QUANTUM MODEL OF PHONON TRANSPORT AND HEAT CONDUCTIVITY IN CARBON NANOCLUSTERS AND NANOTUBES

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Abstract

A complex approach phonon quantum discrete model (PQDM) was developed to describe dynamics, kinetics and statistics of phonons in carbon nanostructures with zero-chirality of both zig-zag and armchair geometry. The model allows include into the pure phonon problem existing interaction with others subsystems: electrons, photons, impurities and defects. We predict that planar C- structures are geometrically stable and may bridge interelectrode space in strong external electric field. The exact solution of generalized thermal conductivity (TC) equation was obtained for nanotubes. Temperature distribution along the tube was derived analytically. The diagonalization procedure for the case of strong ph-ph interaction was proposed. It was shown the quadratic increasing of heat conductivity with the growth of the phonon mean free path (PMFP). Heat capacitance and the entropy of carbon linear tubes were calculated as the function of temperature. Our theoretical approach explains the nature of good TC in carbon and carbon-like materials by existing of the soft vibration branch (low frequency radial breathing mode phonons with high density of states at thermal energies) accompanied by structure hardness (high frequency ϕ- and z-branches) providing big PMFP. TC coefficient for high conducting channel in surrounding medium was calculated. The mechanism of heat conductivity temperature damping was analyzed. Two competitive tendencies produce TC maximum at intermediate temperatures (100-300)K. It was shown the strongly non-linear increasing of effective heat conductivity with the growth nanotubes concentration. It was shown that insertion of armchair nanotube inside a medium or its coating by polyacetylene molecule considerably changes the structure of radial breathing phonons.
1 Motivation

Phonon dynamics in open and closed carbon and carbon-like nets. How many phonon branches are present? Whether exists a simple correlation between differed phonon types for different NT geometries?

Vibrational eigenmode and its amplitudes distribution in the net.

Vibrational eigenmodes, phonons, micro-sound and heat propagation. Phonon mean free path. Sound waves boundary conditions.

The mechanism of temperature damping at high temperatures and concrete law of increasing at low temperatures.

Maximal thermal conductivity for solitary carbon tube is not measured reliably now and changes in wide interval from 200 W/mK to 3000 W/mK for different authors.

The temperature of maximal thermal conductivity for carbon tubes is not surely measured also and may change in wide interval from 150 K to 300 K for different authors.

The question is whether exist differences in thermal conductivity of solitary carbon tubes depending on type (armchair or zig-zag), chirality and diameter. Which physical factors are essential in electron transport through the molecule?

Do phonons (vibrons) participate essentially in electron transport through the molecule?

Are differences in thermal conductivity of solitary carbon tubes, flat carbon structures like graphene and graphite (in plane) essential?
Fig. 2.1 General picture of connected subjects for the problem of phonon propagation in molecular nets.
3 Systems under consideration

Fig. 3.1 A polymer molecule absorbed by armchair nanotube. Absorption bonds are shown by red lines, C-C bonds of the polymer are shown by violet color.

Fig. 3.2 Heat transistor (3-polar contact) on a flat carbon structure connecting three baths at different temperatures $T_l$, $T_u$ and $T_v$.

4 Phonon quantum discrete model (PQDM)

$$\hat{H}_0 = \sum_{s,\sigma} \hbar \omega_{s\sigma} (\hat{b}_{s\sigma}^+ \hat{b}_{s\sigma} + 1/2)$$  
(1)

$$\hat{H}_{\text{int}} = \sum_{i,\sigma} G_{i\sigma} (\hat{b}_{i\sigma}^+ \hat{b}_l + \hat{b}_l^+ \hat{b}_{i\sigma}) + \sum_{r,\sigma} G_{r\sigma} (\hat{b}_{r\sigma}^+ \hat{b}_r + \hat{b}_r^+ \hat{b}_{r\sigma})$$  
(2)

5 Vibrational dynamics. Linear approximation.

Zig-zag NT

$$m \ddot{\rho}_i = -k'(3\rho_i - \rho_{i1} - \rho_{i2} - \rho_{i3})$$  
(3)

$$m \ddot{z}_i = -k(z_i - z_{i1}) - 0.25k(2z_i - z_{i2} - z_{i3})$$  
(4)

$$m \ddot{x}_i = -0.75k(2x_i - x_{i1} - x_{i2}) - k'(x_i - x_{i3})$$  
(5)

Armchair NT
\[ m \ddot{z}_i = -0.75k(2z_i - z_{i1} - z_{i2}) - k'(z_i - z_{i3}) \] (6)

\[ m \ddot{x}_i = -k(x_i - x_{i1}) - 0.25k(2x_i - x_{i2} - x_{i3}) \] (7)

\[ \dot{D}\vec{A} = \omega^2 \vec{A} \] (8)

\[ \omega_{ss}, \vec{A}_{ss}^+ = (C_{s1}, C_{s2}, C_{s3}...C_{sr}), r = 2n(m + 1) \] (9)

Fig. 5.1 The problem’s geometry. Z-axes is perpendicular to the figure plane. It’s shown j and r shifts of an atom.

Fig. 5.2. The problem’s geometry. F is z-axes projection of the force acting between a and b atoms. dz marks the atom a shift along the axes z, dzcos(p/3) is the shift projection.
Fig. 5.3. Sketch of the dynamical matrix for zig-zag tubulene created from a graphene sheet \( \{5,5\} \) containing 60 atoms by its rolling up. Rose-colored spots are diagonal elements, green and blue show two types of bonds, rest elements equal to zero, left and upper red bands contain atomic numbers.

Fig. 5.4. Sketch of the dynamical matrix for armchair tubulene created from a graphene sheet \( \{5,5\} \) containing 60 atoms by its rolling up. Rose-colored spots are diagonal elements, green and blue show two types of bonds, rest elements equal to zero, left and upper red bands contain atomic numbers.
6 Frequency spectrum and DOS. Zig-zag geometry.

\[ g(\omega_{s\sigma}) \approx \frac{1}{\omega_{s\sigma} - \omega_{s-1,\sigma}} \]  

(10)

Fig. 6.1. Radial mode spectrum of zig-zag tubulene created from a graphene sheet \{5,15\} by rolling up around z-axes. The unity of frequency is \( \omega_0 \).

Fig. 6.2 Radial mode DOS function for Fig. 6.1 system. \( h = \text{Int}[35r/50] \).

Fig. 6.3 Azimuth mode spectrum of zig-zag tubulene created from a graphene sheet \{5,15\} by rolling up around z-axes. The unity of frequency is \( \omega_0 \).
Fig. 6.4 Azimuthal mode DOS function (arbitrary units) for graphene sheet \( \{5,15\} \) \( h = \text{Int}[35r/50] \).

Fig. 6.5 Axial mode spectrum of zig-zag tubulene created from a graphene sheet \( \{5,15\} \) by rolling up around z-axes. The unity of frequency is \( \omega_0 \).

Fig. 6.6 Axial mode DOS function (arbitrary units) for tubulene fragment created from a graphene sheet \( \{5,15\} \) by rolling around z-axes. Horizontal axes, frequency in \( \omega_0 \).
7 Frequency spectrum and DOS. Armchair geometry.

Fig. 7.1. Radial mode density of states for armchair tubulene created from a graphene sheet \{8,15\} by rolling up around z-axes. Insertion the same for zig-zag tubulene.
Fig. 7.2 Tangential $j$-mode density of states for armchair tubulene created from a graphene sheet $\{8,15\}$ by rolling up around $z$-axes. Insertion is zig-zag equivalent for this that is $z$-mode DOS. $h=\text{Int}[4r/5]$.

Fig. 7.3 Axial $z$-branch density of states for armchair tubulene created from a graphene sheet $\{8,15\}$ by rolling up around $z$-axes. Insertion is zig-zag equivalent for this that is $\varphi$-mode DOS.
Fig. 7.4 Lower part. Three branches of phonon spectrum for armchair tubulene created from a graphene sheet \{8,15\} by rolling up around z-axes. Upper part. Radial phonon band for zig-zag \{8,15\} NT.

8 Amplitude distribution and knot’s theorem

\[ A_j = \sum_{s,\sigma} |C_{sj}|^2 n_{s\sigma}, \]  \hspace{1cm} (11)

Fig. 8.1 Calculated distribution of vibrational amplitudes of \{8,8\} planar carbon net for the 4-th mode.
Fig. 8.2. Calculated r-branch amplitude distribution $s=5$ along armchair tubulene created from a graphene sheet $\{6,5\}$ by rolling up around marked direction. Transversal knot's lines are degenerated.

Fig. 8.3 r-branch amplitude distribution along zig-zag tubulene created from a graphene sheet $\{6,5\}$ by rolling up around marked direction. 5th state. Longitudinal knot's lines are degenerated.

Fig. 8.4 Calculated mean square amplitude distribution along zig-zag tubulene created from a graphene sheet $15,5$ by rolling up around marked direction. $T=0.03$ eV. Circular arrows show rolling up of the structure.

9  Heat transfer

$$\dot{W}_{l \rightarrow s} = \frac{2\pi}{\hbar} |G_{ls}|^2 g_l(\omega_{s\sigma}) N_l(\omega_{s\sigma}) (1 + n(\omega_{s\sigma}))$$  \hspace{1cm} (12)$$

$$n_s = \frac{\sum |G_{li,s}|^2 cdot g_l(\omega_{s\sigma}) \cdot N_l(\omega_{s\sigma}) + |\sum G_{ir,s}|^2 \cdot g_r(\omega_{s\sigma}) \cdot N_r(\omega_{s\sigma})}{|\sum G_{li,s}|^2 \cdot g_l(\omega_{s\sigma}) + |\sum G_{ir,s}|^2 \cdot g_r(\omega_{s\sigma})}$$ \hspace{1cm} (13)$$

for 3-polar contact

$$n_s = (|\sum G_{li,s}|^2 \cdot g_l(\omega_{s\sigma}) \cdot N_l(\omega_{s\sigma}) + |\sum G_{iu,s}|^2 \cdot g_u(\omega_{s\sigma}) \cdot N_u(\omega_{s\sigma}) + +|\sum G_{id,s}|^2 \cdot g_d(\omega_{s\sigma}) \cdot N_d(\omega_{s\sigma}) ) / (|\sum G_{li,s}|^2 \cdot g_l(\omega_{s\sigma}) + |\sum G_{iu,s}|^2 \cdot g_u(\omega_{s\sigma}) + |\sum G_{id,s}|^2 \cdot g_d(\omega_{s\sigma}) )$$ \hspace{1cm} (14)$$
And for 4-polar contact

\[ n_s = (| \sum_{i_l} G_{i_l,s}^2 \cdot g_l(\omega_{s\sigma}) \cdot N_l(\omega_{s\sigma}) + | \sum_{i_r} G_{i_r,s}^2 \cdot g_r(\omega_{s\sigma}) \cdot N_r(\omega_{s\sigma}) + \\
+ | \sum_{i_u} G_{i_u,s}^2 \cdot g_u(\omega_{s\sigma}) \cdot N_u(\omega_{s\sigma}) + | \sum_{i_d} G_{i_d,s}^2 \cdot g_d(\omega_{s\sigma}) \cdot N_d(\omega_{s\sigma})) / \\
/ (| \sum_{i_l} G_{i_l,s}^2 \cdot g_l(\omega_{s\sigma}) + | \sum_{i_r} G_{i_r,s}^2 \cdot g_r(\omega_{s\sigma}) + | \sum_{i_u} G_{i_u,s}^2 \cdot g_u(\omega_{s\sigma}) + \\
+ | \sum_{i_d} G_{i_d,s}^2 \cdot g_d(\omega_{s\sigma})) \] (15)

\[
\frac{\partial Q}{\partial t} = 2\pi \sum_{s,\sigma} |G_{ls}|^2 |G_{rs}|^2 \omega_{s\sigma} g_l(\omega_{s\sigma}) g_r(\omega_{s\sigma}) \times \\
\quad \times \frac{N_l(\omega_{s\sigma}) - N_r(\omega_{s\sigma})}{|G_{ls}|^2 g_l(\omega_{s\sigma}) + |G_{rs}|^2 g_r(\omega_{s\sigma})} \] (16)

\[ \lambda' = L \left\lvert \frac{\partial Q/\partial t}{T_r - T_l} \right\rvert \] (17)

Approximation

\[ N_l(\omega_{s\sigma}) - N_r(\omega_{s\sigma}) \approx \frac{\partial N(\omega_{s\sigma})}{\partial T} (T_r - T_l) \] (18)

\[ \lambda'(L) = 2\pi L \sum_{s,\sigma} |G_{ls}|^2 |G_{rs}|^2 \omega_{s\sigma} g_l(\omega_{s\sigma}) g_r(\omega_{s\sigma}) \times \\
\quad \times \frac{\partial N(\omega_{s\sigma})/\partial T}{|G_{ls}|^2 g_l(\omega_{s\sigma}) + |G_{rs}|^2 g_r(\omega_{s\sigma})} \] (19)

10 Phonon mean free path and size dependences

\[ \lambda'(l_{ph}) = \frac{2\pi l_{ph}}{T^2} \sum_{s,\sigma} |G_{ls}|^2 |G_{rs}|^2 \omega_{s\sigma}^2 g_l(\omega_{s\sigma}) g_r(\omega_{s\sigma}) \frac{N(\omega_{s\sigma})(N(\omega_{s\sigma}) + 1)}{|G_{ls}|^2 + |G_{rs}|^2} \] (20)

\[ G_{rs} = \sum_{i_r} G_{i_r,s} C_{i_r,s} \] (21)

The mean free path along the tube \( l_{ph} \).

\[ l_{ph} \approx \sqrt{\frac{S}{N}} = \sqrt{\frac{l_d \cdot l_{ph}}{N}}, \quad l_{ph} \approx l_d < \frac{1}{N} > \] (22)

\[ < N > = \frac{1}{\Delta} \int n(\omega) g(\omega) d\omega, \quad l_{ph} \sim \frac{1}{T} \] (23)
Fig. 10.1. One dimensional phonon dynamics. Calculated total thermal conductivity length dependence that includes all vibration branches of armchair NT. $L_{ph}$ is phonon mean free path, $a$ is C- bond length.
11 Thermal coefficient temperature dependence

\[ \lambda_0 = \frac{2\pi a G_0^2}{\hbar \omega_0} k \]  

(24)

Fig. 11.1. Thermal conductivity temperature dependence. Armchair NT. Curve 1 corresponds to z-branch contribution, curve 2 to j-branch and r-branch contribution is presented by curve 3.
12 XII. Generalized phonon transport equation

\[ \dot{W}_{l \to s\sigma} = \frac{2\pi}{\hbar} |G_{ls}|^2 g_l(\omega_{s\sigma}) N_l(\omega_{s\sigma})(1 + n(\omega_{s\sigma})) \] (25)

\[ \frac{\partial n_{s\sigma}}{\partial t} = D_{s\sigma} \frac{\partial^2 n_{s\sigma}}{\partial z^2} \] (26)

\[ D_{s\sigma} = \frac{2\pi l_{ph}}{\hbar} |G_{ls\sigma}|^2 g(\omega_{s\sigma}) \] (27)

\[ G_{ls\sigma} = G_{rs\sigma} = \sum_{i} G_{li} C_{i\sigma} \] (28)

Temperature distribution along the tube

\[ T(z) = \frac{\omega_{s\sigma}}{Ln} \left( 1 + \frac{L}{n_l(\omega_{s\sigma}) + [n_r(\omega_{s\sigma}) - n_l(\omega_{s\sigma})]z} \right) \] (29)
Fig. 12.1 Phonon jumps over a carbon armchair structure (arrows). Nanotubes are ideal one-dimensional systems as to the phonon dynamics.

Fig. 12.2. One dimensional phonon dynamics. Exact temperature distribution along the tube given by (4.4). $T_l, T_r$ are temperatures of baths connecting with tube ends, $L$ is the tube length. End points come together all modal (partial) temperatures for each ss.
Fig.13.1. Averaging procedures and speed of propagation. $a$ is interatomic distance, $\langle x \rangle$ is mean atomic shift, $x$ is extended coordinate of the freedom's degree, $V$ is excitation velocity, $m$ is atom mass, $k$ is elasticity coefficient.

Fig.13.2. Temperature dependence of thermal conductivity coefficient. Two competitive tendencies.

The boundary conditions for microsound spreading through periodic NT complexes

\[
\begin{align*}
0.75ka \frac{\partial \langle z \rangle}{\partial z} + (-1)^{l,r}m\omega^2 \langle z \rangle &= \text{const} \\
\frac{\partial \langle z \rangle}{\partial z} &= \text{const}
\end{align*}
\]  

(30)

\[< z >= Ae^{ifz} + Be^{-ifz} \]  

(31)

A complex approach PQDM was applied to describe phonon dynamics and heat spreading processes in carbon NT-solid medium composite material and in nanotubes embraced by a polymer molecule.

Atomic vibration dynamics was considered for carbon zero-hirality nanotubes connected with solid matrix. Vibrational eigenmodes, density of states and amplitude distribution for tubes inserted into a cylindrical well inside the medium and bounded with its hard inner wall were calculated. Phonon band parameters were analyzed in linear approximation for three types of vibration: azimuthal or tangential $j$-branch, radial breathing mode ($r$-branch) and longitudinal $z$-branch.

It’s shown that phonon propagation in actual nanotubes is characterized by a kind of "compactification" of circular freedom’s degree due to the big phonon mean free path. Nanotubes of actual diameters are ideal one-dimensional phonon and heat conductors.
Phonon band structure was investigated for armchair nanotubes on the base of hierarchical law and system symmetry.

Thermal fluxes and thermal conductivity were considered in PQDM. Temperature dependences were obtained. The mechanism of heat conductivity high temperature damping is cleared. Two competitive tendencies produce thermal conductivity maximum at intermediate temperatures (100-300)K.

The exact solution of generalized thermal conductivity equation was obtained for nanotubes. Temperature distribution along the tube was derived analytically.

Size dependences were considered for thermal conductivity. It was shown the linear increasing of heat conductivity with the growth of the phonon mean free path.

The explanation of the nature of good thermal conductivity in carbon and carbon-like materials by existing of the soft vibration branch (low frequency RBM phonons with high DOS at thermal energies) accompanied by structure hardness (high frequency j- and z-branches) providing big mean free path for phonons (Fig.5.2).

Adding of new layers or new walls to single-walled NT makes breathing r-branch of vibrations harder and causes the sharp decreasing of phonon density of states at the same phonon mean free path.

Pressure decreases thermal conductivity. The effect is connected with total hardening of all bonds and phonon modes going away from active thermal zone.

Melting decreases thermal conductivity by another reason: the phonon’s mean free path becomes small.

Modified Fourier equation of heat propagation in microscopic molecular channel was obtained.

Boundary problem for temperature distribution in channel-medium system was considered in cylindrical symmetry. The method of partial solution building for cylindrical boundary problem was proposed. Temperature distribution isotherms were calculated.

Concentration dependences were considered for thermal conductivity of NT-solid matrix composite. It was shown the strongly non-linear increasing of effective heat conductivity with the growth nanotubes concentration.

Phonon dynamics was considered for carbon zero-chirality nanotubes embraced by polymer molecule. Vibrational eigenmodes, density of states and amplitude distribution for a bounded tube were calculated. Phonon band parameters were obtained in linear approximation for three types of vibration.

It was shown that insertion of armchair nanotube inside a medium or its coating by polyacetilene molecule considerably changes the structure of radial breathing phonons.
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