

## ABOUT SOME THERMODYNAMICAL PROPERTIES OF CYLINDRICAL NANORODS

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Received January 12, 2012

*Abstract.* The thermodynamic phonon properties of cylindrical nanorods are analyzed using the Green’s function method. This method is suitable for analyses of spatially deformed structures and gives possibility for the calculation of mean values of operator products. Two types of Green functions will be found for axial phonons and for disc phonons. As a consequence of the applied new method the thermodynamic characteristics of cylindrical nanorods: internal energy and specific heat were obtained.

*Key words:* Green's function method, nanorods, specific heat.

### 1. INTRODUCTION

Nanorods are structures with rectangular cross section of nanodimension and macroscopic length. Nanodimensions in two directions require the introduction of boundary conditions, which noticeably change the physical characteristics of the system compared to those corresponding to the bulk structure. These changes are antiproportional to the thickness of the structures.

The existence of the phonons in the nanorod is essential for a proper determination of the superconductive properties of the system.

Analyses of nanostructures are very popular in several last years [1–4]. It is caused by advancing of technology of syntheses of nanostructures and also with wide possibilities of application of nanotubes in superconductive devices. The behaviour of some biosystems can be explained by some nanotube properties [5].

Investigations of phonon subsystem are necessary since phonons are always present in every structure and influence to behaviour of electrons, optical excitations, spin waves etc.

In this article we consider the system of  $N$  linear molecular chains connecting molecules lying at the vertices of  $M$  regular polygons whose planes are perpendicular to the chains. It is shown in Fig.1. Molecules in chains are labelled with index  $m$  while molecules in discs (polygons) are labelled with index  $n$ .

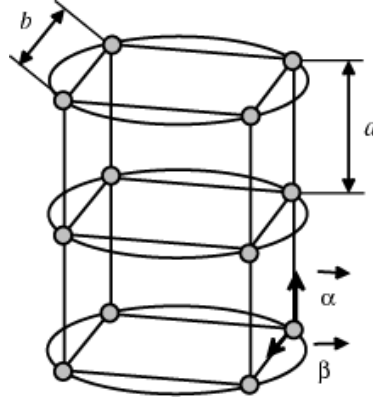


Fig. 1 – Structure scheme of cylindrical nanorods.

We propose that phonons in chains as well as the phonons in discs are of longitudinal type, *i.e.* molecular displacements ( $\alpha$ ) in chains are taken in chain direction, only, while molecular displacements in discs ( $\beta$ ) are directed along lines connecting two nearest molecules of the polygon. Due to this assumption the phonons in chains (in further axial phonons) and phonons in discs (in further disc phonons) are mutually independent. Using this assumption, the phonon Hamiltonian can be written as:

$$H = H_a + H_d, \quad (1)$$

where  $H_a$  is the Hamiltonian of mechanical oscillations along axis, with its expression:

$$H_a = \sum_{m=0}^M \frac{P_{m\alpha}^2}{2M_{mol}} + \frac{1}{4} k_a \sum_{m=0}^M \left[ (\alpha_m - \alpha_{m+1})^2 + (\alpha_m - \alpha_{m-1})^2 \right], \quad (2)$$

and  $H_d$  is the Hamiltonian of subsystem disc phonons:

$$H_d = \sum_{n=0}^N \frac{p_{n\beta}^2}{2M_{mol}} + \frac{1}{4} k_d \sum_{n=0}^N \left[ (\beta_n - \beta_{n+1})^2 + (\beta_n - \beta_{n-1})^2 \right], \quad (3)$$

where  $p_\alpha$  and  $p_\beta$  are the corresponding momentum;  $M_{mol}$  is the mass of the molecule and  $k_a$  and  $k_d$  are the stretch Hook's constants.

The simplest boundary conditions, consisting absence of layers labelled with  $m = -1$  and  $m = M + 1$  will be assumed. The more real boundary conditions include the changes of boundary Hook's constants with respect to those of internal layers. For the molecules lying in the discs the symmetry is not disturbed, but obvious cyclical condition is valid:  $C_n = C_{N+1+n}$ , where  $C$  denotes arbitrary physical characteristics of the system of disc molecules [6, 7].

The paper is organized as follows: The stepwise Green's functions method for the axial phonons and then, for the disc phonons is illustrated in Section 2. Its application to obtain some thermodynamic properties is given in the Section 3. The conclusions are presented in the last section.

## 2. GREEN'S FUNCTIONS METHODS

Thermodynamic and kinetic properties of cylindrical quantum dots will be analysed with the help of two-time temperature Green's functions.

Two types of Green functions will be found for axial phonons: one is of the type displacement-displacement, while another is of the type momentum-momentum.

The Green's function of two interacted particles of the type displacement-displacement is defined as thermal mean value of the commutator of two displacement operators, in the Heisenberg picture,  $\alpha_n(t)$  and  $\alpha_m(0)$ :

$$A_{nm}(t) \equiv \langle\langle \alpha_n(t) | \alpha_m(0) \rangle\rangle = \theta(t) \langle [\alpha_n(t), \alpha_m(0)] \rangle, \quad (4)$$

where  $\langle \alpha_n(t) \alpha_m(t') \rangle = \text{Tr} \{ \alpha_n(t) \alpha_m(t') \exp(-H/k_B T) \}$  and  $\langle\langle \dots \rangle\rangle$  is only a notation.

Its equations of motion can be written as:

$$\frac{d}{dt} A_{nm}(t) = \theta(t) \langle [\dot{\alpha}_n(t), \alpha_m(0)] \rangle, \quad (5)$$

where  $\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0 \end{cases}$  is Heaviside's step function.

Using the equation of motion

$$\dot{\alpha}_n = \frac{1}{i\hbar} [\alpha_n, H_a] = \frac{P_{na}}{M_{mol}}, \quad (6)$$

we reduce (5) at:

$$\frac{d}{dt} A_{nm}(t) = \frac{1}{M_{mol}} \ll p_{n\alpha}(t) | \alpha_m(0) \gg. \quad (7)$$

Now look for Green's function  $\ll p_{n\alpha}(t) | \alpha_m(0) \gg$ :

$$\begin{aligned} \frac{d}{dt} \ll p_{n\alpha}(t) | \alpha_m(0) \gg &= -i\hbar \delta_{nm} \delta(t) C_a \left[ \ll \alpha_{n+1}(t) | \alpha_m(0) \gg + \right. \\ &\left. + \ll \alpha_{n-1}(t) | \alpha_m(0) \gg - 2 \ll \alpha_n(t) | \alpha_m(0) \gg \right]. \end{aligned} \quad (8)$$

Differentiating (5) with respect to time and substituting (6) we obtain the equation:

$$\frac{d^2}{dt^2} A_{nm}(t) = -\frac{i\hbar}{M_{mol}} \delta_{nm} \delta(t) + \frac{k_a}{M_{mol}} \left[ A_{n+1,m} + A_{n-1,m} - 2A_{n,m} \right]. \quad (9)$$

After time-frequency Fourier-transformation:

$$A_{nm}(t) = \int_{-\infty}^{+\infty} d\omega e^{-i\omega t} A_{nm}(\omega), \quad \delta(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega e^{-i\omega t}, \quad (10)$$

we obtain for (9) the follow relation:

$$A_{n+1,m}(\omega) + A_{n-1,m}(\omega) + \gamma A_{n,m}(\omega) = \Phi_{n,m}; \quad \Phi_{n,m} = \frac{i\hbar}{2\pi} \frac{1}{k_a} \delta_{n,m}, \quad (11)$$

with

$$\gamma = \frac{M_{mol}}{k_a} \omega^2 - 2. \quad (12)$$

Since the layers  $m = -1$  and  $m = M + 1$  are absent, it is clear that  $A_{-1,m}(\omega) = A_{N+1,m}(\omega) = 0$ . In boundary layers 0 and  $M$  change Hook's constants, but we shall assume that their changes are negligible. Taking into account all said before, becomes clear that (11) goes over to three systems of difference equations:

$$A_{n+1,m} + A_{n-1,m} + \gamma A_{n,m} = \Phi_{n,m}; \quad 1 \leq n \leq M - 1, \quad (13)$$

$$A_{1,m} + \gamma A_{0,m} = \Phi_{0,m}; \quad n = 0, \quad (14)$$

$$A_{M-1,m} + \gamma A_{M,m} = \Phi_{M,m}; \quad n = M. \quad (15)$$

The solution of the system (13)-(15) will be looked for in the form:

$$A_{n,m} = \sum_{\mu=1}^{M+1} a_{\mu m} \sin(n+1) \varphi_{\mu}, \quad (16)$$

where the parameter  $\varphi_\mu$  is playing role of wave vector is given by:

$$\varphi_\mu = \frac{\pi\mu}{M+2}; \quad \mu = 1, 2, 3, \dots, M+1 \quad (17)$$

and the index  $\mu$  characterizing wave vector in the direction of the chain can't take values 0 and  $M+2$  because it leads to  $\sin(M+1)\varphi_\mu = 0$ .

Taking into account that:

$$a_{\mu m}(\omega) = \frac{2}{M+2} G_\mu(\omega) \sin(m+1)\varphi_\mu, \quad (18)$$

we obtain from replacement (16) in (13) and after some elementary calculus in (14), (15):

$$G_\mu(\omega) = \frac{i\hbar}{2\pi} \frac{1}{k_a} \frac{1}{2\cos\varphi_\mu + \gamma}. \quad (19)$$

After substitution parameter  $\gamma$  from (12) we obtain:

$$G_\mu(\omega) = \frac{1}{M_{mol}} \frac{i\hbar}{2\pi} \frac{1}{\omega^2 - \omega_\mu^2} \quad (20)$$

or, in terms of simple fractions:

$$G_\mu(\omega) = \frac{i\hbar}{2\pi} \frac{1}{2M_{mol}\omega_\mu} \left( \frac{1}{\omega - \omega_\mu} - \frac{1}{\omega + \omega_\mu} \right); \quad \omega_\mu^2 = 4 \frac{k_a}{M_{mol}} \sin^2 \frac{\varphi_\mu}{2}. \quad (21)$$

It can be seen that the minimum frequency in short molecular chain:

$$(\omega_\mu)_{\min} = 2 \sqrt{\frac{k_a}{M_{mol}}} \sin \frac{\pi}{M+2} \quad (22)$$

is different from zero. In the infinite chain the minimal frequency is equal to zero. Since we deal with acoustic phonons, the above conclusion practically means that acoustic phonons in short chain possess energy gap, *i.e.* for excitation of central phonons in short chain the minimal, different from zero, energy must be inserted. This fact has positive repercussions to realization of superconductive effect in short chains.

With help of spectral intensity  $I_G(\omega)$  one can find configuration correlation functions [5]:

$$\langle \alpha(0)\alpha(t) \rangle_\mu = \int_{-\infty}^{+\infty} d\omega e^{-i\omega t} I_G(\omega),$$

$$I_G(\omega) = \frac{\hbar}{2M_{mol}\omega_\mu} \left[ \frac{\delta(\omega - \omega_\mu)}{e^{\frac{\hbar\omega}{\Theta}} - 1} - \frac{\delta(\omega + \omega_\mu)}{e^{\frac{\hbar\omega}{\Theta}} - 1} \right], \quad (23)$$

$$\begin{aligned} \langle \alpha(0)\alpha(t) \rangle = & \frac{2}{M+2} \frac{\hbar}{2M_{mol}} \sum_{\mu=1}^{M+1} \frac{1}{\omega_\mu} \left[ \frac{e^{-it\omega_\mu}}{e^{\frac{\hbar\omega_\mu}{\Theta}} - 1} - \frac{e^{it\omega_\mu}}{e^{\frac{\hbar\omega_\mu}{\Theta}} - 1} \right] \cdot \\ & \cdot \sin(n+1)\varphi_\mu \sin(m+1)\varphi_\mu, \end{aligned} \quad (24)$$

where  $\Theta = k_B T$ .

We prefer to use  $\Theta$  instead  $\beta = \frac{1}{k_B T}$ , on the one hand because of the relevance on the next calculations. On the other hand, we will to avoid the confusion between  $\beta = \frac{1}{k_B T}$  and  $\beta_n$  – molecular displacements in discs along lines connecting two nearest molecules of the polygon.

Carrying out the calculation procedure quite similar to the calculation procedure for Green's function we obtain the correlation function in momentum space ( $\mu$ -space)  $\langle p_{m\alpha}(0)p_{n\alpha}(t) \rangle_\mu$ :

$$\begin{aligned} \langle p_{m\alpha}(0)p_{n\alpha}(t) \rangle = & \frac{1}{M+2} \frac{\hbar C_a}{\Omega_a^2} \sum_{\mu=1}^{M+1} \omega_\mu \left[ \frac{e^{-it\omega_\mu}}{e^{\frac{\hbar\omega_\mu}{\Theta}} - 1} - \frac{e^{it\omega_\mu}}{e^{\frac{\hbar\omega_\mu}{\Theta}} - 1} \right] \cdot \\ & \cdot \sin(n+1)\varphi_\mu \sin(m+1)\varphi_\mu. \end{aligned} \quad (25)$$

The relation obtained will be used for calculation of some thermodynamic characteristics for cylindrical quantum dots, or more precise, for calculation of the contributions of axial phonons to thermodynamic properties.

Phonon characteristics in discs will be examined by Green's functions of the type displacement-displacement:

$$D_{nm}(t) \equiv \langle \langle \beta_n(t) | \beta_m(0) \rangle \rangle = \theta(t) \langle [\beta_n(t), \beta_m(0)] \rangle. \quad (26)$$

Following the same procedure that in the case of axial phonons, we obtain for the configuration correlation functions the formula:

$$\langle \beta_m(0)\beta_n(t) \rangle = \frac{1}{N+1} \frac{\hbar}{2M_{mol}} \sum_{\nu=1}^{N+1} \frac{1}{\omega_\nu} \left[ \frac{e^{-it\omega_\nu}}{e^{\frac{\hbar\omega_\nu}{\Theta}} - 1} - \frac{e^{it\omega_\nu}}{e^{\frac{\hbar\omega_\nu}{\Theta}} - 1} \right] e^{i(n-m)\varphi_\nu}, \quad (27)$$

where the parameter :  $\varphi_\nu = \frac{2\pi\nu}{N+1}$   $\nu = 0, 1, 2, 3, \dots, N+1$ .

The correlation function in momentum space is given by:

$$\langle p_{m\beta}(0) p_{n\beta}(t) \rangle = \frac{1}{N+1} \frac{\hbar}{M_{mol}} \sum_{v=1}^{N+1} \omega_v \left[ \frac{e^{-it\omega_v}}{e^{\frac{\hbar\omega_v}{\Theta}} - 1} - \frac{e^{it\omega_v}}{e^{\frac{\hbar\omega_v}{\Theta}} - 1} \right] e^{i(n-m)\varphi_v}. \quad (28)$$

The relation obtained will be used for calculation of the contributions of phonons in discs to thermodynamic properties.

### 3. RESULTS FOR THERMODYNAMIC PARAMETERS OF CYLINDRICAL NANORODS

It should be noticed in the beginning, that thermodynamical properties will be investigated at low temperatures, when  $e^{\frac{\hbar\omega}{\Theta}} \gg 1$ . In this case the second term in correlation functions (24) and (26) approximately goes over to  $e^{-i\omega t}$ . This term does not depend on temperature and obviously comes from zero oscillations. As it was said earlier, the contributions of zero oscillations will not be taken into account, and consequently this term will be omitted in further analyses.

In further will be used the following expressions for configurational correlation functions, obtained from (25) and (27) with above assumption:

$$\langle \alpha(0) \alpha(t) \rangle = \frac{\hbar}{M_{mol}} \frac{1}{M+2} \sum_{\mu=1}^{M+1} \frac{1}{\omega_{\mu}} e^{-\frac{\hbar\omega}{\Theta} - it\omega_{\mu}} \cdot \sin(n+1)\varphi_{\mu} \sin(m+1)\varphi_{\mu}, \quad (29)$$

$$\langle \beta_m(0) \beta_n(t) \rangle = \frac{\hbar}{2M_{mol}} \frac{1}{N+1} \sum_{v=1}^{N+1} \frac{1}{\omega_v} e^{-\frac{\hbar\omega}{\Theta} - it\omega_v + i(n-m)\varphi_v}. \quad (30)$$

The same requirements for momentum correlation functions give:

$$\langle p_{m\alpha}(0) p_{n\alpha}(t) \rangle = \frac{\hbar}{M_{mol}} \frac{1}{M+2} \sum_{\mu=1}^{M+1} \omega_{\mu} e^{-\frac{\hbar\omega}{\Theta} - it\omega_{\mu}} \cdot \sin(n+1)\varphi \sin(m+1)\varphi, \quad (31)$$

$$\langle p_{m\beta}(0) p_{n\beta}(t) \rangle = \frac{\hbar}{M_{mol}} \frac{1}{N+1} \sum_{v=1}^{N+1} \omega_v e^{-\frac{\hbar\omega}{\Theta} - it\omega_v + i(n-m)\varphi_v}. \quad (32)$$

The following approximations will be used, too:

a. The approximation of small wave vectors:

$$\omega_v \approx \frac{\pi\Omega_d}{M+2}; \quad \omega_{\mu} \approx \frac{2\pi\Omega_a}{N+1}; \quad \Omega_a = \sqrt{\frac{k_a}{M_{mol}}}; \quad \Omega_d = \sqrt{\frac{k_d}{M_{mol}}}.$$

- b. The finite geometrical progression whose quotient contains factor  $e^{-\frac{C}{\Theta}}$  will be approximately considered as infinite ones.
- c. The mathematical forms of the type  $\frac{e^x}{(e^x - 1)^2}$  and  $\ln(1 + e^{-x})$  will be approximately taken equal to  $e^{-x}$ , if  $x$  contains factor  $-\frac{C}{\Theta}$ .

The total internal energy of cylindrical nanorods is the sum of the internal energy of axial phonons and of the internal energy of disc phonons:

$$\langle H \rangle = \langle H_a \rangle + \langle H_d \rangle, \quad (33)$$

$$U_a = \langle H_a \rangle = \hbar\Omega_a e^{-\frac{\pi\hbar\Omega_a}{(M+2)\Theta}} \left\{ \frac{\pi}{4(M+2)} + \frac{M+2}{\pi} \sin^2 \frac{\pi}{2(M+2)} - \frac{1}{2\pi} \sin^2 \frac{\pi}{M+2} \right\}, \quad (34)$$

$$U_d = \langle H_d \rangle = \hbar\Omega_d e^{-\frac{2\pi\hbar\Omega_d}{(N+1)\Theta}} \left\{ \frac{\pi}{2(N+1)} + \frac{N+1}{2\pi} \sin^2 \frac{\pi}{2(N+1)} \right\}. \quad (35)$$

The specific heat of cylindrical quantum dot can be found by differentiating the internal energy with respect to temperature. So we obtain in accordance with general formula:

$$C_V = \frac{\partial \langle H \rangle}{\partial T} = \frac{\partial \langle H \rangle}{\partial \Theta} \frac{\partial \Theta}{\partial T} \quad (36)$$

the following result:

$$C_V = \frac{\pi k_B}{M+2} \left( \frac{\hbar\Omega_a}{\Theta} \right)^2 e^{-\frac{\pi\hbar\Omega_a}{(M+2)\Theta}} \left\{ \frac{\pi}{4(M+2)} + \frac{M+2}{\pi} \sin^2 \frac{\pi}{2(M+2)} - \frac{1}{2\pi} \sin^2 \frac{\pi}{M+2} \right\} + \frac{2\pi k_B}{N+1} \left( \frac{\hbar\Omega_d}{\Theta} \right)^2 e^{-\frac{2\pi\hbar\Omega_d}{(N+1)\Theta}} \left\{ \frac{\pi}{2(N+1)} + \frac{N+1}{2\pi} \sin^2 \frac{\pi}{2(N+1)} \right\}. \quad (37)$$

From the results obtained, it can see that the internal energy as well as the specific heat decrease exponentially at low temperatures. It means that cylindrical nanorods behave as a rigid body at low temperature, *i.e.*, population of mechanical oscillation is very small. This makes suitable conditions for appearance of high temperature superconductivity.

At extremely low temperatures the specific heat is given by:

$$C_V = k_B \left( \frac{\pi\hbar}{M+2} \right)^2 \Omega_a \frac{1}{\Theta^2} e^{-\frac{\pi\hbar\Omega_a}{(M+2)\Theta}}. \quad (38)$$



It is seen that specific heat of cylindrical quantum nanodot is exponentially small.

In the middle temperature range the formula for specific heat of cylindrical quantum nanodot is:

$$C_V = 2k_B (M + 2) \frac{\Theta}{\pi \hbar \Omega_a}. \quad (39)$$

As it is seen specific heat linearly increases with temperature. It should be pointed out that specific heat in bulk structure behaves in the same way as specific heat of nanostructures in middle temperature range but in the interval  $\Theta \in [0, \Theta_M]$ , where  $\Theta_M \sim \Theta_D$  ( $\Theta_D$  is Debye's temperature).

#### 4. CONCLUSIONS

The method for calculation of Green's function of spatially deformed structure appears here and is very use full for to obtain some thermodynamic properties of the nanorods. The usual approach in analyses of spatially deformed structures, consisting in calculation of spatially diagonal Green's functions in the broken symmetry direction cannot reproduce the spatial dependence of such structures [8–10]. In this approach the spectral dependence of physical characteristics of deformed structures was lost. The new method presented here doesn't suffer from this failure.

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