

# The bulk modulus of C<sub>60</sub> molecules and crystals: A molecular mechanics approach

Rodney S. Ruoff

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

Arthur L. Ruoff

Materials Science and Engineering, Cornell University, Ithaca, New York 14853

(Received 28 May 1991; accepted for publication 19 July 1991)

In this letter, the bulk modulus of an individual C<sub>60</sub> 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<sub>60</sub> crystals of C<sub>60</sub> will have a bulk modulus of roughly 668 GPa under hydrostatic pressures. The calculated bulk modulus for a single C<sub>60</sub> "buckyball" therefore suggests the possibility that a C<sub>60</sub> crystal could be the most incompressible material known, at a pressure above about 50 GPa.

The truncated icosahedral C<sub>60</sub> molecule has been produced in macroscopic amounts,<sup>1</sup> and its structure proven.<sup>2,3</sup>

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.<sup>5</sup> In addition a pair-potential method has been used to compute the equation of state of C<sub>60</sub> crystals.<sup>6</sup> Finally, a macroscopic elastic continuum approach has been used to estimate the stiffness of C<sub>60</sub> molecules.<sup>7</sup> 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<sub>60</sub>, 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<sub>60</sub> 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

$$p = B_0 |\Delta V/V|, \quad (1)$$

where  $B_0$  is the bulk modulus.

Each of the 60 C's in C<sub>60</sub> is equidistant from the center of mass of C<sub>60</sub>. 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

$$F_r = P[(A_p/5)0.9375 + \frac{2}{5}A_H 0.9125],$$

$$F_r = 1.1128x^2P. \quad (2)$$

The  $\frac{1}{5}$  arises because each carbon is connected to one pentagon and the  $\frac{2}{5}$  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<sub>60</sub>. If  $F_x$  is the force along a bond,  $3(F_x/2)\Delta x = F_r\Delta r$ , and

$$P = \frac{3}{1.1128} \frac{F_x x}{x^2 2r}. \quad (3)$$

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

$$\Delta x/\Delta r = c = x/r, \quad (4)$$

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

$$P = 0.449(k/r) |\Delta V/V| \quad (5)$$

and

$$B_0 = 0.449(k/r). \quad (6)$$

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<sub>60</sub>. 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.<sup>8</sup> 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.<sup>9</sup> The weighting we use is  $\frac{2}{3}k_1 + \frac{1}{3}k_2$ , where  $k_1$  represents the force constant of the

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

<sup>a</sup> $B_0$  obtained from Eq. (6). See discussion in text about choices of  $k$ .

<sup>b</sup> $k$  from benzene, Ref. 10.

<sup>c</sup> $k$  from graphite.

<sup>d</sup> $k$  for  $C_{60}$  by extrapolating from benzene and graphite.

<sup>e</sup> $k$  scaled from  $k$  for graphite; see text.

<sup>f</sup> $k$  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.<sup>10</sup> 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.<sup>11</sup> The vibrational frequencies were, however, obtained by Stanton from a MINDO calculation,<sup>12</sup> and the  $C_{60}$  geometry employed by Wu and co-workers<sup>11</sup> was significantly larger than the experimentally determined<sup>3</sup> geometry. Finally, Cyvin *et al.* have used a value of 4.7 mdyn/Å in a force constant treatment of  $C_{60}$  vibrational frequencies.<sup>13</sup>

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,<sup>3</sup> 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<sup>14</sup> 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)<sup>15</sup> 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<sup>7</sup> 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.<sup>10</sup>) 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<sup>17</sup> give  $B$  (GPa) = 34 + 8.9 $P$  (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 + 4 $P$  (GPa).<sup>18</sup>

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

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

and

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

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,

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

The  $s_{ij}$  are elastic compliances at zero pressure. Using the  $s_{ij}$  of Kelly,<sup>19</sup>  $B_{0c} = 37.3$  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,<sup>20</sup> 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<sup>6</sup> 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.<sup>21</sup> Recent results obtained on C<sub>60</sub> in a diamond-anvil cell with no pressure medium shows that at pressures of about 20 GPa, crystalline C<sub>60</sub> becomes quite stiff, but not as stiff as diamond, while with a pressure medium of methanol-ethanol it stiffens less rapidly.<sup>5</sup> This different behavior is not understood.

A.L.R. acknowledges the support of his research by the Department of Energy through Grant No. DOE-FG02-87ER-45320 and discussions with E. J. Kramer, M. H. E. Martin, S. J. Duclos, K. E. Brister, and R. Hoffmann. R.S.R. appreciates conversations with Thomas Jackman, Sam LaPlaca, Milton Cole, and discussions and communication of preliminary results by Gustavo Scuseria and Marco Haser.

- <sup>1</sup>W. Kraetschmer, L. D. Lamb, K. Fostiropoulos, and D. Huffman, *Nature* **347**, 354 (1990).  
<sup>2</sup>R. Taylor, J. P. Hare, A. K. Abdul-Sada, and H. W. Kroto, *J. Chem. Soc. Chem. Commun.* 1423 (1990).  
<sup>3</sup>C. S. Yannoni, P. P. Bernier, D. S. Bethune, G. Meijer, and J. R. Salem, *J. Am. Chem. Soc.* **113**, 3190 (1991).  
<sup>4</sup>J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanov, A. M. Denenstein, and J. P. McCauley, Jr., *Science* **252**, 1288 (1991).

- <sup>5</sup>S. J. Duclos, K. E. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel, *Nature* **351**, 380, 1991.  
<sup>6</sup>Y. Wang, D. Tománek, and G. F. Bertsch, *Phys. Rev. Rapid Commun.* (accepted for publication).  
<sup>7</sup>R. S. Ruoff and A. L. Ruoff, *Nature* **350**, 663 (1991).  
<sup>8</sup>R. S. Ruoff and A. L. Ruoff, MSC Report No. 7159, Cornell University, 1991.  
<sup>9</sup>G. Scuseria (private communication) *Chem. Phys. Lett.* **176**, 423 (1991).  
<sup>10</sup>B. L. Crawford and F. A. Miller, *J. Chem. Phys.* **17**, 249 (1949).  
<sup>11</sup>Z. C. Wu, D. A. Jelski, and T. F. George, *Chem. Phys. Lett.* **137**, 291 (1987).  
<sup>12</sup>R. E. Stanton and M. Newton, *J. Phys. Chem.* **92**, 2141 (1988).  
<sup>13</sup>S. J. Cyvin, E. Brendsdal, B. N. Cyvin, and J. Brunvoll, *Chem. Phys. Lett.* **143**, 377 (1988).  
<sup>14</sup>D. S. Bethune, C. Meijer, W. C. Tang, and H. J. Rosen, *Chem. Phys. Lett.* **174**, 219 (1990).  
<sup>15</sup>K. K. Chawla, *Composite Materials* (Springer, New York, 1987), p. 178.  
<sup>16</sup>Y. K. Vohra and A. L. Ruoff (unpublished).  
<sup>17</sup>M. Hanfland, H. Beister, and K. Syassen, *Phys. Rev.* **39**, 23 598 (1989).  
<sup>18</sup>H. J. McSkimin and P. Andreatch, *J. Appl. Phys.* **43**, 2944 (1972).  
<sup>19</sup>B. T. Kelly, *Physics of Graphite* (Applied Science, Englewood, NJ, 1981).  
<sup>20</sup>A. L. Ruoff, H. Xia, H. Luo, and Y. K. Vohra, *Rev. Sci. Instrum.* **61**, 3830 (1990).  
<sup>21</sup>A. L. Ruoff and H. Luo, *J. Appl. Phys.* **70**, 2066 (1991).