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Elastic and other associated properties of C_{60}

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Considering that Coulomb interactions contribute a negligible amount to the cohesive energy in C_{60}, which has an fcc structure at room temperature, we used Girifalco potential function in our calculations; C_{60} is spherical in nature and rotates rather freely at room temperature. From this potential we evaluated the second-order elastic constants (SOEC's), their pressure derivatives, and the third-order elastic constants (TOEC's). The SOEC's are found to be in good agreement with other literature values reported so far. The pressure derivative of bulk modulus is found to be 3.8 which compares favorably with Duclos values while the theoretical literature value is reported to be high. The pressure derivatives of the SOEC's are found to be high compared with those of glassy, amorphous materials, alloys, and metals. Furthermore, the derivatives are all found to be positive. The TOEC's are all found to be negative resembling those of polymers like polystyrene. We evaluated the thermal Gruneisen's constant from the potential function and the value obtained is in excellent agreement with experiment. [S0163-1829(97)06201-2]

I. INTRODUCTION

Since the discovery of superconducting properties of C_{60} and the ability to prepare large quantities of this material,[1,2] an enormous amount of work has been carried out on it. The molecules in the solid state are characterized by strong sp^2 bonding with the C_{60} molecule. The carbon atoms are held together by covalent bonds on the surface of a truncated icosahedron and the molecules interact through Van der Waals forces. However, Li *et al.* postulate[3] that there is a weak Coulomb interaction which is less than 10% of the total cohesive energy.[4] This Coulomb interaction is attributable to the difference in lengths of single and double bonds, and, therefore, an accumulation of negative charge on the double bond and a positive charge on the single bond. They calculated the second-order elastic constants (SOEC's). The molecules rotate freely and, therefore, can be approximated by spheres for any purpose; hence, a number of properties can be investigated by treating C_{60} molecules as spheres. A Lennard Jones type of intermolecular potential function is used for theoretical calculation in obtaining the properties of this material.

II. THEORY

An excellent attempt has been made by Girifalco in formulating the potential function.[5] In the future we refer to this potential function as GFP. This potential function has been written as

$$(r)=-\alpha\left[\frac{1}{x(x-1)^3}+\frac{1}{x(x+1)^3}-\frac{2}{x^4}+\frac{1}{x(x-1)^9}+\frac{1}{x(x+1)^9}-\frac{2}{x^{10}}\right]. \tag{1}$$

Here

$$x=r/2a \tag{2}$$

and α and β are constants and are given by

$$\alpha=\frac{N^2A}{12(2a)^6}, \tag{3}$$

$$\beta=\frac{N^2B}{90(2a)^{12}}. \tag{4}$$

Here ''r'' is the distance between the centers of the molecules and ''$2a$'' is the diameter of C_{60} and is equal to 7.1 Å. Furthermore, A and B are constants of the Lennard-Jones 6–12 potential. The values given by Girifalco are $\alpha=74.94\times10^{-15}$ ergs and $\beta=0.13595\times10^{-15}$ ergs, respectively. The shapes of the potential functions for C–C and C_{60}–C_{60} interactions have been given by Girifalco.

In order to evaluate the elastic constants we need the first and second derivatives of the potential function. They are

$$\frac{d\phi(r)}{dr}=\frac{\alpha}{2a}\left[\frac{1}{x^2(x-1)^3}+\frac{3}{x(x-1)^4}+\frac{1}{x^2(x+1)^3}+\frac{3}{x(x+1)^4}-\frac{8}{x^5}\right]-\left[\frac{\beta}{2a}\right]\left[\frac{1}{x^2(x-1)^9}+\frac{9}{x(x-1)^{10}}+\frac{1}{x^2(x+1)^9}+\frac{9}{x(x+1)^{10}}-\frac{20}{x^{11}}\right] \tag{5}$$

and

$$\frac{d^2\phi}{dR^2}=\frac{\alpha}{4a^2}\left[-\frac{2}{x^3(x-1)^3}-\frac{6}{x^2(x^2-1)^4}-\frac{12}{x(x-1)^5}-\frac{2}{x^3(x+1)^3}-\frac{6}{x^2(x+1)^4}-\frac{12}{x(x+1)^5}+\frac{40}{x^6}\right]-\frac{\beta}{4a^2}\left[-\frac{2}{x^3(x-1)^9}-\frac{18}{x^2(x-1)^{10}}-\frac{90}{x(x-1)^{11}}-\frac{2}{x^3(x+1)^9}-\frac{18}{x^2(x+1)^{10}}-\frac{90}{x(x+1)^{11}}+\frac{220}{x^{12}}\right]. \tag{6}$$

Here

$$x=r/2a. \tag{7}$$

In order to calculate the elastic constants we define two quantities η and δ which are given by

$$\eta=\frac{\rho_w R_0^2}{2M}\left[\frac{1}{R}\frac{d\phi}{dR}\right]_{R=R_0}, \tag{8}$$

$$\delta=\frac{\rho_w R_0^3}{2M}\left[\frac{d}{dR}\left(\frac{1}{R}\frac{d\phi}{dR}\right)\right]_{R=R_0}. \tag{9}$$

Here ρ_w is the weight density, R_0 is the equilibrium distance,[5] and M is the mass of the particle. It was shown earlier that for a face centered cubic structure[6]

$$C_{11}=4\eta+2\delta+K_e, \tag{10}$$

$$C_{12}=-4\eta+\delta+K_e, \tag{11}$$

$$C_{44}=4\eta+\delta. \tag{12}$$

TABLE I. Input data used in the calculations of the Girifalco potential.

$A=32.00\times10^{-60}$ ergs cm^6
$B=55.77\times10^{-15}$ ergs cm^{12}
$a_0^*=3.895$ Å
$\alpha=74.94\times10^{-15}$ ergs
$\beta=0.135\times10^{-15}$ ergs
$2a=7.1$ Å
$R_s=10.05$ Å (nearest-neighbor distance in fcc solid)
$B_T=0.134\times10^{12}$ dyn/cm^2

Here K_e is the electronic bulk modulus which in the present case is equal to zero. We evaluate $(d^2\phi/dR^2)_{R=R_0}$ where R_0 is taken $R_0=10.05$ Å and $2a=7.1$ Å. Hence from Eqs. (8) and (9) we get $\eta=0$ and δ as 0.11×10^{12} dyn/cm^2 from which we get the second-order elastic constants through Eqs. (10)–(12) which are given in Table I along with literature and experimental values.

The bulk modulus B_T is related to the potential function as

$$B_T=\frac{N}{9V}\left[R^2\frac{d^2\phi}{dR^2}\right]_{R=R_0} \tag{13}$$

from which we can get $(dB_T/dp)\equiv C_1$.

Girifalco already evaluated the bulk modulus from the potential function[5] and obtained an excellent agreement between the calculated and experimental value. We now calculate C_1 which forms a severe test for the potential function. Just as several experimental values[7–10] for bulk modulus have been reported the values for the pressure derivatives of B are no less. They vary from a value of 4.2 to 9.32 while the theoretical values range[7–11] from a value of 3.8 to 18.1. From Eq. (13) we get for C_1

$$C_1=\frac{NR_0^2}{27B_TV}\left[\frac{d^2\phi}{dR^2}-R\frac{d^3\phi}{dR^3}\right]_{R=R_0}. \tag{14}$$

Differentiating Eq. (6), we get

$$\frac{d^3\phi}{dR^3}=\frac{\alpha}{8A^3}\left[\frac{6}{x^4(x-1)^3}+\frac{18}{x^3(x-1)^4}+\frac{36}{x^2(x-1)^5}+\frac{60}{x(x+1)^6}+\frac{6}{x^4(x+1)^3}+\frac{18}{x^3(x+1)^4}+\frac{36}{x^2(x+1)^5}+\frac{60}{x(x+1)^6}-\frac{240}{x^7}\right]-\frac{\beta}{8a^3}\left[\frac{6}{x^4(x-1)^9}+\frac{54}{x^3(x-1)^{10}}+\frac{270}{x^2(x-1)^{11}}+\frac{990}{x(x-1)^{12}}+\frac{6}{x^4(x+1)^9}+\frac{54}{x^3(x+1)^{10}}+\frac{270}{x^2(x+1)^{11}}+\frac{990}{x(x+1)^{12}}-\frac{2640}{x^{13}}\right]. \tag{15}$$

From Eqs. (6), (7), (14), and (15) we can calculate C_1. The value obtained is 3.8 while the experimental value as reported by Duclos is 5.7±0.6.

A. Calculation of the pressure derivatives of the SOEC

From Eqs. (10), (11), and (12), we get

$$\frac{dC_{11}}{dP}=C'_{11}=4\eta'+2\delta', \tag{16}$$

$$\frac{dC_{12}}{dP}=C'_{12}=-4\eta'+\delta', \tag{17}$$

$$\frac{dC_{44}}{dP}=C'_{44}=4\eta'+\delta'. \tag{18}$$

In order to evaluate η' and δ' we use Eqs. (8) and (9). Here η' and δ' are pressure derivatives of η and δ. From the definition of δ we get

$$\delta=\frac{\rho_w R_0^3}{2M}\left[-\frac{1}{R^2}\frac{d\phi}{dR}+\frac{1}{R}\frac{d^2\phi}{dR^2}\right], \tag{19}$$

we assume $V=KR^3$, and

$$\begin{aligned}\frac{d\delta}{dP}=&\frac{\rho_w R^3}{2B_T M}\left[-\frac{1}{R^2}\frac{d\phi}{dR}+\frac{1}{R}\frac{d^2\phi}{dR^2}\right]_{R=R_0}\\&+\frac{3\rho_w R^2}{2M}\frac{dR}{dV}\frac{dV}{dP}\left[-\frac{1}{R^2}\frac{d\phi}{dR}+\frac{1}{R}\frac{d^2\phi}{dR^2}\right]_{R=R_0}\\&+\frac{\rho_w R^3}{2M}\left[\frac{2}{R^3}\frac{d\phi}{dR}-\frac{1}{R^2}\frac{d^2\phi}{dR^2}+\frac{1}{R}\frac{d^3\phi}{dR^3}\right.\\&\left.-\frac{1}{R^2}\frac{d^2\phi}{dR^2}\right]\left[\frac{R}{3V}\frac{dV}{dP}\right]_{R=R_0}.\end{aligned} \tag{20}$$

Using the fact that $(d\phi/dR)_{R=R_0}$, and after some straightforward algebra, we get

$$\frac{d\delta}{dP}=-\frac{4}{3}\frac{\delta}{B_T}-\frac{\rho_w R_0^3}{6MB_T}\left[\frac{d^3\phi}{dR^3}\right]_{R=R_0}. \tag{21}$$

Similarly,

$$\eta'=\frac{d\eta}{dP}=-\frac{\delta}{3B_T} \tag{22}$$

and using Eqs. (16)–(22) we can evaluate the pressure derivatives of the SOEC's. These are given in Table III.

B. Evaluation of third-order elastic constants (TOEC's)

It was shown by Thurston and Brugger[12] that

$$C_{111}=-\left[5+2\rho_w C_L\left(\frac{dC_L}{dP}\right)\right]C_{11}. \tag{23}$$

Since

$$\rho_w C_L^2=C_{11}, \tag{24}$$

we get

$$\frac{dC_{11}}{dP}-\frac{C_{11}}{B_T}=2\rho_w C_L\frac{dC_L}{dP} \tag{25}$$

from which we evaluate C_{111}.

It was shown by Thurston[13] that the pressure derivatives C'_{11} and C'_{44} are related to the TOEC's as

$$C'_{11}=\frac{-1}{3B_T}[C_{111}+2C_{112}], \tag{26}$$

$$C'_{44}=\frac{-1}{3B_T}[C_{144}+2C_{166}], \tag{27}$$

$$C'_{12}=\frac{-1}{3B_T}[2C_{112}+C_{123}]. \tag{28}$$

While deriving an equation for the attenuation of sound of longitudinal waves Shiren has shown that a constant ''K'' enters the calculation as[13]

$$K=3+\frac{C_{111}}{C_{11}}\quad\text{for }\langle 100\rangle, \tag{29}$$

$$K=3+\frac{1}{\Delta}[0.5C_{111}+1.5C_{112}+6C_{166}]\quad\text{for }\langle 110\rangle, \tag{30}$$

with

$$\Delta=C_{11}+C_{12}+2C_{44} \tag{31}$$

in $\langle 100\rangle$ and $\langle 110\rangle$ directions for cubic crystals from which we get C_{166}.

Thus it is possible to calculate the TOEC's given in Table III. From the Girifalco potential function we calculate both $(d^3\phi/dR^3)_{R=R_0}$ and $(d^2\phi/dR^2)_{R=R_0}$ from which we calculate γ_g^{th}, given by[14,15]

$$\gamma_g^{\text{th}}=\frac{1}{6}a_0^*\frac{d^3/dR^3}{d^2/dR^2}{}_{R=R_0}. \tag{32}$$

Here a_0^* is the equilibrium distance between two carbon atoms,[5] equal to 3.9 Å, while R_0 is the nearest-neighbor distance between two C_{60} molecules in the fcc solid.[5] The value calculated from Eq. (32) is 0.37 which is in excellent agreement with the experimental value[7,16] of 0.4. One may also calculate C_1 from TOEC's through the Birch equation which is given as

TABLE II. Second-order elastic constants in units of 10^{12} dyn/cm^2.

Elastic moduli	Present in units of 10^{12} dyn/cm^2	Literature (Ref. 3) value in units of 10^{12} dyn/cm^2	Expt. (Ref. 10)
C_{11}	0.220	0.300	0.140
C_{12}	0.110	0.140	0.07
C_{44}	0.11	0.16	0.07

TABLE III. Calculated values of pressure derivatives of elastic constants.

C'_{11}	C'_{12}	C'_{44}
25.0	14.0	12.0

$$C_1 = -\frac{1}{9B_T}[C_{111}+6C_{112}+2C_{123}]. \tag{33}$$

However, this equation cannot be expected to give the correct result since the Birch equation of state is found to predict completely wrong results for the bulk modulus. Hence, it is not expected to give good results for the pressure derivative of B_T. In fact, the value obtained is 17.6 while the experimental value[9] as reported by Duclos is 5.7 ± 6.

III. RESULTS AND DISCUSSION

The molecular-dynamics results of Zhang *et al.*[17] clearly indicate that the intermolecular interactions are weak and lead only to minor changes in bond lengths and bond angles after solidification. They further indicate that alternate single and double bonds are preserved in the solid but the distinction between them becomes blurred at moderate and room temperatures and the C_{60} molecules rotate rather freely. Furthermore, Lu *et al.*[4] clearly state that less than 10% contributes to cohesive energy from Coulomb interactions while the rest is contributed from Lennard Jones interactions. Hence, we believe the Girifalco potential is best suited to evaluate the elastic properties. As can be seen from Table II the results of the SOEC's as obtained from this potential are in closer agreement with experimental values[10] than those obtained by Li *et al.*[3]

TABLE IV. TOEC's calculated for C_{60} in units of 10^{12} dyn/cm^2.

TOEC's	C_{60} in units of 10^{12}dyn/cm^2	Polystyrene
C_{111}	-6.240	-0.91
C_{112}	-1.905	-0.38
C_{123}	-1.80	-0.21
C_{166}	-1.605	-0.13
C_{144}	-1.614	-0.08

The pressure derivatives of the SOEC's are given in Table III. The pressure derivatives of C_{60} are rather high compared to other substances such as glasses,[18] or amorphous, and crystalline substances.[19–21] It is too early to conclude that the high value of C'_{11} may be a characteristic of superconducting materials. At any rate it is peculiar and high. The C_1 value as obtained from Eqs. (14) and (15) is 3.8 which is in fair agreement with the Duclos value[9] of 5.7 ± 0.6 while Li *et al.*[3] achieve a value of 18.2.

The calculated TOEC's are given in Table IV. All the calculated TOEC's are found to be negative as in the case of polystyrene, in contrast to amorphous substances,[19–21] where C_{144} is positive and the rest are negative. However, C_{144} is a large negative quantity in C_{60}. So, from the TOEC's of C_{60} it may be inferred that it is a polymer-like substance of carbon.

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