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Original Article

Analytical Expressions for Bulk Modulus of Fullerene C_{60} in Case of Nonlinear Volumetric Deformations

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Abstract: The aim of this work is to establish the bulk modulus expressions of fullerene C_{60} in both linear and nonlinear deformation cases. The Lennard-Jones potential energy is used to calculate the bonding forces between carbon atoms. The research results reveal a formula demonstrating the dependence of the bulk modulus on the volume of the fullerene in the case of significant volume deformation (nonlinear case). Consequently, the bulk modulus of fullerene C_{60} can be determined basing on the volume deformation ratio. A comparison between the bulk modulus in general case (large deformation - nonlinear) and specific case (small deformation - linear) has been made. The results obtained through the Finite Element Method (FEM) and Density function theory (DFT) have affirmed the accuracy of the research results.

Keywords: Fullerene C_{60}, bulk modulus, nonlinear deformation, linear deformation, expression of the bulk modulus.

1. Introduction

Fullerene C_{60} has a geometrically perfect structure, consisting of multiple interconnected rings, forming a closed cage (cage like fused-ring), with *60* vertices and *32* faces, comprising *20* hexagonal and *12* pentagonal faces. Each carbon atom serves as a vertex of these polygons, and the bonds represent the edges of these polygons. Due to its small size, the determination mechanical properties of fullerene C_{60} through experimental methods has a significant challenge in modern physics. In case of impractical experiments, simulations methods become a useful solution. The simulations method is primarily used

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with nanostructures through molecular dynamics (MD) [1, 2]. Numerous publications have been done for the molecular dynamics simulations for fullerene [3, 4]. Additionally, other methods, such as finite element analysis and density function theory, have been used to determine the mechanical characteristics of fullerene [5]. Although the simulations methods offer a means to overcome many limitations of the experiments, they are not fully optimized yet. Specifically, the results of the simulations method demand scrutiny regarding their accuracy. In this case, analytical expressions serve as a important base for comparison with the simulation results [6].

Fullerene possesses noble properties, however, under actions of significant external forces, it can undergo relatively large deformations. Carbon atoms in fullerene not only vibrate in proximity to their equilibrium positions but also exhibit relatively large amplitudes (compared to the lengths of fullerene's edges). However, the analytical results about the bulk modulus have been limited to small deformations (linear case) [6, 7]. This work presents a formula for the bulk modulus of fullerene C_{60} in the case of nonlinear deformation. The bulk modulus of fullerene is defined as the ratio of the pressure applied to the fullerene to the relative volume change [6]. In the case of linear deformation, analytical expressions that demonstrate the relationship between the bulk modulus of fullerene C_{60} and parameters such as bond stiffness, bond length, etc. have also been established [7]. In the cases of large deformations, the bulk modulus of fullerene C_{60} is not stationary, but exhibits volume-dependent function that is demonstrated in sections bellow.

2. Linear Volume Deformation of Fullerene C_{60}

Authors in [7] successfully obtained the relationship between the bulk modulus and the bond stiffness, as well as the geometric characteristics of C_{60} fullerene when it takes small deformation:

$$B \approx \frac{Nka_0 \cos\alpha}{S_0} \tag{1}$$

where $N = 60$ is the number of carbon atoms in fullerene, α represents the angle between the external force and the direction of the bond with $\cos\alpha = 0.202$, and S_0 is the surface area of the fullerene in the non-deformed state ($S_0 = 0.424$ nm², calculated from the areas of all the polygonal surfaces). The bond length $a_0 = 0.1433$ nm. The authors calculate the value of the bulk modulus with different bond stiffness values, k, obtained from [4]. The results are listed in table below.

Table 1. Bond stiffness and bulk modulus of fullerene C_{60}, [7]

Bond stiffness k, N/m	Bulk modulus B, GPa
762	887
708	824
672	782
660	768
635	739

In article [7], the author only provided an approximate method for calculating the bulk modulus of fullerene in a linearly deformed state with a value of $(V_0/V) \approx 1$, hence the bulk modulus in equation (1) is treated as a constant for volume deformation. However, when large non-linear deformation occurs, the bulk modulus of C_{60} will deviate significantly from the calculated results in the linear deformation state. This issue has not been clarified in article [7].

3. Non-linear Volume Deformation of Fullerene C_{60}

Non-linear volume deformation of fullerene C_{60} is considered. Assum that, the bond reaction force generated by the potential energy interaction between carbon atoms, U, and the pressure created by external forces, **F**, acting on all carbon atoms directed towards the center of the molecule C_{60}, as seen in Fig. 1.

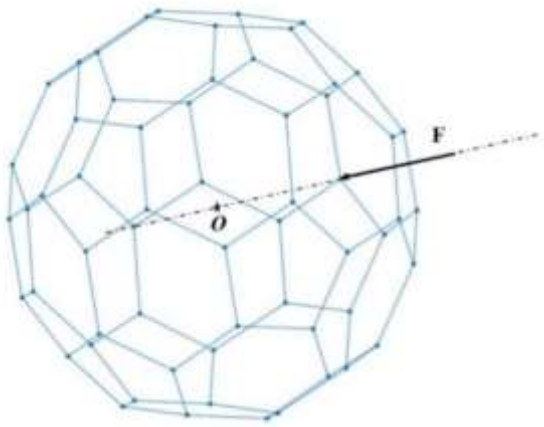

Figure 1. Molecule fullerene C_{60} is deformed under the external forces.

Therefore, the equilibrium equation for any atom with a projection along the direction of the external force is as follows:

$$F + 3U'(r)\cos\alpha = 0, \tag{2}$$

where r is the distance between neighboring atoms in fullerene. The calculation involves the Lennard-Jones potential energy.

$$U(r) = D\left[\left(\frac{a_0}{r}\right)^{12} - 2\left(\frac{a_0}{r}\right)^{6}\right]. \tag{3}$$

In this formula, D is bond energy, which is defined by the difference between the energy at the bottom of the well and the energy at infinity. Replacing the expression of the Lennard-Jones potential energy into equation (2) with the value of the constant $D = ka_0^2/72$, we obtain:

$$F = -\frac{ka_0\cos\alpha}{2}\left[\left(\frac{a_0}{r}\right)^{7} - \left(\frac{a_0}{r}\right)^{13}\right]. \tag{4}$$

Therefore, one can obtain the expression of the pressure acting on the surface of the fullerene molecule according to the following formula:

$$P = \frac{NF}{S} = \frac{Nka_0\cos\alpha}{2S}\left[\left(\frac{a_0}{r}\right)^{13} - \left(\frac{a_0}{r}\right)^{7}\right]. \tag{5}$$

where P is the pressure. Using the following approximate formulas to represent the relationship between pressure and the volume deformation ratio: $r = a_0(V/V_0)^{\frac{1}{3}}$, $S = S_0(V/V_0)^{\frac{2}{3}}$, where S, V are the equivalent surface area and the equivalent volume of the deformed state of the fullerene, respectively. V_0 is the initial volume of the fullerene. Therefore, formula (5) can be modified:

$$P = \frac{Nka_0 \cos\alpha}{2S_0}\left[\left(\frac{V_0}{V}\right)^5 - \left(\frac{V_0}{V}\right)^3\right]. \quad (6)$$

Denote the volumetric strain: $1-(V/V_0)=\Delta V/V_0$; ΔV is the mean volume decrease. After substituting this expression into formula (6), we obtain:

$$P = \frac{Nka_0 \cos\alpha}{2S_0}\left[\left(\frac{V_0}{V}\right)^5 + \left(\frac{V_0}{V}\right)^4\right]\left(\frac{\Delta V}{V_0}\right). \quad (7)$$

The bulk modulus of fullerene is defined as the proportion of the pressure acting on a node of the fullerene and the volumetric strain:

$$B = \frac{P}{\frac{\Delta V}{V_0}} = \frac{Nka_0 \cos\alpha}{2S_0}\left[\left(\frac{V_0}{V}\right)^5 + \left(\frac{V_0}{V}\right)^4\right]. \quad (8)$$

Where B is the bulk modulus of the deformed state of the fullerene. It can be observed that the bulk modulus of C_{60} fullerene is a monotonically increasing function of the volume deformation ratio, V_0/V. In the case of small deformations, with the value $V_0/V \approx 1$, substituting this approximation into Eq. (8), yielded results similar to Eq. (1).

4. Result and Discussion

For fullerene C_{60}, we have corresponding geometric values $N = 60$, $S_0 = 0.424$ nm^2, cosα = *0.202*, a_0 = *0.143* nm. The different values of the bond stiffness k, are taken from Table 1; The volume deformation ratio, V_0/V is given from *0.9* to *1.1*. The dependence of the bulk modulus on the volume deformation ratio with different values of the bond stiffness are demonstrated on the Fig. 2.

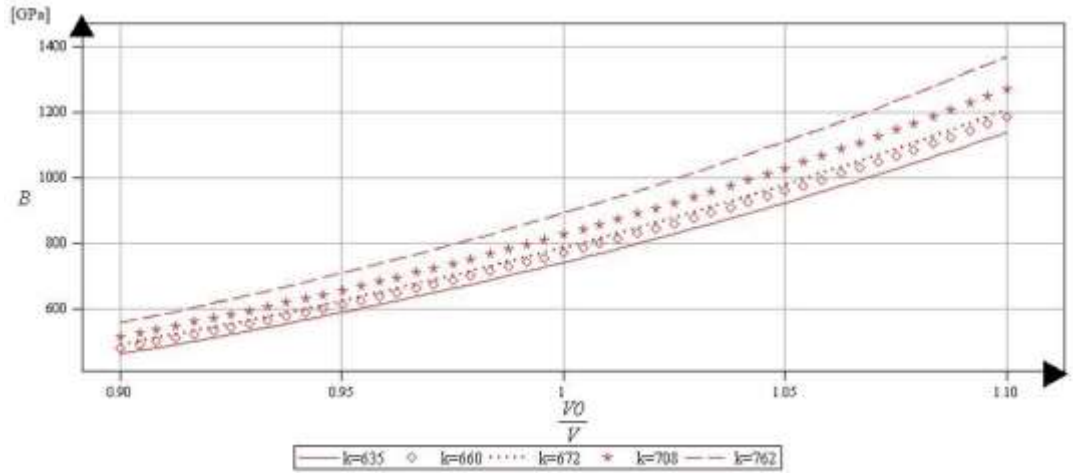

Figure 2. The dependence of the bulk modulus on the volumetric deformation ratio in the nonlinear deformation state.

The bulk modulus increases when the bond stiffness increases. This is coincided with the physical aspect and is also shown in the analytical results of Eq. (8). Besides, it is observed that, when the fullerene volume changes by *5*% - *10*% compared with the original volume, the value of the bulk

modulus has a significant deviations compared with its value in the small deformation case. This can be observed clearer in Fig. 3. In which, B_s is the bulk modulus in the nonlinear deformation case (large deformation), B_0 is the bulk modulus in the linear deformation case (small deformation).

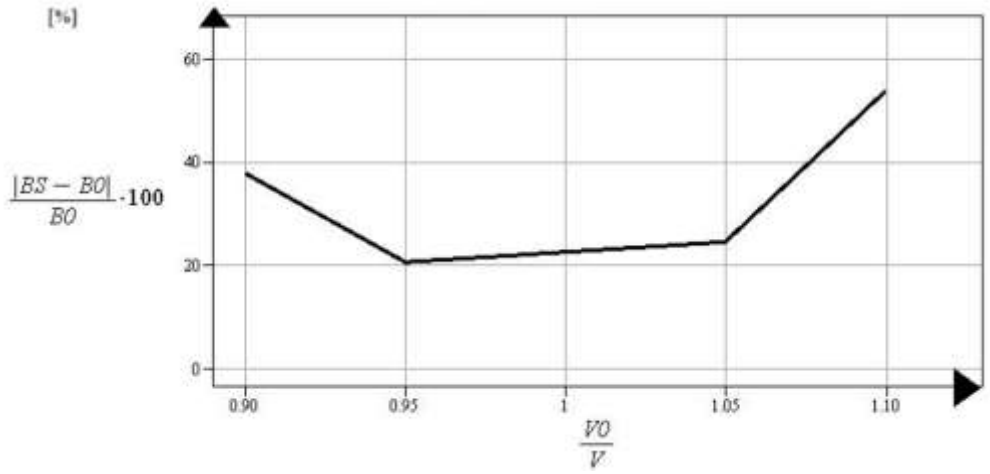

Figure 3. The difference of the bulk modulus in the linear and nonlinear deformation cases.

In Fig. 3, when nonlinear volumetric deformation occurs, the deviations of the bulk modulus is quite large compared with the case of linear deformation (up to *54*% when the fullerene volume is compressed by *10*% compared to the original volume). In addition, this error is not related to the value of the bond stiffness *k*.

In the linear deformation state ($V_0/V \approx 1$), the bulk modulus is compared with the results reported in [5]. In this work, the bulk modulus value of fullerenes C_{60} was determined by the density function theory (DFT) method B_1 equaled *874* GPa (Table 2). Similarly, the comparison with the result determined by the finite element method (FEM) B_2 is equal to *819* Gpa (Table 3).

Table 2. The comparison of bulk modulus fullerene C_{60} with the result determined by the density function theory (DFT)

The bond stiffness *k*, N/m	The bulk modulus in the linear deformation case B_0, GPa	The bulk modulus determined by DFT method B_1, GPa	$\frac{\lvert B_1 - B_0 \rvert}{B_1}.100$, %
762	887	874	1.49
708	824	874	5.72
672	782	874	10.53
660	768	874	12.12
635	739	874	15.44

From Tables 1, 2 it is observed that, the deviations of the bulk modulus of fullerene between the results of this study and the results determined by other methods FEM and DFT in the case of small deformation is less than *10*%. This proves the reliability of the research results. In addition, when the bond stiffness increases, the error is also increased. Besides, some atomistic structural mechanics methods, which are based on the exclusive use of spring elements [8], and based on the beam elements [9], are developed. As senn in [8, 9] the values of bulk modulus obtained were similar to the results obtained in present study.

Table 3.The comparison of bulk modulus fullerene C_{60} with the result determined by the finite element method (FEM)

The bond stiffness k, N/m	The bulk modulus in the linear deformation case B_0, GPa	The bulk modulus determined by FEM method B_2, GPa	$\frac{\lvert B_2 - B_0 \rvert}{B_2}.100,\ \%$
762	887	819	8.30
708	824	819	0.61
672	782	819	4.52
660	768	819	6.23
635	739	819	9.77

5 Conclusion

In this work, the case of nonlinear volume deformation of fullerene C_{60} under pressures created by external forces, which are acting on all carbon atoms in the structure of fullerene C_{60}, is considered. By analytical methods, the bulk modulus obtained in this case is a monotonic function depending on the volume deformation ratio V_0/V, in formula (8). Therefore, it is possible to determine the value of the bulk modulus based on the volume deformation of fullerene C_{60}. Besides, results of this work also show the large deviations of the values of the bulk modulus in two cases of nonlinear deformation and linear deformation. These deviations are up to *54*% when the volume is compressed by *10*% compared to the original volume. The results of the bulk modulus in the linear deformation state are also compared with the values, which have been calculated in [5], with the error from *1.42*% - *15.44*% compared to the result in the case of the quantum mechanical method and *0.61* % - *9.77*% compared to the result in the case of the finite element method. These comparisons also confirm the correctness of the obtained results in our work.

Further, the linear and nonlinear volumetric vibrations of fullerene C_{60} will be considered, thenthe bond stiffness of the molecules fullerenes will also be interpolated from the response of their vibration process.

Acknowledgments

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