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Highlights

- The momentum-momentum Green's functions were used to calculate the diffusion tensor.
- These functions enter into Kubo's formula defining diffusion properties of the system.
- Boundary conditions are included through the Hamiltonian of the film-structure.
- The elements of the diffusion tensor express discrete behavior of the dispersion law
- The diffusion tensor elements are temperature independent.

Diffusion of phonons through (along and across) the ultrathin crystalline films

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Abstract:

Instead of usual approach, applying displacement-displacement Green's functions, the momentum-momentum Green's functions will be used to calculate the diffusion tensor. With this type of Green's function we have calculated and analyzed dispersion law in film-structures. A small number of phonon energy levels along the direction of boundary surfaces joint of the film are discrete-ones and in this case standing waves could occur. This is consequence of quantum size effects. These Green's functions enter into Kubo's formula defining diffusion properties of the system and possible heat transfer direction through observed structures. Calculation of the diffusion tensor for phonons in film-structure requires solving of the system of difference equations. Boundary conditions are included into mentioned system through the Hamiltonian of the film-structure. It has been shown that the diagonal elements of the diffusion tensor express discrete behavior of the dispersion law of elementary excitations. More important result is – that they are temperature independent and that their values are much higher comparing with bulk structures. This result favors better heat conduction of the film, but in direction which is perpendicular to boundary film surface. In the same time this significantly favors appearance 2D superconducting surfaces inside the ultra-thin crystal structure, which are parallel to the boundary surface.

Key words: Thin films, phonons, Green's functions, diffusion tensor

1 Introduction

Phonons are quasi-particles which represent crystal vibrations and they are responsible¹ for heat transfer in all solid materials [1–4]. Furthermore, phonons could affect on electron mobility and optical properties of materials. Phonons, like electrons, could take various energies and form specific dispersion laws depending on the type of crystal oscillation, forming acoustic and optical mode of dispersion branches. Although acoustic phonons

¹Phonons are mainly responsible for heat transfer in insulators and semiconductors, but in metals electrons take significant share in heat processes.

dispersions laws are nearly linear for long-wavelength², this behavior is more complicated with spatial confinement of materials, for example in nanostructure materials [5–9]. Changes of phonon properties in those types of materials are caused by their size, which is comparable with average phonon free path. These facts open opportunity for phonon engineering, i.e. modeling of some characteristic types of nanostructures with desired (or tunable) phonon spectrum and improved (or desirable) electric or thermal properties. Optical phonons on the other hand could be localized in different way – through the electron-phonon scattering rates, rather than through the spatial confinement.

Phonon transport processes determine heat transfer in materials. In nanoscale structures this process is somewhat different from the process in macroscale materials [10–12]. One of the major causes is the fact that in bulk internal scattering processes dominate in heat transfer. If we reduce material to the nanoscale in (at least) one dimension – this leads to the increasing of the phonon scattering (in time units) on the boundaries of nanoscale structures. It is well known that in nanoscale structures surface/volume ratio dramatically increases - so it can be assumed that surface (or boundaries) scattering of phonons dominate (or govern) heat processes in nanomaterials [5–8].

Nanostructures could be highly anisotropic materials, so for this type of structures it could be convenient to describe heat processes with phonon diffusion tensor. Diffusion of heat in dimensionally complex materials is introduced through tensor elements, describing all combinations of phonons diffusion rates [2]. Generally, phonon diffusion tensor could be introduced in isotropic materials (balk or nanostructures) as well, but only with diagonal elements and with all off-diagonal elements equal to zero [1,3,4].

Calculation of phonon diffusion tensor with prediction of phonon dispersion laws and consequently heat transfer processes in nanostructures could yield to better material performance and understanding of phonon engineering [13–15].

Diffusion tensor elements definition through the statistical mean values of velocities [16–18] has necessarily suggested usage of the well known research method based on the two-times temperature depended Green's functions [19–22]. Knowing the Green's functions enables one to find the energy of the ground state of the system, spectrum and the type of elementary excitations, following with thermodynamical properties in equilibrium and non-equilibrium states of the observed system [18–20]. Herein we show the application of Green's functions for defining the way of phonon propagation in bulk-structures and in corresponding ultra-thin crystalline films.

2 Phonon's model

Hamiltonian of the phonon system is given in the form:

$$H = \sum_{\vec{n}} \frac{p_{\vec{n}}^2}{2M_{\vec{n}}} + \sum_{\vec{n}} \frac{C_{\vec{n},\vec{n}\pm\vec{\lambda}}}{2} (u_{\vec{n}}^2 + u_{\vec{n}-\vec{\lambda}}^2 - 2u_{\vec{n}}u_{\vec{n}-\vec{\lambda}}); \quad (1)$$

$$\vec{n} \in (n_x, n_y, n_z); \quad |\vec{\lambda}| = 1,$$

where $M_{\vec{n}} \equiv M$ are molecule masses, $C \equiv C_{\vec{n},\vec{n}\pm\vec{\lambda}}$ – Hook's stretching constants, u are molecule displacements [23–25]. It should be emphasized that the mentioned hamiltonian

²In the same manner optical phonons exhibit no dispersion.

of phonons in the ideal (unbounded) crystalline bulk structure with simple cell is given in the harmonic and nearest neighboring approximation.

Subject of this paper is to examine particularities or changes of properties of ultra thin films, which have the same chemical and crystallographic structure as well as mentioned bulk structures. Model of this film with cross section presented on Fig. 1 contains two boundary surfaces (for $z = 0$ and $z = L \equiv N_z a$, where a is constant of the crystal lattice), i.e. where numbers of crystal planes take values $n_z = 0$ and $n_z = N_z$ with $N_z - 1$ more internal crystal planes, parallel to boundary planes. Thereby observed film has quantum thickness $N_z \leq 10$, while in other directions film being practically unlimited $N_{x,y} \sim 10^8$.

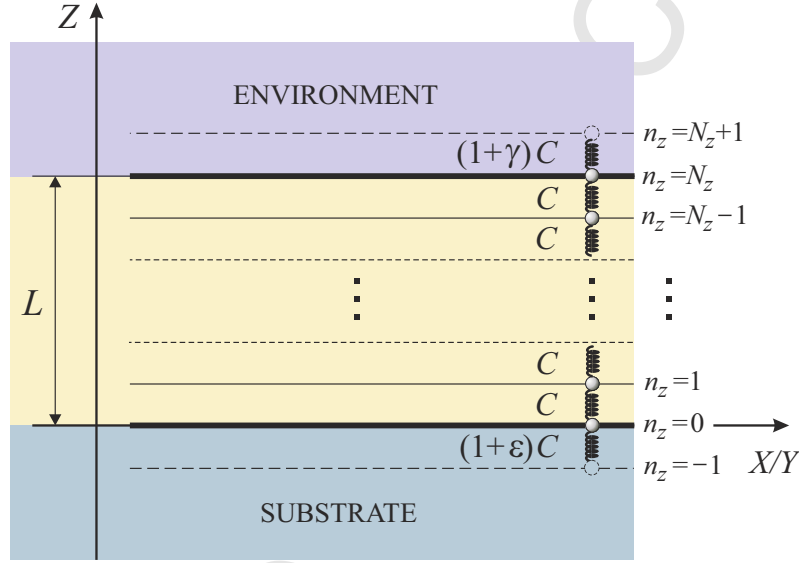


Figure 1: Ultrathin film cross-section in $X(Y) - Z$ plane

We observe ideal thin film³ with cubic crystal structure made on substrate with certain procedure (sputtering, deposition, etc), with basic crystal data given in accordance with the notations on Fig.1):

$$\begin{aligned} C_{\vec{n}, \vec{n} \pm \lambda} = C_{\vec{n} \pm \lambda, \vec{n}} &\equiv C_{n_z, n_z \pm 1} = C_{n_z \pm 1, n_z} \equiv C; & n_z = 1, 2, \dots, N_z - 1; \\ C_{N_z, N_z + 1} = C_{N_z + 1, N_z} &= (1 + \gamma)C, & C_{-1, 0} = C_{0, -1} = (1 + \varepsilon)C, \end{aligned} \quad (2)$$

where ε and γ are real numbers and boundary parameters different from -1 . It is considered that atoms from the boundary planes interact with external medium regardless of the fact that there is no crystal nodes above upper plane (or under lower plane). The boundary motives are "coupled" with modified Hook's forces for the atoms of medium above the film (or atoms of the substrate) [26–29]. In accordance with quoted conditions, elastic constants describing interaction of the boundary planes atoms with external mediums (for example some metal-like substrate and air) are modified with corresponding coefficients ε and γ .

These parameters provide that boundary planes don't behave like a stiff walls, but also define change of elastic interaction. This change of interaction refers to the motive

³Ideal film contains no deformations or distribution of crystal (with no vacancy, impurities etc.). Hence, term "ideal" refers to non-violation crystal structure, and not in sense of spatial limitlessness.

(atoms, ions or molecules) of the boundary planes of the film with the nearest motives of surrounding medium: increasing of interaction with $\varepsilon, \gamma > 0$ or decreasing with $-1 < \varepsilon, \gamma < 0$. In the case of $\varepsilon, \gamma < -1$, characteristic of interaction wouldn't be elastic any more. For $\varepsilon, \gamma = -1$ the stiff walls effect appears, with all boundary surfaces being non-flexible and with all motives inside them being "frozen" along z -direction [30–32]. It should be mentioned that case with $\varepsilon, \gamma = 0$ known as the film with free boundary surfaces, is particularly interesting one, while it has exact analytical solution for the dispersion law.

Hamiltonian of the described crystal film phonon subsystem has the same form as with bulk crystal (1), but the fact that layers for the $n_z \leq -1$ and for the $n_z \geq N_z + 1$ are absent should be taken into consideration, which could be stated with:

$$u_{\alpha; n_x, n_y, j} = 0; \quad -1 \geq j \wedge j \geq N_z + 1; \quad j \notin [0, N_z]. \quad (3)$$

3 Green's functions of phonon system

Consider Green's function impulse-impulse type:

$$G_{\vec{n}\vec{m}}(t) \equiv \langle \langle p_{\vec{n}}(t) | p_{\vec{m}}(0) \rangle \rangle = \Theta(t) \langle [p_{\vec{n}}(t), p_{\vec{m}}(0)] \rangle_0, \quad (4)$$

with equation of motion [20–22]:

$$i\hbar \frac{d}{dt} G_{\vec{n}\vec{m}}(t) = i\hbar \delta(t) \delta_{\vec{n}\vec{m}} + \langle \langle [p_{\vec{n}}(t), H(t)] | p_{\vec{m}}(0) \rangle \rangle, \quad (5)$$

where: the step-function is $\Theta(t) = 0, t < 0$ and $\Theta(t) = 1, t \geq 0$, and $\delta_{\vec{n}\vec{m}}$ is Kronecker's symbol. Calculating the commutator $[p_{\vec{n}}(t), H(t)]$ with initial Hamiltonian of the observed model structure (which includes nearest neighbor: $\vec{m} = \vec{n} \pm \vec{\lambda}; |\vec{\lambda}| = 1$), equation of motion for the Green's function takes the following form:

$$\begin{aligned} \frac{d}{dt} \langle \langle p_{\vec{n}}(t) | p_{\vec{m}}(0) \rangle \rangle &= C_{\vec{n}} [\langle \langle u_{\vec{n}+\vec{\lambda}}(t) | p_{\vec{m}}(0) \rangle \rangle + \\ &+ \langle \langle u_{\vec{n}-\vec{\lambda}}(t) | p_{\vec{m}}(0) \rangle \rangle - 2 \langle \langle u_{\vec{n}}(t) | p_{\vec{m}}(0) \rangle \rangle]. \end{aligned} \quad (6)$$

In this equation Green's functions of movement–momentum type appear. When they are calculated, the following equalities are obtained:

$$\begin{aligned} \frac{d}{dt} \langle \langle u_{\vec{n}}(t) | p_{\vec{m}}(0) \rangle \rangle &= i\hbar \delta_{\vec{n}, \vec{m}} \delta(t) + \frac{1}{M} \langle \langle p_{\vec{n}}(t) | p_{\vec{m}}(0) \rangle \rangle; \\ \frac{d}{dt} \langle \langle u_{\vec{n}+\vec{\lambda}}(t) | p_{\vec{m}}(0) \rangle \rangle &= i\hbar \delta_{\vec{n}+\vec{\lambda}, \vec{m}} \delta(t) + \frac{1}{M} \langle \langle p_{\vec{n}+\vec{\lambda}}(t) | p_{\vec{m}}(0) \rangle \rangle; \\ \frac{d}{dt} \langle \langle u_{\vec{n}-\vec{\lambda}}(t) | p_{\vec{m}}(0) \rangle \rangle &= i\hbar \delta_{\vec{n}-\vec{\lambda}, \vec{m}} \delta(t) + \frac{1}{M} \langle \langle p_{\vec{n}-\vec{\lambda}}(t) | p_{\vec{m}}(0) \rangle \rangle, \end{aligned} \quad (7)$$

where $\delta_{\vec{n}, \vec{m}}$ and $\delta_{\vec{n} \pm \vec{\lambda}, \vec{m}}$ are Kronecker's operators, and $\delta(t)$ is Dirac's delta-function.

If Fourier's transformations of frequency – time type are introduced:

$$\langle \langle \alpha_{\vec{n}}(t) | \beta_{\vec{m}}(0) \rangle \rangle = \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \langle \langle \alpha_{\vec{n}} | \beta_{\vec{m}} \rangle \rangle_{\omega},$$

when Fourier image $\langle\langle u_{\vec{n}}|p_{\vec{m}}\rangle\rangle_{\omega}$ is substituted into equation for $\langle\langle p_{\vec{n}}|p_{\vec{m}}\rangle\rangle_{\omega}$, one finally obtains:

$$\begin{aligned} \langle\langle p_{\vec{n}}|p_{\vec{m}}\rangle\rangle_{\omega} &= \frac{i\hbar C_{\vec{n}}}{\pi \omega^2} + \frac{C_{\vec{n}}}{M \omega^2} \left(2 \langle\langle p_{\vec{n}}|p_{\vec{m}}\rangle\rangle_{\omega} - \right. \\ &\quad \left. - \langle\langle p_{\vec{n}+\vec{\lambda}}|p_{\vec{m}}\rangle\rangle_{\omega} - \langle\langle p_{\vec{n}-\vec{\lambda}}|p_{\vec{m}}\rangle\rangle_{\omega} \right). \end{aligned} \quad (8)$$

The system of difference equations for Green's functions follows from here:

$$\begin{aligned} \langle\langle p_{\vec{n}+\vec{\lambda}}|p_{\vec{m}}\rangle\rangle_{\omega} + \langle\langle p_{\vec{n}-\vec{\lambda}}|p_{\vec{m}}\rangle\rangle_{\omega} + \\ + \left(\frac{M\omega^2}{C_{\vec{n}}} - 2 \right) \langle\langle p_{\vec{n}}|p_{\vec{m}}\rangle\rangle_{\omega} = \frac{i\hbar}{2\pi C_{\vec{n}}} \delta_{\vec{n},\vec{m}}, \end{aligned} \quad (9)$$

By solving this system of difference equations we find the Green's functions which figures in it. For the sake of simplicity we introduce the following marks $\langle\langle p_{\vec{n}\pm\vec{\lambda}}|p_{\vec{m}}\rangle\rangle_{\omega} \equiv G_{\vec{n}\pm\vec{\lambda},\vec{m}}(\omega)$ and $\langle\langle p_{\vec{n}}|p_{\vec{m}}\rangle\rangle_{\omega} \equiv G_{\vec{n},\vec{m}}(\omega)$, so eq.(9) turns into:

$$G_{\vec{n}+\vec{\lambda},\vec{m}}(\omega) + G_{\vec{n}-\vec{\lambda},\vec{m}}(\omega) + S_{\vec{n}}(\omega) G_{\vec{n},\vec{m}}(\omega) = R \delta_{\vec{n},\vec{m}}, \quad (10)$$

where are: $S_{\vec{n}}(\omega) \equiv (\omega/\Omega_{\vec{n}})^2 - 2$, $\Omega_{\vec{n}}^2 = C_{\vec{n}}/M$ and $R \equiv i\hbar/(2\pi C_{\vec{n}})$. This equation de facto represents system of $(N_x + 1)(N_y + 1)(N_z + 1) \rightarrow \infty$ of identical non-homogeneous difference equations of the second order (because $N_{x,y,z} \sim 10^8$).

3.1 Bulk-case

In this case, solution of the difference equation (10) could be calculated by spatial Fourier transformation ($\vec{n} \rightarrow \vec{k}$) of the type:

$$G_{\vec{n},\vec{m}}(\omega) = \frac{1}{N} \sum_{\vec{k}} e^{-i(\vec{n}-\vec{m})\vec{k}} G_{\vec{k}}(\omega); \quad \delta_{\vec{n},\vec{m}} = \frac{1}{N} \sum_{\vec{k}} e^{-i(\vec{n}-\vec{m})\vec{k}},$$

which transforms it to algebraic equation. After slight ordering operations, solutions for the Green's functions takes the following form:

$$G_{\vec{k}}(\omega) = \frac{i\hbar}{4\pi M \Omega_b} \left(\frac{1}{\omega - \omega_{\vec{k}}} - \frac{1}{\omega + \omega_{\vec{k}}} \right). \quad (11)$$

Based on the standard theory for the Green's functions [20–22], we could calculate phonon dispersion law for the bulk-structure from the poles of the Green's functions:

$$E_{\vec{k}} \equiv \hbar \omega_{\vec{k}} = 2 E_b \sqrt{\sin^2 \frac{ak_x}{2} + \sin^2 \frac{ak_y}{2} + \sin^2 \frac{ak_z}{2}}, \quad (12)$$

where $E_b \equiv \hbar \Omega_b = \hbar \sqrt{C/M}$. To compare this relation with the appropriate one for the film structure, we will re-write in following (dimensionless) form:

$$\begin{aligned} \mathcal{E}_{\vec{k}} = \mathcal{F}_{xy} + \mathcal{G}_z; \quad \mathcal{E}_{\vec{k}} &\equiv \left(\frac{E_{\vec{k}}}{2 E_b} \right)^2; \\ \mathcal{F}_{xy} = \sin^2 \frac{ak_x}{2} + \sin^2 \frac{ak_y}{2}; \quad \mathcal{G}_z &= \sin^2 \frac{ak_z}{2}. \end{aligned} \quad (13)$$

Expression (12) represents well known acoustic phonon spectrum [18–20]. In classical representation this spectrum takes form $E_{\vec{k}} \equiv E(k)$, for all values $k_i \in [0, \pi/a]$, $i = (x, y, z)$ from the first Brillouin zone.

Unlike this, we would graphically represent $\mathcal{E}_{\vec{k}}$ in function of \mathcal{F}_{xy} , for the different values of the function \mathcal{G}_z – in form of parametric function. As k_i being changing in interval $[0, \pi]$, so the \mathcal{F}_{xy} and \mathcal{G}_z change in interval: $\mathcal{F}_{xy} \in [0, 2]$ and $\mathcal{G}_{xy} \in [0, 1]$. From equation (13) one can see that $\mathcal{E}_{\vec{k}}$ is linear function \mathcal{F}_{xy} for $\mathcal{G}_z = \text{const}$, i.e. $\mathcal{E}_{\vec{k}}|_{\mathcal{G}_z=0} \in [0, 2]$ and $\mathcal{E}_{\vec{k}}|_{\mathcal{G}_z=1} \in [1, 3]$. Those two parallel lines determine boundaries of the zone with changing of the $\mathcal{E}_{\vec{k}}$: the first determine lower, and the second determine upper boundary. Between these two boundaries there are practically infinite parallel lines – possible phonon energies. Hence, this zone is continual and presented in Fig. 2.

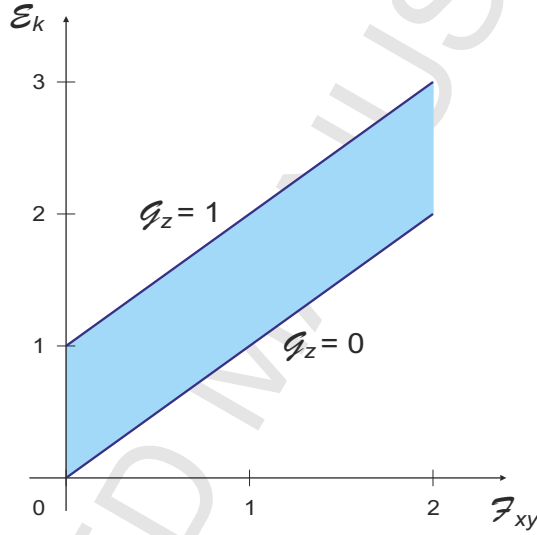


Figure 2: Energy spectra of phonons in simple bulk-crystals

3.2 Film-case

Considering boundary conditions in film structures, instead one difference equation (10) which has represented all nodes of crystal, here we obtain along z -axes the system of $N_z + 1$ difference equations:

– for $n_z = 0$,

$$\begin{aligned}
 & G_{n_x+1, n_y, 0; m_x, m_y, m_z} + G_{n_x-1, n_y, 0; m_x, m_y, m_z} + \\
 & + G_{n_x, n_y+1, 0; m_x, m_y, m_z} + G_{n_x, n_y-1, 0; m_x, m_y, m_z} + \\
 & + \left(\frac{\omega}{\Omega}\right)^2 G_{n_x, n_y, 0; m_x, m_y, m_z} + G_{n_x, n_y, 1; m_x, m_y, m_z} - \\
 & - (6 + \varepsilon) G_{n_x, n_y, 0; m_x, m_y, m_z} = R \delta_{n_x, m_x} \delta_{n_y, m_y} \delta_{0, m_z},
 \end{aligned} \tag{14}$$

– for $1 \leq n_z \leq N_z - 1$,

$$\begin{aligned}
 & G_{n_x+1, n_y, n_z; m_x, m_y, m_z} + G_{n_x-1, n_y, n_z; m_x, m_y, m_z} + \\
 & + G_{n_x, n_y+1, n_z; m_x, m_y, m_z} + G_{n_x, n_y-1, n_z; m_x, m_y, m_z} + \\
 & + G_{n_x, n_y, n_z+1; m_x, m_y, m_z} + G_{n_x, n_y, n_z-1; m_x, m_y, m_z} + \\
 & + \left(\frac{\omega}{\Omega}\right)^2 G_{n_x, n_y, n_z; m_x, m_y, m_z} - 6 G_{n_x, n_y, n_z; m_x, m_y, m_z} = R \delta_{n_x, m_x} \delta_{n_y, m_y} \delta_{n_z, m_z},
 \end{aligned} \tag{15}$$

– for $n_z = N_z$,

$$\begin{aligned}
 & G_{n_x+1, n_y, N_z; m_x, m_y, m_z} + G_{n_x-1, n_y, N_z; m_x, m_y, m_z} + \\
 & + G_{n_x, n_y+1, N_z; m_x, m_y, m_z} + G_{n_x, n_y-1, N_z; m_x, m_y, m_z} + \\
 & + \left(\frac{\omega}{\Omega}\right)^2 G_{n_x, n_y, N_z; m_x, m_y, m_z} + G_{n_x, n_y, N_z-1; m_x, m_y, m_z} - \\
 & - (6 + \gamma) G_{n_x, n_y, N_z; m_x, m_y, m_z} = R \delta_{n_x, m_x} \delta_{n_y, m_y} \delta_{N_z, m_z}.
 \end{aligned} \tag{16}$$

Applying partial spatial Fourier transformation (due to the breaking of the symmetry along z -axes)

$$G_{n_x, n_y, n_z; m_x, m_y, m_z}(\omega) = \frac{1}{N} \sum_{k_x, k_y} e^{-ia[(n_x-m_x)k_x + (n_y-m_y)k_y]} G_{n_z, m_z}(k_x, k_y; \omega) \tag{17}$$

onto system of equations (14) – (16), and with small algebraic operations we obtain next system of equations:

$$(\varrho_k - \varepsilon) G_{0, m_z} + G_{1, m_z} = R \delta_{0, m_z} \tag{18}$$

$$\vdots \quad \vdots \quad \vdots \quad \vdots$$

$$G_{n_z-1, m_z} + \varrho_k G_{n_z, m_z} + G_{n_z+1, m_z} = R \delta_{n_z, m_z} \tag{19}$$

$$\vdots \quad \vdots \quad \vdots \quad \vdots$$

$$G_{N_z-1, m_z} + (\varrho_k - \gamma) G_{N_z, m_z} = R \delta_{N_z, m_z} \tag{20}$$

where are: $G_{n_z, m_z} \equiv G_{n_z m_z}(k, \omega)$, $k = \sqrt{k_x^2 + k_y^2}$ and

$$\begin{aligned}
 \varrho_k & \equiv \varrho_k(\omega) = S_b - 4 \mathcal{F}_{xy} \equiv \varrho = \\
 & = \frac{\omega^2}{\Omega_b^2} - 4 \sin^2 \frac{ak_x}{2} - 4 \sin^2 \frac{ak_y}{2} - 2.
 \end{aligned} \tag{21}$$

We calculate the system of equations (18) – (20) introducing substitution:

$$G_{n_z m_z}(k, \omega) = A \sin n_z k_z a + B \sin (n_z - 1) k_z a, \tag{22}$$

where a -is lattice constant, k_z is component of wave vector along z -axes, A and B are constants which could be calculated from boundary conditions. If we take this expression into system (18) – (20) and slightly arrange, we obtain:

$$G_{n_z m_z}(k, \omega) = \frac{i\hbar}{2\pi M} \frac{\omega_k}{\Omega} \frac{1}{\omega^2 - \omega_k^2}, \tag{23}$$

where are

$$\begin{aligned}\omega_{\vec{k}} &\equiv \omega_{k_x, k_y, k_z} = 2\Omega \sqrt{\sin^2 \frac{ak_x}{2} + \sin^2 \frac{ak_y}{2} + \sin^2 \frac{ak_z}{2}}, \\ \Omega &\equiv \sqrt{\frac{C}{M}}; \quad k_x = \frac{\pi\nu_x}{N_x a}; \quad k_y = \frac{\pi\nu_y}{N_y a}; \\ \nu_{x/y} &\in \left[-\frac{N_{x/y}}{2}, +\frac{N_{x/y}}{2} \right]; \quad N_{x/y} \sim 10^8,\end{aligned}\quad (24)$$

while we get k_z as solution of transcendental equation:

$$\cot(N_z - 1)ak_z = \frac{4 \cos^3 ak_z + 2(\varepsilon + \gamma) \cos^2 ak_z + (\varepsilon\gamma - 3) \cos ak_z + \varepsilon\gamma}{\sin ak_z [2(\varepsilon + \gamma) \cos ak_z - 4 \cos^2 ak_z - (1 + \varepsilon\gamma)]}. \quad (25)$$

In the "cut-off" case (for: $\varepsilon = \gamma = 0$) – crystalline film with free surfaces:

$$k_z = \frac{\pi\nu_z}{a(N_z + 2)}; \quad \nu_z = 1, 2, 3, \dots, N_z + 1. \quad (26)$$

One can see that k_x and k_y levels are equidistant and practically their number is infinite, while k_z levels lose their equidistant nature, due to the confinement of structure with their number being $N_z + 1$, $N_z \leq 10$.

Based on eqs.(24) and (26), dispersion law can be rewrite in almost same form as for bulk, eq. (13), i.e.:

$$\begin{aligned}\mathcal{E}_{\vec{k}} &\equiv \mathcal{E}_k(k_z) = \mathcal{F}_{xy} + \mathcal{G}(z); & \mathcal{E}_{\vec{k}} &\equiv \left(\frac{\hbar \omega_{\vec{k}}}{2E_b} \right)^2; \\ \mathcal{F}_{xy} &= \sin^2 \frac{ak_x}{2} + \sin^2 \frac{ak_y}{2}; & \mathcal{G}(z) &= \sin^2 \frac{ak_z}{2},\end{aligned}\quad (27)$$

but function $\mathcal{G}(z)$ is discrete one and has as many values ($N_z + 1$) as values of k_z – which is defined with (26).

On the Fig. 3 dispersion law for the crystalline film with free surfaces and with four layers in z -direction ($N_z + 1 = 5$) is shown. It is evident that inside continual bulk zone there are 5 discrete energy levels in total. Also, it is evident that the lowest level is always higher than zero (in bulk the lowest level fall down to zero!), and that means that in film structures optical phonons occur! Similarly, the highest level is below bulk maximum. This is surely quantum size effect (QSE).

Now it should be noticed that from the form of function dependence $\mathcal{G}(z) \equiv \mathcal{G}(\nu_z) = \sin^2 \frac{\pi \nu_z}{2 N_z + 2}$, $\nu_z = 1, 2, 3, \dots, N_z + 1$ one can conclude that along z -direction standing wave can be formed. Along x and y direction form plane waves, similar to bulk where plane waves form along all directions.

During our research paper we have been analysing model of ultrathin crystalline film (UTCF) with perturbed boundary parameters, therefore, we "included" both effects which can occur at nanoscopic samples: quantum size (QSE) and confinement effects (CFE). In studies of effect of this process on the macroscopic properties of these samples (e.g., their thermodynamic behavior), the problem of theoretical analysis is finding dispersion law of elementary excitations in exact – analytical form.

In the phonon subsystems in nano-structures, the only analytically solvable problem of finding phonon state is in the case of "free surfaces" (when the boundary values of parameters are equal zero).

This case is considered in our work and our primary objective was to examine the impact of the QSE on thermal propagation through UTCF. Unusual behavior has indicated the occurrence of gap in the phonon spectrum, which is a direct consequence of the QSE and only along the directions where there are nanoscopic borders. The size of that gap, to later calculations of UTCF thermal properties, we were able to determine only in the analytically solvable case, therefore for the model UTCF with free surfaces. And that's what we did and showed these results!

It is true that we "have lost" a part of physically interesting processes that are associated with the appearance of one or two localized phonon state of the boundary surfaces, which may apply only to larger and positive values of boundary parameters. This research, with the help of our own developed and adapted for the UTCF software package, are being finalized and will be presented in our next manuscript. It is evident that the CFE (in the form of changes in the values of the boundary parameters from -100% to +250%), only changes (increases or decreases) already achieved QSE.

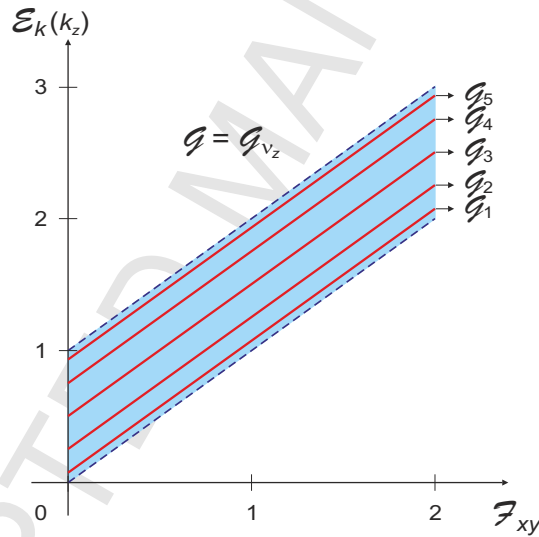


Figure 3: Energy spectra of phonons in ultrathin crystalline film

Certainly, another picture/situation will be obtained with confinement effects (CFE) included, while for different values of boundary parameters ε and γ energy level position could be drastically changed. However this is not subject of this research, and we are going back to the main problem – calculation of phonon diffusion tensor in film, which could be done after finding dispersion law, i.e. Green's functions.

4 Diffusion tensor of phonon system

According to Kubo formula [33–35] the diffusion tensor is defined as:

$$D_{ij}(k) = \lim_{\delta \rightarrow 0^+} \int_0^{\infty} dt e^{-\delta t} \langle \hat{v}_i(0) \hat{v}_j(t) \rangle, \quad (28)$$

where \hat{v}_i and \hat{v}_j are velocity operators (in Heisenberg representation) of oscillating of molecules in crystal along the crystallographic direction $i, j \in (x, y, z)$, and δ is perturbation parameter; $\langle \hat{v}_i(0) \hat{v}_j(t) \rangle$ are corresponding correlation functions.

Correlation functions will be calculated starting from the definition [16–18,33] – spectral theorem:

$$\lim_{\delta \rightarrow +0} [G_{\bar{n}\bar{m}}(\omega + i\delta) - G_{\bar{n}\bar{m}}(\omega - i\delta)] = \left(e^{\hbar\omega/\theta} - 1 \right) \mathcal{C}_{\bar{n}\bar{m}}^G(\omega),$$

where $\mathcal{C}_{\bar{n}\bar{m}}^G(\omega)$ is time – frequency Fourier's transform of the correlation function $\mathcal{C}_{\bar{n}\bar{m}}^G(t)$. For $t = 0$ the correlation functions represent the average values of the appropriate operators product.

To find the correlation functions $\langle \hat{v}_i(0) \hat{v}_j(t) \rangle$ that is figuring in the equation for diffusion coefficient, we start from Green's function of momentum–momentum type $\langle \langle p_i(t) | p_j(0) \rangle \rangle$ since $\hat{v}_i = \frac{\hat{p}_i}{m}$ and $\hat{v}_j = \frac{\hat{p}_j}{m}$, and averaging will be done with big canonic ensemble [35–37], while the boundary conditions will be considered in the system of equations for crystalline films Green's function [38–40].

Based on eqs. (11) and (12) for bulk, i.e. (23) and (24) for films, the appropriate correlation functions are:

$$\langle p_f(t) p_f(0) \rangle = \frac{\hbar C}{\omega_k} \left(\frac{e^{-i\omega_k t}}{e^{\hbar\omega_k/\theta} - 1} - \frac{e^{i\omega_k t}}{e^{\hbar\omega_k/\theta} - 1} \right) \quad (29)$$

and, if we go back to the formula which defines the diffusion coefficients $D_{ij}(k)$ of the phonon system, one obtains:

$$D_{ij}(k) = \lim_{\delta \rightarrow 0^+} \frac{\hbar C}{M^2 \omega_k} \times \int_0^{\infty} \left(e^{-\delta t} \frac{e^{-i\omega_k t}}{e^{\hbar\omega_k/\theta} - 1} - e^{-\delta t} \frac{e^{i\omega_k t}}{e^{\hbar\omega_k/\theta} - 1} \right) dt, \quad (30)$$

what finally gives:

$$D_{ij}^f(k) = \left| i \frac{\hbar C}{M^2 \langle \omega_k^2 \rangle} \right|. \quad (31)$$

The results of here conducted calculation are the following:

1) The diffusion tensor of phonon system is diagonal, that is $D_{ii}(k) = \frac{\hbar C}{M^2 \langle \omega_k^2 \rangle}$.

2) The eigenvalues have higher values for the lower frequencies.

This means that the diffusion of phonons, and heat transfer, is more intensive in the film than in bulk, but only along the privileged (z) direction:

$$D_{ii}^f(k) \equiv \frac{\hbar C}{M^2 \langle \omega_f^2(k_f) \rangle} \gg D_{ii}^b(k) \equiv \frac{\hbar C}{M^2 \langle \omega_b^2(k_b) \rangle},$$

because: $\langle \omega_f^2(k_z) \rangle \ll \langle \omega_b^2(k_z) \rangle$.

- 3) Beside that, the eigenvalues are temperature independent, for both bulk and film structures. This conclusion is very significant because it justifies the macroscopic theories of heat conduction from which it is taken, and that diffusion coefficient is temperature independent.

This fact and the effects that it could cause is very important in the theory of phonon engineering [41–50], especially regarding contemporary nanostructures for high-temperature superconductivity.

5 Conclusion

Research about quantum size and confinement effects on direction of energy/heat flow through the nano crystals is conducted by determination of phonon diffusion tensor in ultra-thin crystalline films, and then by comparison of the tensor elements with the phonon diffusion tensor elements in bulk. For that analysis it was necessary to calculate phonon state and spectra. Those results are compatible and supplement the results obtained in previous research [23–26,30–32].

Comparison of the phonon spectra and states between bulk structures (with no deformations) and film structures (i.e. structures with translational broken symmetry) yields to conclusions:

- 1) In bulk structures mechanical vibrations in all directions appear. These vibrations are plane waves. In film structures superposition of plane waves in XY -planes and standing waves in z -direction appear.
- 2) all three acoustic frequencies disappear, but in films some minimal frequency exists. Value of that frequency is function of film thickness and actually represent energy gap for phonon creation. To create phonons film should be heated to sufficient temperature and below that activation temperature film behave as "frozen".
- 3) Type of atoms from which film is made of also determine energy gap. Type of crystal structure especially along z -direction and type and concentration of injected atoms (or impurities) play significant roles.

Calculation and analysis of phonon diffusion tensor in ultra-thin crystalline film showed existence of privileged direction for heat transfer throughout film. This direction connects boundary surfaces of film, with heat transfer more intensive comparing with other mutually vertical directions (in our model denoted as x and z). Therefore, in all planes parallel to the boundary planes heat transfer is attenuated.

Literature text-book data for conventional (low temperature) superconductors, that is well before 1986, pointed to the fact that samples of the large and small dimensions of the boundary surface, such as thin crystalline films, had better superconducting properties

(e.g., higher critical parameters: T_C , j_C , H_C), than the respective bulk-samples of the same chemical and crystallographic structure!

In this work we have not done the research of superconducting properties of UTCF, we seriously worked and published that in our works, cited here under Refs. [39,40], and three decades ago in [51], where we especially emphasized the importance and role of the 2D: 1D (sub) structure in the recorded 2D superconductive transfer at then a completely new – high-temperature superconducting Cu–O ceramics.

This attitude and the possibility of "replacement" of acoustic – by optical phonons in order to increase the value of critical parameters, was known and implied a lot before the discovery of high-temperature superconducting Cu–O ceramics (for example, in Ref. [52]).

However, the occurrence of an energy gap in the spectrum of acoustic phonons – conditioned by the QSE, imposed a small comment and compared to potential mechanism of partly ideally electrical and partly superconductive transfer charge through UTCF, in terms of the impact of the size of that gap of optical type phonons on the activation, i.e. on temperature of the superconductive transition.

Therefore, experimental data show that if bulk and film structures are made of same material, the films exhibit better superconducting characteristics. This fact could be supported with following:

- 1) Superconductors have some collective characteristics, which represent quantum-mechanical behavior on macroscopic level. This behavior appear in film structures too, where standing phonon waves along z -direction represent collective behavior.
- 2) Electric resistance in conductors is caused by phonons. Film-structures have energy gap, so that below that energy (or activation temperature) there are no phonons at all (or no mechanical vibrations). In this case conditions for super-conductive (or resistance-less) electric currents are achieved.
- 3) Better conditions for superconductivity effects arise along directions with attenuated heat transfer. Based on results in this research it could be confirmed that in crystalline film structures quasi 2D superconductivity occurs.

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