Model for Compression of Fullerenes and Carbon Nanotubes

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ABSTRACT

The new materials of carbon, solid C_{60} and Carbon Nanotubes (CNT) are important for various technological applications. One of the reasons of their technological applications could be based upon the fact that they have lot of empty space in their molecules as well as in their unit cells, when bulk quantities of these are taken in the form of either C_{60} solid or Nanoropes. Their compressibility studies have revealed extremely interesting results showing tremendous reversible compression, arousing curiosity and interest. Carbon nanotubes have been found to be compressible reversibly up to about 65% of their original volume when subjected to pressures of about 20Kbar. This enormous volume compression in such materials under moderate pressures is conceived to be of great significance for understanding and interpreting the mechanism based on molecular level understanding related to shock compression in these materials.

We undertake a model study accounting for unit cell deformations by applying pressures up to 3 Gpa and develop a pressure compression relation. We use the anharmonicity of the intermolecular potential energy to calculate Gruneisen parameters and the temperature increase due to an adiabatic pressure application. This work reports uses a rigid molecule model for calculations related to some ingredients, whereas experimental pressure compression data.

Keywords: carbon nanotubes, nanoropes, fullerenes, C_{60}, shock compression, Gruneisen parameters.

1 THEORETICAL PROCEDURE

First principles based atomistic modeling is an emerging technology to predict materials response at extreme conditions where experiments are difficult or impossible to perform. Alternatively, a simpler model potential approach can be utilized. Before we outline the model potential approach, we start by writing down a few expressions responsible for heating under shock pressure application in a material.

Solid materials get heated due to the shock compression. Anharmonic lattice dynamics plays a key role in determining the temperature increase as a result of compression in the material. When an anharmonic solid material is compressed, the gain in the energy goes into heating of the material. A shock compression from a volume V_0 to V_1 under shock pressure p_i starting from initial pressure p_0 deposits energy in solid material \Delta E given by:

\[ \Delta E = \frac{1}{2} (P_1 + P_0) (V_0 - V_1), \]

(1)

This energy changes the entropy in accordance with the laws of thermodynamics,

\[ TdS = dE + pdV. \]

(2)

However, we also can rewrite Eq. (2) as

\[ dS = \frac{C_v}{T}dT + \frac{1}{T} \left[ p + \left( \frac{\partial E}{\partial V}_T \right) \right] dV, \]

(3)

Where

\[ \left( \frac{\partial E}{\partial V} \right)_T = T \frac{\beta}{\kappa} - p \]

(4)

\[ \beta, \kappa \] being the volume thermal expansion coefficient and isothermal compressibility defined as

\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]

(5)

\[ \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \]

(6)

As a result, Eq. (2) can be written as
\[
dS = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dV ,
\]

(7)

This has also been expressed in terms of bulk Gruneisen parameters, \( \Gamma \)
\[
dS = \frac{C_v}{T} dT + \frac{\Gamma C_v}{V} dV
\]

(8)

with
\[
\beta = \Gamma \kappa C_v / V .
\]

(9)

Also the entropy change due to increases in internal energy caused by shock compression i.e.
\[
dE = \frac{1}{2} (V_0 - V_1) dp - \frac{1}{2} pdV ,
\]

(10)

This results in a temperature increase due to shock compression from \( V_0 \) to \( V \) as
\[
T_i = T_o \exp \left[ \frac{-\beta}{\kappa C_v} (V_0 - V) / V_0 \right] \\
+ \frac{\Gamma}{\kappa C_v} e^{\Gamma V_0 / V_0 - \Gamma V} dV
\]

(11)

Evaluation of temperature rise requires evaluation of the thermodynamic quantities like thermal expansion, bulk modulus \( (B = 1 / \kappa) \) and \( C_v \). These can be obtained from the details of model potential which we now describe.

1.1 Model Potential

The inter-tube (or inter-C\(_{60}\) molecule, as the case may be) potential energy \( U_{i\kappa,j\kappa'} \) between two nanotubes (molecules), identified by \( \kappa \) molecule in unit cell index \( i \), \( \kappa' \) molecule in cell \( j \), can be written as a pair-wise sum of C-atom-atom potentials (C-C) on these two molecules, i.e.
\[
U_{i\kappa,j\kappa'} = \sum_{ij} V(r_{ij}),
\]

(12)

where the sum in Eq. 12 includes all the N atoms in each of the nanotube molecules, and \( V(r) \) is the C-C potential. We take the potential \( V(r) \), where \( r \) is the distance between the C-C atoms, to be given by
\[
V(r) = -A / r^6 + B \exp(-\alpha r)
\]

(13)

The interaction parameters \( A, B \) and \( \alpha \) have been obtained from the set provided by Kitaigorodski\(^3\).

The total potential energy \( \Phi \) can be obtained by carrying out the lattice sum, knowing the position of the lattice points,
\[
\Phi = 1 / 2 \sum_{i\kappa,j\kappa'} U_{i\kappa,j\kappa'}
\]

(14)

The potential energy obtained in this way is a function of the lattice parameter and orientations of the molecules in the unit cell. A minimization of the potential energy is necessary to obtain the equilibrium orientations and lattice parameter. Some of the results as obtained for bunches of some CNT are presented in Table I. Fig. 1 shows the minimized energy at the equilibrium distance.

Table-I Lattice parameter as calculated for various Nanobunches

<table>
<thead>
<tr>
<th>Tube Type</th>
<th>Diameter (in nm)</th>
<th>Lattice parameter (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Present</td>
</tr>
<tr>
<td>(10,10)</td>
<td>1.356</td>
<td>1.667</td>
</tr>
<tr>
<td>(17,0)</td>
<td>1.332</td>
<td>1.642</td>
</tr>
<tr>
<td>(12,6)</td>
<td>1.242</td>
<td>1.570</td>
</tr>
</tbody>
</table>

Using the minimized energy, the harmonic force contents can be easily obtained leading to the evaluation of dynamical matrix which when diagonalized leads to the phonon frequencies. We show in Fig.1 the calculated cohesive energy as a function of lattice energy.

1.2 Pressure Effects and Bulk Modulus

An application of a hydrostatic pressure \( p \) alters the total potential energy such that
\[
\Phi_p = \Phi + p \Delta V
\]

(15)

where \( \Delta V \) is the increase in volume due to an application of pressure \( p \).
Table II: Bulk Modulus of SWNT Crystal (10,10)

<table>
<thead>
<tr>
<th>Calculated Bulk modulus (Gpa)</th>
<th>Other work (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31 GPa</td>
<td>32 GPa</td>
</tr>
</tbody>
</table>

Therefore, a minimization of the new potential energy leads to the p-V curve. This is shown in fig. 2.

![Fig. 1. Calculated potential energy per unit length as a function of the lattice parameter](image)

Fig. 2: The p-V curve calculated for SWNT crystal of (10,10) CNT bunch. The length of the CNT has been taken to be about 6nm arising from 1000 C atom tube. The points on the curve show calculated data points \( V = \frac{1}{2} a l \).

This data also immediately enables one to evaluate the bulk modulus, \( B = -V (\frac{\partial V}{\partial p}) \). The results for B at p=0 thus calculated are presented in Table-II.

1.3 Gruneisen Parameters

Gruneisen parameters, \( \gamma_q \), which are related to the volume derivatives of the phonon frequencies,

\[ \gamma_q = \left( \frac{\partial \ln \omega_q}{\partial \ln V} \right), \]

can also be straightforwardly calculated from pressure dependence of phonon frequencies. A hydrostatic pressure leads to new volume as discussed above and new potential energy. The dynamical matrix is recalculated and pressure dependent phonon frequencies are obtained which correspond to volume dependent phonon frequencies.

1.4 Thermal expansion

Once the Gruneisen parameters and bulk modulus have been obtained as discussed above thermal expansion,

\[ \varepsilon = \frac{1}{2V_B} \sum_q \gamma_q \hbar \omega_q \coth \left( \frac{\hbar \omega_q}{2kT} \right). \]  

As a result the temperature increase under shock compression can be calculated eq. 11.

2 RESULTS AND DISCUSSION

With the details of theoretical procedure and model assumed as described, we have calculated the heating due to compression of C_{60} solid and nanoropes. For C_{60} solid, the compression ratio at various pressures has been calculated for the rigid molecule model, whereas, for nanoropes, we use the experimental data of compression. On the basis of the model calculation, assuming that \( L^2 \) at 20Kbar a compression of 65% of its initial volume is obtained, we find a temperature increase of about 4000K for CNT bunches. This is because of an exponential temperature increase which directly depends on the compression ratio. Results for C_{60} solid are shown in Fig. 3 and Fig. 4. We also present results for Naphthalene using similar model in the same diagram. In our calculations, while calculating the temperature increase, we calculate only the dominant component, as expressed in the first line of Eq. 11.
Fig. 3: Compression ratio as a function of hydrostatic pressure for C_{60} (solid curve) and naphthalene (dashed curve, ref. 6).

Because of larger compression achieved for C_{60} solid as compared to Naphthalene, a much larger temperature increase is expected when C_{60} solid is compressed similarly. In addition, the Gruneisen parameters for solid C_{60} as well as for nanoropes turn out to be larger by a factor of about 3, we expect heating in these materials to be much larger. Nanoropes have significantly larger heating because amount of compression is much larger for similar pressure application.

Fig. 4: Temperature rise due to shock compression of C_{60} solid. The dashed curve represents similar results for naphthalene for compression.

3 CONCLUSION

Carbon nanotube bunches are very important new materials, also because of significant volume compression. This seems to result in extremely high temperature increase as compared to other materials. As pointed out here, the heating is controlled through anharmonicity of the potential function and gives us important control parameters, one of them being the Gruneisen parameter. In the text, it has been described and has been obtained from phonon frequency derivative with respect to volume. The other parameters being related to thermal expansion coefficient and bulk modulus. The expressions enlisted here tell us that (i) if we know how much shock compression (V_0-V_1) is there under an application of certain shock pressure, and (ii) if we know the basic ingredients like bulk modulus (B), volume expansion coefficient (β) and heat capacity (C_p) of a material, we know how much temperature rise would be there. It appears to us that the significance of these materials stem from a very high value of Gruneisen parameters as well as high value of volume compression. It is necessary to redo the whole calculation by removing several approximations, especially related to rigid molecule approximation. However, the fact that because of larger value of Gruneisen parameter and high compression ratio, the nanoropes would continue to draw attention for their shock absorbing properties linked with heating.

REFERENCES