Theoretical analysis of telescopic oscillations in multi-walled carbon nanotubes

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Abstract

A simplified theory of the telescopic oscillations in multiwalled carbon nanotubes is developed. The explicit expressions for the telescopic force constants (longitudinal rigidity) and frequencies for telescopic oscillations are derived depending on interacting tubes diameters and lengths. The contribution of small-amplitude telescopic oscillations to low temperature characteristics of nanotubes such as specific heat are estimated.

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) are the first discovered nanoscopic quasi-1D nanostructures (1). Each MWCNT consists of some nested single-walled nanotubes (shells) held mostly by van der Waals forces (2).

The telescopic motion ability of inner shells (3) and their unique mechanical properties (4) permit to use multi-walled nanotubes as main movable arms in coming nanomechanical devices. The variety of gadgets of this kind was already suggested such as a possible mechanical gigahertz oscillator (linear bearing) (3; 5), nanoswitch (6), nanorelay, nanogear (7), nanorail, reciprocating nano-engine (8). Therefore the analysis of mechanic characteristics of MWCNT is an important objective of study. The present work is just devoted to a simplified
continuum version of this problem. The continuum model for telescopic oscillations, in which each shell of MWCNT is considered as continuous infinitesimally thin cylinder is described in the next section. The third section devoted to the description of the small (thermal) and large-amplitude oscillations for DWCNT and MWCNT in the framework of proposed model. Note that the similar continuum model was used recently for the investigation of the suction energy and large amplitude telescopic oscillations in DWCNT (9, 10). The contribution of temperature-induced oscillations into the tubes heat capacity within Debye model is also discussed. In the last section the obtained results are compared with the available experimental data (3).

2. Intertube interaction in MWCNT within continuum model

The interaction energy of two shells of the multi-walled tube is modelled as the sum of pair interaction potentials of atoms from different shells. In doing so we took for the potential energy of two atoms at the distance \( l \) the Lennard-Jones potential

\[
E_{LJ}(l) = -\frac{\gamma_6}{l^6} + \frac{\gamma_{12}}{l^{12}},
\]

with attractive and repulsive constants \( \gamma_6 = 2.43 \times 10^{-24} \text{ J nm}^6 \) and \( \gamma_{12} = 3.859 \times 10^{-27} \text{ J nm}^{12} \) borrowed from (2). In accordance with this approximation the total intertube interaction energy has form

\[
U = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \left( -\frac{\gamma_6}{(\mathbf{r}_{1,i} - \mathbf{r}_{2,j})^6} + \frac{\gamma_{12}}{(\mathbf{r}_{1,i} - \mathbf{r}_{2,j})^{12}} \right),
\]

where \( \mathbf{r}_{1,i} \) and \( \mathbf{r}_{2,j} \) are radius-vectors of the inner and outer tube’s atoms respectively.

As in (2) we used instead of (1) the continuum model, for which

\[
U(\Delta z) = \sigma^2 r_1 r_2 \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 \int_0^{L_2+\Delta z} dz_1 \int_0^{L_2} dz_2 \left( \frac{\gamma_{12}}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos(\theta_1 - \theta_2) + (z_1 - z_2)^2)^6} \right.

\left. - \frac{\gamma_6}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos(\theta_1 - \theta_2) + (z_1 - z_2)^2)^3} \right),
\]

(2)
where \(r_1\) and \(r_2\) are inner and outer tubes radii, \(L_1\) and \(L_2\) are their lengths (from now on we assume that \(L_1 \leq L_2\)) and \(\Delta z\) is the distance between tubes outer edges and \(\sigma\) is the surface density of carbon atoms in graphene, which almost independent on the tube chirality,

\[
\sigma = \frac{4}{3\sqrt{3}} \frac{b}{b^2} = 38.2 \text{ nm}^{-2},
\]

where \(b = 0.142 \text{ nm}\) is the interatomic distance in graphene.

The integration over variables \(z_1\) and \(z_2\) can be easily carried out analytically, but obtained expressions are too cumbersome to be presented here.

It’s trivial, that system energy is minimal when the inner tube is completely retracted into the outer tube. In terms of hypergeometric functions the minimum interaction energy is given by expression

\[
U_{\text{min}} = \frac{3}{2} \pi^3 \sigma^2 r_1 r_2 \min(L_1, L_2) \times
\]

\[
\times \left( \frac{21}{32} \frac{2F_1 \left( \frac{1}{2}, \frac{11}{12}, 1, \frac{4r_1 r_2}{(r_1 + r_2)^2} \right)}{\gamma_{12} (r_1 + r_2)^{11}} \right) - \gamma_{16} \frac{2F_1 \left( \frac{1}{2}, \frac{5}{2}, 1, \frac{4r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^5}, \quad (3)
\]

where

\[
2F_1 \left( \frac{1}{2}, J, 1, \frac{4r_1 r_2}{(r_1 + r_2)^2} \right) = \frac{(r_1 + r_2)^2 J}{2\pi} \int_{-\pi}^{\pi} \frac{d\theta}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^J}.
\]

![Figure 1: The intertube interaction energy for the (5,5)@(10,10) DWCNT with 10nm and 20nm lengths](image)
3. Telescopic oscillations in DWCNT

If the outer tube is rigidly mounted, then the longitudinal motion of the internal tube is described by primitive equation:

\[ a_z(\Delta z) = -\frac{1}{m} \frac{\partial U(\Delta z)}{\partial z}, \quad (4) \]

where \( a \) is the acceleration of the inner tube with mass \( m \).

We ignore here the contribution of some defect-induced dissipative forces since for high-quality nanotubes they are several orders lower than the retraction force due to self-healing mechanism (3; 5; 11).

By (4) the motion of inner tube is cyclic with period

\[ \tau = \frac{\sqrt{2mL}}{\int_{L_2 - L_1 - \Delta z_0}^{\Delta z_0} \sqrt{E_0 - U(\Delta z)} \, d(\Delta z)} \]

where \( \Delta z_0 \) is determined by relations \( U(\Delta z_0) = U(L_2 - L_1 - \Delta z_0) = E_0 \).

Due to the special form of potential (2) we can separate out two limit form of motion:

1) steady movement for \( \Delta z_0 \gg b \) while the potential is just linear in \( \Delta z \);
2) small oscillations when \( \Delta z_0 \to 0 \) and the potential is just quadratic in \( \Delta z \).

3.1. Large-amplitude oscillations in DWCNT

In the case of displacement \( \Delta z_0 \) greater than few nanometers the potential energy is mostly linear with respect to displacement \( \Delta z \) except small-displacement zone with quadratic potential energy contribution of which can

![Figure 2: Longitudinal intertube interaction force for (5,5)@(10,10) DWCNT with 10nm and 20nm lengths](image)
be neglected. In such a case the oscillatory period can be derived from simple formulas for the steady and uniformly accelerated motion. For equal-lengthes tubes the period has form

\[ \tau(E_0) = 4 \sqrt{\frac{2(E_0 - U_{\text{min}})}{a_z F_z}} = 4 \sqrt{\frac{2m(E_0 - U_{\text{min}})}{F_z}}, \]

where \( F_z \) is the longitudinal component of retraction force:

\[ F_z = \frac{3\pi^3 \sigma^2}{2} \frac{r_1 r_2}{r_1^2} \left( \frac{21}{32} \gamma_1 \gamma_2 2F_1 \left( \frac{1}{2}, \frac{11}{2}, 1, \frac{4r_1 r_2}{(r_1 + r_2)^2} \right) \right) - \frac{2F_1 \left( \frac{1}{2}, \frac{5}{2}, 1, \frac{4r_1 r_2}{(r_1 + r_2)^5} \right)}{(r_1 + r_2)^5}, \]

where \( F_{z0} \) is approximately constant for tubes of large radius.

![Figure 3: Dependence of \( F_{z0} \) on tube's radius for the 50nm-length DWCNT](image)

In terms of the maximal displacement \( \Delta z_0 \) the period can be written as follows

\[ \tau(\Delta z_0) = 4 \sqrt{\frac{2\Delta z_0}{a_z}} = 4 \sqrt{\frac{2m\Delta z_0}{F_z}}. \]

If \( L_2 > L_1 \) then the steady motion contribution is included and

\[ \tau(E_0) = \tau_{\text{accelerated}} + \tau_{\text{steady}} = 4 \sqrt{\frac{2m(E_0 - U_{\text{min}})}{F_z}} \left( 1 + \frac{F_z}{4} \frac{L_2 - L_1}{E_0 - U_{\text{min}}} \right). \]

\[ \tau(\Delta z_0) = 4 \sqrt{\frac{2m\Delta z_0}{F_z}} \left( 1 + \frac{L_2 - L_1}{4\Delta z_0} \right). \]
Since the period is proportional to the square root of inner tube mass, then for the same maximal displacements and the same immobile outer shell the oscillatory period of inner tube is proportional to the inverse square of its mass. At the same time the oscillatory period does not depend on tubes diameters.

If the outer tube is also mobile, then the above expressions for periods remain valid with \( m_1 \) replaced by the reduced mass

\[
M = \frac{m_1 m_2}{m_1 + m_2}.
\]

Note that the interaction energy of atoms forming the tubes rapidly decreases with the interatomic distance. Therefore it is enough to consider only interaction of adjacent tubes in MWCNT. Since some adjacent shells of MWCNT can be rigidly glued by defects, then glued tubes should be considered as double-sided shells with integrated masses.

3.2. Thermal oscillations of DWCNT

For low temperatures the telescopic oscillations are the least frequency 1D modes in DWCNT. Therefore for \( T \to 0 \) by Boltzmann theorem their energy is

\[
E = k_B T.
\]

For small oscillations the maximal potential energy of DWCNT coincides with \( E \):

\[
U_{\text{max}} = \frac{k(\Delta z_0)^2}{2} = E,
\]

where \( k \) is the rigidity parameter. Taking into account that in the harmonic approximation rigidity is the potential energy second derivative with respect to the inner tube longitudinal displacement and assuming the tube’s radius is much smaller of its length for \( L_1 = L_2 \) yield

\[
k(r_1, r_2) = 4\pi \sigma^2 r_1 r_2 \int_0^{2\pi} \left( \frac{\gamma_6}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^3} - \frac{\gamma_{12}}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^6} \right) d\theta.
\]

The harmonic oscillations frequency for this \( k(r_1, r_2) \) is

\[
\omega_{\text{harmonic}} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}.
\]
and the amplitude of longitudinal thermal oscillations can be estimated as follows

$$\Delta z_0 = \sqrt{\frac{2k_B T}{k}} \approx \sqrt{6} \cdot 10^{-3} \sqrt{T}, \text{nm.}$$

We see in particular that $\Delta z_0$ is few times lesser than graphene lattice parameter.

To model the intertube interaction force $F(r_1, r_2, L_1, L_2, \Delta z)$ in the case of $L_1 \neq L_2$ depending on the inner tube edge position $\Delta z$ let us assume that the axis of outer tube coincides with the interval $[0, L_2]$ of real axis and introduce two parameters:

$$F_0(r_1, r_2, L_1, L_2) = \frac{3\pi^3 \sigma^2}{4} r_1 r_2 \text{sgn}(L_2 - L_1) \left( \frac{21}{32} \gamma_{12} \frac{2 F_1 \left( \frac{1}{3}, \frac{1}{2}, 1, \frac{4 r_1 r_2}{(r_1 + r_2)^2} \right)}{r_1 + r_2} - \frac{2 F_1 \left( \frac{1}{3}, \frac{1}{2}, 1, \frac{4 r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^3} \right),$$

$$k(r_1, r_2, L_1, L_2) = 4\pi^2 r_1 r_2 \sigma^2 \left( \gamma_{12} \left[ \frac{2 F_1 \left( \frac{1}{3}, \frac{1}{2}, 1, \frac{4 r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^3} + \frac{2 F_1 \left( \frac{1}{3}, \frac{1}{2}, 1, \frac{4 r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^2 + (L_1 - L_2)^2} \right] \right)^6$$

$$-\gamma_6 \left[ \frac{2 F_1 \left( \frac{1}{3}, \frac{6}{7}, 1, \frac{4 r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^6} + \frac{2 F_1 \left( \frac{1}{3}, \frac{6}{7}, 1, \frac{4 r_1 r_2}{(r_1 + r_2)^2 + (L_1 - L_2)^2} \right)}{(r_1 + r_2)^2 + (L_1 - L_2)^2} \right] = k_0 r_2,$$

where $k_0$ is almost independent of $r_1, r_2$ for rather large values of these parameters. For $r_1 > 10 \text{nm}$ we have $k_0 \approx -3.7 \frac{\text{nN}}{\text{nm}}$.

For small maximum retractions of inner tube ($\Delta z < 0.3 \text{nm}$) $F(r_1, r_2, L_1, L_2, \Delta z)$ can be written as follows

$$F(r_1, r_2, L_1, L_2, \Delta z) = \begin{cases} F_0 + k \Delta z, & 0.3 \text{nm} < \Delta z < x_0 \\ 0, & x_0 < \Delta z < L_2 - L_1 - x_0 \\ -F_0 + k \cdot (L_2 - L_1 - \Delta z), & L_2 - L_1 - x_0 < \Delta z < L_2 - L_1 + 0.3 \text{nm} \end{cases}$$

Here $x_0 = \frac{|F_0|}{k}$ is the displacement, which makes the longitudinal retraction force equals to zero, $k(r_1, r_2, L_1, L_2)$ is the DWCNT longitudinal rigidity and $F_0(r_1, r_2, L_1, L_2) = F(r_1, r_2, L_1, L_2, 0)$. 7
In case of tubes with significantly different lengths (|L_1 - L_2| \gtrsim 1\,nm) the formula (5) takes on form

\[ k_{L_1 
eq L_2}(r_1, r_2) = 4\pi^2 r_1 r_2 \sigma^2 \left( \gamma_{12} \frac{\,_{2}F_{1} \left( \frac{1}{2}, \frac{12}{7}, 1, \frac{4r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^{12}} - \gamma_{6} \frac{\,_{2}F_{1} \left( \frac{1}{7}, \frac{6}{7}, 1, \frac{4r_1 r_2}{(r_1 + r_2)^2} \right)}{(r_1 + r_2)^{6}} \right) \]

and in the case of equal lengths

\[ k_{L_1 = L_2}(r_1, r_2) = 2k_{L_1 
eq L_2}(r_1, r_2). \]

The oscillation cycle can be considered as

\[ \tau = \tau_{steady} + \tau_{accelerated} = \frac{2(|L_2 - L_1| - 2x_0)}{V_{max}} + 2\pi \sqrt{\frac{m}{k}}, \]

where \( V_{max} = \sqrt{\frac{2}{m}(E(\Delta z_0) - U_{min})} \) is the maximum inner tube velocity and \( U_{min} = U \left( \frac{-|L_2 - L_1|}{2} \right) \) is the system minimum potential energy defined by (3).

With an accuracy of several percent previous equation can be approximated by

\[ \tau = 2 \sqrt{\frac{m}{k}} \left( \frac{|L_2 - L_1| - 2x_0}{|\Delta z_0 + x_0|} + \pi \right). \]

Since the system’s longitudinal rigidity depends only on the tubes radii and inner tube mass is directly proportional to the product of its length and radius, then

\[ \omega_{\text{harmonic}} \sim \sqrt{\frac{1}{\tau}}. \]

4. Thermal Oscillation Frequencies in MWCNT

Considering the long-amplitude oscillations of multi-walled nanotube we assumed that some nanotube’s shells can be bounded by the defects, but in the case of thermal oscillations we should take into account the motion of all shells because amplitudes of their oscillations are of the same order and much lesser then interatomic distance.

The MWCNT’s thermal oscillations frequencies were obtained by solving the system of equations for longitudinal displacements of tubes with forces defined by the expression above for the intertube potential. In the continuum model
arbitrary multi-walled nanotube can be characterized by the inner shell radius $r_0$, number of shells $n$ under consideration and the constant distance between adjacent shells ($d = 0.34 \text{nm}$).

Considering only adjacent shells interaction we find explicit values of the consequent MWCNT eigenfrequencies $\omega_i, i = 1..n$. The least eigenvalue is always equals to zero corresponding to the whole nanotube translational motion. The numerical analysis shows that the maximal frequency depends on the MWCNT characteristics but in case of tube with large number of shells ($n \gtrsim 10$) it tends to the asymptotic value which depends only on the tubes length:

$$\omega_{\text{max}} = \frac{280}{\sqrt{L}} \text{GHz}.$$  

The obtained value of maximal frequency is seems too low for real tubes because defects may rise the longitudinal rigidity of MWCNT. The minimal oscillation frequency strongly depends on the number of shells and can be found using the following interpolation formula

$$\omega_{\text{min}} = \frac{4.46 \times 10^{11}}{\sqrt{L}} \frac{e^{-0.0128n}}{n^{0.9365}} \text{GHz}. \quad (7)$$

Using obtained frequencies we calculated the contribution of tube’s telescopic oscillations to the individual MWCNT internal energy

$$E(T) = \sum_{\omega_i \neq 0} \hbar \omega_i \left( \frac{1}{2} + \frac{\hbar}{k_B T} \exp \left( \frac{\hbar \omega_i}{k_B T} \right) - 1 \right),$$

where $k_B$ is the Boltzmann constant and $T$ is an absolute temperature, and specific heat

$$C_v(T) = \frac{\partial E(T)}{\partial T} = \sum_{\omega_i \neq 0} k_B \left( \frac{1}{2} \frac{\hbar \omega_i}{k_B T} \sinh \left( \frac{\hbar \omega_i}{2 k_B T} \right) \right)^2. \quad (8)$$

By (8) if $k_B T \ll \hbar \omega_{\text{min}}$, then

$$C_v(T) \simeq k_B \left( \frac{\hbar \omega_{\text{min}}}{k_B T} \right)^2 \exp \left( - \frac{\hbar \omega_{\text{min}}}{k_B T} \right)$$

while $C_v(T) \simeq nk_B$ if $k_B T \gg \hbar \omega_{\text{max}}$.

It is well known that under the Debye temperature the bulk solid specific heat decreases as a cubic function of the temperature and for the one dimensional
Figure 4: Frequencies of small telescopic oscillations for the 50nm-length MWCNT with 20 shells

Figure 5: The maximal and minimal oscillation frequency for 30nm-length MWCNT for different number of shells
structures such decreasing is given by the linear function. In the case of MWC-NTs the telescopic oscillation induced specific heat decreases exponentially in the range of small temperatures and the corresponding Debye-like temperature is

\[ T_D = \frac{n\omega_{\text{min}}}{2k_B} = \frac{1.7}{\sqrt{L}} e^{-0.0128n} \text{ n}_0^{0.9365} K, \]

where \( \omega_{\text{min}} \) is given by (7). As a result of MWCNTs specific heat exponential decreasing their specific heat may be several orders higher than that of environment for \( T \gg T_D \) while for \( T \ll T_D \) these values change over. For the natural carbon nanotubes \( T_D \) varies in the interval \( 10^{-3} \div 1 K \).

5. Summary

The explicit expressions for longitudinal rigidities and frequencies of small and large-amplitude telescopic oscillations of DWCNT and MWCNT were deduced in the framework of continuum Lennard-Jones model borrowed from (2). The difference between frequencies calculated by obtained formulas and those found by numerical methods with account of discrete structure of nanotubes lies within the 5%-range. Besides the obtained frequencies of telescopic oscillations of MWCNT are in good agreement with available experimental data (3). Therefore the considered Lennard-Jones continuum model is seemingly well facilitated for description of telescopic trembling of MWCNT.

Acknowledgments

Authors are grateful to Prof. V.M.Adamyan for the significant help.

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