Power Spectrum Estimation of Fullerene at Different Temperatures

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Abstract—The power spectrum of a fullerene has been calculated using classical molecular dynamics simulation. The empirical bond-order Tersoff-Brenner potential has been utilized for carbon-carbon interaction with rises in temperature. The total energy, potential energy and power spectra of fullerene (C₆₀) have been evaluated. It is observed that the power spectra of fullerene are shifted from higher frequencies to lower frequencies with decrement in the frequencies as the temperature increases. It is interesting to note that the main peaks showed universal temperature dependence in fullerene (C₆₀) and the nature of the simulated results agree well with the experimental results available in literature.

Keywords— Fullerene, Tersoff-Brenner potential and Power spectrum

In this molecule, each carbon atom of fullerene has four valence electrons is bounded to the three nearest carbon atoms. The molecule fullerene (C₆₀) is formed by 30 double and 60 single bounds. The distances between atoms in single and double bonds of fullerene (C₆₀) are 1.45 and 1.37 Å, respectively. In the study of the electronic properties of the C₆₀ it is frequent considered that only the four valence electrons 2s, 2px, 2py, 2pz of each carbon atom. Each of the 60 atomic orbitals 2pz is aligned in the radial direction i.e. leading to the p molecular states. The other three atomic orbitals 2s, 2px, 2py are distributed in the tangential plane to the molecular surface at the carbon atom position producing s molecular states in the direction of the molecular bonds. The lineal combination of these three orbitals at each atomic site produces three sp² hybrid orbitals, one is in the direction of the double bond and the other two are aligned with the single bonds. The 60 p orbitals are relevant for the conductivity properties of the molecule, as in the case of graphite, and the 180 s orbitals are mainly responsible for the elastic properties (see Fig.1). In order to study the effect of temperature on carbon nanotube vibrational properties, a fullerene (C₆₀) is taken.

Figure 1 Pure fullerene with 60 atoms

III. CALCULATIONS

The potential is based on the bond-order concept plus contains many-body terms. It was designed to be highly transferable [5]; furthermore has proven to be reasonably accurate in describing structural and elastic properties of carbon in such different bonding structures as diamond, graphite and hydrocarbons.
The common ways to integrate the bond order potential within the molecular force field have been discussed. [22] They are based either on partitioning, or switching-on no bonded interactions. If the phenomenon investigated does not involve structural changes in the bonding network, as in the case with fullerene, the situation is simplified and in the simulation we treat fullerene (C\textsubscript{60}) as a molecule; thus defining no bonded interactions as intermolecular only. The Hamiltonian of the fullerene (C\textsubscript{60}) is given by

\[ H = \sum_i \left( \frac{p_i^2}{2m_i} + U(r_i) \right) \]  

(1)

where

\[ U(r_{ij}) = V_A(r_{ij}) - \overline{B}_{ij} V_A(r_{ij}) \]  

(2)

Where the attractive, \( V_A(r_{ij}) \), and repulsive, \( V_R(r_{ij}) \), parts of the potential are modeled by a general Morse function,

\[ V_R(r_{ij}) = f_c(r_{ij}) \frac{D^{(e)}_{ij}}{S_{ij} - 1} \exp \left[ -\sqrt{2}S_{ij}\beta_{ij}(r_{ij} - R_0) \right] \]  

(3)

\[ V_A(r_{ij}) = f_c(r_{ij}) \frac{D^{(e)}_{ij}S_{ij}}{S_{ij} - 1} \exp \left[ -\sqrt{2}/S_{ij}\beta_{ij}(r_{ij} - R_0) \right] \]  

(4)

Parameters of potential model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_0/\text{Å} )</td>
<td>1.315</td>
</tr>
<tr>
<td>( D^{(e)}_{ij}/\text{eV} )</td>
<td>6.325</td>
</tr>
<tr>
<td>( B_{ij} )</td>
<td>1.5</td>
</tr>
<tr>
<td>( S_{ij} )</td>
<td>1.29</td>
</tr>
<tr>
<td>( a_{ij} )</td>
<td>0</td>
</tr>
<tr>
<td>( \delta )</td>
<td>0.80469</td>
</tr>
<tr>
<td>( R_1/\text{Å} )</td>
<td>1.7</td>
</tr>
<tr>
<td>( R_2/\text{Å} )</td>
<td>2</td>
</tr>
<tr>
<td>( a_0 )</td>
<td>0.011304</td>
</tr>
<tr>
<td>( b_0 )</td>
<td>19</td>
</tr>
<tr>
<td>( c_0 )</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The cut-off function, \( f_c(r_{ij}) \), is unity for first neighbors and zero otherwise. The many-body nature of the potential is hidden in the bond order parameter \( \overline{B}_{ij} \), which is a function of the coordination, \( \theta_{ijk} \).

\[ \overline{B}_{ij} = \frac{1}{2} \left( \left[ 1 + \sum_{k \neq i,j} \exp(\alpha_{ijk}(r_{ij} - r_{jk}))G_j(\theta_{ijk}) \right]^{-\delta} \right. \]  

\[ + \left. \left[ 1 + \sum_{k \neq i,j} \exp(\alpha_{ijk}(r_{ij} - r_{ik}))G_j(\theta_{ijk}) \right]^{-\delta} \right) \]  

(5)

Where \( \theta_{ijk} \) is the angle between \( r_{ij} \) and \( r_{ik} \), prime on sums denotes summation over first neighbors only, and \( G_j(\theta_{ijk}) \) is three-parameter angular function,

\[ G_j(\theta_{ijk}) = a_0 \left[ 1 + \frac{c_0^2}{d_0^2/(1 + \cos \theta_{ijk})^2} \right] \]  

(6)

The force on atom \( i \) arising from a bond-order potential,

\[ f_i = -\nabla_i U_{\text{tot}} \]  

\[ = -\sum_{j \neq i} \left( \frac{\partial U_A(r_{ij})}{\partial r_{ij}} - \frac{\partial U_A(r_{ij})}{\partial r_{ij}} - U_A \frac{\partial \overline{B}_{ij}}{\partial r_{ij}} \right) r_{ij} \]  

(7)

All parameters of this model are recorded in the Table I match with the original paper of Brenner.[21] Molecular dynamics simulations were performed on samples formed by rolling a perfect graphene sheet to form fullerene (C\textsubscript{60}). The system contains 60 carbon atoms. Periodic boundary conditions were used in the direction of fullerene (C\textsubscript{60}) axis to avoid boundary effect. The initial condition for each molecule is usually assigned by giving the velocity in the random directions for all monatomic molecules. The Maxwell-Boltzmann velocity distributions are obtained after some equilibration calculations. The equilibrium system is calculated for constant temperature. The simple temperature control of the equilibrium system can be computed by just scaling the velocity of molecules as \( v_i' = v_i \sqrt{T_c/T} \) with the current temperature \( T \) and the desired temperature \( T_c \). This control has to be applied in many steps because of the relaxation of potential energy.
All simulations were achieved in the micro-canonical ensemble using the leapfrog Verlet algorithm with a time step of 2 fs. First, the system was run for typically 10,000 time steps. This was done to obtain a desired temperature by coupling the system to a thermostat with the specified temperature using the Nose–Hoover method. Initially, the equilibration period non-bonded interactions in the form of Lennard-Jones potential were added to all pairs separated by at least three neighbors. This facilitates equi-partitioning of the energy between different modes of fullerene (C\textsubscript{60}). The phonon spectral densities were computed according to linear response theory from the Fourier transform of the velocity autocorrelation function, 

\begin{equation}
    g(k, \nu) = \mathcal{F} \{ \langle v(t) \cdot v(0) \rangle \} \\
    = \int_0^\infty dt \exp(2\pi i \nu t) \sum_j \exp(i k \mathbf{r}_j) \frac{\langle v_j(t) \cdot v_j(0) \rangle}{\langle v_j(0)^2 \rangle}
\end{equation}

IV. RESULTS AND DISCUSSION

The potential energies of fullerene (C\textsubscript{60}) are given by these in eqn. (2) and are shown in figure 2. The temperatures are maintained with Nose–Hoover thermostat and the total energy is calculated through equation (1) which is shown in figure 3. In both figures the green, dark blue, red and brown colours represent the potential energy at 1200K, 900K, 600K and 300K respectively.
The power spectrum of fullerene (C\textsubscript{60}) is presented in figure 4.

![Figure 4 Power Spectrum of C\textsubscript{60}](image)

Each simulated power spectra represents the distribution of power among the various vibrations of respective model atoms at that particular temperature. The simulated power spectrum of fullerene gives two significant peaks at three different temperatures 300K, 600K, 900K and four significant peaks at 1200K temperature. The temperature dependence calculated peaks of carbon nanotubes are also observed experimentally [20]. Similarly the power spectrum of fullerene (C\textsubscript{60}) gives four significant peaks at 300K, 600K, 900K and 1200 K temperature as shown in figure 4. With rise in temperature, the distribution of power again redistributes among the various model atoms. It is significant to note that different peaks in each spectra of each model appear to move from higher frequency to lower frequency as the temperature increase. Besides the main peaks of each spectrum broaden in width, decreases in intensity as the temperature increase. The decreases peak shift frequency, broaden width, decreases intensity in fullerene with rise in temperature are known as the temperature dependence peaks. The temperature dependences have been measured experimentally in various carbon materials, such as SWNTs, [23-27] multi-walled carbon nanotubes (MWNTs), [28]) double-walled carbon nanotubes (DWNTs [22]) and graphite.[24] Strong temperature dependences of Raman scattering spectra have been pragmatic from in-situ measurements performed during the growth stage of SWNTs. [27]

The present result is comparable to experimental result that the fullerene may be damaged or burned when high power excitation laser light is tightly focused with a high magnification objective lens. Thus the intensity and the frequency of each model get changes after changing the respective model temperature. In one paper temperature dependence of Raman scattering only from single-walled carbon nanotubes has calculated i.e. undefined radial breathing mode peaks at high temperatures leaving the all spectra of carbon nanotube [29]. Though the fullerene nature of temperature dependency in present power spectra and simulated Raman temperature dependency in carbon nanotube are almost same [29] yet in present power spectrum paper represent the power of each model gets redistributed among its model atoms as the temperature change. This is due to the an-harmonic components of bonding force become important owing to phonon-phonon relations at high temperatures. Thus the an-harmonicity supports thermal expansion and decreases the force constant of bonds.

V. CONCLUSION

Various peaks of fullerene have been measured using classical molecular dynamics simulation and the empirical bond-order Tersoff-Brenner potential at four different temperatures.
The peaks shift of the carbon nanotubes and fullerene exhibited universal temperature dependence for all carbon nanotubes samples and all excitation wavelengths investigated, hence the temperature of fullerene samples can conveniently be measured based on the changes in the peak position. The peaks also demonstrated temperature dependences, such as downshifts of the Raman frequency with broadening of the peak width, and reduction in the intensities with increasing temperature. Besides it is demonstrated that the several peaks could not be assigned to any chiral indices which the intensities of those unassigned peaks were very weak at room temperature (300K) and increased with increasing temperature.

REFERENCES