DYNAMICS OF ENDOHEDRAL FULLERENE
K$^+$@C$_{60}$ INSIDE SINGLE WALLED
CARBON NANOTUBE: MD SIMULATION
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Abstract: K$^+$@C$_{60}$ endohedral fullerenes inside armchair, zigzag and chiral nanotubes were simulated using the MD technique. The structure of the endohedral fullerene sample was estimated by calculating the radial distribution function. The angular and translational velocity autocorrelation functions and their Fourier transforms were also calculated. The frequency dependence of potassium ion vibrations in different nanotubes at room temperature was observed and discussed. A dependency between the angular motion of endo-fullerenes and the nanotube chirality was found.

Keywords: endo-fullerenes, doped C$_{60}$, nanotubes, potassium ion, confined geometry

1. Introduction

Fullerenes, new allotropes of carbon, have attracted scientific attention ever since they were discovered [1]. The empty space inside a fullerene cage is a good place to accommodate a wide variety of atoms and small molecules [2]. Endo-fullerenes have been synthesized and investigated by several experimental and theoretical methods [3–5].

Among them, such metal atoms as potassium ions are usually taken as fullerene dopants [6]. The external field controlled dynamics of K$^+$@C$_{60}$ has been also reported [7]. Another interesting carbon structure is the nanotube. Carbon nanotubes reveal many interesting physical properties [8–12]. Composites of endo-fullerenes and carbon nanotubes have many interesting electrical and mechanical properties that make them candidates for a nanoelectronic switching devices [13]. The study of nanosystems attracts scientific attention because their properties differ from those of bulk materials [14–20]. The purpose of this work was a computer simulation study of the dynamics of endohedral fullerenes inside a small nanotubes.

2. Computational procedure

The C$_{60}$ molecule and the nanotube were treated as rigid bodies with discrete sites. The interaction between each interacting non-charged site in the C$_{60}$ molecules
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and the nanotube or a potassium ion was described by the Lennard-Jones potential
\[ V_{L-J}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \]
and the interaction between positive charges of potassium ions was described by the Coulomb potential
\[ V_C(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 r_{ij}}, \]
where \( r_{ij} \) was the distance between the \( i \)-th and \( j \)-th atoms of a pair of different molecules, \( Z_n \) denoted the charges of each \( n \)-th site, \( e \) was the electron charge. The \( \sigma \) and \( \varepsilon \) parameters of the potential used in the simulation are given in Table 1. The parameters of unlike atoms were calculated with the Lorentz-Berthelot rules:
\[ \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \] (1)

The classical equations of motion were solved by the Adams-Moulton predictor-corrector algorithm [21]. The integration time step used in simulation was 1 fs. The calculations were carried out for an NVT ensemble. The system was equilibrated to the desired temperature by a Berendsen thermostat [21] for \( 10^6 \) MD steps. The Berendsen thermostat was switched on during the collection of MD data. The temperature was defined from the energy equipartition principle:
\[ T = \frac{2 \bar{E}_k}{f d k_B}, \] (2)
where \( k_B \) was the Boltzmann constant, \( \bar{E}_k \) was the average kinetic energy over the ensemble, the coefficient \( f_d = 6N - 6 \) was a sum of the total number of translational (3\(N\)) and rotational (3\(N\)) degrees of freedom minus 3 translational and 3 rotational degrees of whole nanosystem movement, \( N \) was the total number of molecules. The total momentum of molecules was conserved to within 0.05%. The autocorrelation functions of linear \( \vec{v} \) of K\(^+\) and angular \( \vec{\omega} \) velocities of C\(_{60}\) and SWCNT molecule were calculated by averaging the translational velocity autocorrelation function
\[ C_v(t) = \langle \vec{v}(0) \cdot \vec{v}(t) \rangle / \langle \vec{v}(0) \cdot \vec{v}(0) \rangle \]
and the angular velocity autocorrelation function
\[ C_\omega(t) = \langle \vec{\omega}(0) \cdot \vec{\omega}(t) \rangle / \langle \vec{\omega}(0) \cdot \vec{\omega}(0) \rangle \]
over \( 10^5 \) time origins. The origins were separated by a time interval equal to 50 integration time steps.

<table>
<thead>
<tr>
<th>Atom (site)</th>
<th>( \varepsilon ) [10(^{-21}) J]</th>
<th>( \sigma ) [10(^{-10}) m]</th>
<th>( m ) [10(^{-26}) kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.387</td>
<td>3.4</td>
<td>1.99</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.48</td>
<td>3.56</td>
<td>6.49</td>
</tr>
</tbody>
</table>

3. Results and discussion

The endo-fullerene model was formed by placing a K\(^+\) ion inside a fullerene cage which was followed by inserting five endohedral fullerenes into a carbon nanotube (Figure 1). The simulation was prepared for three nanotubes, which differed in chirality and diameter (Figure 2). All the nanotubes used in the calculations had the same length of 5 nm. The surface of nanotube was treated as a rigid body. The confined geometry of the system was checked by calculating the radial distribution function \( g(r) \) of the C\(_{60}\) molecules at \( T = 300 \) K in a (10,10) armchair nanotube (Figure 3). The plot suggests a solid state structure of endo-fullerenes. The nanotube chirality does not change the structure. The nanotube diameter influences the structure of
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Figure 1. Instantaneous configuration of $K^+@C_{60}$ in the armchair $(10,10)$ nanotube at $T = 300\,\text{K}$.

Figure 2. Nanotubes of different chirality cross-sections.

$endo$-fullerenes, see the dashed line in Figure 3. The smaller the nanotube diameter is, the larger the near neighbor distance between the fullerene molecules located inside the nanotube. The fullerene molecules seems to be a bit loosely packed due to an additional interaction with the nanotube surface. The motion of $K^+@C_{60}$ inside the nanotube was investigated by calculating the mean square displacement $\langle \Delta r^2(t) \rangle$ (Figure 4). The slope of the function at higher temperatures shows slow motion of the $endo$-fullerenes inside the nanotube. The bumping in the plot is associated with the vibrations of the $C_{60}$ molecule between the nanotube walls. The dynamics of the fullerenes changes with the diameter of the nanotubes (Figure 5). Less space for movement in the nanotube gives a lower amplitude of vibrations and the molecules move slower along the nanotube long axis. The rotation of the $C_{60}$ molecules is reflected in the $C_{\omega}(t)$ function at three temperatures for the armchair nanotube $(10,10)$. In
Figure 3. Radial distribution function of C$_{60}$ molecules for two different chirality vectors at $T = 300$ K

the lower temperature ($T = 200$ K) the first dip at $t = 4$ ps is visible. The rising of the temperature causes this first dip ($T = 350$ K) to disappear. The relaxation of the angular velocity occurs within 60 ps at $T = 200$ K and 140 ps at $T = 350$ K. Some more interesting behavior was observed in the plot of the $C_\omega(t)$ function depending on the chirality and the diameter at the same temperature of $T = 300$ K (Figure 7). The correlation function $C_\omega(t)$ for the nanotubes with larger diameters decays featureless and very slowly, up to 180 ps. On the other side in the smaller nanotubes, the function $C_\omega(t)$ decays also featureless but much faster, approaching almost zero at $t \approx 6$ ps. The last plot for the armchair (10,10) shows a small dip at 2 ps, this can be related to different chirality of nanotubes. The chiral ones (10,8) and (16,3) have some prepared path that ease the C$_{60}$ molecule rotation. The charged K$^+$ ions potentially generate electromagnetic waves of a frequency proportional to their vibrational motion. To investigate this property, the translational velocity autocorrelation function of the K$^+$ ion at $T = 300$ K in a armchair nanotube was calculated (Figure 8). A first look at this plot reveals at least two characteristic frequencies. A fast vibration of the ion against the fullerene cage is combined with the motion along the nanotube. The function $C_v(t)$ decays to zero within 15 ps. The cosine Fourier transform of the $C_v(t)$ shows two frequency bands (Figure 9). The sharp peak at $\nu = 158$ cm$^{-1}$ is the oscillation frequency of the K$^+$ ion in a fullerene cage [22]. Several peaks show up between 0–40 cm$^{-1}$ in the low frequency band. These can be related to the slow motion of fullerenes. The lower peak at $\nu = 7.56$ cm$^{-1}$ can be related to bouncing along the nanotube long axis and the higher groups of peaks can be related to an interaction between the endo-fullerenes and the nanotube surface. A modification
Figure 4. Mean square of the $C_{60}$ molecule center of mass displacement at three temperatures; the molecules are inside the armchair carbon nanotube with chirality (10,10)

Figure 5. Mean square of the $C_{60}$ molecule center of mass displacement at $T = 300$ K; the molecules are inside three different nanotubes with different chiralities and diameters.
Figure 6. $C_\omega(t)$ function of the C$_{60}$ molecules in the armchair (10,10) carbon nanotube at three temperatures.

Figure 7. $C_\omega(t)$ function of the C$_{60}$ molecule for three different chiralities of carbon nanotubes at $T = 300$ K.
Figure 8. $C_{v}(t)$ function of K$^+$ ions inside the armchair (10,10) carbon nanotube at $T = 300$ K.

Figure 9. Cosine Fourier transform of the $C_{v}(t)$ function of K$^+$ ions inside fullerenes at $T = 300$ K in the armchair (10,10) nanotube.
Figure 10. $C_v(t)$ function of $\text{K}^+$ ions at $T = 300\text{K}$ in the chiral (10,8) carbon nanotube

Figure 11. Cosine Fourier transform of the $C_v(t)$ function of $\text{K}^+$ ions at $T = 300\text{K}$ in the chiral (10,8) carbon nanotube
of the nanotube diameter and chirality effects the $C_v(t)$ correlation function. For a nanotube with chirality $(10,8)$ and diameter $d = 1.25 \text{ nm}$ the function $C_v(t)$ decays faster, within $8 \text{ ps}$ (Figure 10). The cosine Fourier transform of this function shows a new band in the frequency range from $75$ to $100 \text{ cm}^{-1}$ (Figure 11). This band can be related to the bumping motion of fullerenes between tight nanotube walls.

4. Conclusions

A simulation of small cluster of five K$^+@C_{60}$ inside a carbon nanotube shows a few interesting properties. First of all, the potassium atom vibrations inside the cage strongly depend on the carbon nanotubes diameter. The angular motion of endo-fullerene in chiral nanotubes is easier than in an armchair nanotube. This property of K$^+@C_{60}$ can be used for probing the nanotube structure. These studies may contribute to future experimental and computational research of endohedral fullerenes in confined geometries.

References

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