The bulk modulus of C_{60} molecules and crystals: A molecular mechanics approach

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In this letter, the bulk modulus of an individual C_{60} molecule is calculated in terms of the C,C bond force constant. A range of values for the bulk modulus is obtained with literature values for the force constant. The values obtained all exceed the bulk modulus (441 GPa) of diamond. With a C,C bond force constant equal to that between adjacent carbon atoms in graphite, 7.08 mdyn/Å, a bulk modulus of 903 GPa is obtained. On the basis of a simple composite model it is calculated that single closest-packed C_{60} crystals of C_{60} will have a bulk modulus of roughly 668 GPa under hydrostatic pressures. The calculated bulk modulus for a single C_{60} "buckyball" therefore suggests the possibility that a C_{60} crystal could be the most incompressible material known, at a pressure above about 50 GPa.

The truncated icosahedral C_{60} molecule has been produced in macroscopic amounts,[1] and its structure proven.[2,3]

Its equation of state has been studied to 1.2 GPa (Ref. 4) with an ethanol-methanol medium and to 20 GPa under nonhydrostatic conditions and also with an ethanol-methanol medium.[5] In addition a pair-potential method has been used to compute the equation of state of C_{60} crystals.[6] Finally, a macroscopic elastic continuum approach has been used to estimate the stiffness of C_{60} molecules.[7] In the present letter an atomic bonding model is used to compute their bulk modulus in terms of the C,C stretching force constant k and the known geometry of C_{60}, an approach that is likely to be considered more acceptable to chemists and physicists than the macroscopic approach used earlier.

This equation is used with literature values for k to obtain a range of values for the bulk modulus of a single C_{60} and these values are compared with the bulk modulus of diamond, the least compressible substance presently known.

The equation relating the fractional change in volume $\Delta V/V$ to applied pressure p is

$$p=B_0|\Delta V/V|, \tag{1}$$

where B_0 is the bulk modulus.

Each of the 60 C's in C_{60} is equidistant from the center of mass of C_{60}. Let the radius r equal this distance. If hydrostatic pressure is applied, the radial inward force F on each C is the same.

Let x be the bond length and $A_p = 1.7205x^2$the area of a regular pentagon and $A_H = 2.5981x^2$ the area of a regular hexagon. Then a force balance gives

$$F_r=P[(A_p/5)0.9375+\tfrac{2}{6}A_H0.9125],$$

$$F_r=1.1128x^2P. \tag{2}$$

The $\frac{1}{5}$ arises because each carbon is connected to one pentagon and the $\frac{2}{6}$ because each carbon is connected to two hexagons. The factors 0.9375 and 0.9125 resolve the force normal to the pentagon and hexagon, respectively, along the line connecting the carbon atom to the center of mass of the C_{60}. If F_x is the force along a bond, $3(F_x/2)\Delta x=F_r\Delta r$, and

$$P=\frac{3}{1.1128}\frac{F_x}{x^2}\frac{x}{2r}. \tag{3}$$

Since $x=cr$, where c is a constant,

$$\Delta x/\Delta r=c=x/r, \tag{4}$$

and since $F_x = k\Delta x$ and $\Delta V/V = 3\Delta x/x$ we have

$$P=0.449(k/r)|\Delta V/V| \tag{5}$$

and

$$B_0=0.449(k/r). \tag{6}$$

Equation (6) is appropriate for a regular truncated icosahedron, with all 90 edge lengths equal. Equation (6) can easily be extended to the case where there are two different bond lengths, and two different C,C stretching force constants. An alternative method can be used to derive Eq. (6), and involves equating the stored elastic potential energy in the 90 bonds to the work done in compressing C_{60}. We use $r=3.52$ Å, corresponding to $x = 1.433$ Å. The force balance is carried out at $r = 3.52$ Å where the pressure P equals the applied pressure P. Since we consider the molecule to be a homogeneous elastic solid with a bulk modulus B_0, the pressure throughout is P. We take values for k from the literature, and with Eq. (6) calculate B_0. The values are collected in Table I.

There are a range of k values quoted in Table I. One can derive a k for a bond connecting carbon atoms in the hexagonal planar array in graphite from the known compliances, and $k=7.08$ mdyn/Å.[8] Scuseria has obtained preliminary results from *ab initio* calculations at the TZP SCF level (electron correlation not included) that yield a "weighted" k of 6.72 mdyn/Å.[9] The weighting we use is $\frac{2}{3}k_1 + \frac{1}{3}k_2$, where k_1 represents the force constant of the

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TABLE I. B_0 of C_{60} for some choices of k[a].

k (mdyn/Å)	B_0 (GPa)	Ref.
7.62	972	b
7.08	903	c
6.35	810	d
6.60	842	e
6.72	826	f

[a]B_0 obtained from Eq. (6). See discussion in text about choices of k.
[b]k from benzene, Ref. 10.
[c]k from graphite.
[d]k for C_{60} by extrapolating from benzene and graphite.
[e]k scaled from k for graphite; see text.
[f]k from preliminary theoretical results, Ref. 9.

pentagon edge bond, and k_2 represents the force constant of the bond shared by two hexagons. The k value obtained from a force field fit to the measured frequencies of benzene is a bit higher, equal to 7.62 mdyn/Å.[10] Wu, Jelski, and George obtained values of k_1 and k_2 that provide a weighted average of 10.3 mdyn/Å for k in their treatment of C_{60} vibrational frequencies.[11] The vibrational frequencies were, however, obtained by Stanton from a MINDO calculation,[12] and the C_{60} geometry employed by Wu and co-workers[11] was significantly larger than the experimentally determined[3] geometry. Finally, Cyvin *et al.* have used a value of 4.7 mdyn/Å in a force constant treatment of C_{60} vibrational frequencies.[13]

The formal bond order of bonds in C_{60} is equivalent to that of graphite, 1.33 (assigning benzene a value of 1.5). The bond distance in graphite is 1.412 Å, similar to the weighted bond length of 1.433 for C_{60}. This suggests to us that k for C_{60} will likely be close to that of k for graphite. In fact, if one uses the C,C bond distances for benzene and graphite, and plots k vs x, the extrapolated value of k for C_{60} (weighted $x = 1.43$ Å) is 6.35 mdyn/Å. It is also interesting to scale the force constant of graphite, 7.08 mdyn/Å by the number of bonds per unit area, assuming equal bond lengths in C_{60} and graphite. The scaling factor is 0.932, and this yields 6.60 mdyn/Å.

The reader should note that the k values from the literature are used here only for the regular C_{60} with edge length $x = 1.433$ Å. The reason that other force constants are not needed in our derivation of the bulk modulus is that we are implicitly making the assumption that only the C,C bond lengths change, that is, all angles are invariant with applied F_r. This must be true when one hydrostatically presses on the regular C_{60}. For the case when one starts with two unequal bond lengths x_1 and x_2, the ratio x_1/x_2 will likely change as pressure is applied. Because x_1 and x_2 are so close, 1.45 and 1.40 Å,[3] the expression for the bulk modulus of our somewhat idealized C_{60} is easily extended for two slightly dissimilar bond lengths.

One should take the k's in Table I as values that can be used to provide an estimated range of values of B_0 for one C_{60}. Better values for k will become available when experimental data such as measured vibrational frequencies[14] and volume changes with very high applied pressure are fit.

The fcc closest-packed C_{60} crystal (considering the C-60 as touching spheres) is 26% empty volume. Multiplying the B_0's in Table I by 0.74 provides a first-order estimate of the bulk modulus of a single crystal (composite of C_{60} and empty space)[15] subjected to a sufficient hydrostatic pressure (such that the soft spheres are compressed so that hard-sphere contact occurs). The range of values obtained is 623–720 GPa. To estimate the pressure at which hard-sphere contact might occur, we make an analogy between the compression of graphite and C_{60} single crystals. (In our earlier paper[7] we based this estimate on unpublished results in which it was found that graphite becomes very stiff at 20 GPa; however this is associated with an unknown transition.[16]) We expect the bonds between the different buckyballs to behave in approximately the same manner as the bonds between the layers of graphite. Initially graphite is quite compressible but as its volume decreases (almost entirely due to the layers getting closer) its bulk modulus increases rapidly with pressure. Measured experimental values[17] give B (GPa) $= 34 + 8.9P$ (GPa). We expect that approximately the same pressure would be needed to compress C_{60} crystals so that hard-sphere contact occurs. This suggests the possibility that C_{60} crystals at pressures above about 50 GPa will have a larger bulk modulus than diamond at atmospheric pressure. However we note that the diamond bulk modulus also is increasing with pressure according to B (GPa) $= 441 + 4P$ (GPa).[18]

The pressure dependence of the bulk modulus of crystalline materials in general can be described sufficiently well for the present needs by a linear relation for $P < B_0/2$. However in the case of graphite (which we are using as an approximation for crystalline C_{60}) we will be involved with $P > B_0$, so we use a Lennard–Jones potential to describe the compression of graphite planes in the c direction (normal to the layers) with the result that

$$P = \frac{B_{0c}}{6}\left[\left(\frac{\sigma}{L}\right)^{11} - \left(\frac{\sigma}{L}\right)^{5}\right] \tag{7}$$

and

$$B_c = \frac{B_{0c}}{6}\left[11\left(\frac{\sigma}{L}\right)^{11} - 5\left(\frac{\sigma}{L}\right)^{5}\right]. \tag{8}$$

Here $L = c/2, \sigma = c_0 = 3.3504$, and B_{0c} is the response of the fractional changes in the lattice parameter c with pressure,

$$\Delta c/c_0 = -(s_{33} + 2s_{13})P = -P/B_{0c}. \tag{9}$$

The s_{ij} are elastic compliances at zero pressure. Using the s_{ij} of Kelly,[19] $B_{0c} = 37.3$ GPa. To a first approximation we ignore the change in the area of the graphite layers that are elastically very stiff in tension (or compression). In this way we find that at 50 GPa, the bulk modulus of graphite exceeds that of diamond (661 GPa). While diamond is known to be stable to 416 GPa,[20] it is possible that C_{60} (which we modeled as graphite) will have a phase transition prior to 50 GPa (the balls could buckle) and the above conclusion would need reconsideration. A similar value, 78 GPa, was found by Wang and co-workers[6] by a different technique. This leads to the possible use of C_{60} crystals as an intensifier in a diamond-anvil cell in the

multimegabar regime, and may make possible reaching the terapascal range.[21] Recent results obtained on C_{60} in a diamond-anvil cell with no pressure medium shows that at pressures of about 20 GPa, crystalline C_{60} becomes quite stiff, but not as stiff as diamond, while with a pressure medium of methanol-ethanol it stiffens less rapidly.[5] This different behavior is not understood.

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