Elastic Properties of Carbon Nanotubes and Nanoropes

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Elastic properties of carbon nanotubes and nanoropes are investigated using an empirical force-constant model. For single and multiwall nanotubes the elastic moduli are shown to be insensitive to structural details such as the helicity, the radius, and the number of walls. The tensile Young's modulus and the torsion shear modulus of tubes are comparable to that of the diamond, while the bulk modulus is smaller. Nanoropes composed of single wall nanotubes have the ideal elastic properties of high tensile stiffness and light weight. [S0031-9007(97)03859-3]

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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 structural details such as the tube radius and the helicity. It has been speculated that nanotubes also possess 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 tubes of a few Å in radius. Most samples of nanotubes are either multiwall or crystalline ropes of single wall tubes.

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

The force-constant model.—In an empirical force-constant model, the atomic interactions near the equilibrium structure are approximated by the sum of pairwise 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 empirically determined by fitting to measured elastic constants and phonon frequencies. The local structure of a nanotube wall is constructed from the conformal mapping of the graphitic sheet onto a cylindrical surface. For a typical nanotube of a few nm in radius, the curvature is small enough that one expects short-range atomic interactions to be similar to that in the graphite. Thus, the set of parameters developed for intraplane interactions in graphite [8] is used for all intrawall interactions in nanotubes.

The different walls in a multiwall tube are not as well registered as they are in the single crystal graphite. Thus, the interlayer interaction parameters in crystalline graphite cannot be adopted for the interwall interaction. Instead, we model the interwall interaction by the summation of pairwise van de Waals interactions, $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6)]$. 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, was determined by fitting the interlayer distance and the elastic constant c_{33} of the single crystal graphite [11].

Single wall nanotubes.—Following the notation of White *et al.* [12], each single wall 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 unit cell vectors of the graphite sheet. The nanotube structure is obtained by the conformal mapping of a graphite strip onto a cylindrical surface. The nanotube radius is given by $R = a_0\sqrt{3(n_1^2 + n_2^2 + n_1n_2)}/2\pi$, where $a_0 = 1.42$ Å is the C-C bond length. In principle, force constants depend on the size of the tube while overlaps of π orbitals and orbital mixing depend on the curvature. However, such dependence is very weak [13]. In this paper we neglect this effect and concentrate on the dependence on the geometry and interwall 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 the 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 I lists the bulk, Young's, and shear (referred to as the torsional shear) moduli calculated for selective examples of single wall nanotubes. An important quantity in determining the values of elastic constants is the wall thickness h of nanotubes. For multiwall nanotubes, measured interwall distance is close to that interlayer distance in graphite, $h = 3.4$ Å. Thus, it is reasonable to take the interwall distance as the wall thickness. We use $h = 3.4$ Å for all single wall nanotubes. This enables us to compare the results between tubes of different size and the number of walls. For comparison, elastic moduli of the graphite [11] and that of the diamond [14] are also listed in Table I.

From the examination of the numbers in Table I, 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 of the graphitic sheet*. (3) *Single wall nanotubes are stiff in both the axial direction and the basal plane*.

The value of the Young's modulus obtained, $Y \sim 1$ TPa, is almost five time smaller than that previously calculated for small radius tubes [7]. However, in that calculation the tube wall thickness used is the π orbital extension $h = 0.66$ Å. Since elastic constants scale with the energy density or the inverse of the wall thickness, our results agree with the earlier calculations if the same wall thickness is used.

Multiwall nanotubes.—The interwall distance in all experimentally observed multiwall nanotubes is comparable to that in graphite. This puts a constraint on possible combinations of single wall tubes to form multiwall tubes. We have calculated elastic moduli for many different combinations. It is found that elastic properties are insensitive to different combinations as long as the constraint—interwall distance ≈ 3.4 Å— is satisfied. Because of this insensitivity, we use the results for one series of multiwall tubes to illustrate our conclusions. The series chosen is constructed from $(5n, 5n), n = 1, 2, 3, \ldots$, single wall tubes. This is one of the most likely structures for multiwall tubes as its interwall distance is very close to that actually observed [15].

Table II lists the calculated elastic coefficients and the bulk, Young's, and shear moduli for this series of nanotubes up to ten walls. The experimental values for the graphite and the diamond are also listed for comparison. One observes that the elastic moduli are essentially insensitive to the number of walls. The same is true for all other multiwall tubes we have calculated. From Table II and its comparison with Table I, one concludes that (1) *The elastic moduli vary little with the number of walls*. (2) *The interwall van de Waals interactions do not affect significantly the elastic moduli of multiwall nanotubes*. (3) *There is a large anisotropy in elastic properties of both single wall and multiwall nanotubes*. The Young's modulus of multiwall 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 substantially 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 the experiment. In their estimation the isotropic model was assumed. Our results clearly show that this is a large anisotropy in elastic properties, and that analysis of experimental data should take this into account. More recent direct measurements

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

(n_1, n_2)	R	C_{11}	C_{33}	B	Y	M	ν
(5, 5)	0.34	0.397	1.054	0.191	0.971	0.436	0.280
(6, 4)	0.34	0.397	1.054	0.191	0.972	0.437	0.280
(7, 3)	0.35	0.397	1.055	0.190	0.973	0.454	0.280
(8, 2)	0.36	0.397	1.057	0.190	0.974	0.452	0.280
(9, 1)	0.37	0.396	1.058	0.191	0.974	0.465	0.280
(10, 0)	0.39	0.396	1.058	0.190	0.975	0.451	0.280
(10, 10)	0.68	0.398	1.054	0.191	0.972	0.457	0.278
(50, 50)	3.39	0.399	1.054	0.192	0.972	0.458	0.277
(100, 100)	6.78	0.399	1.054	0.192	0.972	0.462	0.277
(200, 200)	13.5	0.399	1.054	0.192	0.972	0.478	0.277
Graphite[a]		1.06	⋯	0.0083	1.02	0.44	0.16
Graphite[b]		⋯	0.036	0.0083	0.0365	0.004	0.012
Diamond[c]		1.07	1.07	0.442	1.063	0.5758	0.1041

[a]Graphite in 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 multiwall nanotubes constructed from the $(5n, 5n), n = 1, 2, 3, \ldots$ series of single wall tubes. N—number of walls, R—radius of the outermost wall in nm. B, Y, M are bulk, Young's, and shear moduli (in TPa).

n	R	C_{11}	C_{33}	B	Y	M	ν
1	0.34	0.397	1.05	0.191	0.97	0.436	0.280
2	0.68	0.412	1.13	0.194	1.05	0.455	0.270
3	1.02	0.413	1.15	0.194	1.08	0.464	0.269
4	1.36	0.412	1.17	0.194	1.09	0.472	0.269
5	1.70	0.411	1.18	0.194	1.10	0.481	0.269
6	2.03	0.411	1.18	0.194	1.10	0.491	0.269
7	2.37	0.410	1.18	0.194	1.11	0.502	0.269
8	2.71	0.410	1.19	0.194	1.11	0.514	0.269
9	3.05	0.410	1.19	0.194	1.11	0.527	0.269
10	3.39	0.410	1.19	0.194	1.11	0.541	0.269

TABLE III. Elastic moduli (in TPa), lattice constant a_0 (nm), and the cohesive energy per atom E_0 (meV) of crystalline nanoropes composed of single wall (n, n) tubes. R (nm) is the radius of a single wall tube.

n	R	C_{11}	C_{33}	B	Y	a_0	E_0
5	0.33	0.066	0.795	0.015	0.795	0.99	33.5
6	0.40	0.071	0.736	0.017	0.736	1.13	30.1
7	0.47	0.078	0.687	0.018	0.687	1.26	28.2
8	0.54	0.082	0.641	0.020	0.641	1.40	26.2
9	0.61	0.085	0.600	0.021	0.600	1.54	24.7
10	0.67	0.090	0.563	0.022	0.563	1.67	23.5
11	0.74	0.098	0.532	0.025	0.532	1.81	22.5
12	0.81	0.102	0.502	0.026	0.502	1.94	21.6
13	0.88	0.106	0.475	0.028	0.475	2.08	20.7
14	0.94	0.111	0.452	0.030	0.452	2.21	19.9
15	1.01	0.118	0.430	0.033	0.430	2.35	19.3

of the multiwall suggest the Young's modulus to be $\sim 1-1.2$ TPa [16], in better agreement with our calculations.

Crystalline nanoropes.—The new method of producing single wall nanotubes also produces bundles of nanotubes or nanoropes. [2] These nanoropes consist of 100–500 single wall nanotubes of uniform size arranged in hexagonal order. Because of the weak intertube interactions, one expects these ropes to be flexible in the basal plane, yet very stiff along the axial direction.

We use the same model described above to calculate the elastic constant of nanoropes. Because of extreme disparity between the intertube and intratube interactions, we neglect the coupling between the two interactions. (This may lead to some error, but considering the simplicity of the current model such approximation is appropriate.) Thus, the lattice constant a_0 and the cohesive energy E_0 are determined by intertube van de Waals interaction only. By minimizing the total intertube interactions we find that the equilibrium lattice constant a_0 and the cohesive energy per atom scales with the tube radius R as $a_0 = 2R + 3.2$ Å, $E_0 = 61.5(\text{meV})/\sqrt{R(\text{Å})}$. Table III summarizes the bulk properties of nanoropes with the nanotube radius ranging from 0.33 nm [the (5,5) tube] to 1 nm [the (15,15) tube]. For a typical nanorope composed of the (10,10) tube, $R = 6.78$ Å, $a_0 = 16.8$ Å, and $E_0 = 23$ meV. The cohesive energy is comparable to that of the C_{60} solid (33 meV per C atom). The density of such a nanorope, 1.3 g/cm^3, is only one-half that of the graphite and one-third that of the diamond. Nanoropes are much lighter than regular carbon fibers.

The elastic constant ropes are calculated in a similar way by considering a small deviation from the equilibrium structure. The results are listed in Table III for selections of nanoropes. From the table, one observes that (1) *Nanoropes are extremely anisotropic. The basal plane is soft (small c_{11}) while the axial direction is very stiff (large c_{33}).* This unique property is in sharp contrast to the graphite and makes nanoropes superior to conventional carbon fiber in making strong composite materials. (2) *The Young's modulus is about one-half that of the diamond. It decreases with the nanotube radius. But per unit mass nanorope is stiffer than the diamond.* The weak intertube interactions make the rope flexible as individual tubes can easily rotate and slide with respect to each other. This is supported by the experimental scanning electron microscopy images, where long nanoropes are observed to be well bent and tangled [2]. (3) *Nanoropes possess the ideal properties of high tensile moduli and light weight*. These unique properties should make nanoropes useful in many applications.

In conclusion, we have investigated elastic properties of nanotubes and nanoropes using an empirical force-constant model. The simplicity of the model enables us to explore the dependence of elastic moduli on the nanotube geometry. It is shown that elastic properties of single and multiwall nanotubes are insensitive to the radius, helicity, and the number of walls. The Young's modulus (~ 1 TPa) and shear modulus (~ 0.5 TPa) calculated are comparable to that of the diamond. A crystalline rope of nanotubes is very anisotropic in its elastic properties—soft on basal plane and stiff along the axial direction. The unusual properties of nanorope—light, flexible, stiff—make them ideal materials for composite and nano scale engineering.

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