

Stiffness of a solid composed of C_{60} clusters

Yang Wang, D. Tománek, and G.F. Bertsch

*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-1116
and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116*

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We calculate the equilibrium structure of fullerite, a solid composed of C_{60} clusters, as a function of external pressure. We find that at zero pressure, carbon atoms in neighboring "fullerene" clusters are no closer than 2.65 Å apart and interact by pairwise van der Waals forces. At increasing pressures, we observe a gradual transition to a hard-core repulsion between neighboring clusters. Only at high pressures, beyond ≈ 70 GPa, does the bulk modulus of fullerite exceed that of diamond.

Recently, Krätschmer *et al.* developed a new technique to synthesize C_{60} clusters in bulk quantities¹ which attracted much attention of the scientific community and the public. Based on their earlier experiments, Kroto *et al.* postulated an uncommon "hollow soccer ball" (or "fullerene") structure for the isolated clusters themselves.² When crystallized, C_{60} clusters form a solid with a face-centered cubic structure which has been given the name "fullerite." In spite of the considerable effort invested in understanding the equilibrium properties of C_{60} clusters,³ many open questions remain regarding the material properties of fullerite. So far, based on x-ray diffraction data,^{1,4} fullerite has been shown to be a close-packed molecular solid with a face-centered cubic structure and with a nearest-neighbor distance $D = 10.04$ Å. Extended x-ray-absorption fine-structure data⁵ indicate an average carbon-carbon nearest-neighbor distance $d_{C-C} = 1.42$ Å which is the same as in graphite. This bond length corresponds to a radius $R = 3.55$ Å of the fullerene cluster. In other words, the closest distance between two surfaces of adjacent clusters is $d = 2.9$ Å at zero pressure. Raman and infrared spectroscopy data^{5,6} confirm that the "soccer ball" structure of C_{60} is preserved in the solid. Pressure-dependent x-ray diffraction data, obtained in a diamond anvil cell, indicate a large change of the bulk modulus of fullerite as a function of pressure.⁷

In our paper, we determine the static and elastic properties of fullerite as a function of pressure. We present a

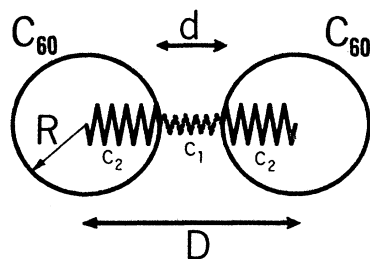


FIG. 1. Schematic drawing of the forces involved in the interaction between neighboring C_{60} clusters in fullerite. The weak van der Waals bond between these clusters can be mapped onto an anharmonic soft spring (spring constant c_1). The compressibility of the "hard" C_{60} fullerene cluster itself can be described by a hard anharmonic spring (spring constant c_2).

physical model, based on first-principles calculations, for the cohesion of the solid. In our investigation, we focus on the interesting question, whether fullerite can become less compressible than diamond.

When fullerite is compressed, part of the volume reduction comes from squeezing the clusters closer together, and part from the compressions of the clusters themselves. Our model exploits this distinction to make a tractable calculation without the full-scale apparatus of the local-density-approximation (LDA) theory.⁸

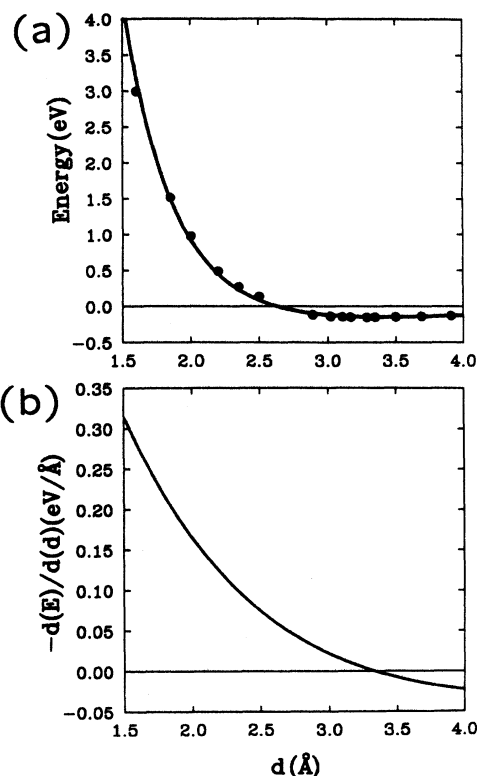


FIG. 2. (a) Binding energy of hexagonal graphite (with respect to isolated layers, per carbon atom) as a function of the interlayer spacing d . The solid line represents a modified Morse fit [Eqs. (1) and (2)] to *ab initio* LDA results of Ref. 10. (b) Negative gradient of the energy given in (a), corresponding to the interlayer force.

While the LDA is computationally feasible with present computers,³ it does not provide the insight possible with a simplified treatment. Also, the LDA does not have any fundamental significance for purely van der Waals forces which dominate the interaction at large separations between the C_{60} clusters. A schematic picture of the model is shown in Fig. 1. Effectively, there are two spring constants, c_1 associated with the interaction between clusters and c_2 associated with the compression of the clusters themselves.

Under external pressure, we expect the C_{60} to not deviate much from a spherical shape due the twelfold coordination with neighboring clusters. Also, the symmetry of the lattice is incompatible with the symmetry of C_{60} , so the specific nonspherical aspects of its geometry should not play an important role. This is supported by the low activation energy of only ≈ 0.15 eV (per cluster) for molecular rotation.⁹ We shall therefore treat the clusters in a spherical approximation.

The C_{60} surface is similar to a curved piece of graphite, with predominantly sp^2 bonding and a nearest-neighbor distance of $d_{C-C} = 1.42$ Å. Owing to the large equilibrium separation of $d=2.9$ Å between C_{60} clusters, their mutual interaction is mainly due to a van der Waals force which should be very similar to the interaction between layers of graphite. We shall base this part of our model on the LDA results for interactions between graphite layers.¹⁰ Our expectation, confirmed by the analysis, is that the

individual clusters are highly incompressible compared to the interaction between clusters. Thus, for low pressures at least, there is a close relationship between the compressibility of fullerite and the c -axis compressibility of graphite.

We shall model the van der Waals interaction assuming that atoms in the neighboring graphite layers interact pairwise,¹¹ as

$$E = \sum_i \sum_j U(r_{ij}). \quad (1)$$

The pair interaction is constructed to reproduce the *ab initio* LDA calculations for the binding energy of graphite.¹⁰ We use a modified Morse potential of the form

$$U(r) = D_e[(1 - e^{-\beta(r-r_e)})^2 - 1] + E_r e^{-\beta' r}. \quad (2)$$

Here, i, j denote atoms in adjacent graphite layers, D_e is the equilibrium binding energy of these atoms, r_e is the equilibrium distance between these atoms, and E_r describes an additional hard-core repulsion. β and β' describe the distance dependence of these interactions. The binding energy of graphite as a function of the interlayer distance d , obtained using Eqs. (1) and (2), is shown in Fig. 2(a) together with the LDA data. The corresponding interlayer force is shown in Fig. 2(b). The parameters used in Eq. (2) are listed in Ref. 12.

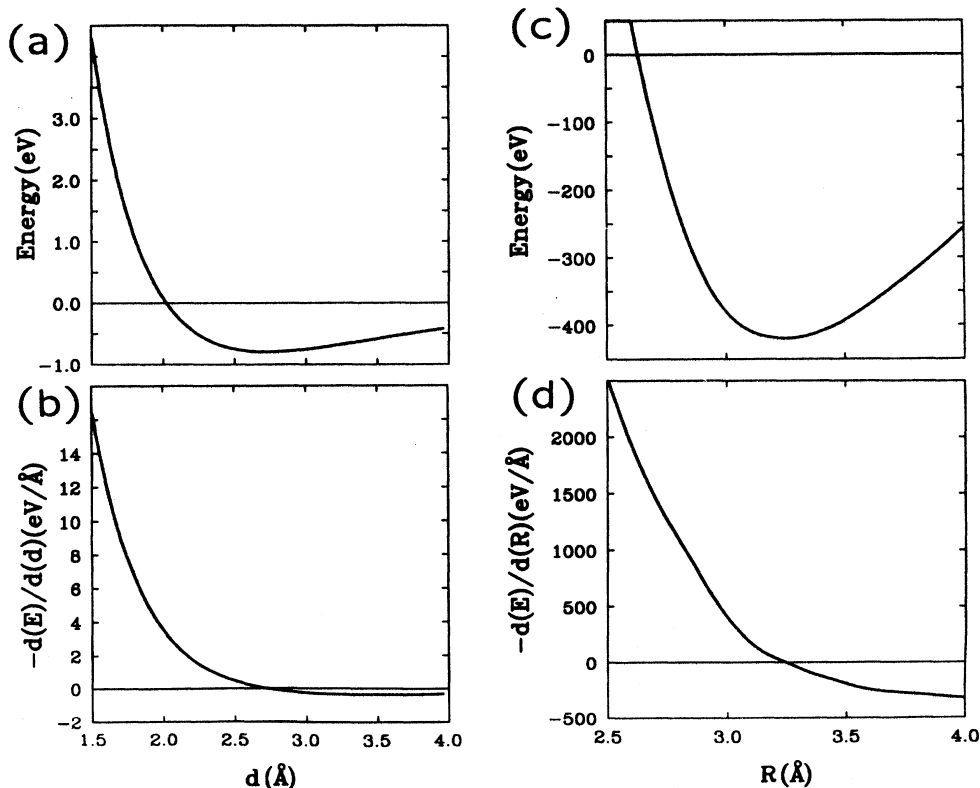


FIG. 3. (a) Interaction energy between two C_{60} fullerene clusters as a function of the closest approach distance d (see Fig. 1). (b) Negative gradient of the interaction energy in (a), corresponding to the pairwise force between neighboring C_{60} clusters. (c) Binding energy of an isolated C_{60} fullerene cluster as a function of the cluster radius R . (d) Negative gradient of the binding energy given in (c). Note the difference in scales between (b) and (d).

Since the van der Waals interaction is long ranged, it is convenient to replace the double sum in Eq. (1) by a double integral which averages over the atomic sites. The interatomic binding energy U is then replaced by the energy \tilde{U} corresponding to the interaction energy between two small areas ΔA in adjacent graphite layers. Then,¹²

$$E = \int_{A_1} dr_1 \int_{A_2} dr_2 U(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (3)$$

$$\tilde{U}(r) = \tilde{D}_e[(1 - e^{-\beta(r-r_e)})^2 - 1] + \tilde{E}_r e^{-\beta'r}. \quad (4)$$

We use Eqs. (3) and (4) to determine the interaction energy E_{vdW} between neighboring C_{60} clusters and note that the double integral extends over the surface areas of both clusters. In case the direct line connecting the area elements at \mathbf{r}_1 and \mathbf{r}_2 contains a part of any cluster, we neglect the corresponding contribution to the double integral due to screening. The resulting pairwise interaction energy between neighboring clusters is shown in Fig. 3(a). The corresponding force, given in Fig. 3(b), indicates that at zero pressure, the distance of closest approach between neighboring C_{60} clusters is $d = 2.65 \text{ \AA}$.

We calculate the binding energy E_{60} of an isolated C_{60} cluster using a modified tight-binding Hamiltonian,¹³ which had been tested successfully in previous studies of the equilibrium structure and vibration modes of small Si_n clusters.¹⁴ The breathing mode of the C_{60} cluster is described by the dependence of the binding energy on the cluster radius R , as shown in Fig. 3(c). The restoring force, shown in Fig. 3(d), is zero at the equilibrium radius $R_{\text{eq}} = 3.25 \text{ \AA}$.

With all force constants at hand, we can now proceed to calculate the equation of state of fullerite. The solid can now be viewed as an fcc lattice of fullerenes represented by mass points and connected with strongly anharmonic nearest-neighbor springs, shown in Fig. 1. In compressed fullerite, the equilibrium geometry minimizes the binding energy per C_{60} cluster in the fcc structure,

$$E_{\text{coh}}(D) = 6E_{\text{vdW}}(d) + E_{60}(R) \quad (5)$$

with fixed $D = d + 2R$, corresponding to a unit cell volume $V = D^3/\sqrt{2}$. The first term in this equation correctly avoids double counting the nearest-neighbor van der Waals bonds, and the second term is the energy of an isolated C_{60} . The binding energy of fullerite $E_{\text{coh}}(V)$ is shown in Fig. 4(a). At $T = 0$, one obtains the pressure from $p = -dE_{\text{coh}}/dV$ and the bulk modulus from $B = -V(\partial p/\partial V)$.

In Figs. 4(b) and 4(c), we show the dependence of the cell volume and the bulk modulus on the external pressure. From these results it is obvious that the elastic behavior of fullerite resembles closely that of an inert gas solid. At very small pressures, the interactions between clusters are dominated by the compressible van der Waals bonds causing a very low bulk modulus $B \approx 0.2 \text{ Mbar}$. With increasing external pressure, the clusters themselves are compressed at a high cost in energy, causing a large increase in the bulk modulus. We found it instructive to compare the bulk modulus of fullerite at high pressures to diamond. The diamond data of Ref. 15, ob-

tained using LDA calculations, are shown in Fig. 4(c) by a dashed line. From our calculation, we conclude that the compressibility of fullerite exceeds that of diamond only at pressures exceeding $\approx 70 \text{ GPa}$.

As discussed earlier, fullerite can be viewed as an fcc solid consisting of heavy mass points representing C_{60} clusters, with nearest-neighbor interactions. In Fig. 5, we show the phonon band structure of this lattice. The relatively low vibration frequencies result from the heavy mass of the clusters and the weak van der Waals interactions at $p=0$.

For the sake of completeness, we should mention the possibility of fullerite turning locally into diamond under very large pressures. The mechanism is very similar to that discussed by Fahy, Louie, and Cohen for the conversion of rhombohedral graphite with sp^2 bonding to dia-

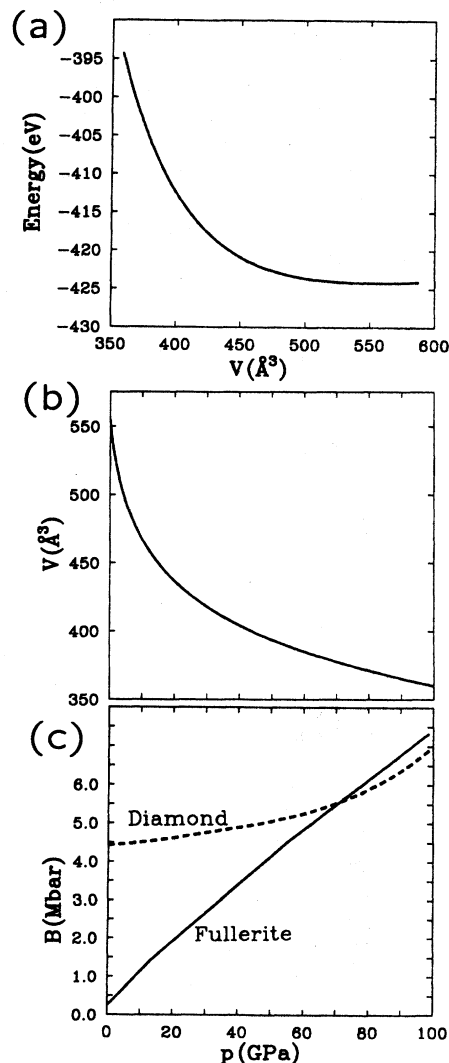


FIG. 4. (a) Binding energy of fcc fullerite (per C_{60} cluster, with respect to isolated carbon atoms) as a function of cell volume V . (b) Pressure dependence of the equilibrium cell volume V of fullerite. (c) Pressure dependence of the bulk modulus B of fullerite (solid line), as compared to diamond (dashed line, from Ref. 15).

mond with sp^3 bonding.¹⁶ This transition is initiated in graphite by a strong interlayer coupling occurring when interlayer and intralayer carbon nearest-neighbor bonds are comparable. In fullerite, this transition should occur when the distance of closest approach between adjacent fullerene clusters d is close to 1.5 Å. This occurs at the upper end of the pressure scale in Figs. 3(b) and 3(c) and should be more easily achieved in fullerite than in graphite.

In this study, we used Eqs. (3) and (4) to calculate the interaction between neighboring clusters which have been approximated by spherical shells. As mentioned earlier, the atomic granularity of the clusters is averaged out to a large degree. Based on our expression in Eqs. (1) and (2), we find a residual activation energy for cluster rotation of the order of 0.1 eV (per cluster), in fair agreement with experimental data.⁹

In summary, we calculated the equilibrium structure of fullerite, a solid composed of C₆₀ clusters, as a function of external pressure. We found that at zero pressure, carbon atoms in neighboring "fullerene" clusters are no closer than 2.65 Å apart and interact by pairwise van der Waals forces. At increasing pressures, we found a gradual transition to a hard-core repulsion between neighboring

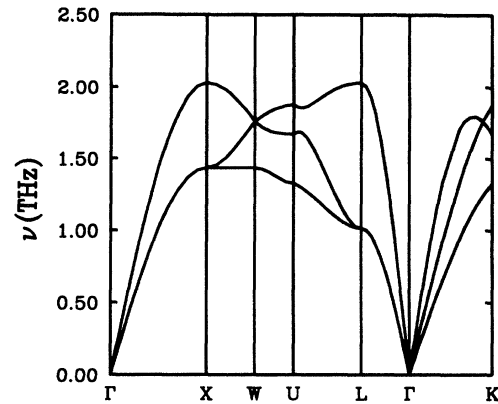


FIG. 5. Phonon dispersion relation $\nu(\mathbf{k})$ of bulk fullerite with fcc structure.

clusters. Only at high pressures beyond ≈ 70 GPa, the bulk modulus of fullerite should exceed that of diamond.

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