Mechanical properties of fullerite of various composition

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Abstract. Molecular dynamics simulation is used to study the structures of fullerite of various composition as well as their mechanical properties. Fullerites based on fullerene C_60 with simple cubic and face-centered packing, fullerene-like molecule C_48 and fullerene C_240 with simple cubic packing are studied. Compliance and stiffness coefficients are calculated for fullerites C_60 and C_48. For fullerite C_240, C_60, and C_48, deformation behavior under the effect of hydrostatic compression is also investigated. It is shown that the fullerenes in the fullerite remain almost spherical up to high values of compressive strain, as a result of which the fullerite is an elastic medium up to densities of 2.5 g/cm^3. The increasing stiffness and strength under an applied compression is found for all the considered fullerites.

1. Introduction
In recent years, more and more attention has been attracted by bulk carbon nanomaterials, which demonstrate new interesting properties. For example, bulk carbon nanostructures created on the basis of graphene flakes, carbon nanotubes and fullerenes [1-4], diamond-like phases [5-16], to name a few are of considerable interest. Such properties of these materials as superconductivity, field emission, non-wetting of the surface, ultrahigh specific surface area combined with electrical conductivity seem very promising for various applications: in the fields of catalysis, separation, gas storage, electronics, electrode materials, supercapacitors, etc. [17-22]. Economical and environmentally friendly methods of obtaining such materials are being developed during last decades.

One of the interesting structures, which were studied to the present moment both experimentally and theoretically, is fullerite, a material formed by fullerenes deposited in an ordered lattice. The fullerite crystal C_60 has a cubic structure with a face-centered cubic (FCC) lattice, which has a lattice constant of 14.2 Å and a density of 1.65±0.03 g/cm^3 can be easily produced experimentally. At room temperature, hexagonal packing of molecules is observed, although FCC stacking is preferable. At room temperature, the molecular centers form a regular FCC crystal lattice, but the molecules themselves freely rotate around their centers. In [23], where the influence of deformation on the physical properties of C_{240} fullerenes was studied, it is shown that even a small deformation leads to a shift in the electronic spectra. The bulk modulus of fullerite C_{60} increases rapidly with increasing pressure. To date, studies have been made on the elastic properties of polycrystalline fullerite samples, and measurements of Young's modulus on single-crystal samples of small dimensions [24, 25]. Earlier measurements of the elastic constants of some diamond-like structures and fullerites can be found in [26-29]. The elastic moduli c_{11}, c_{12} and c_{44} of single-crystal C_{60} were determined by measurement of ultrasound velocities and found to be equal to ~15 GPa, ~9 GPa and ~6 GPa correspondingly [26]. The relaxation contribution [27] and temperature behavior [28, 29] of the elastic modulus is also discussed.
One of the interesting and important areas of research is the search for materials with unusual mechanical properties. Analysis of the elastic properties of various carbon nanostructures showed that they can have a negative Poisson's ratio [30-33] which is quite rare property [12, 14, 34-44]. To date, auxeticity was found mostly for carbon nanotubes [34-37] or graphene which is already known to have some negative parameters, for example, negative thermal expansion, potential auxeticity at various conditions, such as very high temperatures [38] or resonance under fully blocked boundary conditions [39]. Effect of different factors on auxeticity was studied for graphene [31, 40, 41]. For example, corrugation can be effectively used to tailor graphene properties [31, 42]. The lowering of Poisson’s ratio was found due to an introduction of low concentrations of vacancies. In recent years, graphene kirigami has been investigated due to its specific properties under deformation [43] and unusual auxetic behavior [44]. Thus, carbon nanostructures can be considered as very promising in case of search for such auxetic structures.

The aim of this work is to consider the fullerite crystals of various compositions and study their mechanical properties by molecular dynamics simulation. Three types of fullerite with different crystal packing are considered.

2. Simulation details

The simulation cell of fullerite is created on the basis of fullerenes C$_{60}$ and C$_{240}$ and the fullerene-like molecule C$_{48}$. Initial structures are prepared with the help of home-made programs written by authors, which allow to combine different structural elements in three-dimensional structures, such as fullerite. The single structural element is shown in figure 1a. Structure based on C$_{60}$ have SC (simple cubic) and FCC (face-centered) packing, fullerites based on the fullerene-like molecule C$_{48}$ and fullerene C$_{240}$ have SC packing. Examples of the structures with different crystal packing are shown in figure 1b, c.

![Figure 1](image)

Figure 1. (a) Fullerenes C$_{48}$, C$_{60}$ and C$_{240}$ correspondingly. Fullerite based on (b) fullerene-like molecule C$_{48}$ with SC stacking (c) fullerene C$_{60}$ molecule with FCC stacking.

The simulation cell includes 4 structural units respectively along the x, y and z directions. Structural units of the material were randomly oriented in space. In view of the high symmetry of the fullerene molecules, it can be considered that this material is a crystalline body and has translational symmetry. Periodic boundary conditions along the x, y and z directions are applied.

The simulation is carried out using molecular dynamics simulation using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software package [45], where the interaction of
carbon atoms is described by the AIREBO interatomic interaction potential [46]. The Lennard-Jones potential, which is an integral part of the AIREBO potential, has a minimum potential energy of 0.024 eV at a distance $r = 3.4 \text{Å}$. This part of the AIREBO potential is used to describe the pairwise Van der Waals interatomic forces between the structural elements (fullerenes). This potential is based on the well-known Tertsoff potential, and have been actively used to study carbon structures and widely used to study various carbon structures and their properties [47-53]. Equations of motion of atoms were integrated according to the Verle method of the fourth order of accuracy with an integration step of 0.2 fs. All numerical experiments are carried out at 300 K. The Nose-Hoover thermostat is used for thermalisation of the system. At the initial moment, the structure relaxed until a local or global minimum of potential energy is reached.

To calculate the compliance moduli $s_{ij}$, a linearly increasing stress with one non-zero component is applied to the simulation cell and the corresponding strain components are calculated. It turned out that for strains less than 2%, stress-strain curves are practically linear and from the slopes of these curves the required constants $s_{ij}$ can be calculated from Hooke’s law. This technique is described in details in [12, 14].

For a cubic crystal, it is sufficient to calculate only three modulus of compliance from expression

$$
\begin{align*}
\left[ \varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6 \right] &= \left[ s_{11}, s_{12}, s_{12}, 0, 0, 0 \right] \begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{pmatrix},
\end{align*}
$$

To study the deformation behavior, the simulation cell is subjected to deformation-controlled hydrostatic compression $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = -\varepsilon$, where $\varepsilon \geq 0$ it is a parameter that increases monotonically with the velocity $\dot{\varepsilon} = 0.02 \text{ ps}^{-1}$. Test calculations with lower strain rates (four and eight times lower) did not reveal noticeable changes in the results. In the process of deformation, the hydrostatic pressure $p = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) / 3$ and material density $\rho$ are calculated. The bulk modulus is calculated as $B = \rho (\Delta p / \Delta \rho)$.

3. Results and discussion

3.1. Fullerite $C_{48}$ and $C_{60}$

The values of the compliance and stiffness coefficients of fullerite $C_{48}$ and $C_{60}$ obtained by molecular dynamics, are presented in tables 1 and 2. The results show a qualitative agreement with the previously known moduli of rigidity of fullerite $C_{60}$, determined experimentally in [26-29]. However, the calculated values are several times larger. This can be explained by the fact that the experimentally obtained single crystals of fullerite contain many defects and, in addition, experimental measurements are carried out at finite temperatures, while the calculations presented in this work were carried out for an ideal crystal at zero temperature.

| Table 1. Compliance coefficients for three structures. |
|-----------------------------------------------|
| $s_{11}$, TPa$^{-1}$ | $s_{44}$, TPa$^{-1}$ | $s_{12}$, TPa$^{-1}$ |
| $C_{48}$ | 10.5 | 6.61 | -4.68 |
| $C_{60}$ SC | 43.3 | 218 | -1.87 |
| $C_{60}$ FCC | 0.052 | 0.0348 | -0.0224 |
Table 2. Stiffness coefficients for three structures.

|       | $c_{11}$   | $c_{44}$   | $c_{12}$   |
|-------|------------|------------|------------|
| $C_{60}$ | 331 MPa   | 151 MPa   | 265 MPa   |
| $C_{60}$ SC | 23.2 MPa | 4.59 MPa | 1.05 MPa |
| $C_{60}$ FCC | 55.3 GPa | 28.7 GPa | 41.8 GPa |

In figure 2 hydrostatic pressure as the function of density is shown for three types of fullerite. It is observed that for all the structures the pressure is zero when $\rho < 1$ g/cm$^3$ and increases monotonically with $\rho$ afterwards. This is because when $\rho < 1$ g/cm$^3$ fullerenes are far away from each other, and only start to interact when $\rho < 1$ g/cm$^3$. Accordingly, the zero strain level ($\varepsilon = 0$) is set at the point when $\rho = 1$ g/cm$^3$ and this convention is used hereafter. As it can be seen, all fullerene crystals can be compressed until very high densities, even close to the diamond density. Since AIREBO potential cannot adequately describe bonds destruction and transition to the amorphous state, compression is stopped at the density 2.8 g/cm$^3$ while crystalline order still can be identified.

Figure 2. Hydrostatic pressure as the function of the material density at 300 K for fullerite $C_{60}$ FCC (red solid line), fullerite $C_{60}$ SC (blue dotted line) and fullerite $C_{48}$ SC (green dashed line).

Two structures with SC packing behave differently from the fullerite $C_{60}$ with FCC packing. For SC structures, pressure is much higher than for FCC structure because fullerenes in SC packing cannot reorganize in the simulation cell, while for FCC packing they have some free space for further compression. Fullerenes in FCC structures have the same round shape until very high densities, while fullerenes in SC structures slightly crumple under compression.

Elastic constants for three fullerite crystal are presented in table 3, where $G_1$ and $G_2$ are the maximum and minimum values of shear modulus. Bulk modulus is calculated as $B = 1/3(c_{11}+2c_{12})$. Results are in good agreement with experimental work [26].

Table 3. Elastic coefficients for three structures.

|       | $B$      | $G_1$   | $G_2$   |
|-------|----------|---------|---------|
| $C_{60}$ | 287 MPa | 151 MPa | 0.033 MPa |
| $C_{60}$ SC | 8.43 MPa | 4.58 MPa | 0.011 MPa |
| $C_{60}$ FCC | 46.3 GPa | 28.7 GPa | 6.72 GPa |

3.2. Fullerite $C_{240}$

In figure 3a the dependence of the hydrostatic pressure on the density for $T = 300$ K is shown. From the inset in figure 3a it can be seen that there is a linear relationship between $\rho$ and $\varepsilon$ up to $\varepsilon = 0.03$. The stress-strain curve allows to estimate the bulk modulus, which is $B = 0.35$ GPa. Pressure-density curve

Loading of fullerite was followed by subsequent unloading. The corresponding curves are shown in figure 3b, where the loading curve is shown by a solid line, and the unloading curves from different compression strain are shown by dashed lines. Value $\rho^*$ corresponds to the value of the density, after
which irreversible changes take place in the structure and its return to the original state is impossible. Unloading from a density higher than critical, results in a deviation of the unloading curve from the initial one. As can be seen from the figure 3b, fullerite remains almost an elastic medium till the high densities, and only at density values greater 2.5 g/sm$^3$ the discharge curve does not coincide with the loading curve, although the course of the curves remains the same.

![Figure 3](image)

Figure 3. (a) Dependence of the hydrostatic pressure on the material density at $T = 300$ K. The inset shows the curve of the dependence of hydrostatic pressure on deformation for a small strain range. (b) Loading (solid lines) and unloading (dashed lines) curves from different strain levels.

4. Conclusion

The mechanical and structural properties of fullerite of various composition have been studied by molecular dynamics. The increasing stiffness and strength under an applied compression is found for all the considered fullerenes. The estimation of the volume modulus of the structure considered gives $B = 0.35$ GPa, which is much lower than the values ~9 GPa, obtained at room temperature for fullerite $C_{60}$ in [26] and present work. Such a difference in the values is easy to explain, taking into account the ratio of the sizes of fullerenes $C_{60}$ and $C_{240}$ and presence of various defects in experimental samples.

The high strength of fullerite is explained by the fact that fullerenes retain a convex shape close to spherical up to high values of strain and their collapse occurs instantaneously when the critical value of compression is reached. This also explains the fact that fullerite $C_{240}$ is an elastic medium until the density lower than 2.5 g/cm$^3$ and unloading leads to an almost complete restoration of the initial structure. Fullerenes in fullerites $C_{60}$ and $C_{48}$ also remain stable and spherical with the well-defined crystalline order. However, FCC $C_{60}$ sustain lower pressure in comparison with SC structures.

This study, showing a significant difference in the bulk modulus of fullerenes of different dimensions and packing, poses the question of the effect of the size of a single building element of the cluster and its crystal packing. Obviously, the density of clusters consisting of different structural units will play an important role in assessing the mechanical properties and the effect of hydrostatic deformation on the behavior of the material, which, however, requires further research. Moreover, it is also interesting to study non-symmetric fullerenes, such as $C_{70}$ and giant fullerenes as $C_{960}$ because those fullerite crystals can also be produced experimentally.

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