The Young's Modulus of Single-Walled Carbon Nanotubes

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Abstract

A new numerical method for calculating the Young's modulus of carbon nanotubes which avoids ambiguities that have plagued other attempts is validated. Molecular dynamics simulations that utilize the Tersoff Potential are used to model various single-walled carbon nanotubes under different strains to achieve this validation. Data is taken from an armchair, zigzag, and chiral carbon nanotube. The calculated Young's moduli are all around $Y = 1$ TPa, in agreement with existing experimental data.

1 Introduction

Carbon nanotubes (CNTs) were discovered in 1952 by L. V. Radushkevich and V. M. Lukyanovich, but they were not brought to the attention of the scientific community until 1991, when Sumio Iijima discovered CNTs in the soot of graphite electrodes after an arc discharge [1]. Since then, the exciting properties of CNTs have led to a host of proposed applications, many of which are currently being realized.

A convenient way to think about CNTs is to think of them as a sheet of graphene rolled up into a tube and capped on either end with a part of a buckyball. Graphene is a hexagonal lattice of carbon atoms connected by sp^2 bonds. Multiple stacked sheets of graphene compose the common form of carbon called graphite. A buckyball is a carbon molecule in the shape of a sphere. The CNT is capped in such a way so that every carbon atom is bonded to three other carbon atoms.

The way that the graphene is rolled up determines what is called the chirality of the nanotube. CNTs can be grouped into three categories based on chirality: armchair, zigzag, and chiral (Fig. 1). Armchair CNTs contain carbon-carbon bonds which are perpendicular to the tube's axis, while zigzag CNTs contain bonds that are parallel to the tube's axis. Chiral CNTs

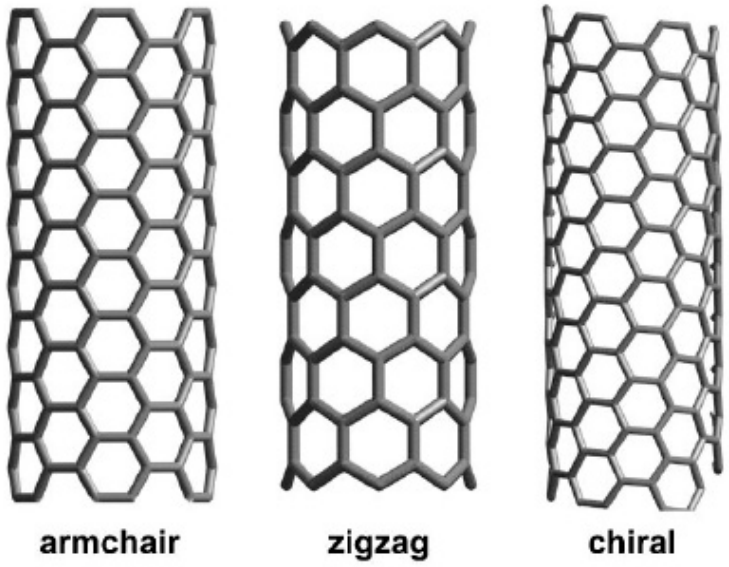

Figure 1: An example of each of the three types of CNT chiralities [2].

contain bonds neither perpendicular nor parallel to the axis of the tube. Each category is named for the nanotubes' edge pattern.

Each CNT can be uniquely identified with the index pair (n, m), $n \geq m$. All armchair CNTs have index pairs of the form $(n, 0)$, and all zigzag CNTs have index pairs of the form (n, n). A great deal of useful information is contained in the index pair. For example, the radius of a given CNT is

$$r = \frac{l\sqrt{3(n^2 + m^2 + nm)}}{2\pi}$$

where the carbon-carbon bond length $l = 1.42$ Å[3].

Carbon nanotubes demonstrate a number of unique properties. They are the stiffest material known, yet they are also very bendable [4, 5]. CNTs are only a few nanometers in diameter, but they can range in length from a few nanometers to 18 centimeters [6]. Depending on the tube geometry and the strain that the nanotube is experiencing, CNTs can be either metallic or semiconducting [7]. CNTs can also be nested inside one other to create multi-walled carbon nanotubes (MWCNTs). Carbon nanotubes without other nanotubes nested within them are referred to as single-walled carbon nanotubes (SWCNTs) to differentiate them from MWCNTs.

The proposed applications of CNTs promise to affect fields such as nanotechnology, materials science, and electronics [8, 9, 10, 11]. They range from space elevator cables to synthetic muscles [8, 9]. Although many of these applications have not yet come to fruition, advances

in the application of CNTs have already been made. For example, carbon nanotubes are already used to make various composite materials stronger and more stiff, and their addition to motors and transistors is rapidly allowing motors and transistors to become smaller than they have ever been before [10, 11].

Unfortunately, production and characterization problems currently hinder the advancement of CNT applications. The current method of CNT production, for example, is still relatively primitive. CNTs can easily be produced, but at the moment it is all but impossible to specifically create large quantities of nanotubes with a predetermined chirality or length [12]. Widespread use of carbon nanotubes requires cost-effective and reliable methods of production, but at the moment such methods of production have not been discovered.

A second problem hindering the application of CNTs is the uncertainty surrounding their mechanical properties. Many of the values that are used to describe mechanical properties of materials have traditionally assumed that the material being described is macroscopic. The microscopic nature of CNTs poses new challenges to the definition of the aforementioned values that have not yet been resolved. In this paper, validation is provided to a new characterization of one of the most important values, Young's modulus, which circumvents many of the problems that have hampered previous attempts to precisely define it.

2 Young's Modulus

2.1 Background

Young's modulus is a value associated with a material that represents that material's stiffness. In other words, Young's modulus relates the stress applied to the material with the resulting strain of the material. The Young's modulus of a material must be known before the material can be used in many practical applications, but there is currently disagreement over how to define Young's modulus for carbon nanotubes.

This disagreement stems mostly from the fact that Young's modulus is only properly defined for continuous materials, while CNTs are crystalline materials. For continuous, bulk materials, Young's modulus is defined as $Y = \frac{\sigma}{\varepsilon}$, where σ is the axial stress and ε is the axial strain. Axial stress, in turn, can be written as $\sigma = \frac{F}{A}$, where F is the force applied over the cross-sectional area A (Fig. 2). Young's modulus, therefore, requires an unambiguous cross-sectional area. For continuous materials, defining the cross-sectional area is quite simple. For discrete materials such as carbon nanotubes, however, this task is ambiguous.

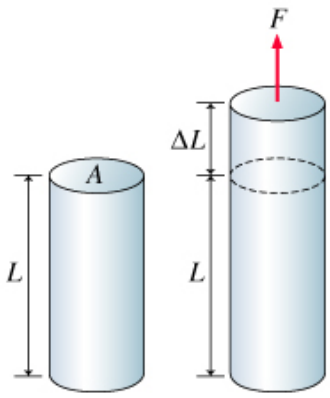

Figure 2: Young's Modulus for continuous materials [13]. Axial strain $\varepsilon = \frac{\Delta L}{L}$, or $\varepsilon = \frac{\Delta L}{L_0}$.

2.2 Methods of Defining Young's Modulus

The cross-sectional area of carbon nanotubes is ambiguous for two main reasons. The first reason is that the force is not applied uniformly, but is applied at discrete points due to the CNTs' crystalline structure. The second reason is that the discrete points to which the force is applied are distributed around the circumference of the nanotube, not uniformly across the entire cross-sectional area.

The cross-sectional area of CNTs has been defined differently by different researchers. A common definition of the cross-sectional area is that of a solid cylinder or prism [14]. Another popular definition of A is that of a hollow cylinder with a thickness [14].[1] Still others have opted to define the much more straightforward circumference instead of the troublesome cross-sectional area [14]. This method views the CNT as basically one-dimensional and produces a value called the surface Young's modulus. This surface Young's modulus is applicable in some situations, but it is not the same value as Young's modulus and so doesn't completely solve the original problem of defining Y.

2.3 The Second Derivative of the Strain Energy Density

These different methods of defining A predictably produce different values of Young's moduli. Young's modulus is supposed to be a constant of the material, so these attempts to define the cross-sectional area seemingly fail. But recently, an application from elastics has led to a new method of defining Young's modulus for CNTs to be proposed. This new method defines Young's modulus as the second derivative of the strain energy density with respect

[1] 3.4 Å is the most common thickness, since it is the distance of separation between layers of graphene in graphite. Other values have also been used, though.

to the axial strain [14]. This method circumvents the problem of having to define the cross-sectional area of CNTs and so has the potential to finally and definitively define Young's modulus.

In the case of carbon nanotubes under axial strain, the strain energy of the CNT is its internal elastic potential energy. The internal elastic potential energy U_e of a CNT experiencing axial strain is

$$U_e = \int \frac{YA\Delta L}{L_0}\,\mathrm{d}L = \frac{YA}{L_0}\int \Delta L\,\mathrm{d}L = \frac{YA\Delta L^2}{2L_0}$$

where A is the cross-sectional area, L_0 is the initial length, ΔL is the change in length, and Y is Young's modulus. The internal elastic potential energy per unit volume, or the internal elastic potential energy density, can be written as

$$V = \frac{Y\Delta L^2}{2L_0^2}$$

where $V = \frac{U_e}{AL_0}$. Since $\varepsilon = \frac{\Delta L}{L_0}$, we can write

$$V = \frac{1}{2}Y\varepsilon^2$$

and then take the second derivative or the internal elastic potential energy density, or strain energy density, with respect to strain to find Young's modulus: $\frac{d^2V}{d\varepsilon^2} = Y$.

3 Method

3.1 Molecular Dynamics Simulation

Molecular dynamics simulations are a type of simulation program that models materials on the molecular scale. These programs first read a potential that describes the interactions between atoms, as well as information on atomics masses, initial positions, and initial velocities. From this information, the programs calculate the force on each atom due to atoms around it. Then, the programs solve for the acceleration of each particle and perform a double integration to find the change in position of each atom. Finally, the programs apply the position changes and repeat the process as many times as required.

A molecular dynamics simulation tool called XMD was utilized to create a program that simulates SWCNTs experiencing strain [15]. After creating the nanotube, the program sets the temperature of the nanotube, and also implements the Tersoff Potential to model the

interactions between the carbon atoms. The program allows the CNT to reach mechanical equilibrium, and then begins to gradually increase the strain that the CNT is under until the CNT reaches maximum strain.[2] Inputs for the final program include chirality, length of CNT, duration of incremental strain increase, maximum strain, and temperature. Outputs include particle displacement, the product of internal stress and atomic volume, and internal potential energy, which in this case is also the strain energy. Data was gathered from three SWCNTs: a (5,5) armchair CNT, a (9,0) zigzag CNT, and a (6,4) chiral CNT. The temperature was set to $T = 0$ K.

3.2 Finite Size Scaling Analysis

Molecular dynamics simulations produce reliable results only when edges and boundaries are not a significant portion of the material being simulated. In other words, simulations which model materials that are too small usually produce nonphysical results. So, in order to run an efficient simulation that still produces reliable results, the molecular dynamics program should be made to simulate CNTs with the shortest length that still produces realistic data. In order to find this optimum length, finite size scaling analysis is necessary.

The XMD program requires that the length of a CNT be inputted in terms of unit lengths that are determined by the program. The length of a unit length changes for each CNT, as it is dependent on chirality of the nanotube. For the (5,5) armchair CNT the unit length is about 3.566 nm, for the (9,0) zigzag CNT the unit length is about 3.692 nm, and for the (6,4) chiral CNT the unit length is about 3.689 nm. Young's moduli for CNTs of unit lengths 1-7 were calculated (Fig. 3). The Young's moduli for lengths of 1-3 units were all quite large. Starting with lengths of 4 units, though, the calculated Young's moduli ceased to change dramatically, although they slowly begin to increase. Since CNTs with lengths of 4 units are the shortest CNTs that follow this trend, they are most likely the nanotubes with the smallest length that can reliably model actual CNTs.

4 Results and Analysis

After plotting the strain against the strain energy, the second derivative of the graph's best fit parabola was taken to find the product of Young's modulus and atomic volume.[3] The average atomic volume can be easily calculated from the particle displacement data, so it was divided out to calculate Young's modulus.

[2]Mechanical equilibrium is defined in this case as the state of the CNT in which the internal potential energy of the CNT is constant. Experimentation determined that CNTs in the XMD program reach mechanical equilibrium after $2.5 * 10^{-10}$ seconds.

[3]The output from the XMD program was strain energy, not strain energy density. This is why, after taking the second derivative, the resulting value was not Young's modulus, but was the product of Young's modulus and atomic volume.

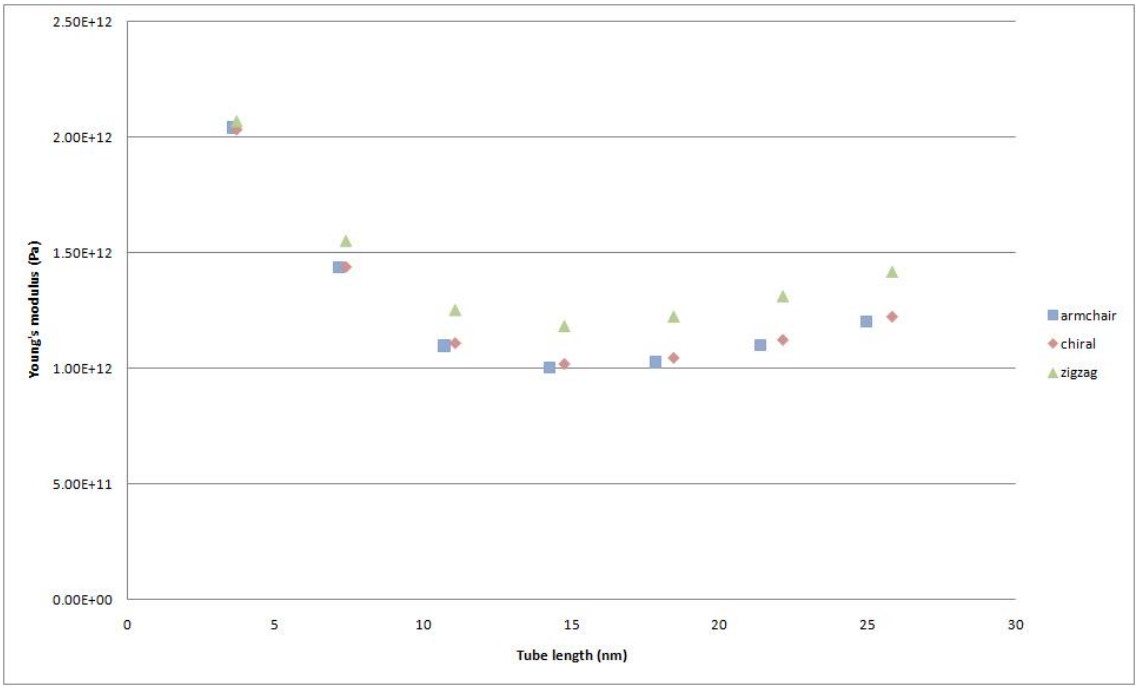

Figure 3: Young's moduli for the three CNT chiralities of different lengths. The maximum strain that the CNTs experienced in the simulation that produced the data for this graph was .01, but very similar trends appeared in simulations of CNTs under all levels of strain.

(5,5) armchair CNT
$.958571 \pm .04928$ TPa
(9,0) zigzag CNT
$1.14569 \pm .04615$ TPa
(6,4) chiral CNT
$.987279 \pm .03549$ TPa

Table 1: Estimated values for Young's modulus of CNTs calculated with the definition of Y.

(5,5) armchair CNT
$.954444 \pm .04797$ TPa
(9,0) zigzag CNT
$1.12272 \pm .06231$ TPa
(6,4) chiral CNT
$.967868 \pm .04884$ TPa

Table 2: Values for Young's modulus of CNTs under various strains calculated with the new method.

In order to check the reliability of the simulations that produced these results, Young's modulus was also derived by using the definition of Young's modulus: $Y = \frac{\sigma}{\varepsilon}$. Since the internal stress is a response to the strain, the applied axial stress σ could be estimated from it. Then, the strain ε was graphed against the stress σ, and the slope of the resulting line, which is Young's modulus Y, was calculated. Only resulting lines that had $R^2 \geq .999$ were considered valid and below the yield point of the CNT, and so only CNTs experiencing strains of .04 or less were considered. The results of this check are listed in Table 1.

The resulting Young's moduli from the simulations are listed in Table 2. They correlate closely with the data in Table 1, confirming the accuracy of the results. Experimental data sets the estimated Young's modulus of any given CNT is around 1 TPa [3]. So, the results in Table 2 are also in agreement with the experimental data.

5 Future Directions

The XMD program created for this project can be used as a base for many other simulations involving CNTs. For example, future work could examine the effects of temperature or chirality on Young's modulus. Since the program created during this project and the results it produced are reliable, the relationship between applied axial stress and the resulting axial strain can be calculated for CNTs of any chirality. This ability to correlate stress and strain removes one of the major obstacles preventing the use of CNTs in many practical applications. Now that more is known about the mechanical properties of CNTs, future work could begin to relate the mechanical properties with other properties of CNTs, such as electrical properties of the nanotubes.

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