Background

On a macroscopic level, distinguishing between mechanical and thermal forms of energy is a relatively simple task – the science of thermodynamics is based on the clear distinction between work and heat. When making observations on the molecular scale, however, these definitions become less clear-cut. Both forms of energy are the result of the motion of individual atoms and can be expressed as the total kinetic energy of a collection of molecules. The goal of this work is to model the flow of energy from mechanical oscillations into thermal vibrations in carbon nanotubes without tracking the trajectory of every atom in the system.

Characterized by a strength-to-weight ratio up to 200 times that of steel and a thermal conductivity twice that of diamond, carbon nanotubes (CNT) have been suggested for a wide variety of technological applications. [1] In particular, CNTs may constitute an ideal reinforcing element in polymer-based ablative composite materials. [2] In addition to transporting thermal energy throughout an ablative heat shield in a controllable way, the mechanical properties of CNTs could contribute significant ballistic impact resistance to microscopic projectiles. [3] For the purpose of designing CNT-reinforced polymer composites for this application, it is necessary to understand how mechanical energy is dissipated in a network of CNTs.

In order to analyze this problem, computational simulations of dynamic energy transfer in single CNTs were conducted, with the dissipation of stretching and bending energies investigated separately. Results from detailed atomistic simulations are used to introduce energy dissipation mechanisms into a computationally efficient mesoscopic model.

Significance

The transformation of energy at the nanoscale is of extreme importance for the operation of nanodevices and materials. Although the static characteristics of CNTs have been researched extensively, very little literature exists concerning their dynamic properties. Thermal dissipation among uncorrelated degrees of freedom has been included in mesoscopic models of other molecular systems. [5,6] This work goes further, however, by suggesting a method for artificially transferring energy among highly correlated oscillations in complex molecules at a mesoscopic level. Ultimately, the resulting mesoscopic model will be indispensable in the engineering of novel CNT-based materials and devices.

Methodology

Atomistic simulations were conducted using constant energy Molecular Dynamics. Interatomic interactions were calculated according to the AIREBO potential parameterized for carbon [4]. The CNT sample chosen for simulation consisted of 100 40-atom unit cells and two C260 fullerene hemispherical caps (Figs 1-2).

In the mesoscopic representation, the CNT was discretized into 13 cylindrical segments defined by 14 nodes. In the simulations, nodes interacted according to the Lagrangian

$$L = \frac{1}{2} \sum_i m_i \dot{x}_i^2 - \sum_i U_{str}^i - \sum_i U_{bnd}^i ,$$  \hspace{1cm} (1)

with explicit models for the anharmonic stretching potential energy $U_{str}^i$ and the bending potential energy, including bending-buckling, $U_{bnd}^i$. [7,8,9] These models were parameterized according to experimental bulk properties of CNTs. Simulations were then carried out by integrating the resulting equations of motion at constant energy. Although both potentials permitted the fracture of the CNT at the critical strain or bending angle, respectively, the design of the dynamic simulations intentionally avoided such events. Prior simulations with this mesoscopic formulation confirmed that it correctly reproduces low frequency acoustic waves. [7]

In both the atomistic and mesoscopic representations, the CNT samples were equilibrated at a constant temperature $\theta_{init}$ for a minimum of 100ps. In the case of stretching simulations, the samples were instantaneously
stretched in the axial direction at a homogeneous strain rate \( \varepsilon \),

\[ x_i' = x_i^t, \quad x_i'' = x_i^t, \quad x_i^3 = (1 + \varepsilon) x_i^3. \]  

(2)

For bending simulations, the coordinates were transformed to a specified radius of curvature \( R_c \), measured from the centerline of the CNT, while maintaining the centerline length and orthogonal cross-sections. The atomic velocities were also rotated accordingly,

\[ x_i' = R_c \sin \left( \frac{x_i^t}{R_c} \right) + x_i \sin \left( \frac{x_i^t}{R_c} \right), \]

\[ x_i'' = R_c \cos \left( \frac{x_i^t}{R_c} \right) + x_i \cos \left( \frac{x_i^t}{R_c} \right), \]

\[ x_i^3 = x_i^3 \cos \left( \frac{x_i^t}{R_c} \right) - x_i^3 \sin \left( \frac{x_i^t}{R_c} \right). \]  

(3)

A mode analysis technique was employed in order to compare results between atomistic and mesoscopic simulations. In a linear system in the limit of small oscillations, the displacement of a single node can be written as the sum over the contributions of all normal modes \( \rho_i^{(n)} \) in the system,

\[ x_i(t) - x_i(0) = \sum_{n=1}^{N} \rho_i^{(n)} C_i^{(n)} \cos(\omega_n t + \phi_n). \]  

(5)

Exploiting the orthogonality of these normal modes, the kinetic energy \( T^{(n)} \) of one mode is

\[ T^{(n)}(t) = \frac{1}{2} \left( \sum_{j=1}^{N} m_j^{12} \hat{x}_i(t) \rho_i^{(n)} \right)^2. \]  

(6)

Although the total numbers of modes differ, all modes available in the mesoscopic model are common between the two representations. The kinetic energy corresponding to the mesoscopic representation could thus be extracted from atomistic simulations as

\[ T_{meso}(t) = \sum_{n=1}^{N_{req}} T^{(n)}(t). \]  

(7)

**Results**

As expected, the amplitude of low frequency oscillations induced by stretching and bending was observed to decay with time in the atomistic simulations. In the case of stretching, thermalization occurred by means of three distinct mechanisms dependent on the initial strain rate.

**Stretching Decay Mechanism I**

The decay of low amplitude (less than 3.3%) strain rate at an initial temperature of 40.6K) longitudinal oscillations can be modeled as a variable rate exponential decay. Making a harmonic approximation for the stretching potential in the limit of small oscillations, it can be assumed that all normal modes will have equal energy in thermal equilibrium. The rate of exponential decay should thus approach zero as the temperature of the mesoscopic modes \( \theta_{meso} \) approaches the temperature of the higher frequency modes \( \theta_{thermal} \). This can be achieved by adding a velocity-dependent decay term to the equations of motion for mesoscopic nodes,

\[ m_i \ddot{x}_i = \nabla \sum_{j=1}^{N} U_{ij}^{str} - \gamma (\theta_{meso} - \theta_{thermal}) \dot{x}_i. \]  

(8)

where \( \gamma \) is the exponential decay rate.

Expressing \( \gamma \) as a piecewise function in time,

\[ \gamma(t) = \gamma_i, \quad t_{i-1} < t < t_i, \]  

(9)

gives a function that can be fitted to the \( T_{meso} \) calculated from atomistic results,

\[ \langle T_{meso}(t) \rangle \propto \exp(-2\gamma_i t). \]  

(10)

(Fig 3). At higher initial temperatures, \( \gamma \) tends towards a linear function of \( (\theta_{meso} - \theta_{thermal}) \).
**Stretching Decay Mechanism II**

At higher strain rates (3.3-5.7% at an initial temperature of 40.6K), the oscillations decay as in mechanism I until a critical time at which the longitudinal motion is rapidly damped (Fig A1). This phenomenon is due to dynamic coupling between longitudinal stretching modes and radial breathing modes. This coupling causes the amplitude of low frequency radial breathing modes to increase exponentially until the critical compression necessary to induce axial buckling is reached. Initiation of buckling facilitates the rapid transfer of energy into thermal vibrations.

An analogous effect due to stretching-bending coupling was observed in the mesoscopic model, which does not include radial breathing in its formulation. The exponential increase in the amplitude of bending modes, culminating in the initiation of buckling, can be seen in Fig 4.

**Stretching Decay Mechanism III**

For initial strain rates higher than 5.7% at an initial temperature of 40.6K, the majority of the mechanical stretching energy was thermalized within one period of oscillation (Fig A2). This rapid decay is also a result of axial buckling, initiated by the summation of two compressive unloading waves at the midpoint of the CNT. Because tensile stresses do not induce axial buckling, initially compressed CNTs required two periods of oscillations to exhibit the same rapid decay, as both tensile waves reflected from the free ends as compressive stesses.

**Bending Decay Mechanism**

Bending oscillations were found to decay in a similar manner to stretching mechanism I in all cases. If initially bent past the bending buckling limit, the sample CNT continued to buckle and relax cyclically until damping brought the amplitude of the oscillations back under the buckling limit. In simulations beginning with an initial radius of curvature greater than this limit, bending buckling was never initiated.

**Conclusions**

The results from atomistic simulations have elucidated the mechanical energy dissipation mechanisms in CNTs and provided sufficient data to introduce these mechanisms artificially in the mesoscopic model. These corrections will improve the mesoscopic model's description of nonequilibrium processes, such as high velocity impact phenomena (Fig A3).

An understanding of mechanical and thermal energy transfer at the molecular level is essential to the development of nanodevices and nanomaterials. A fully developed mesoscopic model including this information allows for the intelligent engineering of new composite materials capable of withstanding both extreme aerodynamic heating and ballistic impact from airborne debris, two critical goals for the design of safe heat shield materials in aerospace applications.
**Dynamic Simulation of Energy Dissipation in Carbon Nanotubes**

**William Jacobs**

**Fig A1: Stretching Decay Mechanism II**

\[ \theta_{\text{init}} = 40.6K \]

4\% initial strain

\[
\begin{align*}
0\text{ps} & \quad \text{onset of axial buckling} \quad \sim 14\text{ps} \quad 20\text{ps} \\
\end{align*}
\]

**Fig A2: Stretching Decay Mechanism III**

\[ \theta_{\text{init}} = 40.6K \]

10\% initial strain

\[
\begin{align*}
0.1\text{ps} & \quad \text{onset of axial buckling} \quad 1.0\text{ps} \\
\end{align*}
\]
Dynamic Simulation of Energy Dissipation in Carbon Nanotubes

(a) Initial Projectile Velocity 100m/s
Mechanical impact energy distributed evenly throughout the thin film.

(b) Initial Projectile Velocity 1000m/s
Mechanical impact energy confined to the vicinity of the projectile.

Fig A3: Mesoscopic simulations of high velocity impact. A spherical projectile (50nm diameter) collided at normal incidence and perforated a thin film (100nm thickness) composed of a network of CNT bundles. CNTs are colored according to intertube interaction energies, with warmer colors indicating higher energies. The exclusion of mechanical energy dissipation mechanisms and higher frequency thermal vibrational modes prevented the absorption of impact energy by the thin film and resulted in unphysically elevated simulation temperatures.
References


