

## Energies of fullerenes

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(Received 10 August 1992)

To understand fullerenes, it is crucial to determine the energies, and hence the relative stabilities, of different structures. Here we introduce an approach to calculating and understanding these energies, by applying elasticity theory. Explicit formulas are given for the energies of ball-shaped molecules, graphite tubules, and the recently proposed negative-curvature fullerenes. Extensive atomistic calculations confirm the validity of the formulas. These results provide a general perspective on the relative stability of the different fullerenes.

Since the discovery of the  $C_{60}$  molecule, there has been intense interest in the graphitelike forms of carbon called "fullerenes."<sup>1</sup> This family includes not only molecules,<sup>1</sup> but also tubules<sup>2</sup> and crystalline forms with negative curvature.<sup>3-5</sup>

The most important single property of any fullerene is its energy. The energy (along with kinetic factors) controls the abundance, and even the existence, of the respective fullerenes. Yet the only approach until now has been to calculate numerically the energies of specific individual molecules. Such calculations<sup>4-8</sup> have already increased our knowledge of fullerene energetics; but it seems essential to go further, and identify those factors which determine the energies, in order to achieve a more fundamental understanding.

Here, we introduce an approach for calculating and understanding the energies of fullerenes. By viewing fullerenes as distorted graphite sheets (including topological defects) and applying elasticity theory, explicit formulas are derived for the energies of three major, topologically distinct classes of fullerenes. The accuracies of these formulas are confirmed in two ways: by extensive atomistic calculations over a large range of sizes, using a valence force model, and by comparison with quantum-mechanical calculations reported by Zhang *et al.*<sup>7</sup> for a large number of molecules.

Three types of fullerenes have been studied, distinguished by their different topologies. Ball-shaped molecules such as  $C_{60}$  were discovered first, and can now be synthesized in quantity.<sup>1</sup> Even simpler, and of potential importance, are "tubules."<sup>2</sup> And recently, several authors have considered the possibility of fullerenes similar to balls in their local structure, but with sevenfold rings instead of fivefold rings.<sup>3-5</sup> This results in three-dimensional crystals consisting of graphitic sheets of negative Gaussian curvature (i.e., locally saddle shaped rather than spherical). While such fullerenes have not yet been synthesized, their calculated properties are quite intriguing.<sup>4,5</sup>

Tubules are essentially bent graphite sheets, so they are obvious candidates for the application of classical elasticity theory. However, such an approach has apparently never been considered for the other fullerenes, which in-

volve topological defects. These fullerenes can be viewed as graphite sheets containing arrays of disclinations of  $60^\circ$  (fivefold rings) or  $-60^\circ$  (sevenfold rings). The formation energy of a disclination is just the energy stored in the elastic strain field around it, plus a constant term from local effects. Thus in these cases too elasticity theory is applicable.

For each class of fullerenes, we derive the expression for its elastic energy, and compare this with detailed atomistic calculations. (In all cases, energies are given relative to an equal number of atoms in graphite.) In the most important class, the ball-like molecules, we can compare with quantum-mechanical calculations reported by Zhang *et al.*,<sup>7</sup> using a tight-binding method. In addition, for all three classes, we have carried out extensive calculations over a large range of sizes, using an empirical interatomic potential for carbon.<sup>9</sup> This potential was optimized for diamond, and gives somewhat lesser accuracy for graphite, but the absolute accuracy of the calculated energies is not a central issue here. Our principle interest is in demonstrating the ability of continuum elasticity theory to reproduce the results of detailed atomistic calculations, whether classical or quantum mechanical.

We begin with a brief treatment of the tubules, because they are the simplest fullerenes, consisting entirely of sixfold rings. Such tubules are in general helical in structure,<sup>2</sup> presumably because of a growth mode somewhat analogous to metal "whiskers" (which grow helically around a screw dislocation). A helical structure can be formed without in-plane strain, by curving a graphite sheet in a direction which is not an axis of lattice symmetry; this is assumed to be the actual structure.

The energy to bend a sheet into a tube is

$$E = \frac{1}{2}c_0\kappa^2, \quad (1)$$

where  $E$  is the energy per unit area,  $c_0$  is an elastic constant (with units of energy) for curvature out of the plane, and  $\kappa$  is the mean curvature of the cylinder, i.e., the inverse of the radius of curvature. Since the graphite sheet has hexagonal symmetry, it is elastically isotropic; so the bending energy depends only on the radius of curvature, and not on the direction of bending (i.e., not on the heli-

cal pitch). We therefore need only perform atomistic calculations for tubules with zero helical pitch.

For a tubule that wraps around in  $M$  lattice periods with zero helical pitch, the curvature is  $\kappa = 2\pi/Ma$ , where  $a$  is the graphite lattice constant (2.46 Å). The area is  $a^2\sqrt{3}/2$  per sixfold ring. Figure 1 shows calculated energies of such tubules, for  $60 \leq M \leq 140$ , versus  $\frac{1}{2}\kappa^2$ . The highly linear behavior confirms the validity of Eq. (1). The slope gives the inferred values of the elastic constant,  $c_0 = 1.02$  eV, in reasonable agreement with the value of 1.2 eV extracted from the measured phonon spectrum of graphite.<sup>10</sup>

We now turn to the most extensively studied fullerenes, the ball-shaped molecules.<sup>1</sup> The simplest ball is a pentagonal dodecahedron, consisting of 20 atoms forming 12 fivefold rings. From this, a series of larger balls (including  $C_{60}$ ) can be generated by adding sixfold rings, e.g., with an "inflation" procedure.<sup>11</sup> We have calculated the energies of eight such balls of icosohedral symmetry, the largest having 2160 atoms. The results are given in Table I.

These energies can be understood by viewing a ball as an array of 12 disclinations in a graphite sheet. The energetics of single disclinations have already been treated in detail by Seung and Nelson.<sup>12</sup> However, it is worthwhile to explicitly derive the energy for the case at hand. A single fivefold ring in a sheet of graphite represents a  $60^\circ$  disclination. Such a disclination can be formed by cutting a  $60^\circ$  wedge out of a sheet of graphite, and joining the cut edges so that all atoms are correctly bonded. This deformation causes the sheet to pucker into a cone.

If the in-plane elastic constants of the graphite sheet are arbitrarily large, compared to that for bending out of the plane, then the sheet is said to be "inextensional." In this limit, the shape around a single disclination is precisely conical. The half-angle of the cone is  $\sin^{-1}(\frac{5}{6})$ . At a distance  $r$  from the apex, measured along the cone face, the cone radius (i.e., the distance from face to axis) is  $\rho = \frac{5}{6}r$ . The curvature is locally cylindrical, with curvature  $\kappa = \cos\theta/\rho = (\frac{11}{25})^{1/2}/r$ .

Thus from Eq. (1), the energy density in the elastic strain field of the cone is  $c_0 \frac{11}{50} r^{-2}$ . The total energy cost of a fivefold ring includes a constant local contribution  $\lambda_5$  plus the integrated energy in the surrounding strain field:

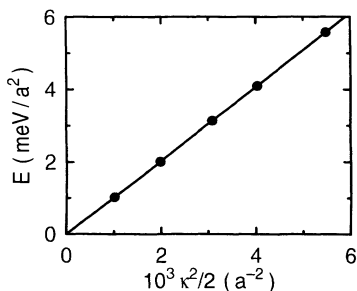


FIG. 1. Energy of graphite tubules, per unit area, vs  $\kappa^2/2$ , where  $\kappa$  is the mean curvature. The slope gives the elastic constant  $c_0 = 1.02$  eV for bending out of the plane.

TABLE I. Calculated energies  $E$  of fullerenes, relative to an equal number of atoms in an infinite sheet of graphite. Also given are the number of atoms  $N_a$  and the number  $m_n$  of rings of size  $n=5,6,7$ . For the negative-curvature structures ( $m_7 > 0$ ), which are infinite crystals, all numbers are per primitive cell.

$N_a$	$E$ (eV)	$m_5$	$m_6$	$m_7$
60	39.92	12	20	0
80	41.80	12	30	0
180	48.55	12	80	0
240	50.90	12	110	0
540	56.76	12	260	0
720	58.85	12	350	0
1620	64.63	12	800	0
2160	66.63	12	1070	0
168	17.77	0	56	24
504	47.40	0	224	24
1512	74.70	0	728	24
216 <sup>a</sup>	25.38	0	80	24
216 <sup>b</sup>	22.88	0	80	24

<sup>a</sup>From Ref. 5, fcc.

<sup>b</sup>From Ref. 5, simple cubic.

$$E_5 = \lambda_5 + \int_{r_{\min}}^{r_{\max}} c_0 \frac{11}{50} r^{-2} 2\pi \frac{5}{6} r dr$$

$$= \lambda_5 + \frac{11}{30} \pi c_0 \ln(r_{\max}/r_{\min}). \quad (2)$$

The lower limit of integration  $r_{\min}$  is arbitrary, since changing  $r_{\min}$  changes the energy only by an additive constant, which can be absorbed into  $\lambda_5$ . Nevertheless, it is helpful to choose a physically appropriate value of  $r_{\min}$ . It seems reasonable to associate one ring of atoms (the fivefold ring) with the disclination, so we take  $r_{\min} = a\sqrt{3}/2$ . (In graphite, starting from the center of a hexagon, this distance is midway between the first and second shell of atoms.)

Since we are viewing the ball as composed of 12 cones, each with a fivefold ring at its apex, the upper limit  $r_{\max}$  is just half the distance between fivefold rings. The center-to-center distance between fivefold rings is just  $2r_{\max} = \sqrt{N_a}/20a$ , where  $N_a$  is the number of atoms in the fullerene. Hence the total energy per fivefold ring, Eq. (2) can be written

$$E_5 = \lambda_5 + \frac{11}{60} \pi c_0 \ln(N_a/60). \quad (3)$$

With our choice for  $r_{\min}$ ,  $\lambda_5$  is just the energy per fivefold ring in the structure which consists precisely of 12 distinct fivefold rings, i.e.,  $C_{60}$ .

Figure 2 shows the total energies of balls from Table I, divided by 12 (i.e.,  $E_5$ , the energy per fivefold ring), versus  $c_0 \ln(N_a/60)$ . The energies fall very nearly on a straight line, as predicted by Eq. (3). The y intercept, which gives the "local" energy  $\lambda_5$  of the fivefold rings, is 3.36 eV. This is in fortuitously good agreement with the value of 3.55 eV from *ab initio* calculations,<sup>6</sup> but somewhat larger than the value of 2.1 eV inferred from experi-

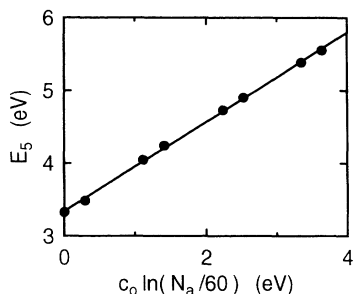


FIG. 2. Energy per fivefold ring  $E_5$  vs  $c_0 \ln(N_a/60)$  for fullerene balls. Line is least-squares fit; slope and  $y$  intercept are 0.61 and 3.36 eV.

mental measurements<sup>13</sup> or 2.0 eV from tight-binding calculations.<sup>7</sup>

The slope is 0.61, about 6% larger than the predicted value  $\frac{11}{60}\pi$ . This small discrepancy presumably arises because the cones are joined at their bases, constraining their shape. Any deviation from the perfect rotational symmetry assumed in the derivation of Eqs. (2) and (3) will preserve the logarithmic behavior, but with a larger coefficient.

For sufficiently large symmetric molecules, the elastic analysis should be quite generally valid. However, much of the current interest in fullerenes centers on molecules of moderate size, and with lower symmetry. To see how well the theory describes these cases, we show in Fig. 3 the energies calculated by Zhang *et al.*, using a quantum-mechanical tight-binding approach, for a range of fullerene sizes.<sup>7</sup> For each size  $N_a$ , the energy shown corresponds to the lowest-energy structure found. All sizes  $N_a \geq 50$  treated in Ref. 7 are included. There is some slight scatter associated with reduced symmetry and with electronic effects, but the data fall nearly on a smooth curve.

The solid curve in Fig. 3 corresponds to the predicted form, Eq. (3), i.e., energy per atom  $E + (A + B \ln N)/N$ . The two parameters  $A$  and  $B$  are fitted to the two data which should best obey elasticity theory, the icosohedral molecules of size  $N_a = 180$  and 240. Yet even though the theoretical curve is fitted only to two extremely large and

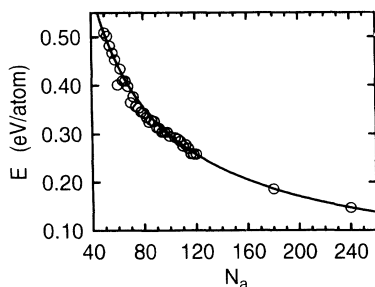


FIG. 3. Energy per atom vs size  $N_a$ , for lowest-energy structure of each size  $N_a \geq 50$ , as calculated by Zhang *et al.* (Ref. 7). Solid line is the prediction of Eq. (3), i.e.,  $E = (A + B \ln N)/N$ , with  $A$  and  $B$  fitted to icosohedral molecules of size  $N_a = 180$  and 240.

symmetric molecules, it gives a strikingly good overall description of the energies of all molecules down to  $N_a = 50$ . Moreover, the coefficient  $B$ , which should be proportional to the elastic constant  $c_0$ , agrees to within 8% with that in Fig. 2. Thus, despite the complexities of structure and of electronic effects, the energies of fullerenes are, overall, remarkably well described by Eq. (3).

We now turn to structures with negative Gaussian curvature. These are considerably more complex than icosohedral molecules. The exact shape of a single *negative* disclination is not known, even in the inextensional limit. Nevertheless, the strain must still fall off as  $r^{-1}$ , giving a logarithmic form like Eq. (3). Seung and Nelson have calculated the coefficient of the logarithm numerically for a single  $-60^\circ$  disclination in the inextensional limit.<sup>12</sup> With that coefficient, the energy per sevenfold ring can be written

$$\begin{aligned} E_7 &= \lambda_7 + 2.28c_0 \ln(r_{\max}/r_{\min}) \\ &= \lambda_7 + 1.14c_0 \ln(N_a/168), \end{aligned} \quad (4)$$

where  $r_{\max}$  and  $r_{\min}$  are chosen just as for balls above, and  $N_a$  now refers to the number of atoms per primitive cell, rather than per molecule.

The calculated energies of several negative-curvature structures are given in Table I. All those considered here have fcc structure, with 24 sevenfold rings per primitive cell, and various numbers of sixfold rings. These include the structure proposed by Vanderbilt and Tersoff,<sup>4</sup> two others generated from this by the inflation procedure,<sup>11</sup> and the fcc structure proposed by Lenosky *et al.*<sup>5</sup> The calculated energies are shown in Fig. 4, with  $E_7$  plotted versus  $c_0 \ln(N_a/168)$ . A simple-cubic structure from Ref. 5 is included in Table I but not in Fig. 4.

The slope in Fig. 4 is 1.07, 6% less than the estimate of Eq. (4). This is the same magnitude of discrepancy found above in the case of balls. The  $y$  intercept is  $\lambda_7 = 0.75$  eV  $\ll \lambda_5$ . This means that in terms of *local* structure, sevenfold rings are energetically less costly than fivefold rings. Thus, for example, the negative-curvature structure  $C_{168}$ , while closely analogous to  $C_{60}$ , has much lower energy per atom. As discussed by Vanderbilt and Tersoff,<sup>4</sup> this is because negative Gaussian curvature (seven-

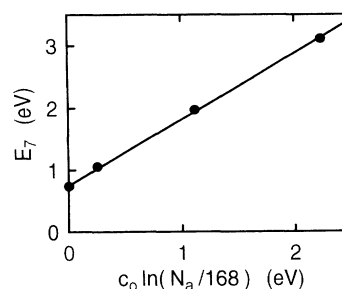


FIG. 4. Energy per sevenfold ring  $E_7$  vs  $c_0 \ln(N_a/168)$ , for fullerenes with negative Gaussian curvature. Line is least-squares fit; slope and  $y$  intercept are 1.07 and 0.75 eV.

fold rings) can be accommodated without large bond-angle distortions, and so is energetically preferable to positive curvature (fivefold rings). However, the mean square curvature associated with buckling around a sevenfold ring is nearly twice as large as that around a fivefold ring. For sufficiently large structure, the energy of the long-range strain field will dominate, leading to a reversal of ordering, with fivefold rings becoming lower in energy than sevenfold rings. However, this reversal occurs at an extremely large size, where the energy per atom is in any case quite small.

In conclusion, we have derived explicit formulas for the energies of a variety of fullerenes, including balls, tubes, and negative-curvature structures. The accuracy

of these formulas is confirmed by atomistic calculations over a large range of sizes. For balls, where extensive data from quantum-mechanical calculations are available, the theoretical formula gives a strikingly accurate description of the overall behavior, despite the complexities of electronic structure and geometry. In all cases the energy is well approximated by the elastic energy of out-of-plane bending, plus a fixed energy cost for fivefold or sevenfold rings.

It is a pleasure to acknowledge helpful discussions with David DiVincenzo, David Nelson, and David Vanderbilt. I am grateful to B. L. Zhang for providing results of Ref. 7 prior to publication.

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