Equation of state and bulk modulus of C$_{60}$ solid

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The soft core DY potential model for C$_{60}$ solid is critically examined in the light of theoretical and experimental studies. It is found that the soft core DY potential deviates largely as far as the theory and experiment are concerned. A simple model is, therefore, proposed to study the effect of pressure on C$_{60}$ solid. The model is applied to study the equation of state (EOS) and pressure dependence of bulk modulus in the light of other relations. A good agreement between theory and experiment supports the validity of the model proposed.

Keywords: Fullerite, Bulk modulus, Equation of state

1 Introduction
The fullerenes are the carbon molecules with closed-cage structure and nearly spherical in appearance. Fullerites are the assemblages of fullerenes exhibiting interactions that range between weak van der Waals forces up to covalent one. C$_{60}$ molecules condense to form a solid of weakly bound molecules. This crystalline state is a new form of solid carbon, besides the diamond and graphite. The structure of C$_{60}$ at room temperature has been investigated by X-ray and neutron diffraction, which shows that C$_{60}$ unit forms a face centered cubic (fcc) structure. Much of the work in science is centered on the solid phase of C$_{60}$. Duclos et al. performed the experimental measurements of EOS of C$_{60}$ fullerite to pressure of 200 kbar at room temperature. Birch-Murnaghan (BM) EOS and Vinet EOS were used to fit the experimental data. The BMEOS and Vinet EOS may be regarded as the standard EOSs for C$_{60}$ solid. It was found that up to this pressure range there is no significant change in the bonding character. Both the C$_{60}$ molecule and the fcc fullerite structures were found to be stable up to hydrostatic compression to this pressure. Sun computed the isotherms of C$_{60}$ solid using original Girifalco potential, modified Girifalco potential, the hard core DY potential, the soft core DY potential and compared the results with the experimental data reported by Duclos et al. Sun concluded that soft core DY potential gives the best agreement with the experimental data of Duclos et al.

Sun also reported the pressure dependence of bulk modulus using original Girifalco potential, hard core DY potential and soft core DY potential. Thus, it is expected that the results of bulk modulus as reported by Sun must be in good agreement with the BMEOS and Vinet EOS. Thus, it is legitimate and may be useful to present a critical analysis of the results reported by Sun in the light of BMEOS and Vinet EOS and to include some simpler model.

2 Method of Analysis
Duclos et al. presented the experimental measurements of the room temperature EOS of C$_{60}$ fullerite to pressure of 200 kbar. The BMEOS and Vinet EOS were used to fit the experimental data. The BMEOS is given by Ref. (5).

\[
P = \frac{3}{2} B_0 \left[ \left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3} \right] \times \left[ 1 + \frac{3}{4} (B'_0 - 4) \left(\frac{V_0}{V}\right)^{2/3} - 1 \right]
\]

… (1)

The bulk modulus corresponding to this EOS is as follows:

\[
B = \frac{1}{2} B_0 \left( 7 x^{-7} - 5 x^{-5} \right) + \frac{3}{8} B_0 A_1 \left( 9 x^{-9} - 14 x^{-7} + 5 x^{-5} \right)
\]

… (2)
where
\[ x = \left( \frac{V}{V_0} \right)^{\frac{1}{3}} \] and \[ A_1 = (B'_0 - 4) \]

Vinet EOS is as follows:\(^3\)
\[ P = 3(1-x)B_0 \left[ \exp \eta (1-x) \right] / x^2 \] \quad \ldots (3)
where \[ \eta = \frac{3(B'_0 - 1)}{2} \]

The bulk modulus corresponding to this EOS is as follows:\(^3\)
\[ B = \frac{B_0}{x^3} \left[ 1 + \left( \frac{3}{2}(B'_0 - 1)x + 1 \right)(1-x) \right] \times \exp \left[ \frac{3}{2}(B'_0 - 1)(1-x) \right] \] \quad \ldots (4)

The Murnaghan EOS has already been used for fullerene molecule in different forms\(^4\). In the present study, we use Murnaghan EOS to study C\(_{60}\) solid and extend the theory which modifies the Murnaghan\(^6,7\) EOS. In addition to the Murnaghan EOS, this theory has the power to predict several other EOSs viz. Tait, Suzuki and Shanker\(^8,9\) and improves the results\(^7\) obtained from BMEOS and Vinet EOS. The detailed analysis is available elsewhere\(^6-9\) and the mathematical form reads as follows:
\[ P = \frac{B_0}{A} \left[ \exp A \left( 1 - \frac{V}{V_0} \right)^{-1} \right] + \alpha_0 B_0 (T - T_0) \] \quad \ldots (5)

or
\[ \frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} \left( P - \alpha_0 B_0 (T - T_0) \right) \right] \] \quad \ldots (6)

At \( T = T_0 \), Eq. (5) gives the following relation for bulk modulus:
\[ \frac{B}{B_0} = \frac{V}{V_0} \exp A \left[ 1 - \frac{V}{V_0} \right] \] \quad \ldots (7)

Eq. (5) under certain conditions gives the Murnaghan EOS, which is as follows:
\[ P = \frac{B_0}{B'_0} \left[ \exp \left( \frac{-B'_0 \ln \frac{V}{V_0}}{B_0} \right) - 1 \right] \] \quad \ldots (8)

and bulk modulus is given by:
\[ \frac{B}{B_0} = \left( \frac{V}{V_0} \right)^{-\delta} \] \quad \ldots (9)

3 Results and Discussion

We have used different formulations as described above to study the EOS of C\(_{60}\) solid. These are BMEOS, Vinet EOS, Kumar EOS and Murnaghan EOS. The input data\(^1\) required are \( B_0 = 181 \) kbar and \( B'_0 = 5.7 \). The results obtained are shown in Fig. 1 along with the experimental data\(^1\) as well as those reported by Sun\(^4\) based on soft core DY potential. It is found that up to 100 kbar all the formulations give good results which agree with the experimental data\(^1\). The deviations occur at the pressure above 100 kbar. In this pressure range the results obtained from BMEOS, Vinet EOS and Kumar EOS are almost similar and agree well with the experimental data\(^1\). Moreover, the results obtained from Murnaghan EOS and that reported by Sun\(^4\) deviate largely as pressure increases.
A more critical test of the EOS is the bulk modulus, which depends on the higher order derivative. We have, therefore, used all these formulations to predict the pressure dependence of bulk modulus. The results obtained are shown in Fig. 2 along with the results obtained by Sun\(^4\). It is found that the results obtained by Sun\(^4\) deviate largely as compared with the results obtained from the formulation based on BMEOS and Vinet EOS. Moreover, there is a good agreement between the formulations based on Kumar and Vinet EOS.

4 Conclusions

An experimental study of the EOS of C\(_{60}\) solid has been formed by Duclos et al\(^1\). These researchers concluded that their experimental results agree well with BMEOS and Vinet EOS. A theoretical study based on potential model has been performed by Sun\(^4\). Sun\(^4\) concluded that his results agree well with the experimental data of Duclos et al\(^1\). Since the results of Duclos et al\(^1\) agree with BMEOS and Vinet EOS and the results of Sun\(^4\) agree with the Duclos et al\(^1\). It is, therefore, desirable that the results of Sun\(^4\) must agree with the BMEOS and Vinet EOS. This should also be true for the properties such as bulk modulus. In the present paper, we have discussed this in detail. The present study shows that for EOS the model developed by Sun\(^4\) agree with the experimental data\(^1\) as well as BMEOS and Vinet EOS up to 100 kbar. There are deviations above this pressure range. Further, for bulk modulus, the result based on the model of Sun\(^4\) does not agree with the bulk modulus obtained from BMEOS and Vinet EOS. However, it is found that there is a simple model (Eq.5) which agrees with the experimental data\(^1\) well for entire pressure range. The bulk modulus obtained from this model also agrees well with the results based on Vinet EOS. We, therefore, recommend this model for the detailed study of fullerites under varying conditions of pressure and temperature.

References