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ANALYTICAL EXPRESSIONS FOR BULK MODULI AND FREQUENCIES OF VOLUMETRICAL VIBRATIONS OF FULLERENES C_{20} AND C_{60}

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In the present paper simple analytical expressions connecting bulk moduli for fullerenes C_{20} and C_{60} with stiffness of interatomic bond and geometrical characteristics of the fullerenes are derived. Ambiguities related to definition of the bulk modulus are discussed. Nonlinear volumetrical deformation of the fullerenes is considered. Pressure-volume dependence for the fullerenes under volumetrical compression are derived. Simple analytical model for volumetrical vibrations of the fullerenes is proposed. The expression connecting frequencies of volumetrical vibrations for fullerenes C_{20} and C_{60} with parameters of interatomic interactions are obtained.

Keywords: fullerenes, bulk modulus, vibrations, eigenfrequency, natural frequency.

1. Introduction

The discovery of unique physical and mechanical properties of fullerenes in the end of XXth century [1] have strongly increased scientific interest to these carbon nanostructures. The fullerenes are closed spheroidal surfaces, made of pentagons and hexagon with carbon atoms in tops. During the last several decades a great number of fullerenes have been synthesized [2, 3]. However it is notable that only two of them, C_{20} and C_{60}, have perfect geometrical shape (dodecahedron and truncated icosahedron respectively). Due to the small size of fullerenes experimental investigation of their physical and mechanical properties is still a challenge problem for the modern physics. That is why only few characteristics of fullerenes can be measured. In the case when experimental methods are not applicable, computer simulation becomes almost the only method for investigation. The main methods for computer simulation of nanostructures are classical [4] and *ab initio* [5] molecular dynamics (MD). A great number of papers is devoted to both classical and *ab initio* MD simulation of fullerenes [6, 7]. Though computer simulations allow to overcome many limitations of real experiment, they are still not a "panacea". In particular, results of computer simulations require verification and validation. In this situation simple analytical models allowing to check the quality of the results are very important [8].

In the present paper simple analytical formulas for equivalent bulk moduli of fullerenes C_{20} and C_{60} are a derived. The following definition for bulk modulus is used. A bulk modulus of the fullerene is a proportionality factor between the pressure exerted on the fullerene and relative change of volume in case of small volumetric deformations [8]. The ambiguity of definition for the pressure exerted on the fullerene is discussed. Three definitions of the pressure, differing in the way of calculation of the equivalent surface area of the fullerene, are considered. Analytical expressions connecting bulk moduli of fullerenes C_{20} and C_{60} with micro- parameters (bond stiffness, bond length, etc.) are derived. The expressions are compared with a result of paper [8]. Bulk moduli of the fullerenes are calculated for different values of bond stiffness reported in literature. The dependence of pressure on volumetrical deformation of the fullerene is derived in the case of large deformations. Linearized equation of volumetrical vibrations of the fullerenes is presented. Corresponding eigenfrequency is calculated. The comparison with experimental data [10] is discussed.

2. Linear volumetrical deformation of fullerenes C_{20} and C_{60}

Let us assume that pressure exerted on the fullerene is carried out by the external forces of magnitude F acting on each carbon atom. Forces are directed to the center of the molecule. Consider the case of small volumetrical deformations. In this case angles between atoms do not change during the deformation. Then forces acting between atoms depend on interatomic distances only. Let us assume that atoms in the fullerene interact via pair central forces proportional to deformation of the bond. From the symmetry reasons all atoms in the fullerene are equivalent. Therefore the reasoning is carried out for one specific atom. Using symmetry one can show that equation of equilibrium for the given atom in a projection to direction of corresponding external force has the following form

$$F = -3ka_0\varepsilon\cos\alpha, \tag{1}$$

where α is an angle between the external force and direction of the bonds (α is identical for all bonds of the given atom); k is a stiffness of the bond; ε is a relative deformation of the bond; a_0 is an equilibrium bond length. It is important to note that the angle α doesn't change in the course of deformation. Let us use the expression connecting deformation of the bond ε and volumetrical deformation $\Delta V/V_0 = (V - V_0)/V_0$, where V and V_0 are volumes of the fullerene in deformed and undeformed states. In the case of small deformations the expression has form

$$\frac{\Delta V}{V_0} \approx 3\varepsilon. \tag{2}$$

Substituting expression (2) into formula (1) one obtains

$$F = -ka_0\cos\alpha\frac{\Delta V}{V_0}. \tag{3}$$

Let us define the pressure acting on fullerene as follows

$$P \overset{\text{def}}{=} \frac{NF}{S} \approx -\frac{Nka_0\cos\alpha}{S_0}\frac{\Delta V}{V_0}, \tag{4}$$

where N is a number of carbon atoms in the fullerene (N=20 for C_{20} and N=60 for C_{60}), S_0 is an equivalent surface area of the fullerene in undeformed state. Thus, one have the following expression for bulk moduli of fullerenes C_{20} and C_{60}

$$B = N\frac{a_0k\cos\alpha}{S_0}. \tag{5}$$

Note that equivalent surface area S_0 in formulas (4), (5) is in principle not unique. Therefore in the present paper three different definitions of S_0 are considered: area of the inscribing sphere, area of the circumscribing sphere and the surface area (the area of dodecahedron and truncated icosahedron respectively). Geometrical characteristics of fullerenes C_{20} and C_{60} required for calculation of the bulk modulus are presented in Table 1. Using the characteristics, bulk moduli of the fullerenes are calculated for different values of S_0 (see Table 2). The following value of bond length is used: $a_0 = 0.1433$ nm. Values of bond stiffness k, presented in Table 2, are taken from the paper [8]. Different values corresponds to different types of experiments (see paper [8] for details). Note that maximal difference between values of k is approximately 17%. One can see from Table 2 that bulk modulus B of fullerene C_{20} is approximately twice larger than the similar value for fullerene C_{60}. The value of bulk modulus essentially depends on a choice of the

Table 1. Geometrical characteristics of undeformed fullerenes C_{20} and C_{60}. Here R_c, S_0^c are radius and surface area of the sphere circumscribed around the fullerene, R_i, S_0^i are radius and surface area of inscribed sphere, S_0^p is a surface area of corresponding polygon.

	C_{20}		C_{60}	
	Formula	Value	Formula	Value
R_c	$a_0/(2\cos\alpha)$	0.201 nm	$a_0/(2\cos\alpha)$	0.355 nm
R_i	$a_0\sqrt{10(25+11\sqrt{5})}/20$	0.160 nm	$3a_0\sqrt{3}(3+\sqrt{5})/12$	0.325 nm
S_0^c	$4\pi R_c^2$	0.507 nm^2	$4\pi R_c^2$	1.58 nm^2
S_0^i	$4\pi R_i^2$	0.320 nm^2	$4\pi R_i^2$	1.33 nm^2
S_0^p	$3a_0^2\sqrt{5(5+2\sqrt{5})}$	0.424 nm^2	$15\left(2\sqrt{3}+\mathrm{ctg}\frac{\pi}{5}\right)a_0^2$	1.49 nm^2
$\cos\alpha$	$\frac{2}{\sqrt{3}(1+\sqrt{5})}$	0.357	$\sqrt{\frac{1+2\cos\frac{3}{5}\pi}{10+2\cos\frac{3}{5}\pi}}$	0.202

Table 2. Stiffness of the bond and bulk moduli of fullerenes C_{20} and C_{60}

Area	Bond stiffness, N/m	bulk modulus B, GPa	
		fulleren C_{20}	fulleren C_{60}
circumscribed sphere	762	1538	834
	708	1429	775
	672	1356	736
	660	1332	723
	635	1282	695
inscribed sphere	762	2436	997
	708	2263	926
	672	2148	879
	660	2110	863
	635	2030	830
polyhedron	762	1838	887
	708	1708	824
	672	1621	782
	660	1592	768
	635	1532	739

equivalent surface area S_0. Maximum difference between values B, calculated for different S_0, is 37% for C_{20} and 16% for C_{60}. Note that the values of bulk modulus of fullerene C_{60}, presented in Table 2, do not coincide with results of paper [8]. In paper [8] another definition for pressure acting on the fullerene was used. It was assumed that pressure is carried by normal forces distributed on a surface of the truncated icosahedron. Obviously the given way of loading can not be realized in practice. Therefore physical meaning of the definition used in paper [8] is not clear.

3. Nonlinear volumetrical deformation of fullerenes C_{20} and C_{60}

Let us consider nonlinear deformation of fullerenes C_{20} and C_{60}. Assume that compression of the bond is described by pair potential U. Also assume that pressure is carried out by external forces of value F, acting on all carbon atoms. Forces are directed to the center of the molecule. Then the projection of equilibrium equation for some specific atom on the directions of corresponding external force has the following form

$$F + 3U'(r)\cos\alpha = 0, \tag{6}$$

where r is a distance between the nearest neighbors in the fullerene. Resolving the given equation with respect to F and substituting the result onto definition for pressure (4) one obtains

$$P\left(\frac{V}{V_0}\right) = -\frac{3Na_0\cos\alpha}{S_0}\left(\frac{V_0}{V}\right)^{\frac{2}{3}} U'\left(a_0\left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right), \tag{7}$$

Here the following identities are used $r = a_0\,(V/V_0)^{\frac{1}{3}}$, $S = S_0\,(V/V_0)^{\frac{2}{3}}$, where S is a surface area of the fullerene in the deformed state. Formula (7) defines pressure-volume dependence for the fullerene in the case of large volumetrical deformations. For example, let us calculate this dependence for Lennard-Jones potential

$$U(r) = D\left[\left(\frac{a_0}{r}\right)^{12} - 2\left(\frac{a_0}{r}\right)^{6}\right], \tag{8}$$

where D is a bond energy, a_0 is an equilibrium distance between atoms in the fullerene. Substituting (8) into (7) one obtains

$$P\left(\frac{V}{V_0}\right) = \frac{Nka_0\cos\alpha}{2S_0}\left(\frac{V_0}{V}\right)^{3}\left[\left(\frac{V_0}{V}\right)^{2} - 1\right], \tag{9}$$

where the well-known relation between bond energy and stiffness for Lennard—Jones potential $D = ka_0^2/72$ was used. Linearizing formula (9) for the case of small deformations one can obtain the expression for bulk modulus that exactly coincides with formula (5).

4. Volumetrical oscillations of fullerenes C_{20} and C_{60}

Let us calculate the frequency of small volumetrical vibrations of fullerenes C_{20} and C_{60}. Assume that atoms in the fullerene interacts via linear pair central forces. Only interactions between the nearest neighbors are taken into account. Then equation of motion for some specific atom in the fullerene has the following form

$$m\,\ddot{\mathbf{r}}_0 = k\sum_{i=1}^{3}(\mathbf{r}_i - \mathbf{r}_0), \tag{10}$$

where m is a mass of carbon atom, $\mathbf{r}_0$ and $\mathbf{r}_i$ are radius-vectors of the specific atom and its neighbor number i with respect to the center of the fullerene. In the case of volumetrical vibrations radius-vectors can be represented in the following form $\mathbf{r}_i = r_0\mathbf{e}_i, i = 0, .., 3$. Substituting these expressions into equation of motion (10) one obtains

$$m\,\ddot{r}_0\,\mathbf{e}_0 = kr_0\sum_{i=1}^{3}(\mathbf{e}_i - \mathbf{e}_0) \Rightarrow m\,\ddot{r}_0 = -3kr_0(\cos(2\alpha) + 1). \tag{11}$$

where the identity $\mathbf{e}_0 \cdot \mathbf{e}_i = -\cos(2\alpha), i = 1..3$ was used. Then equation of motion takes simple scalar form

$$m\,\ddot{r}_0 + 6k\cos^2\alpha\, r_0 = 0. \tag{12}$$

Therefore the eigenfrequency of volumetrical vibrations of the fullerenes is determined by the following expression

$$\omega = \sqrt{\frac{6k}{m}}\cos\alpha. \tag{13}$$

One can see that the only difference between values of ω for fullerenes C_{20} and C_{60} is in the value of angle α. Let us calculate the frequencies assuming that $m = 1.994 \cdot 10^{-26}$ kg, $k = 635$ N/m [8]. Then one obtains $\omega = 156.0$ THz for C_{20} and $\omega = 88.20$ THz for C_{60}. The experimental value of the frequency of volumetrical vibrations of the fullerenes is not reported in literature. However one can carry out the order of magnitude analysis. In paper [10] the first eigenfrequency of fullerene C_{60} is determined using Raman spectroscopy. It is shown that the frequency is equal to 8.19 THz. Obviously the frequency of volumetrical vibrations should be approximately one order higher then the first eigenfrequency. Thus results of the present paper qualitatively coincide with experimental data [10]. However more accurate comparison is required.

5. Conclusion

In the present paper simple analytical expressions connecting bulk moduli B for fullerenes C_{20} and C_{60} with interatomic bond stiffness and geometrical characteristics of the fullerenes were presented. It was shown that B depends on a choice of the equivalent surface area. Maximum difference between values of B, calculated for different S_0 and identical value of the bond stiffness is 37% for C_{20} and 16% for C_{60}. Nonlinear volumetrical deformation of the fullerene was considered. It was assumed that compression of the bond is described by pair potential of the general form. Simple analytical formula for pressure-volume dependence for the fullerenes under volumetrical compression was derived. For example, Lennards-Jones potential was considered. It was shown that at high compressions the pressure is increasing asymptotically as $(V_0/V)^5$. Volumetrical vibrations of the fullerenes are considered. An analytical expression connecting frequencies of volumetrical vibration for fullerenes C_{20} and C_{60} with parameters of interatomic interactions was derived. The following values of the frequencies were obtained: $\omega = 156.0$ THz for C_{20} and $\omega = 88.20$ THz for C_{60}.

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