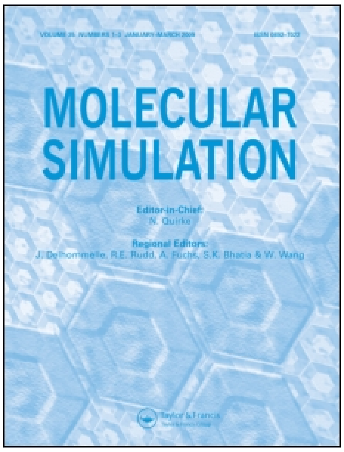

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Model for compression of fullerenes and carbon nanotubes

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The new materials of carbon, solid C_{60} and carbon nanotubes (CNT) [1,4] are important for various technological applications. One of the reasons for their technological applications could be based upon the fact that they have a 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 which has aroused curiosity and interest. CNT have been found to be compressible reversibly up to about 65% of their original volume when subjected to pressures of about 20 kbar. 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 uses some components calculated from a rigid molecule model, whereas others are taken from experimental pressure compression data.

Keywords: Carbon nanotubes; Nanoropes; Fullerenes; C_{60}; Shock compression; Gruneisen parameters

1. Theoretical procedure

First principles based atomistic modeling [5,7] is an emerging technology to predict a 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 will start by writing down a few expressions responsible for heating under shock pressure application in a material.

Solid materials become heated [6] due to the shock compression. Anharmonic lattice dynamics play 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 P_1, (assuming a starting value P_0) results in compression in volume from V_0 to V_1 and deposits energy in solid material ΔE given by:

$$\Delta E = \frac{1}{2}(P_1 + P_0)(V_0 - V_1). \tag{1}$$

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

$$T\,\mathrm{d}S = \mathrm{d}E + p\mathrm{d}V. \tag{2}$$

However, using $E \equiv E(V,T)$, we can rewrite equation (2) as

$$\mathrm{d}S = \frac{C_v}{T}\mathrm{d}T + \frac{1}{T}\left[p + \left(\frac{\partial E}{\partial V}\right)_T\right]\mathrm{d}V, \tag{3}$$

Where

$$\left(\frac{\partial E}{\partial V}\right)_T = T\frac{\beta}{\kappa} - p \tag{4}$$

β, κ being the volume thermal expansion coefficient and isothermal compressibility defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{5}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{6}$$

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As a result, equation (2) can be written as

$$\mathrm{d}S = \frac{C_v}{T}\,\mathrm{d}T + \frac{\beta}{\kappa}\,\mathrm{d}V. \tag{7}$$

This has also been expressed [6] in terms of bulk Gruneisen parameter Γ,

$$\mathrm{d}S = \frac{C_v}{T}\,\mathrm{d}T + \frac{\Gamma C_V}{V}\,\mathrm{d}V \tag{8}$$

with

$$\beta = \Gamma\kappa C_V/V. \tag{9}$$

Also the entropy change due to increases in internal energy caused by shock compression i.e.

$$\mathrm{d}E = \frac{1}{2}(V_0 - V_1)\,\mathrm{d}p - \frac{1}{2}p\,\mathrm{d}V. \tag{10}$$

This results in a temperature increase due to shock compression from V_0 to V as

$$T_1 = T_0 \exp\left[\frac{\beta}{\kappa C_V}(V_0 - V)/V_0\right] + \int_{V_0}^{V_1} \frac{fV}{C_v} e^{\Gamma/V(V_0-V_1)}\,\mathrm{d}V \tag{11}$$

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 $U_{l\kappa,l'\kappa'}$ between two nanotubes (molecules), identified by κ molecule in unit cell index l, κ' molecule in cell l', can be written as a pair-wise sum of C-atom–atom potentials (C–C) on these two molecules, i.e.

$$U_{l\kappa,l'\kappa'} = \sum_{ij} V(r_{ij}), \tag{12}$$

where the sum in equation 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

$$V(r) = -A/r^6 + B\exp(-\alpha r) \tag{13}$$

The interaction parameters A, B and α have been obtained from the set provided by Kitaigorodski [3].

Table 1. Lattice parameter as calculated for various nanobunches.

		Lattice parameter (in nm)	
Tube type	Diameter (in nm)	Present	Expt.
(10,10)	1.356	1.667	1.678
(17,0)	1.332	1.642	1.652
(12,6)	1.242	1.570	–

The total potential energy Φ can be obtained by carrying out the lattice sum, knowing the position of the lattice points,

$$\Phi = \frac{1}{2}\sum_{l\kappa,l'\kappa'}{}' U_{l\kappa,l'\kappa'} \tag{14}$$

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 1. Figure 1 shows the minimized energy at the equilibrium distance.

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 figure 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

$$\Phi_p = \Phi + p\Delta V \tag{15}$$

where ΔV is the increase in volume due to an application of pressure p.

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

This data also immediately enables one to evaluate the bulk modulus, $B(= -V(\partial p/\partial V))$. The results for B at $p = 0$ thus calculated are presented in table 2, and other parameters in table 3.

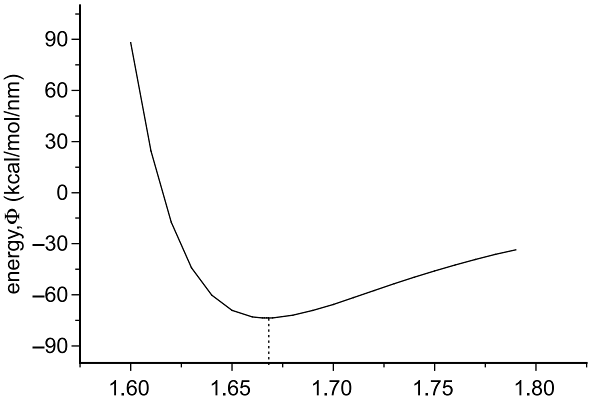

Figure 1. Calculated potential energy per unit length as a function of the lattice parameter.

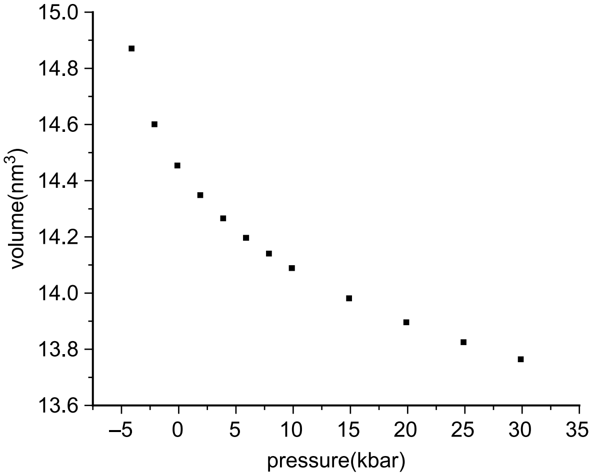

Figure 2. The p–V curve calculated for SWNT crystal of (10,10) CNT bunch. The volume is of about 6 nm long tubes ($V = \frac{\sqrt{3}}{2}a^2 l$) having 1000 C atoms in each tube.

1.3 Gruneisen parameters

Gruneisen parameters, γ_{qj}, which are related to the volume derivatives of the phonon frequencies,

$$\gamma_{qj} = -\left(\frac{\partial \ln \omega_{qj}}{\partial \ln V}\right), \qquad (16)$$

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,

$$\in = \frac{1}{2V_0 B}\sum_{qj}\gamma_{qj}\hbar\omega_{qj}\coth\frac{\hbar\omega_{qj}}{2kT}. \qquad (17)$$

As a result, the temperature increase under shock compression can be calculated equation 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 [1,2] at 20 kbar a compression of 65% of its initial volume is obtained, we find a temperature increase of about 4000 K 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 figures 3 and 4. It however, needs to be mentioned that Elliott *et al.* [9] report collapse of the nanotubes above 20 kbar pressures, rather than reversible compression [1]. The disagreement in quantitative threshold pressure between the simulation results of Elliott *et al.* and the measurements of Chesenkov *et al.* [1] needs to be investigated further by them. Our theoretical results bring out the parameters that are responsible for heating under shock compression, and some estimates have been made assuming no structural phase changes occur during compression. It is interesting to note that even in the results of Elliott *et al.*, about 65% compression is achieved before the collapse at threshold pressure, indicating that our results should be applicable in this pressure range. Yildrin *et al.* [10] do report interesting interlinking of carbon nanotubes at high pressures, which appear as different phases under high pressures. Such findings would require fresh calculations to estimate the amount of heating, but the identification of what controls heating has already been done here. Nevertheless, for experimental investigation of their findings, one could for example

Table 2. Bulk modulus of SWNT crystal (10,10).

Calculated bulk modulus (Gpa)	*Other work (Gpa)*
31	32

Table 3. Calculated lattice and averaged Gruneisen parameters of various CNT bunches.

Tube	*Radius (in Å)*	*Lattice constant (in Å)*	$\frac{1}{nm}\sum_{q=1}^{n}\sum_{j=1}^{m}\gamma_{qj}$
(5,5)	3.46	9.885	11.04
(10,10)	6.78	16.672	18.73
(15,15)	10.32	23.44	26.27

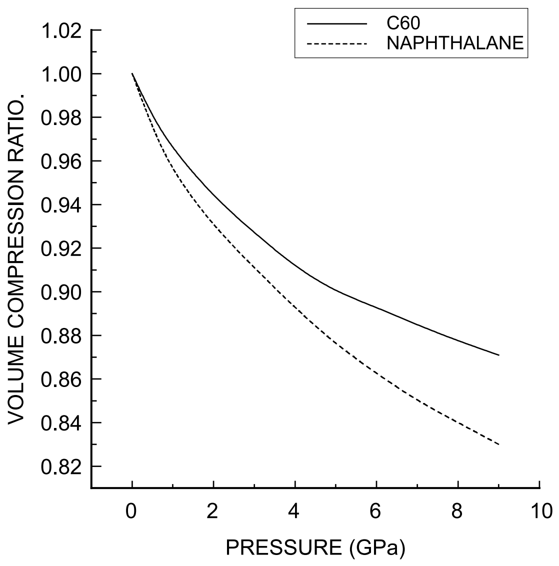

Figure 3. Compression ratio as a function of hydrostatic pressure for C_{60} (solid curve) and naphthalene (dashed curve, [6]).

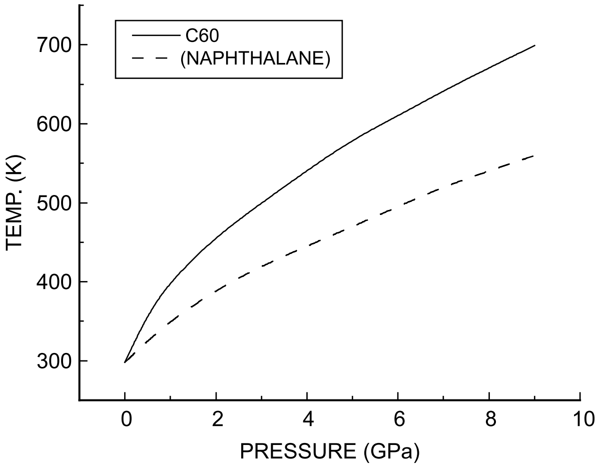

Figure 4. Temprature rise due to shock compression of C_{60} solid. The dashed curve represents similar results for naphthalene for compression.

follow a procedure [11] as adopted for studying C_{60} phases using ion beam irradiation. 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 equation 11. 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.

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_v) of a material, we know how much temperature rise would be there. It appears to us that the significance of these materials stems from a very high value of Gruneisen parameters as well as a high value of volume compression. It is necessary to redo the whole calculation by removing several approximations, especially related to rigid molecule approximation. However, because of the larger value of Gruneisen parameter and high compression ratio, the nanoropes would continue to draw attention for their shock absorbing properties linked with heating.

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