Elastic Properties of Carbon Nanotubes and Nanoropes

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(February 7, 2008)

Abstract

Elastic properties of carbon nanotubes and nanoropes are investigated using an empirical force-constant model. For single and multi-wall nanotubes the elastic moduli are shown to be insensitive to details of the structure such as the helicity, the tube radius and the number of layers. The tensile Young's modulus and the torsion shear modulus calculated are comparable to that of the diamond, while the the bulk modulus is smaller. Nanoropes composed of single-wall nanotubes possess the ideal elastic properties of high tensile elastic modulus, flexible, and light weight.

PACS numbers: 61.46+w, 36.40+d

I. Introduction

The discoveries of carbon nanotubes[1] and the new efficient method of producing them[2] stimulate a great interest in these novel materials. The electronic[3] and magnetic properties[4] of nanotubes depend sensitively on the structural details such as the tube radius and the helicity. It has been speculated that nanotubes also posses novel mechanical properties. Recent measurements have inferred a Young's modulus that is several times that of the diamond.[5]

The mechanical properties of small single-wall nanotubes have been studied by several groups using molecular dynamics simulations.[6,7] A Young's modulus several times greater than that of the diamond was predicted. However, those calculations were restricted to small single-wall nanotubes of few Å in radius. Most samples of nanotubes are either multi-wall or crystalline ropes of single-wall nanotubes.

A practical method of investigating elastic properties is to use the empirical force-constant model. The phonon spectrum and elastic properties of the graphite has been successfully calculated using such models.[8] The similarity in local structure between the graphite and the nanotubes ensure that a similar model is applicable for nanotubes. The advantage of such a model is that it can be easily applied to nanotubes of different size, helicity, and number of layers. One such model has been used to predict the phonon spectrum of small single-wall nanotubes.[9] Here we present results of applying a similar model to calculate elastic properties of single and multi-wall nanotubes of various size and geometry, and that of crystalline nanoropes composed of single-wall nanotubes.

II. The Force-constant Model

In an empirical force-constant model, the atomic interactions near the equilibrium structure are approximated by the sum of pair-wise harmonic potentials between atoms. In the most successful model for the graphite, interactions up to fourth-neighbor in-plane and out-of-plane interactions are included.[8] The force constants are empirical determined by fitting to measured elastic constants and phonon frequencies.

The local structure of a nanotube layer can be constructed from the conformal mapping of the graphitic sheet on to a cylindrical surface. For a typical nanotube of few nm in radius, the curvature is small enough that one expects short-range atomic interactions to be very close to that in the graphite. Thus, we adopt the same parameters developed by Al-Jishi et al.[8] for graphite for intra-plane interactions in all nanotubes.

The different layers in a multi-wall nanotube are not well registered as they are in the single crystal graphite. Thus, one can not adopt the same set of parameters for the interlayer interactions. Instead, we model the interlayer interactions in nanotube by the summation of pair-wise van de Waals interactions, $U(r) = 4\epsilon\left((\sigma/r)^{12} - (\sigma/r)^{6}\right)$. Such a model has been used successfully to calculate the bulk properties of C_{60} solid.[10] The van de Waals parameter $\sigma = 3.4$Å , $\epsilon = 12$meV, were determined by fitting the interlayer distance and the elastic constant c_{33} of the single crystal graphite.[11]

III. Single-Layer Nanotubes

Following the notation of White et al.[12], each single-layer nanotube is indexed by a pair of integers (n_1, n_2), corresponding to a lattice vector $\mathbf{L} = n_1\mathbf{a_1} + n_2\mathbf{a_2}$ on the graphite plane, where $\mathbf{a_1}, \mathbf{a_2}$ are the graphite plane unit cell vectors. The structure of the nanotube is obtained by the conformal mapping of a graphite strip onto a cylindrical surface. The nanotube radius is given by $R = a_o\sqrt{3(n_1^2 + n_2^2 + n_1 n_2)}/2\pi$, where $a_o = 1.42$Å is the C-C bond length.

In principle, force constants depend on the size of the nanotube as overlaps of π orbitals change with the nanotube curvature.[13] However, Such dependence is very weak. In this paper, we neglect this effect and concentrate on the dependence of elastic properties on the geometry and interlayer interactions.

The elastic constants are calculated from the second derivatives of the energy density with respect to various strains.[14] The tensile stiffness as measured by Young's modulus is defined as the stress/strain ratio when a material is axially strained. For most materials, the radial dimension is reduced when it is axially elongated. The ratio of the reduction in radial

dimension to the axial elongation defines the Poisson ratio ν. We first calculate the Poisson ratio by minimizing the strain energy with respect to both the radial compression and the axial extension. The Young's modulus Y is then calculated from the second derivative of the strain energy density with respect to the axial strain at the fixed ν.

Table.1 lists the bulk, Young's and shear (referred to the torsional shear) moduli calculated for selective examples of single-wall nanotubes. An important quantity in determining values of elastic constants is the wall thickness h of nanotubes. Previous calculations has taken $h = 0.66$Å for single layer nanotubes which leads to the unusual large Young's modulus.[7] For multi-wall nanotubes, all experiments indicate that the interlayer distance is the same as that in the graphite, $h = 3.4$Å. Thus, it is reasonable to take the interlayer distance $h = 3.4$Å as the wall thickness. We use the same values for all single multi-wall nanotubes. This enables us to compare results across nanotubes of different size and number of layers. For comparison, elastic moduli of the graphite[11] and that of the diamond[14] are also listed.

Examine the numbers in Table.1 one concludes that: (1) *Elastic moduli are insensitive to the size and the helicity.* (2) *The Young's and shear moduli of nanotubes are comparable to that of the diamond and that if in-plane graphite.* (3) *Single-wall nanotubes are stiff in both the axial direction and the basal plane.*

VI. Multi-wall Nanotubes

The interlayer distance in all experimentally observed multi-wall nanotubes is comparable to that in graphite. This puts a constrain on possible combinations of single-wall nanotubes to form multi-wall nanotubes. We have calculated elastic moduli for many different combinations. It is found that elastic properties are insensitive to different combinations as long as the constrain – interlayer distance ≈ 3.4Å – is satisfied. Because of this insensitivity we use results for one series of multi-wall nanotubes to illustrate our main points. The series chosen is constructed from $(5n, 5n), n = 1, 2, 3 \cdots$ single-wall tubes. This is one of the most likely structure for multi-wall tubes as its interlayer distance is very close to

that actually observed.[15]

Table.2 lists the calculated elastic coefficients and the bulk, Young's, and shear modulus for this series of nanotubes up to 10 layers. The experimental values for the graphite and the diamond are also listed for comparison. One observes that the elastic moduli are essentially independent of the number of layers. The same is true for all other multi-wall nanotubes we have calculated. From Table.2 and its comparison with Table.1 one concludes: (1) *The elastic moduli vary little with the number of layers.* (2) *The interlayer van de Waals interactions contribute less than 10% to the elastic moduli of multi-wall nanotubes.*

The Young's modulus of multi-wall nanotubes was deduced recently by Treacy et al.[5] from the thermal vibrations of anchored tubes. Their values range from 0.4 to 4 TPa with the average values of 1.6 TPa. These results are substantial larger than our calculated values of 1 TPa. The discrepancy may be due to the large uncertainty in how to estimate the Young's modulus from their experiments. In their estimation the isotropic model was assumed, our results clearly show that this is not true. More recent direct measurement of the multi-wall nanotubes using the AFM technique and the Euler's buckling criteria has yield a result of 1 TPa,[16] in agreement with our calculations.

V. Crystalline Nanoropes

The discovery of a new efficient method of producing bulk quantity of single-wall nanotubes has made it possible to make crystalline ropes of nanotubes.[2] These nanoropes consist of 100 to 500 single-wall nanotubes of uniform size. Due to the weak inter-tube interactions one expects these rope to be flexible in the basal plane, yet very stiff along the axial direction.

We use same model described above to calculate the lattice constant and elastic moduli of these nanoropes. Table.3 summarize the bulk properties of nanoropes with nanotubes radius ranging from 1nm (the (5,5) tube) to 2nm (the (13,13) tube). Due to extreme disparity between the inter-tube and intra-tube interactions, we have neglected the coupling between the two interactions. Thus, the lattice constant a_0 and the cohesive energy E_0 are determined by inter-tube van de Waals interaction only. It is found that a_0 and the cohesive

energy per atom scales with the tube radius R as $a_0 = 2R{+}3.2$Å , $E_0 = 61.5(meV)/\sqrt{R(\mathring{A}\ )}$. For nanorope composed of the typical (10,10) tube, $R = 6.78$Å , $a_0 = 16.8$Å , $E_0 = 23$meV. The cohesive energy of the rope is comparable to that of the C_{60} solid (33mev).

From Table.3 one observes that: (1) *Nanorope is very anisotropic.* (2) *The basal plane is soft, while the axial direction is very stiff.* (3) *The C_{33} is about half that of the diamond.* The weak inter-tube interaction ensures that the rope is flexible as individual tubes can rotate and slide with respect to each other easily. This is supported by the experimental SEM images where long nanoropes are observed to be well bended and tangled.[2]

VI. Conclusions

We have investigated elastic properties of nanotubes and nanoropes using an empirical force constant model. The simplicity of the model enable us to explore the dependence of elastic moduli on the nanotube geometry. It is shown that elastic properties are insensitive to the radius, helicity, and the number of layers. The calculated Young's modulus ($\sim$ 1 TPa) and shear modulus ($\sim$ 0.5 TPa) are comparable to that of diamond for both single and multi-wall individual nanotubes. Crystalline rope of nanotubes is very anisotropic in its elastic properties – soft on basal plane and stiff along the axial direction. The large Young's modulus and flexibility of nanoropes make them ideal materials for nanometer scale engineering.

Acknowledgments This work is supported by a grant from U.S. Department of Energy, and in part by a grant from The Petroleum Research Foundation.

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TABLES

TABLE I. Elastic moduli of selective single-wall nanotubes. (n_1, n_2) – index, R – radius in nm. B, Y, M are bulk, Young's and shear modulus in units of TPa ($10^{13} dy/cm^2$). ν is the Poisson ratio. Experimental values for the graphite and the diamond are listed for comparison.

(n_1, n_2)	R	B	Y	M	ν
(5,5)	0.34	0.191	0.971	0.436	0.280
(6,4)	0.34	0.191	0.968	0.437	0.284
(7,3)	0.35	0.191	0.968	0.454	0.284
(8,2)	0.36	0.190	0.974	0.452	0.280
(9,1)	0.37	0.191	0.968	0.465	0.284
(10,0)	0.39	0.192	0.968	0.451	0.282
(10,10)	0.68	0.191	0.972	0.457	0.278
(50,50)	3.39	0.192	0.969	0.458	0.282
(100,100)	6.78	0.192	0.969	0.462	0.282
(200,200)	13.56	0.192	0.969	0.478	0.282
Graphite[a]		0.0083	1.02	0.44	0.16
Graphite[b]		0.0083	0.0365	0.004	0.012
Diamond[c]		0.442	1.063	0.5758	0.1041

[a] Graphite along the basal plane.[11]

[b] Graphite along the C axis.[11]

[c] Diamond along the cube axis.[14]

TABLE II. Elastic coefficients and moduli (in TPa) of multi-wall nanotubes constructed from the $(5n, 5n), n = 1, 2, 3 \cdots$ series of single-wall tubes. N – number of layers, R – radius of the out-most layer in nm. B, Y, M are bulk, Young's and shear modulus (in TPa). Values for the graphite and the diamond are listed for comparison.

n	R	C_{11}	C_{33}	C_{44}	C_{66}	C_{13}	Y	M	B
1	0.34	0.397	1.05	0.189	0.134	0.147	0.97	0.436	0.191
2	0.68	0.412	1.13	0.189	0.137	0.146	1.05	0.455	0.194
3	1.02	0.413	1.15	0.189	0.138	0.146	1.08	0.464	0.194
4	1.36	0.412	1.17	0.189	0.138	0.146	1.09	0.472	0.194
5	1.70	0.411	1.18	0.189	0.139	0.146	1.10	0.481	0.194
6	2.03	0.411	1.18	0.189	0.139	0.146	1.10	0.491	0.194
7	2.37	0.410	1.18	0.189	0.139	0.146	1.11	0.502	0.194
8	2.71	0.410	1.19	0.189	0.139	0.146	1.11	0.514	0.194
9	3.05	0.410	1.19	0.190	0.139	0.146	1.11	0.527	0.194
10	3.39	0.410	1.19	0.190	0.139	0.146	1.11	0.541	0.194
Graphite[a]		1.06	0.036	0.004	0.440	0.015	1.02	0.008	0.440
Diamond		1.07	1.07	0.575	0.575	0.125	1.06	0.442	0.575

[a]Young's and shear moduli refer to the basal plane.

TABLE III. Lattice constant a_0 (nm), cohesive energy per atom E_0 (meV), and elastic moduli (in TPa) of crystalline nanorope made of single-wall (n, n) tubes. R(nm) is the radius of single-wall tube.

n	R	a_0	E_0	C_{11}	C_{12}	C_{33}
5	0.33	0.99	33.5	0.066	0.022	0.795
6	0.40	1.13	30.1	0.071	0.024	0.736
7	0.47	1.26	28.2	0.078	0.024	0.687
8	0.54	1.40	26.2	0.082	0.029	0.641
9	0.61	1.54	24.7	0.085	0.029	0.600
10	0.67	1.67	23.5	0.090	0.032	0.563
11	0.74	1.81	22.5	0.098	0.035	0.532
12	0.81	1.94	21.6	0.102	0.036	0.502
13	0.88	2.08	20.7	0.106	0.036	0.475
14	0.94	2.21	19.9	0.111	0.042	0.452
15	1.01	2.35	19.3	0.118	0.043	0.430