Theoretical analysis of telescopic oscillations in multi-walled carbon nanotubes

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A simplified theory of the telescopic oscillations in multi-walled carbon nanotubes is developed. The explicit expressions for the telescopic force constants (longitudinal rigidity) and the frequencies of telescopic oscillations are derived. The contribution of small-amplitude telescopic oscillations to the nanotubes low temperature specific heat is estimated.

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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 multiwalled 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 and nanogear [7], nanorail, reciprocating nanoengine [8]. Therefore the analysis of mechanical characteristics of MWCNT is an important objective of study. The present work is 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 is devoted to the description of the small (thermal) and large-amplitude oscillations for double-walled carbon nanotubes (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 temperatureinduced 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 $\gamma_6 = 2.43 \cdot 10^{-24} \text{ J} \cdot \text{m}^6$ and $\gamma_{12} = 3.859 \cdot 10^{-27} \text{ J} \cdot \text{m}^{12}$ borrowed from [2]. In accordance with this approximation the total intertube interaction energy takes the form

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

where $\mathbf{r}_{1,i}$ and $\mathbf{r}_{2,j}$ are radii vectores of the inner and outer tube's atoms, respectively.

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

$$U(\Delta z) = \sigma^{2} r_{1} r_{2} \int_{0}^{2\pi} d\theta_{1} \int_{0}^{2\pi} d\theta_{2} \int_{L_{2}-L_{1}+\Delta z}^{L_{2}+\Delta z} dz_{1} \times \\ \times \int_{0}^{L_{2}} dz_{2} \left\{ \frac{\gamma_{12}}{[r_{1}^{2} + r_{2}^{2} - 2r_{1}r_{2}\cos(\theta_{1} - \theta_{2}) + (z_{1} - z_{2})^{2}]^{6}} - \frac{\gamma_{6}}{[r_{1}^{2} + r_{2}^{2} - 2r_{1}r_{2}\cos(\theta_{1} - \theta_{2}) + (z_{1} - z_{2})^{2}]^{3}} \right\},$$
(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 $L_1 \le L_2$) and Δz is the distance between tubes outer edges and σ is the surface density of carbon atoms in graphene, which is almost independent on the tube chirality,

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

where b = 0.142 nm is the interatomic distance in graphene. Note that expression (2) governs any one of coaxial DWCNT configurations, but for stable natural multi-walled nanotubes the interlayer distance *d* ranges from 0.342 to 0.375 nm, and that it is a function of the curvature [11].

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 clear, that the 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

$$U_{\min} = \frac{3}{2} \pi^{3} \sigma^{2} r_{1} r_{2} \min (L_{1}, L_{2}) \times \left[\frac{2I}{32} \gamma_{12} \frac{2F_{1} \left(\frac{1}{2}, \frac{11}{2}, 1, \frac{4r_{1}r_{2}}{(r_{1} + r_{2})^{2}} \right)}{(r_{1} + r_{2})^{11}} - \gamma_{6} \frac{2F_{1} \left(\frac{1}{2}, \frac{5}{2}, 1, \frac{4r_{1}r_{2}}{(r_{1} + r_{2})^{2}} \right)}{(r_{1} + r_{2})^{5}} \right],$$
(3)

where

$${}_{2}F_{1}\left(\frac{1}{2}, J, 1, \frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right) = \frac{(r_{1}+r_{2})^{2J}}{2\pi} \times \\ \times \int_{-\pi}^{\pi} \frac{d\theta}{(r_{1}^{2}+r_{2}^{2}-2r_{1}r_{2}\cos\theta)^{J}}.$$
 (4)

3. Telescopic oscillations in DWCNT

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

$$a_z(\Delta z) = -\frac{1}{m} \frac{\partial U(\Delta z)}{\partial z},$$
 (5)

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

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We ignore here the contribution of some defect-induced dissipative forces since for high-quality nanotubes they are by several orders lower than the retraction force due to self-healing mechanism [3,5,12].

By (5) the motion of inner tube is cyclic with the period

$$\tau(E_0) = \sqrt{2m} L \int_{L_2 - L_1 - \Delta z_0}^{\Delta z_0} \frac{d(\Delta z)}{\sqrt{E_0 - U(\Delta z)}}, \qquad (6)$$

where maximal displacement Δz_0 is determined by the equation $U(\Delta z_0) \equiv U(L_2 - L_1 - \Delta z_0) = E_0$.

Due to the special form of potential (2) we can separate out two limiting forms of motion (Fig. 1):

1) steady movement for $\Delta z_0 \gg b$ while the potential is linear in Δz ;

2) small oscillations when $\Delta z_0 \lesssim b$ and the potential is quadratic in Δz .

It is obvious that for real DWCNTs the interaction energy and force are affected by the atomic structure of its shells. As a result the interaction energy is modulated [13] with period defined by the lattice parameters of both shells. The amplitude of energy modulation can reach a value of 1000 K for zigzag@zigzag and 60–100 K for armchair@armchair DWCNTs (for 5 nm length inner shell) and is linear in length.

On the other hand due to incommensurability of atomic lattices for most chiral nanotubes as well as armchair@chiral or zigzag@chiral pairs the modulation period can be much bigger than the whole DWCNT length. This means that impact of the shells structure substantially reduces as the smaller nanotube length increases.

Actually the interaction between two (or more) nanotubes of different length is well-described by the continuum model if the oscillation energy is much higher than 1000 K which corresponds to the great amplitude telescopic motion ($\Delta z_0 \gg b$). The small amplitude oscillations also can be considered within the continuum model for most cases of incommensurate nanotubes for which the energy modulation amplitude varies between 10^{-2} and 10 K.

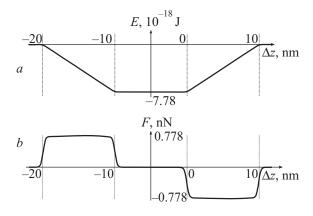


Fig. 1. The intertube interaction energy (*a*) and longitudinal intertube interaction force (*b*) for the (5,5)@(17,1) DWCNT with 10 and 20 nm lengths.

Furthermore, for DWCNTs with shell of equal length the effect of lattice structure on the intertube interaction energy is negligible compared to that of nanotube edges. As a result if $L_2 - L_1 < 0.4$ nm (where 0.4 nm is the van der Waals force saturation displacement) the continuum model is valid regardless of temperature and shells structure.

3.1. Large-amplitude oscillations in DWCNT

When the displacement Δz_0 is greater than few nanometers the potential energy is linear on Δz except smalldisplacement region (with quadratic potential energy) which can be neglected. In such a case the period of oscillation can be derived from simple formulas for the steady and uniformly accelerated motion. For equal-lengths tubes the period takes the form

$$\tau(E_0) = 4\sqrt{\frac{2(E_0 - U_{\min})}{a_z F_z}} = 4\frac{\sqrt{2m(E_0 - U_{\min})}}{F_z}, \quad (7)$$

where F_z is the longitudinal component of retraction force

$$F_{z}(r_{1}, r_{2}) = \frac{3\pi^{3}\sigma^{2}}{2} r_{1}r_{2} \times \left(\frac{21}{32}\gamma_{12} \frac{2F_{1}\left(\frac{1}{2}, \frac{11}{2}, 1, \frac{4r_{1}r_{2}}{(r_{1} + r_{2})^{2}}\right)}{(r_{1} + r_{2})^{11}} - \gamma_{6} \frac{2F_{1}\left(\frac{1}{2}, \frac{5}{2}, 1, \frac{4r_{1}r_{2}}{(r_{1} + r_{2})^{2}}\right)}{(r_{1} + r_{2})^{5}}\right).$$
(8)

Taking into account that $r_2 = r_1 + d$ for natural DWCNTs, expression (8) may be written as

$$F_{z}(r_{1}, r_{2}) \equiv -F_{z0}^{1}(r_{1})r_{1} \equiv -F_{z0}^{2}(r_{2})r_{2}, \qquad (9)$$

where $F_{z0}^{1}(r_{1})$ and $F_{z0}^{2}(r_{2})$ are approximately constant for tubes of rather large radii and their asymptotic value F_{z0} is about 1.54 nN/nm (Fig. 2).

In terms of maximal displacement $\Delta z_0 = (E_0 - U_{\min}) \times |F_z|^{-1}$ the period can be rewritten as follows:

$$\tau = 4\sqrt{\frac{2\Delta z_0}{|a_z|}} = 4\sqrt{\frac{2m\Delta z_0}{|F_z|}}.$$
 (10)

If $L_2 > L_1$ then the region of steady motion also contributes to (6):

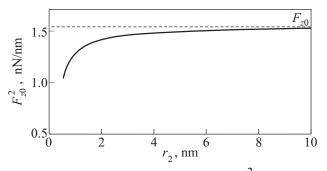


Fig. 2. The external shell radius dependence of F_{z0}^2 for the natural DWCNT with interlayer distance d = 0.34 nm.

$$\tau = \tau_{\text{accelerated}} + \tau_{\text{steady}} = 4 \frac{\sqrt{2m(E_0 - U_{\min})}}{|F_z|} \times \left(1 + \frac{|F_z|}{4} \frac{L_2 - L_1}{E_0 - U_{\min}}\right) = 4 \sqrt{\frac{2m\Delta z_0}{|F_z|}} \left(1 + \frac{L_2 - L_1}{4\Delta z_0}\right). (11)$$

Actually the oscillatory period does not depend on inner tube radius r_1 (if it is sufficiently large) since both the inner tube mass *m* and retraction force F_z are linear with r_1 .

If the outer tube is also mobile, then the above expressions for periods remain to be valid with m 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 smallest frequency 1D modes in DWCNT. Therefore for $T \rightarrow 0$ by Boltzmann theorem their mean energy is $\overline{E} = k_B T$.

For small oscillations the maximal potential energy of DWCNT coincides with \overline{E} :

$$U_{\max} = \frac{k(\Delta z_0)^2}{2} = \overline{E},$$
 (12)

where k is the rigidity parameter. Taking into account that in harmonic approximation the rigidity is the second derivative of potential energy on the inner tube longitudinal displacement and assuming the tube radius is much smaller of its length we obtain for $L_1 = L_2$ the following expression:

$$k(r_{1}, r_{2}) = 4\pi\sigma^{2}r_{1}r_{2} \times \\ \times \int_{0}^{2\pi} \left(\frac{\gamma_{6}}{(r_{1}^{2} + r_{2}^{2} - 2r_{1}r_{2}\cos\theta)^{3}} - \frac{\gamma_{12}}{(r_{1}^{2} + r_{2}^{2} - 2r_{1}r_{2}\cos\theta)^{6}} \right) d\theta.$$
(13)

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

$$\omega_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}},\tag{14}$$

and the amplitude of longitudinal thermal oscillations can be estimated using the next relation:

$$\frac{\Delta z_0}{\sqrt{T}} = \sqrt{\frac{2k_B}{k}} \approx \sqrt{6} \cdot 10^{-3} \, \frac{\text{nm}}{\sqrt{\text{K}}}.$$
(15)

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It can be shown that Δz_0 is few times smaller than the graphene lattice parameter even for $T \sim 300$ K.

the inner tube edge position Δz let us assume that the axis of outer tube coincides with the interval $[0, L_2]$ of real axis and introduce two parameters:

1

the intertube interaction То model force $F(r_1, r_2, L_1, L_2, \Delta z)$ in the case of $L_1 \neq L_2$ depending on

$$F_{0}(r_{1},r_{2},L_{1},L_{2}) = \frac{3\pi^{3}\sigma^{2}}{4}r_{l}r_{2}\operatorname{sgn}(L_{2}-L_{1})\left[\gamma_{12}\frac{21}{32}\frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{11}{2},\frac{1}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{11}} - \gamma_{6}\frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{5}}\right], \quad (16)$$

$$k(r_{1},r_{2},L_{1},L_{2}) = 4\pi^{2}r_{l}r_{2}\sigma^{2}\left\{\gamma_{12}\left[\frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{12}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{12}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{12}{2},\frac{4r_{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] - \gamma_{6}\frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{12}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{4r_{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] - \gamma_{6}\frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{12}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{4r_{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] - \gamma_{6}\frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{12}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}{2},\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}+(L_{1}-L_{2})^{2}}\right)}{(r_{1}+r_{2})^{2}} + \frac{{}^{2}F_{1}\left(\frac{1}{2}\frac{5}$$

1

where k_0 is almost independent of r_1, r_2 for rather large values of these parameters. For $r_1 > 10$ nm we have $k_0 \approx -3.7 \text{ nN/nm}^2$.

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:

$$F(r_1, r_2, L_1, L_2, \Delta z) = \begin{cases} F_0 + k\Delta z, & 0.3 \text{ nm} < \Delta z < x_0, \\ 0, & x_0 < \Delta z < L_2 - L_1 - x_0, \\ -F_0 + k(L_2 - L_1 - \Delta z), & L_2 - L_1 - x_0 < \Delta z < L_2 - L_1 + 0.3 \text{ nm}. \end{cases}$$
(18)

Here $x_0 = |F_0/k|$ 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 $F_0(r_1, r_2, L_1, L_2) = F(r_1, r_2, L_1, L_2, 0)$.

In case of tubes with significantly different lengths $(|L_1 - L_2| \gtrsim 1 \text{ nm})$ the expression (17) takes the form

$$k_{L_{1}\neq L_{2}}(r_{1},r_{2}) = 4\pi^{2}r_{1}r_{2}\sigma^{2}\left[\gamma_{12}\frac{2F_{1}\left(\frac{1}{2},\frac{12}{2},1,\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{12}} - \gamma_{6}\frac{2F_{1}\left(\frac{1}{2},\frac{6}{2},1,\frac{4r_{1}r_{2}}{(r_{1}+r_{2})^{2}}\right)}{(r_{1}+r_{2})^{6}}\right], (19)$$

and in the case of equal lengths $k_{L_1=L_2}(r_1, r_2) = 2k_{L_1\neq L_2}(r_1, r_2)$.

The oscillation cycle can be considered as

$$\tau = \tau_{\text{steady}} + \tau_{\text{accelerated}} = 2 \frac{|L_2 - L_1| - 2x_0}{V_{\text{max}}} + 2\pi \sqrt{\frac{m}{k}}, \quad (20)$$

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 by approximated by

$$\tau = 2\sqrt{\frac{m}{k}} \left(\frac{|L_2 - L_1| - 2x_0}{|\Delta z_0 + x_0|} + \pi \right).$$
(21)

Since the longitudinal rigidity depends only on the tubes radii and the inner tube mass is proportional to the product of its length and radius, then the harmonic oscillation frequency scales on the length as $\omega_0 \sim L^{-1/2}$.

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From the above discussion it is clear that for $T \leq 300$ K the continuum model is valid for the DWCNTs with incommensurate shells but ceases to be true for commensurate (armchair@armchair, zigzag@zigzag) and some quasi-commensurate configurations. As an example, for the majority of zigzag@chiral and armchair@chiral DWCNTs the considered thermal oscillations are possible for temperatures higher than 0.01–1 K. As for the chiral@chiral configurations, in some cases the shells atomic structure impact may becomes negligible even for $T \sim 10^{-3}$ K.

3.3. Thermal oscillation frequencies in multi-walled CNTs

Considering the long-amplitude oscillations of multiwalled 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. For simplicity assume that all MWCNT's shells are equal in length.

We obtained the MWCNT's thermal oscillations frequencies 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 , the number of shells n under consideration and the constant distance between adjacent shells (d = 0.34 nm).

Considering only adjacent shells interaction we find explicit values of the consequent MWCNT eigenfrequencies $\omega_i, i = \overline{1...n}$ (Fig. 3). The smallest eigenvalue is always equal to zero corresponding to the whole nanotube translational motion. The 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 (Fig. 4):

$$\omega_{\text{max}} = \frac{280}{\sqrt{L}} \,\text{GHz}\,. \tag{22}$$

The obtained value of maximal frequency is underestimated for real tubes because defects may increase the lon-

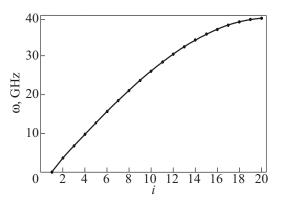


Fig. 3. Frequencies of small telescopic oscillations for the 50 nm-length MWCNT with 20 shells.

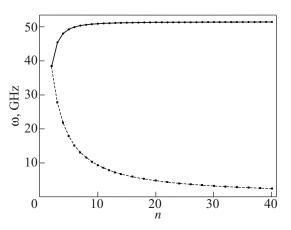


Fig. 4. The maximal (\bullet) and minimal (\bullet) oscillation frequency for 30 nm-length MWCNT for different number of shells.

gitudinal rigidity of MWCNT. The minimal oscillation frequency strongly depends on the number of shells (as a result of increasing of the outer shell mass) and can be found using the following interpolation formula (Fig. 4):

$$\omega_{\min} = \frac{4.46 \cdot 10^{11}}{\sqrt{L}} \frac{e^{-0.0128n}}{n^{0.9365}} \,\text{GHz}\,.$$
 (23)

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

$$E(T) = \sum_{\omega_i \neq 0} \hbar \omega_i \left[\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar \omega_i}{k_B T}\right) - 1} \right],$$
 (24)

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

$$C_{\nu}(T) = \frac{\partial E(T)}{\partial T} = \sum_{\omega_i \neq 0} k_B \left[\frac{\frac{1}{2} \frac{\hbar \omega_i}{k_B T}}{\sinh\left(\frac{1}{2} \frac{\hbar \omega_i}{k_B T}\right)} \right]^2.$$
 (25)

By (25) if $k_B T \ll \hbar \omega_{\min}$, then

$$C_{\nu}(T) \simeq k_B \left(\frac{\hbar\omega_{\min}}{k_B T}\right)^2 \exp\left(-\frac{\hbar\omega_{\min}}{k_B T}\right)$$
 (26)

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 structures such decreasing is given by the linear function. In the case of MWCNTs the telescopic oscillation induced specific heat decreases exponentially in the range of small temperatures and the corresponding Debye-like temperature is

$$T_D = \frac{\hbar\omega_{\min}}{2k_B} = \frac{1.7}{\sqrt{L}} \frac{e^{-0.0128n}}{n^{0.9365}} \,\mathrm{K},\tag{27}$$

where ω_{\min} is given by (23). As a result of exponential decreasing MWCNT's 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} –1 K.

If MWCNT's shells have different lengths the hampering of low-energy telescopic motion by the lattice structure causes the abrupt increase of the oscillation frequency and also leads to the specific heat exponential decreasing. Moreover for most MWCNTs the thermal oscillations freezing-out as a result of both processes takes place within the same temperature range from 10^{-3} to 1-10 K.

For the temperature T = 1 K (assuming that $T > T_D$) the telescopic oscillations contribution to the total nanotube's specific heat may run as high as 50% for the relatively small double-walled nanotubes (L = 20 - 30 nm, $r_2 \sim 1$ nm). For the ten-walled MWCNTs of length L == 50 nm and external radius r = 2.5 nm the telescopic oscillation specific heat is about 0.025 J/(kg·K) and phonon contribution is in the range 0.2 to 0.3 J/(kg·K) [14]. The maximal electronic contribution for metallic SWCNT is estimated to be ten times smaller than that of lattice oscillations [14]. As for all semiconducting nanotubes (which are the majority of natural MWCNTs) the electronic specific heat is negligible. Taking into account the 1D structure phonon specific heat linear decreasing in the considered temperature region it is reasonable to expect that for $T \lesssim 10^{-1}$ K (if it is higher than T_D) the telescopic oscillation contribution may become dominant.

4. 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]. Besides the obtained frequencies of telescopic oscillations of MWCNT are in good agreement with available experimental data [3] and results of numerical simulations [15–17].

For example, the thermal oscillation frequency of 12.21 nm (7,0)@(9,9) DWCNT obtained in Ref. 15 is (75±8) GHz while the considered model gives 62 GHz. The retraction force F_z for the (9,0)@(12,0) DWCNT obtained in [16,17] is 1.6 nN and using Lennard-Jones parameters from [16] it yields $F_z = 1.54$ nN. For (5,5)@(10,10) and (10,10)@(15,15) DWCNTs the maximum retraction

forces ratio is 1.67 by our model and 1.7 in [18]. So, the difference between frequencies calculated by our analytical formulas and those found by numerical methods with account of discrete structure of nanotubes lies within the 5%-range.

It is worth to be mentioned that investigation of multiwalled nanotube oscillations by using exact expression for the two-shell retraction force and longitudinal rigidity is not computationally intensive in contrast to the molecular dynamics simulations. This permits us easily to calculate (within the bounds of continuum model) all oscillation frequencies and corresponding parameters (such as specific heat) of any MWCNT regardless of number of shells and their configuration.

Therefore the considered Lennard-Jones continuum model is seemingly well suited for description of telescopic trembling of MWCNT.

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- 1. S. Iijima, Nature 354, 56 (1991).
- L.A. Girifalco, M. Hodak, and R.S. Lee, *Phys. Rev.* B62, 013104 (2000).
- 3. J. Cumings and A. Zettl, Science 289, 602 (2000).
- M.M.J. Treasy, T.W. Ebbesen, and J.M. Gibson, *Nature* 381, 678 (1996).
- 5. Q. Zheng and Q. Jiang, Phys. Rev. Lett. 88, 045503 (2002).
- 6. L. Forro, Science 289, 560 (2000).
- 7. D.W. Srivastava, Nanotechnology 8, 186 (1997).
- 8. Z.C. Tu and X. Hu, Phys. Rev. B72, 033404 (2005).
- D. Baowan and J.M. Hill, Z. Angew. Math. Phys. 58, 857 (2007).
- D. Baowan, N. Thamwattana, and J.M. Hill, Communications in Nonlinear Science and Numerical Simulation 13, 1431 (2008).
- C.H. Kiang, M. Endo, P.M. Ajayan, G. Dresselhaus, and M.S. Dresselhaus, *Phys. Rev. Lett.* 81, 1869 (1998).
- A. Kis, K. Jensen, S. Aloni, W. Mickelson, and A. Zettl, *Phys. Rev. Lett.* 97, 025501 (2006).
- W. Guo, Y. Guo, H. Gao, Q. Zheng, and W. Zhong, *Phys. Rev. Lett.* **91**, 125501 (2003).
- J.C. Lasjaunias, K. Biljaković, Z. Benes, J.E. Fischer, and P. Monceau, *Phys. Rev.* B65, 113409 (2002).
- J.L. Rivera, C. McCabe, and P.T. Cummings, *Nanotechnology* 16, 186 (2005).
- S.B. Legoas, V.R. Coluci, S.F. Braga, P.Z. Coura, S.O. Dantas, and D.S. Galvao, *Nanotechnology* 15, S184 (2004).
- S.B. Legoas, V.R. Coluci, S.F. Braga, P.Z. Coura, S.O. Dantas, and D.S. Galvao, *Phys. Rev. Lett.* **90**, 055504 (2003).
- 18. J.W. Kang and J.H. Lee, Nanotechnology 19, 285704 (2008).