilevered SWCNT with a tip mass $\alpha^2 = \sqrt{140/11}$, $\mu = 140/33$ and for a bridged SWCNT with a mass at the midpoint $\alpha^2 = \sqrt{6720/13}$, $\mu = 35/13$. 

![Comparison of sensing results](image)
Validation of sensor equations - FE model

The theory of linear elasticity is used for both the CNT and the bacteria. FE model: number of degrees of freedom = 55401, number of mesh point = 2810, number of elements (tetrahedral element) = 10974, number of boundary elements (triangular element) = 3748, number of vertex elements = 22, number of edge elements = 432, minimum element quality = 0.2382 and element volume ratio = 0.0021. Length of the nanotube is 8 nm and length of bacteria is varied between 0.5 to 3.5 nm.
Validation of sensor equations - model data

Table: Geometrical and material properties for the single-walled carbon nanotube and the bacterial mass.

<table>
<thead>
<tr>
<th></th>
<th>SWCNT</th>
<th>Bacteria (E Coli)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L ) ( = 8 \text{ nm} )</td>
<td>( E = 1.0 \text{ TPa} )</td>
<td>( E = 25.0 \text{ MPa} )</td>
</tr>
<tr>
<td>( E ) ( = 1.0 \text{ TPa} )</td>
<td>( \rho = 1.16 \text{ g/cc} )</td>
<td>( \rho = 2.24 \text{ g/cc} )</td>
</tr>
<tr>
<td>( \rho ) ( = 2.24 \text{ g/cc} )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( D ) ( = 1.1 \text{ nm} )</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \nu ) ( = 0.30 \text{ nm} )</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
**Table:** Comparison of frequencies (100 GHz) obtained from finite element simulation with MD simulation for the bridged configuration. For the 8.0 nm SWCNT used in this study, the maximum error is less than about 4%.

<table>
<thead>
<tr>
<th>D(nm)</th>
<th>L(nm)</th>
<th>( f_1 )</th>
<th>( f_2 )</th>
<th>( f_3 )</th>
<th>( f_4 )</th>
<th>( f_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MD</td>
<td>FE</td>
<td>%error</td>
<td>MD</td>
<td>FE</td>
</tr>
<tr>
<td></td>
<td>10.315</td>
<td>10.769</td>
<td>16.859</td>
<td>-4.40</td>
<td>6.616</td>
<td>6.884</td>
</tr>
<tr>
<td></td>
<td>10.478</td>
<td>22.224</td>
<td>-60.90</td>
<td>-112.10</td>
<td>9.143</td>
<td>12.237</td>
</tr>
<tr>
<td></td>
<td>10.478</td>
<td>22.224</td>
<td>-112.10</td>
<td>-40.69</td>
<td>9.143</td>
<td>14.922</td>
</tr>
<tr>
<td>1.1</td>
<td>5.6</td>
<td>MD</td>
<td>FE</td>
<td>%error</td>
<td>MD</td>
<td>FE</td>
</tr>
<tr>
<td></td>
<td>6.616</td>
<td>6.884</td>
<td>12.237</td>
<td>-4.05</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>9.143</td>
<td>14.922</td>
<td>-33.84</td>
<td>-63.21</td>
<td>8.679</td>
<td>8.659</td>
</tr>
<tr>
<td>8.0</td>
<td>5.6</td>
<td>MD</td>
<td>FE</td>
<td>%error</td>
<td>MD</td>
<td>FE</td>
</tr>
<tr>
<td></td>
<td>3.800</td>
<td>3.900</td>
<td>8.659</td>
<td>-2.63</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>3.9</td>
<td>9.034</td>
<td>-4.09</td>
<td>8.801</td>
<td>9.034</td>
</tr>
</tbody>
</table>
The variation of identified mass with bacterial length using the finite element simulation, exact analytical formula and the linear approximation for the cantilevered nanotube. Proposed analytical expressions are in good agreement with the detailed finite element results for longer bacterial length.
Validation of sensor equations - Bridged nanotube

The variation of identified mass with bacterial length using the finite element simulation, exact analytical formula and the linear approximation for the bridged nanotube. Proposed analytical expressions are in good agreement with the detailed finite element results for longer bacterial length.
Validation of sensor equations

The general relationship between the normalized frequency-shift and normalized added mass of the bio-particles in a SWCNT with effective density \( \rho \), cross-section area \( A \) and length \( L \). Relationship between the frequency-shift and added mass of bio-particles obtained from finite element simulation are also presented here to visualize the effectiveness of analytical formulas.
For the cantilevered CNT, the resonance frequencies can be obtained from

\[ f_j = \frac{\lambda_j^2}{2\pi} \sqrt{\frac{EI}{\rho AL^4}} \]  

where \( \lambda_j \) can be obtained by solving the following transcendental equation

\[ \cos \lambda \cosh \lambda + 1 = 0 \]  

The vibration mode shape can be expressed as

\[ Y_j(\xi) = (\cosh \lambda_j \xi - \cos \lambda_j \xi) \]

\[ - \left( \frac{\sinh \lambda_j - \sin \lambda_j}{\cosh \lambda_j + \cos \lambda_j} \right) \left( \sinh \lambda_j \xi - \sin \lambda_j \xi \right) \]

where

\[ \xi = \frac{x}{L} \]

is the normalized coordinate along the length of the CNT. For sensing applications we are interested in the first mode of vibration for which \( \lambda_1 = 1.8751 \).
Cantilevered nanotube resonator with attached masses (DeOxy Thymidine)

(a) DeOxy Thymidine at the edge of a SWCNT
(b) DeOxy Thymidine distributed over the length of a SWCNT

(c) Mathematical idealization of (a): point mass at the tip
(d) Mathematical idealization of (b): distributed mass along the length
Exact dynamic solution

Suppose there is an attached nano/bio object of mass $M$ at the end of the cantilevered resonator in 1(a). The boundary conditions with an additional mass of $M$ at $x = L$ can be expressed as

$$y(0, t) = 0, \quad y'(0, t) = 0, \quad y''(L, t) = 0,$$

and

$$Ey''''(L, t) - M\ddot{y}(L, t) = 0 \quad (25)$$

Here $(\bullet)'$ denotes derivative with respective to $x$ and $(\bullet)$ denotes derivative with respective to $t$. Assuming harmonic solution $y(x, t) = Y(x)e^{i\omega t}$ and using the boundary conditions, it can be shown that the resonance frequencies are still obtained from Eq. (21) but $\lambda_j$ should be obtained by solving

$$(\cos \lambda \sinh \lambda - \sin \lambda \cosh \lambda) \Delta M \lambda + (\cos \lambda \cosh \lambda + 1) = 0 \quad (26)$$

Here

$$\Delta M = \frac{M}{\rho AL} \quad (27)$$

is the ratio of the added mass and the mass of the CNT. If the added mass is zero, then one can see that Eq. (27) reduces to Eq. (22).
These equations are obtained by considering the differential equation and the boundary conditions in an exact manner.

They are complex enough so that a simple relationship between the change in the mass and the shift in frequency is not available.

Moreover, these equations are valid for point mass only. Many biological objects are relatively large in dimension and therefore the assumption that the mass is concentrated at one point may not be valid.

In the fundamental mode of vibration, the natural frequency of a SWCNT oscillator can be expressed as

$$f_n = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}}$$

(28)

Here $k_{eq}$ and $m_{eq}$ are respectively equivalent stiffness and mass of SWCNT in the first mode of vibration.

The equivalent mass $m_{eq}$ changes depending on whether a nano-object is attached to the CNT. This in turn changes the natural frequency.
**Calibration Constants - energy approach**

- Suppose $Y_j$ is the assumed displacement function for the first mode of vibration.
- Suppose the added mass occupies a length $\gamma L$ and its mass per unit length is $m$. Therefore, $M = m \times \gamma L$. From the kinetic energy of the SWCNT with the added mass and assuming harmonic motion, the overall equivalent mass $m_{eq}$ can be expressed as

$$m_{eq} = \rho A L \int_{0}^{1} Y_j^2(\xi)d\xi + M \int_{\Gamma} Y_j^2(\xi)d\xi$$

where $\Gamma$ is the domain of the additional mass. From the potential energy, the equivalent stiffness $k_{eq}$ can be obtained as

$$k_{eq} = \frac{EI}{L^3} \int_{0}^{1} Y_j''^2(\xi)d\xi$$

(29)
From these expressions we have

\[
\frac{k_{eq}}{m_{eq}} = \frac{EI}{\rho AL} \frac{l_3}{I_1} = \left( \frac{EI}{\rho AL^4} \right) \frac{l_3}{I_1 + l_2 \Delta M} \tag{31}
\]

where the mass ratio \(\Delta M\) is defined in Eq. (27). Using the expression of the natural frequency we have

\[
f_n = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} = \frac{\beta}{2\pi} \frac{c_k}{\sqrt{1 + c_m \Delta M}} \tag{32}
\]

where \(\beta = \sqrt{\frac{EI}{\rho AL^4}}\)

The stiffness and mass calibration constants are

\[
c_k = \sqrt{\frac{l_3}{l_1}} \quad \text{and} \quad c_m = \frac{l_2}{l_1} \tag{33}
\]

Equation (32), together with the calibration constants gives an explicit relationship between the change in the mass and frequency.
Calibration Constants - point mass

- We first consider the cantilevered CNT with an added point mass. For the cantilevered CNT, we use the mode shape in (23) as the assumed deflection shape $Y_j$. The value of $\lambda_j$ appearing in this equation is 1.8751. Using these the integral $I_1$ can be obtained as

$$I_1 = \int_0^1 Y_j^2(\xi)d\xi = 1.0 \quad (34)$$

- For the point mass at the end of the cantilevered SWNT we have

$$m(\xi) = M\delta(\xi - 1) \quad (35)$$

- Using these, the integral $I_2$ can be obtained as

$$I_2 = \int_0^1 \delta(\xi - 1)Y_j^2(\xi)d\xi = Y_j^2(1) = 4.0 \quad (36)$$

- Differentiating $Y_j(\xi)$ in Eq. (23) with respect to $\xi$ twice, we obtain

$$I_3 = \int_0^1 Y_j''^2(\xi)d\xi = 12.3624 \quad (37)$$
Using these integrals, the stiffness and mass calibration factors can be obtained as

\[ c_k = \sqrt{\frac{l_3}{l_1}} = 3.5160 \quad \text{and} \quad c_m = \frac{l_2}{l_1} = 4.0 \]  \hspace{1cm} (38)

Now we consider the case when the mass is distributed over a length \( \gamma L \) from the edge of the cantilevered CNT. Since the total mass is \( M \), the mass per unit length is \( M/\gamma L \). Noting that the added mass is between \((1 - \gamma)L\) to \( L\), the integral \( l_2 \) can be expressed as

\[ l_2 = \frac{1}{\gamma} \int_{\xi=1-\gamma}^{1} Y_j^2(\xi) d\xi; \quad 0 \leq \gamma \leq 1 \]  \hspace{1cm} (39)

This integral can be calculated for different values of \( \gamma \).
Calibration Constants - non-dimensional values

**Table:** The stiffness \((c_k)\) and mass \((c_m)\) calibration constants for CNT based bio-nano sensor. The value of \(\gamma\) indicates the length of the mass as a fraction of the length of the CNT.

<table>
<thead>
<tr>
<th>Mass size</th>
<th>Cantilevered CNT</th>
<th>Bridged CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(c_k)</td>
<td>(c_m)</td>
</tr>
<tr>
<td>Point</td>
<td>3.5160152</td>
<td>4.0</td>
</tr>
<tr>
<td>mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>((\gamma \to 0))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.1)</td>
<td>3.474732666</td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.2)</td>
<td>3.000820053</td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.3)</td>
<td>2.579653837</td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.4)</td>
<td>2.212267400</td>
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</tr>
<tr>
<td>(\gamma = 0.5)</td>
<td>1.898480438</td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.6)</td>
<td>1.636330135</td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.7)</td>
<td>1.421839146</td>
<td></td>
</tr>
<tr>
<td>(\gamma = 0.8)</td>
<td>1.249156270</td>
<td></td>
</tr>
</tbody>
</table>
The resonant frequency of a SWCNT with no added mass is obtained by substituting $\Delta M = 0$ in Eq. (32) as

$$f_{0n} = \frac{1}{2\pi} c_k \beta$$ (40)

Combining equations (32) and (40) one obtains the relationship between the resonant frequencies as

$$f_n = \frac{f_{0n}}{\sqrt{1 + c_m \Delta M}}$$ (41)

The frequency-shift can be expressed using Eq. (41) as

$$\Delta f = f_{0n} - f_n = f_{0n} - \frac{f_{0n}}{\sqrt{1 + c_m \Delta M}}$$ (42)

From this we obtain

$$\frac{\Delta f}{f_{0n}} = 1 - \frac{1}{\sqrt{1 + c_m \Delta M}}$$ (43)

Sensor equation based on calibration constants
Sensor equation based on calibration constants

- Rearranging gives the expression

\[
\Delta M = \frac{1}{c_m \left(1 - \frac{\Delta f}{f_0 n}\right)^2} - \frac{1}{c_m}
\]  

(44)

- This equation completely relates the change in mass with the frequency-shift using the mass calibration constant. The actual value of the added mass can be obtained from (44) as

\[
M = \frac{\rho AL}{c_m} \frac{\left(c_k^2 \beta^2\right)}{\left(c_k \beta - 2\pi \Delta f\right)^2} - \frac{\rho AL}{c_m}
\]  

(45)

This is the general equation which completely relates the added mass and the frequency shift using the calibration constants.
Validation based on molecular mechanics simulation

- In the calculation, GAUSSIAN 09 computer software and the universal force field (UFF) developed by Rappe et al. are employed.
- The universal force field is a harmonic force field, in which the general expression of total energy is a sum of energies due to valence or bonded interactions and non-bonded interactions

\[
E = \sum E_R + \sum E_\theta + \sum E_\phi + \sum E_\omega + \sum E_{VDW} + \sum E_{el} \quad (46)
\]

The valence interactions consist of bond stretching \((E_R)\) and angular distortions.

- The angular distortions are bond angle bending \((E_\theta)\), dihedral angle torsion \((E_\phi)\) and inversion terms \((E_\omega)\). The non-bonded interactions consist of van der Waals \((E_{VDW})\) and electrostatic \((E_{el})\) terms.
- We used UFF model, wherein the force field parameters are estimated using general rules based only on the element, its hybridization and its connectivity.
Comparison with MD simulations

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>Present analysis</th>
<th>MD simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>5.26</td>
<td>0.220</td>
<td>1.113</td>
</tr>
<tr>
<td>5.62</td>
<td>0.195</td>
<td>1.005</td>
</tr>
<tr>
<td>5.99</td>
<td>0.174</td>
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<td>6.35</td>
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<td>7.07</td>
<td>0.128</td>
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<tr>
<td>7.44</td>
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<td>0.548</td>
</tr>
<tr>
<td>8.52</td>
<td>0.089</td>
<td>0.492</td>
</tr>
</tbody>
</table>

Table: Natural frequencies of a (5,5) carbon nanotube in THz - Cantilever boundary condition. First four natural frequencies obtained from the present approach is compared with the MD simulation [Duan et al, 2007 - J. App. Phy] for different values of the aspect ratio.
Zigzag (5,0) SWCNT of length 8.52 nm with added DeOxy Thymidine (a nucleotide that is found in DNA)

(a) Point mass on a cantilevered CNT.

(b) Distributed mass on a cantilevered CNT. The length of the mass varies between 0.05L to 0.72L from the edge of the CNT.

Figure: Identified attached masses from the frequency-shift of a cantilevered CNT. The proposed calibration constant based approach is validated using data from the molecular mechanics simulations. The importance of using the calibration constant varying with the length of the mass can be seen in (b). The point mass assumption often used in cantilevered sensors, can result in significant error when the mass is distributed in nature.
## Error in mass detection

<table>
<thead>
<tr>
<th>Point mass</th>
<th>Distributed mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative frequency shift</td>
<td>% error</td>
</tr>
<tr>
<td>0.0929</td>
<td>13.9879</td>
</tr>
<tr>
<td>0.1790</td>
<td>28.1027</td>
</tr>
<tr>
<td>0.2165</td>
<td>11.1765</td>
</tr>
<tr>
<td>0.2956</td>
<td>34.2823</td>
</tr>
<tr>
<td>0.3016</td>
<td>10.9296</td>
</tr>
<tr>
<td>0.3367</td>
<td>12.4422</td>
</tr>
<tr>
<td>0.3477</td>
<td>2.1427</td>
</tr>
<tr>
<td></td>
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</tbody>
</table>
Bridged nanotube resonator with attached masses (DeOxy Thymidine)

(a) DeOxy Thymidine at the centre of a SWCNT
(b) DeOxy Thymidine distributed about the centre of a SWCN

c) Mathematical idealization of (a): point mass at the centre
(d) Mathematical idealization of (b): distributed mass about the centre
Zigzag (5,0) SWCNT of length 8.52 nm with added DeOxy Thymidine (a nucleotide that is found in DNA)

Figure: Identified attached masses from the frequency-shift of a bridged CNT. The proposed calibration constant based approach is validated using data from the molecular mechanics simulations. Again, the importance of using the calibration constant varying with the length of the mass can be seen in (b). However, the difference between the point mass and distributed mass assumption is not as significant as the cantilevered case.
## Error in mass detection

<table>
<thead>
<tr>
<th>Relative frequency shift ($\Delta f / f_{0n}$)</th>
<th>% error</th>
<th>Relative frequency shift ($\Delta f / f_{0n}$)</th>
<th>Normalized length ($\gamma$)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0521</td>
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<td>0.0901</td>
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<td>0.2000</td>
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<td>4.2630</td>
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</tr>
<tr>
<td>0.2094</td>
<td>0.5273</td>
<td>0.2859</td>
<td>0.4000</td>
<td>11.5109</td>
</tr>
<tr>
<td>0.2237</td>
<td>7.6267</td>
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<td>0.5000</td>
<td>13.4830</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3284</td>
<td>0.6000</td>
<td>23.3768</td>
</tr>
</tbody>
</table>
Simulation methods

Overview of nonlocal continuum mechanics

Computational methods for nano sensors

Adhikari (Swansea)

February 5, 2016
Experiments at the nanoscale are generally difficult at this point of time. On the other hand, atomistic computation methods such as molecular dynamic (MD) simulations are computationally prohibitive for nanostructures with large numbers of atoms. Continuum mechanics can be an important tool for modelling, understanding and predicting physical behaviour of nanostructures. Although continuum models based on classical elasticity are able to predict the general behaviour of nanostructures, they often lack the accountability of effects arising from the small-scale. To address this, size-dependent continuum based methods are gaining in popularity in the modelling of small sized structures as they offer much faster solutions than molecular dynamic simulations for various nano engineering problems. Currently research efforts are undergoing to bring in the size-effects within the formulation by modifying the traditional classical mechanics.
Overview of nonlocal continuum mechanics

Nonlocal continuum mechanics

- One popularly used size-dependant theory is the nonlocal elasticity theory pioneered by Eringen [1983], and has been applied to nanotechnology.

- Nonlocal continuum mechanics is being increasingly used for efficient analysis of nanostructures viz. nanorods, nanobeams, nanoplates, nanorings, carbon nanotubes, graphenes, nanoswitches and microtubules. Nonlocal elasticity accounts for the small-scale effects at the atomistic level.

- In the nonlocal elasticity theory, according to Eringen [1983], the small-scale effects are captured by assuming that the stress at a point as a function of the strains at all points in the domain.

- Nonlocal theory considers long-range inter-atomic interactions and yields results dependent on the size of a body.

- Some of the drawbacks of the classical continuum theory could be efficiently avoided and size-dependent phenomena can be explained by the nonlocal elasticity theory.
The basic equations for a nonlocal isotropic linear homogenous elastic body can be expresses as

\[ \sigma_{ij,j} = 0, \]

\[ \sigma_{ij}(x) = \int_{V} \phi(|x - x'|, \alpha)t_{ij}dV(x'), \quad \forall x \in V \]  

(47)

\[ t_{ij} = H_{ijkl}\varepsilon_{kl}, \]

\[ \varepsilon_{ij} = 1/2(u_{i,j} + u_{j,i}) \]

The terms \( \sigma_{ij}, t_{ij}, \varepsilon_{kl} \) and \( H_{ijkl} \) are the nonlocal stress, classical stress, classical strain and fourth-order elasticity tensors respectively. The volume integral is over the region \( V \) occupied by the body. Equation (47) couples the stress due to nonlocal elasticity and the stress due to classical elasticity.

The kernel function \( \phi(|x - x'|, \alpha) \) is the nonlocal modulus. The nonlocal modulus acts as an attenuation function incorporating into constitutive equations the nonlocal effects at the reference point \( x \) produced by local strain at the source \( x' \).
Nonlocal continuum mechanics

- The term $|\mathbf{x} - \mathbf{x}'|$ represents the distance in the Euclidean form and $\alpha$ is a material constant that depends on the internal (e.g. lattice parameter, granular size, distance between the C-C bonds) and external characteristics lengths (e.g. crack length, wave length).

- Material constant $\alpha$ is defined as $\alpha = (e_0 a)/l$. Here $e_0$ is a constant for calibrating the model with experimental results and other validated models. The parameter $e_0$ is estimated such that the relations of the nonlocal elasticity model could provide satisfactory approximation to the atomic dispersion curves of the plane waves with those obtained from the atomistic lattice dynamics.

- The terms $a$ and $l$ are the internal (e.g. lattice parameter, granular size, distance between C-C bonds) and external characteristics lengths (e.g. crack length, wave length) of the nanostructure. Equation (47) effectively shows that in nonlocal theory, the stress at a point is a function of the strains at all points in the domain. The classical elasticity can be viewed as a special case when the kernel function becomes a Dirac delta function.
The direct use of equation (47) in boundary value problems results in **integro-partial differential equations** and they are generally difficult to solve analytically.

For this reason, a differential form of nonlocal elasticity equation is often beneficial. According to Eringen this can be achieved for a **special case** of the kernel function given by

$$
\phi(|x - x'|, \alpha) = \left(2\pi \ell^2 \alpha^2\right) K_0 \left(\sqrt{x \cdot x}/\ell \alpha\right)
$$

(48)

Here $K_0$ is the modified Bessel function. The **equation of motion** in terms of nonlocal elasticity can be expressed as

$$
\sigma_{ij,j} + f_i = \rho \ddot{u}_i
$$

(49)

where $f_i$, $\rho$ and $u_i$ are the components of the body forces, mass density, and the displacement vector, respectively.
The terms $i, j$ take up the symbols $x, y, \text{ and } z$. The operator $(\ddot{\bullet})$ denotes double derivative with respect to time. Assuming the kernel function $\phi$ as the Green’s function, Eringen proposed a differential form of the nonlocal constitutive relation as

$$\sigma_{ij,j} + \mathcal{L}(f_i - \rho \ddot{u}_i) = 0 \quad (50)$$

where

$$\mathcal{L}(\bullet) = [1 - (e_0 a)^2 \nabla^2](\bullet) \quad (51)$$

and $\nabla^2$ is the Laplacian.

Using this equation the nonlocal constitutive stress-strain relation can be simplified as

$$\left(1 - \alpha^2 l^2 \nabla^2\right)\sigma_{ij} = t_{ij} \quad (52)$$

One can use this relationship and derive the equation of motion using conventional variational principle. In the next subsections we consider the dynamics of nonlocal road, beam and plate using this approach.
Values of different nonlocal parameters used in literature.

<table>
<thead>
<tr>
<th>Nonlocal Parameters</th>
<th>Magnitudes</th>
<th>Researchers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>0.142 nm</td>
<td>(Sudak, 2003)</td>
</tr>
<tr>
<td>$e_0$</td>
<td>0.39</td>
<td>(Eringen, 1983)</td>
</tr>
<tr>
<td></td>
<td>0.288</td>
<td>(Wang and Hu, 2005)</td>
</tr>
<tr>
<td></td>
<td>0-19</td>
<td>(Duan et al., 2007)</td>
</tr>
<tr>
<td>$e_0 a$</td>
<td>0.7 nm</td>
<td>(Wang et al, 2008)</td>
</tr>
<tr>
<td></td>
<td>0-2 nm</td>
<td>(Duan and Wang, 2007)</td>
</tr>
<tr>
<td></td>
<td>&lt;2.1 nm</td>
<td>(Wang, 2005)</td>
</tr>
<tr>
<td>$e_0 a/l$</td>
<td>0-0.8</td>
<td>(Lu et al., 2006)</td>
</tr>
</tbody>
</table>
Our recent book has more detailed discussions on the nonlocal theory:

We consider the frequency of carbon nanotubes (CNT) with attached mass, for example, deoxythymididine molecule.
For the **bending vibration** of a nonlocal damped beam, the equation of motion of free vibration can be expressed by

\[
EI \frac{\partial^4 V(x, t)}{\partial x^4} + m \left( 1 - (e_0 a)^2 \frac{\partial^2}{\partial x^2} \right) \left\{ \frac{\partial^2 V(x, t)}{\partial t^2} \right\} = 0
\]  

(53)

In the **fundamental mode** of vibration, the natural frequency of a nonlocal SWCNT oscillator can be expressed as

\[
f_n = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}}
\]  

(54)

Here \( k_{eq} \) and \( m_{eq} \) are respectively equivalent stiffness and mass of SWCNT in the first mode of vibration.
Following the energy approach, the natural frequency can be expressed as

\[ f_n = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} = \frac{\beta}{2\pi} \frac{c_k}{\sqrt{1 + c_{nl}^2 \theta^2 + c_m \Delta M}} \]  

(55)

where

\[ \beta = \sqrt{\frac{EI}{\rho AL^4}}, \ \theta = \frac{e_0 a}{L} \]  

(56)

The stiffness, mass and nonlocal calibration constants are

\[ c_k = \sqrt{\frac{140}{11}}, \ c_m = \frac{140}{33} \]  

and \[ c_{nl} = \frac{56}{11} \]  

(57)

Equation (55), together with the calibration constants gives an explicit relationship between the change in the mass and frequency.
We consider the frequency of carbon nanotubes (CNT) with attached distributed mass, for example, a collection of deoxythymidine molecules.
Following the energy approach, the natural frequency can be expressed as

\[
 f_n = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} = \frac{\beta}{2\pi} \frac{c_k}{\sqrt{1 + c_{nl}\theta^2 + c_m(\gamma)\Delta M}}
\]  

(58)

where

\[
 \beta = \sqrt{\frac{EI}{\rho AL^4}}, \quad \theta = \frac{e_0 a}{L}, \quad \Delta M = \frac{M}{\rho AL}, \quad c_k = \sqrt{\frac{140}{11}} \quad \text{and} \quad c_{nl} = \frac{56}{11}
\]

(59)

The length-dependent mass calibration constant is

\[
 c_m(\gamma) = \frac{140 - 210\gamma + 105\gamma^2 + 35\gamma^3 - 42\gamma^4 + 5\gamma^6}{33}
\]

(60)

Equation (58), together with the calibration constants gives an explicit relationship between the change in the mass and frequency.
Nonlocal sensor equations

- The resonant frequency of a SWCNT with no added mass is obtained by substituting $\Delta M = 0$ in Eq. (58) as

$$f_{0n} = \frac{1}{2\pi} c_k \beta$$

(61)

- Combining equations (58) and (61) one obtains the relationship between the resonant frequencies as

$$f_n = f_{0n} \frac{f_{0n}}{\sqrt{1 + c_{nl} \theta^2 + c_m(\gamma) \Delta M}}$$

(62)

- The frequency-shift can be expressed using Eq. (62) as

$$\Delta f = f_{0n} - f_n = f_{0n} - f_{0n} \frac{f_{0n}}{\sqrt{1 + c_{nl} \theta^2 + c_m(\gamma) \Delta M}}$$

(63)

- From this we obtain

$$\frac{\Delta f}{f_{0n}} = 1 - \frac{1}{\sqrt{1 + c_{nl} \theta^2 + c_m(\gamma) \Delta M}}$$

(64)
Nonlocal sensor equations

- Rearranging gives the expression

Relative mass detection

\[ \Delta M = \frac{1}{c_m(\gamma) \left(1 - \frac{\Delta f}{f_{0n}}\right)^2} - \frac{c_{nl}}{c_m(\gamma)} \theta^2 - \frac{1}{c_m(\gamma)} \]  

This equation completely relates the change in mass with the frequency-shift using the mass calibration constant. The actual value of the added mass can be obtained from (65) as

Absolute mass detection

\[ M = \frac{\rho AL}{c_m(\gamma)} \frac{(c_k^2 \beta^2)}{(c_k \beta - 2\pi \Delta f)^2} - \frac{c_{nl}}{c_m(\gamma)} \theta^2 \rho AL - \frac{\rho AL}{c_m(\gamma)} \]  

This is the general equation which completely relates the added mass and the frequency shift using the calibration constants.
Zigzag (5,0) SWCNT of length 8.52 nm with added DeOxy Thymididine (a nucleotide that is found in DNA)

(a) Point mass on a cantilevered CNT.

(b) Distributed mass on a cantilevered CNT. The length of the mass varies between 0.05L to 0.72L from the edge of the CNT.

Figure: Normalized mass vs. relative frequency shift for the SWCNT with point mass. The band covers the complete range of nonlocal the parameter $0 \leq \varepsilon_2 \leq 2$nm. It can be seen that the molecular mechanics simulation results reasonably fall within this band (except at $\Delta f / f_{n0} = 0.35$).
Results for optimal values of the nonlocal parameter

(a) Point mass on a cantilevered CNT: $e_0 a = 0.65\text{nm}$.

(b) Distributed mass on a cantilevered CNT. $e_0 a = 0.5\text{nm}$.

**Figure:** Normalized mass vs. relative frequency shift for the SWCNT with point mass with optimal values of the nonlocal parameter $e_0 a$. 
**Error in mass detection: point mass**

Percentage error in the mass detection using cantilevered CNT based biosensors for single biomolecule. The errors are shown for both local and nonlocal elastic theories (with optimised nonlocal parameter $e_0a = 0.65$ nm).

<table>
<thead>
<tr>
<th>Relative frequency shift</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Local elasticity</td>
</tr>
<tr>
<td>0.0929</td>
<td>13.9879</td>
</tr>
<tr>
<td>0.179</td>
<td>28.1027</td>
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<td>12.4422</td>
</tr>
<tr>
<td>0.3477</td>
<td>2.1427</td>
</tr>
</tbody>
</table>
## Error in mass detection: distributed mass

Percentage errors in the mass detection using cantilevered CNT based biosensor for distributed added biomolecules. The errors are shown for both local and nonlocal elastic theories (with optimised nonlocal parameter $e_0 a = 0.5$ nm).

<table>
<thead>
<tr>
<th>Relative frequency shift</th>
<th>Normalized length</th>
<th>Percentage error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>Local elasticity</td>
</tr>
<tr>
<td>0.0929</td>
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</tr>
<tr>
<td>0.153</td>
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<tr>
<td>0.3039</td>
<td>0.7167</td>
<td>7.9455</td>
</tr>
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</table>
Single-layer graphene sheet (SLGS) based sensors

Cantilevered Single-layer graphene sheet (SLGS) with adenosine molecules
Resonant frequencies of SLGS with attached mass

- We model SLGS dynamics as a thin plate in transverse vibration:

\[
D \left( \frac{\partial^4 u}{\partial x^4} + 2 \frac{\partial^2 u}{\partial x^2 \partial y^2} + \frac{\partial^4 u}{\partial y^4} \right) + \rho \frac{\partial^2 u}{\partial t^2} = 0, \\
0 \leq x \leq a; \ 0 \leq y \leq b.
\] (67)

- Here \( u \equiv u(x, y, t) \) is the transverse deflection, \( x, y \) are coordinates, \( t \) is the time, \( \rho \) is the mass density per area and the bending rigidity is defined by

\[
D = \frac{Eh^3}{12(1 - \nu^2)}
\] (68)

- \( E \) is the Young’s modulus, \( h \) is the thickness and \( \nu \) is the Poisson’s ratio. We consider rectangular graphene sheets with cantilevered (clamped at one edge) boundary condition.
Resonant frequencies of SLGS

The vibration mode-shape for the first mode of vibration of the planar SLGS is given by

$$w(x, y) = 1 - \cos \left( \frac{\pi x}{2a} \right) \quad (69)$$

The natural frequency of the system can be alternatively obtained using the energy principle. Assuming the harmonic motion, the kinetic energy of the vibrating plate can be expressed by

$$T = \omega^2 \int_A w^2(x, y) \rho \, dA \quad (70)$$

Here $\omega$ denotes the frequency of oscillation and $A$ denotes the area of the plate. Using the expression of $w(x, y)$ in Eq. (69) we have

$$T = \frac{1}{2} \omega^2 \rho \int_0^a \int_0^b \left( 1 - \cos \left( \frac{\pi x}{2a} \right) \right)^2 \, dx \, dy$$

$$= \frac{1}{2} \omega^2 (ab\rho) \frac{3\pi - 8}{2\pi} \quad (71)$$
Two-dimensional sensors - classical approach

Resonant frequencies of SLGS

- The potential energy can be obtained as

\[ U = \frac{D}{2} \int_A \left\{ \left( \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} \right)^2 - 2(1 - \nu) \left[ \frac{\partial^2 w}{\partial x^2} \frac{\partial^2 w}{\partial y^2} - \left( \frac{d^2 w}{dx^2} y \right)^2 \right] \right\} dA \]  \hspace{1cm} (72)

- Using the expression of \( w(x, y) \) in (69) we have

\[ U = \frac{D}{2 \rho} \int_0^a \int_0^b \left( \frac{\partial^2 w}{\partial x^2} \right)^2 \, dx \, dy = \frac{1}{2} \pi^4 D \, b(1/32) \]  \hspace{1cm} (73)

- Considering the energy balance, that is \( T_{\text{max}} = U_{\text{max}} \), from Eqs. (83) and (73) the resonance frequency can be obtained as

\[ \omega_0^2 = \left( \frac{\pi^4 D}{a^4 \rho} \right) \frac{1/32}{(3\pi - 8)/2\pi} \]  \hspace{1cm} (74)
Resonant frequencies of SLGS with attached mass

(a) Masses at the cantilever tip in a line
(b) Masses in a line along the width
(c) Masses in a line along the length
(d) Masses in a line with an arbitrary angle
Resonant frequencies of SLGS with attached mass

- Using the energy approach, the resonance frequency can be expressed in a general form as

\[
\omega_{a,b,c,d}^2 = \frac{1}{2} \left\{ \frac{1}{8} \pi^4 b(1/32) \frac{D}{a^4 \rho} + \alpha_{a,b,c,d} M \right\} = \left( \frac{\pi^4 D}{a^4 \rho} \right) \frac{1/32}{(3\pi - 8)/2\pi + \mu \alpha_{b,c,d}}
\]  

(75)

- Here the ratio of the added mass

\[
\mu = \frac{M}{M_g}
\]  

(76)

- \(\alpha_{a,b,c,d}\) are factors which depend on the mass distribution:

\[
\alpha_a = 1, \quad \alpha_b = (1 - \cos(\pi \gamma/2))^2
\]  

(77)

\[
\alpha_c = \frac{3\pi \eta + [\sin((\gamma + \eta)\pi) - \sin(\gamma \pi)] - 8[\sin((\gamma + \eta)\pi/2) - \sin(\gamma \pi/2)]}{2\pi \eta}
\]  

(78)

\[
\alpha_d = \frac{3\pi \eta \cos(\theta) + [\sin((\gamma + \eta \cos(\theta))\pi) - \sin(\gamma \pi)] - 8[\sin((\gamma + \eta \cos(\theta))\pi/2) - \sin(\gamma \pi/2)]}{2\pi \eta \cos(\theta)}
\]  

(79)
Sensor equation

The relative added mass of the bio-fragment can be obtained from the frequency shift as

\[ \mu = \frac{1}{c_n \left(1 - \frac{\Delta f}{f_0}\right)^2} \left(1 - \frac{1}{c_n}\right) \]  

(80)

Relative mass detection for 2D sensors

<table>
<thead>
<tr>
<th>Mass arrangement</th>
<th>Calibration constant (c_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case (a): Masses are at the cantilever tip in a line</td>
<td>(2\pi/(3\pi - 8))</td>
</tr>
<tr>
<td>Case (b): Masses are in a line along the width</td>
<td>(2\pi(1 - \cos(\pi \gamma/2))^2/(3\pi - 8))</td>
</tr>
<tr>
<td>Case (c): Masses are in a line along the length</td>
<td>((3\pi \eta + [\sin((\gamma + \eta)\pi) - \sin(\gamma \pi)] - 8[\sin((\gamma + \eta)\pi/2) - \sin(\gamma \pi/2)])/\eta(3\pi - 8))</td>
</tr>
<tr>
<td>Case (d): Masses are in a line with an arbitrary angle (\theta)</td>
<td>((3\pi \eta \cos(\theta) + [\sin((\gamma + \eta \cos(\theta))\pi) - \sin(\gamma \pi)] - 8[\sin((\gamma + \eta \cos(\theta))\pi/2) - \sin(\gamma \pi/2)])/\eta \cos(\theta)(3\pi - 8))</td>
</tr>
</tbody>
</table>
Validation with MM simulation (UFF): Case a

(a) SLGS with adenosine molecules at the (b) Identified mass from the frequency shift cantilever tip in a line

**Figure:** Identified attached masses from the frequency-shift of a cantilevered SLGS resonator for case (a). The SLGS mass is 7.57 zg and the mass of each adenosine molecule is 0.44 zg. The proposed approach is validated using data from the molecular mechanics simulations. Up to 12 adenosine molecules are attached to the graphene sheet.
Validation with MM simulation: Case b

(a) SLGS with adenosine molecules in a line along the width

(b) Identified mass from the frequency shift, $\gamma = 0.85$

Figure: Identified attached masses from the frequency-shift of a cantilevered SLGS resonator for case (b). The proposed approach is validated using data from the molecular mechanics simulations. Up to 10 adenosine molecules are attached to the graphene sheet.
Validation with MM simulation: Case d

(a) SLGS with adenosine molecules in a line with an arbitrary angle

(b) Identified mass from the frequency shift, \( \gamma = 0.25, \eta = 0.7 \) and \( \theta = \pi/6 \)

**Figure:** Identified attached masses from the frequency-shift of a cantilevered SLGS resonator for case (d). The proposed approach is validated using data from the molecular mechanics simulations. Up to 10 adenosine molecules are attached to the graphene sheet.
(a) Schematic diagram of single-layer graphene sheets, (b) Nonlocal continuum plate as a model for graphene sheets, (c) Resonating graphene sheets sensors with attached bio fragment molecules such as adenosine.
Nonlocal plate theory for SLGS

We model SLGS dynamics as a thin nonlocal plate in transverse vibration

\[ D \nabla^4 u + m \left( 1 - (e_0 a)^2 \nabla^2 \right) \left( \frac{\partial^2 u}{\partial t^2} \right), \]

\[ 0 \leq x \leq c; \ 0 \leq y \leq b. \]  

Here \( u \equiv u(x, y, t) \) is the transverse deflection, \( \nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x^2} \right) \) is the differential operator, \( x, y \) are coordinates, \( t \) is the time, \( \rho \) is the mass density per area and the bending rigidity is defined by

\[ D = \frac{Eh^3}{12(1 - \nu^2)} \]  

Introducing the non dimensional length scale parameter

\[ \mu = \frac{e_0 a}{c} \]  

the resonance frequency can be obtained as

\[ \omega_0^2 = \left( \frac{\pi^4 D}{c^4 \rho} \right) \left( \frac{1}{(3\pi - 8)/2\pi + \mu^2 \pi^2/8} \right) \]
Nonlocal SLGS with attached masses

(a) Masses at the cantilever tip in a line (b) masses in a line along the width, (c) masses in a line along the length, (d) masses in a line with an arbitrary angle.
Nonlocal resonant frequencies of SLGS with attached mass

Using the energy approach, the resonance frequency can be expressed in a general form as

\[ \omega^2_{a,b,c,d} = \frac{1}{2} \left( \frac{\pi^4 D}{c^3 b} \right) \left\{ cb \rho \left( \frac{3\pi - 8}{2\pi} + \frac{\mu^2 \pi^2}{8} \right) + \alpha_{a,b,c,d} M \right\} \]

\[ = \left( \frac{\pi^4 D}{c^4 \rho} \right) \frac{1/32}{(3\pi - 8)/2\pi + \mu^2 \pi^2 / 8 + \beta \alpha_{b,c,d}} \quad (85) \]

Here the ratio of the added mass

\[ \beta = \frac{M}{M_g} \quad (86) \]

and \( \alpha_{b,c,d} \) are factors which depend on the mass distribution as defined before.
Free vibration response at the tip of the graphene sheet due to the unit initial displacement obtained from molecular mechanics simulation. Here $T_0$ is the time period of oscillation without any added mass. The shaded area represents the motion of all the mass loading cases considered for case (a).
Validation with MM simulation (UFF): Case a

(a) SLGS with adenosine molecules at the cantilever tip in a line

(b) Identified mass from the frequency shift

Figure: Identified attached masses from the frequency-shift of a cantilevered SLGS resonator for case (a). The SLGS mass is 7.57\text{g} and the mass of each adenosine molecule is 0.44\text{g}. The proposed approach is validated using data from the molecular mechanics simulations. Up to 12 adenosine molecules are attached to the graphene sheet.
Validation with MM simulation: Case b

(a) SLGS with adenosine molecules in a line along the width

(b) Identified mass from the frequency shift, $\gamma = 0.85$

**Figure:** Identified attached masses from the frequency-shift of a cantilevered SLGS resonator for case (b). The proposed approach is validated using data from the molecular mechanics simulations. Up to 10 adenosine molecules are attached to the graphene sheet.
Validation with MM simulation: Case d

(a) SLGS with adenosine molecules in a line with an arbitrary angle

(b) Identified mass from the frequency shift, $\gamma = 0.25$, $\eta = 0.7$ and $\theta = \pi/6$

**Figure:** Identified attached masses from the frequency-shift of a cantilevered SLGS resonator for case (d). The proposed approach is validated using data from the molecular mechanics simulations. Up to 10 adenosine molecules are attached to the graphene sheet.
Conclusions

- Principles of fundamental mechanics and dynamics can have unprecedented role in the development of nano-mechanical bio sensors. Nano-sensor market is predicted to be over 20 Billion$ by 2020.
- Mass sensing is an inverse problem - NOT a conventional “forward problem”.
- Due to the need for “instant calculation”, physically insightful simplified (but approximate) approach is more suitable compared to very detailed (but accurate) molecular dynamic simulations.
- Energy based simplified dynamic approach turned out to sufficient to identify mass of the attached bio-objects from “measured” frequency-shifts in nano-scale sensors.
- Closed-form sensor equations have been derived and independently validated using molecular mechanics simulations. Calibration constants necessary for this approach have been given explicitly for point mass as well as distributed masses.
- Nonlocal model with optimally selected length-scale parameter improves the mass detection capability for nano-sensors.


