Z. Phys. D 27, 93–96 (1993)

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Structural rigidity and low frequency vibrational modes of long carbon tubules

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Received: 13 November 1992 / Final version: 3 December 1992

Abstract. We have studied the low frequency vibrational modes and the structural rigidity of long graphitic carbon tubules consisting of 100, 200, and 400 atoms. Our calculations have been performed using an empirical Keating Hamiltonian with parameters determined from first principles. We have found the "beam bending" mode to be one of the softest modes in these structures. The corresponding beam rigity of a "bucky tube" is compared to an found to exceed the highest values found in presently available materials.

PACS: 36.40.+d; 81.20.Sh

The successful synthesis [1] of macroscopic quantities of C_{60} clusters with a fascinating hollow "buckyball" structure [2] has ignited the interest of the scientific community in these and similar structures to an unprecedented degree. More recently, successful synthesis and identification of helical microtubules of graphitic carbon has been reported [3]. These graphite whiskers or "bucky tubes" are topological relatives of the "buckyball" [4] and might have been synthesized in direct current arc in inert gas already in the lat 50's [5]. Most interest in "bucky tubes" has concentrated on their electronic properties which can range from metallic to insulating [6]. In this paper, we present the first study of the mechanical properties of these structures. We show that these structures may be the finest and toughest fibers presently available, as was suggested recently [7].

We focus our study on the low frequency vibrational eigen modes of "bucky tubes" consisting of 100, 200, and 400 carbon atoms which reflect the rigidity of these structures. Among the many possible isomers [8], we consider those which can be generated by splitting the C_{60} "buckyball" into equal halves, and connecting the two "bucky caps" by a graphitic cylinder of variable length. All carbon atoms in the structure are three-fold coordinated. The "bucky tubes", like all members of the fullerene family, consist of a varying number of hexagonal carbon rings (distributed across the caps and the cylinder) and of twelve pentagons (on the caps). The equilibrium structure of a "bucky tube" consisting of 200 atoms is shown in Fig. 1a.

In order to determine the structural rigidity and the vibrational eigen modes of such a complex structure, we use an elastic model with central and angular forces for the nearest neighbor bonds. Such models are currently widely used to describe properties of covalently bonded solids with directional bonding [9–11]. In the present study, we will use the Keating potential [9] which is attractive due to its simple form and its successful application to complex structures such as the C_{60} solid [12] and amorphous silicon [13].

The Keating potential V_K describes potential energy changes with respect to a relaxed reference state, and consists of a bond stretching and a bond bending term. The bond stretching term is a central nearest-neighbor two-body potential. The bond bending part of the potential is a three-body interaction term which is sensitive to changes of the angle between nearest-neighbor bonds.

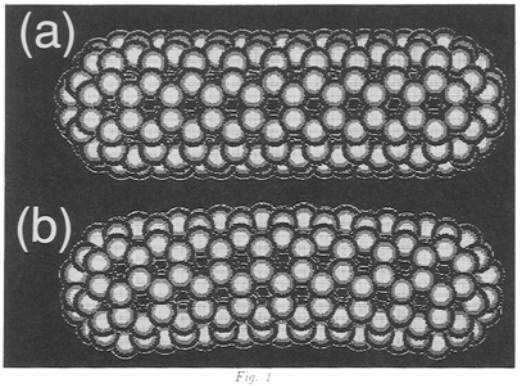

Fig. 1a, b. Schematic view of a "bucky tube" consisting of 200 carbon atoms. **a** Equilibrium geometry. **b** Geometry of the low frequency "beam bending" mode

The Keating potential is given by

$$V_K = \tfrac{1}{2}\alpha \sum_{\substack{\langle i,j\rangle \\ i<j}} \frac{(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij} - |\mathbf{R}_{ij}|^2)^2}{|\mathbf{R}_{ij}|^2} + \tfrac{1}{2}\beta \sum_{\substack{\langle i,j,k\rangle \\ j<k}} \frac{(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij} - \mathbf{R}_{ij}\cdot\mathbf{R}_{ik})^2}{|\mathbf{R}_{ij}|\,|\mathbf{R}_{ik}|}. \quad (1)$$

The first term contains a summation over nearest neighbor pairs and the second term a summation over nearest neighbor triplets (where the vertex i is the nearest neighbor of j and k). $\mathbf{R}_{ij}(\mathbf{r}_{ij})$ denotes the bond vector between atoms i and j before (after) the distortion. In graphite, all nearest neighbor bonds have the same equilibrium length $|\mathbf{R}_{ij}| = R$. In graphite, the angle between nearest neighbor bonds with a common vertex atom is 120°, so that $\mathbf{R}_{ij}\cdot\mathbf{R}_{ik} = -\frac{1}{2}R^2$.

We determined the force constants α and β in the Keating potential using ab initio local density approximation (LDA) [14] total energy calculations for specific distortion modes of graphite. As in our former total energy calculation of graphite [15], we used first-principles pseudopotentials [16], a Gaussian orbital basis, and an energy cutoff of 49 Ry in the Fourier expansion of the charge density.

We have considered three kinds of displacement geometries which correspond to the eigenvectors of different vibrational modes at the Brillouin zone center [15, 17]. The first geometry results from E_{2g_2} mode displacements, where the two sublattices of AA-stacked graphite are shifted within each layer against each other (geometry I). In this mode, both the nearest neighbor bond lengths and the angles change. In the second distortion (geometry II), we only consider changes of angles between nearest neighbor bonds and keep the bond lengths R constant; this distortion does not correspond to an eigen mode of the lattice. The third distortion geometry is a uniform expansion of the graphite lattice (geometry III). Using this geometry, we determined the equilibrium nearest neighbor bond length to be $R = 1.418$ Å, which compares very well with experimental data. We consider these distortions of graphite to be closely linked to low frequency distortions of "bucky tubes" in which we are mainly interested. The use of three different distortions for the calculation of the two force constants α and β gives us an independent reliability test of the Keating potential in (1).

We expect the force constant β, which describes bond bending, to reflect sensitively on the sp^2 hybridization in the flat graphite sheet or possible deviations from this hybridization in case of out-of-plane deformations, similar to those found in "buckyballs" and "bucky tubes". In these structures, the tilting angle between adjacent hexagons and pentagons is 142.622°. We investigated the effect of "buckling" on the force constants by repeating the above LDA calculations for correspondingly buckled graphite. We used the A_{2u} mode of AB-stacked graphite, consisting of a displacement by $\pm\delta_z$ of each of the two sublattices along the z-direction perpendicular to the graphite layers. We have chosen a value for δ_z which gives the above buckling angle of 142.622° between adjacent hexagons, and kept the nearest neighbor bond length constant. We determined the modified force constants for this structure by applying the distortions of geometry I, II, and III. From energy differences for "flat" graphite, which has been distorted according to geometries I and II, we obtain $\alpha = 1.805\times10^5$ dyn/cm and $\beta = 0.662\times10^5$ dyn/cm. This gives a force constant ratio $\beta/\alpha = 0.37$. The analogous calculation, based on energy differences for geometries II and III, leads to the same value for β, but a rather different value for the bond stretching constant, $\alpha = 5.889\times10^5$ dyn/cm. Consequently, we get $\beta/\alpha = 0.11$ for these distortions. This discrepancy is indicative of the failure of the two-parameter Keating model to reproduce the phonon spectrum of graphite correctly, and occurs both for the "flat" and "buckled" graphite. We favor the force constants based on geometries I and II which do not involve a homogeneous lattice expansion and are related to the structural resilience of the "bucky tubes". This choice is supported by the agreement of the C_{60} frequencies determined by the Keating model with $\beta/\alpha = 0.3$ with the observed frequencies [12] and those based on the bond charge model [18]. The discrepancy between the force constants obtained using the different geometry combinations occurs also for "buckled" graphite. As we show in Table 1, the calculated values for α and β are very similar in "flat" and "buckled" graphite. We conclude that the deviation from sp^2 bonding is negligible (or has no effect on the force constants) in carbon fullerenes and their derivatives. In the following, we use the values for "flat" graphite layers.

Table 1. Calculated force constants α and β [defined in (1)] for "flat" and "buckled" graphite, based on LDA

System	α [10^5 dyn/cm]	β [10^5 dyn/cm]	β/α
Graphite ("flat")	1.805	0.662	0.37
Graphite ("buckled")	2.028	0.680	0.34

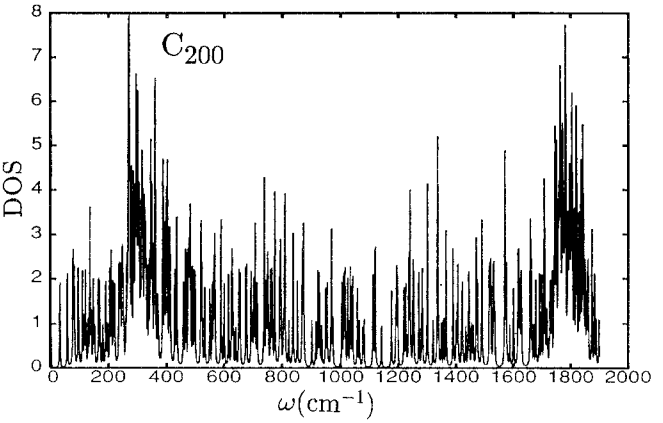

Fig. 2. The vibrational density of states (DOS) as a function of frequency ω for a C_{200} "bucky tube", obtained using the Keating potential. The DOS is given in units of cm and the peaks are artificially broadened; the integral over the frequency range gives the number of vibrational modes

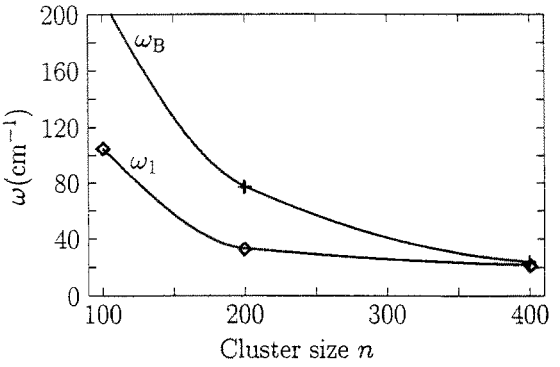

Fig. 3. The lowest vibration frequency, ω_1, and the bending mode frequency, ω_B, as a function of the cluster size n

The equilibrium geometry of the highly symmetric C_{200} "bucky tube" is shown in Fig. 1a. The vibrational eigen modes of this and other "bucky tubes" have been determined using analytic expressions in the force constant matrix. In Fig. 2, we show the vibrational density of states (DOS) as a function of frequency ω for C_{200}. In order to understand the bending rigidity of "bucky tubes", we will focus on the lowest non-trivial eigen modes. We expect one of the lowest modes to be the bending mode which is shown in Fig. 1b for a C_{200} cluster. Some other prominent low frequency modes include an ellipsoidal distortion of the cross section perpendicular to the principal rotation axis, and an internal twist along this axis.

In Fig. 3, we show the dependence of the lowest non-trivial mode ω_1 and the bending-mode ω_B on the cluster size n. We find that for all cluster sizes, this softest mode corresponds to the ellipsoidal distortion of the cross section mentioned above. Both of these low frequency modes are doubly degenerate. We expect and find that the frequency of the bending mode decreases when the length of the "bucky tube" increases. For very long "bucky tubes" (consisting of 500 atoms and more), the bending mode becomes the lowest non-trivial vibrational eigen mode. In the following, we use the eigenvectors of this bending mode to study the "beam rigidity" of "bucky tubes".

We base our comparisons of "beam rigidity" on a single deformation geometry, namely that of a beam with one clamped and one free end [see the inset in Fig. 4a]. The corresponding deformations of a "bucky tube" are derived from its lowest frequency bending mode. For such a frozen-in distorted geometry, we define a "neutral line" by connecting the centers of carbon rings which are locally normal to the cylinder axis. We determine the tangent to this "neutral line" at the one end of the "bucky tube" and define the bending distortion Δz by the distance of the other tube end (in the center of a pentagon) from this tangent.

In Fig. 4a, we show energy differences $\Delta E(\Delta z)$ (with respect to the straight tube) for the C_{100}, C_{200}, and C_{400} "bucky tubes", based on the Keating potential. We found it instructive to compare the bending rigidity of "bucky tubes" to the beam rigidity of Iridium, a material with a very high Young's modulus of $Y(\mathrm{Ir}) = 5.2 \times 10^{11}\ \mathrm{N/m^2}$.

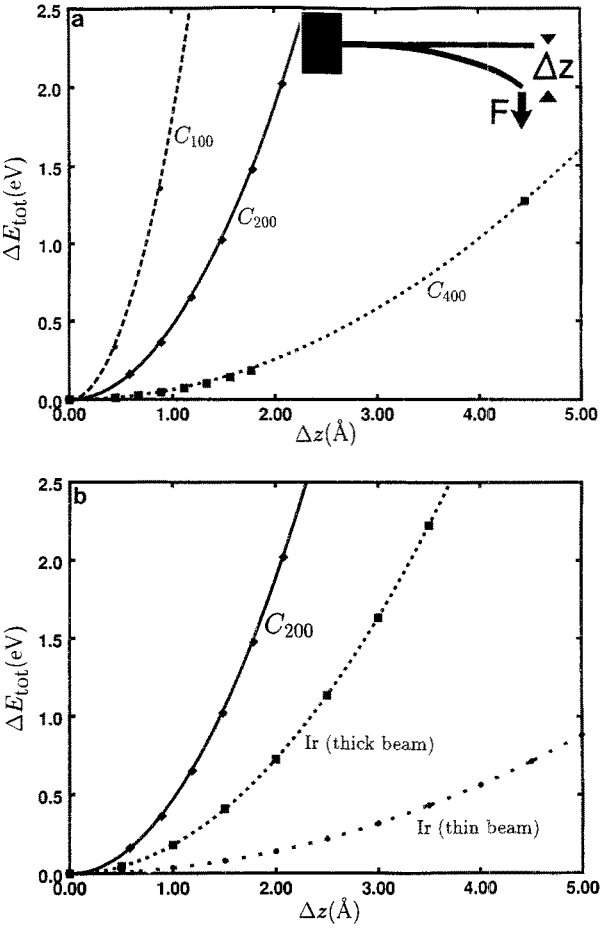

Fig. 4. The total energy change ΔE_{tot} as a function of the bending distortion Δz, **a** for C_{100}, C_{200} and C_{400} "bucky tubes", and **b** for C_{200} in comparison to an Ir beam. The beam bending geometry is shown in the inset of a, the results for a C_{200} "bucky tube" are compared to a "thin" and a "thick" cylindrical Ir beam (see text). The data points are connected by second order polynomials

In Fig. 4b, we show the total energy changes ΔE_{tot} as a function of bending for the C_{200} "bucky tube". We compare these results to an elasticity theory calculation [19] for a solid cylindrical beam of Iridium of same length as the C_{200} cluster, $l = 23.52$ Å. For the sake of fair comparison, we consider thin Ir beams with a radius of $r = 3.31$ Å, the same as the radial distance of carbon atoms in a "bucky tube", and thick beams with a radius increased by half the interlayer separation in graphite [20], i.e. $r = 4.99$ Å. Once a point force F is applied to one end of this beam (while the other end is clamped, as shown in the inset of Fig. 4a), the displacement Δz is given by [19]

$$\Delta z = -\frac{l^3}{3\,YI} F, \tag{2}$$

where I is the area moment of inertia of the beam. For a solid cylindrical beam with a cross-section A, I is given by

$$I = \int_A z^2 \mathrm{d}A = \frac{\pi r^4}{4}. \tag{3}$$

Table 2. Force constants for the bending mode of different structures. Results for "bucky tubes" are based on (1) and the result for an Ir beam on (2)

System	c_B [10^5 dyn/cm]
C_{100}	0.575
C_{200}	0.151
C_{400}	0.021
Ir (beam) [a]	0.011
Ir (beam) [b]	0.058

[a] Radius $r = 3.31$ Å and length $l = 23.52$ Å
[b] Radius $r = 4.99$ Å and length $l = 23.52$ Å

For small displacements Δz, we define a force (or spring) constant for bending as $c_B = F/\Delta z$. The values of c_B for the C_{100}, C_{200}, and C_{400} "bucky tubes" are listed in Table 2. For the thin Ir beam ($r = 3.31$ Å) we find $c_B = 11.13 \times 10^3$ dyn/cm and for the thick Ir beam ($r = 4.99$ Å) we get $c_B = 5.8 \times 10^3$ dyn/cm. Both these values are substantially lower than the corresponding value for C_{200}. From Table 2 we infer that c_B decreases when the length of the "bucky tube" increases, which is directly related to the softening of the bending mode shown in Fig. 3. Clearly, the continuum approach used in (2) is probably stretched to the limit of its validity when calculating the deformations of an extremely thin Ir wire, where deviations from an isotropic medium and atomic structure become significant. Nevertheless, (2) is still expected to give the right order of magnitude estimate for the spring constant of this wire. Based on the results presented in Table 2, we conclude that "bucky tubes" are about one order of magnitude stiffer than an Ir wire of comparable size. Naturally, we expect the beam rigidity of multi-walled tubules (consisting of nested cylinders) to be much higher. Such multi-walled structures have been recently generated by several groups [21].

In conclusion, we have calculated the structural rigidity and the low frequency vibrational modes of long carbon tubules consisting of 100, 200, and 400 carbon atoms. We used a nearest neighbor Keating potential with parameters obtained from first principles calculations. We have shown that "bucky tubes" have a very high structural rigidity which is about one order of magnitude larger than that of a cylindrical Ir wire. Such a large beam rigidity, combined with a low mass density, should make the "bucky tubes" an ideal component in future graphite fiber composite materials.

We would like to thank Michael A. Schlüter and George F. Bertsch for stimulating discussions. This research was supported by the National Science Foundation under Grant No. PHY-8920927. G.O. acknowledges partial financial support from the Swiss National Science Foundation and Kommission zur Förderung der wissenschaftlichen Forschung.

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