Phonon Contribution in Thermodynamic Properties of Single Quantum Dot

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In this paper, we have theoretically and analytically examined the impact of the quantum size effect on mechanical and thermodynamic properties of the single crystalline quantum dot. Spectra of allowed phonon energies, as well as thermodynamic characteristics, are analyzed using the method of two-time dependent Green's functions. The internal energy of the system as well as the thermal capacitance of the quantum dot in a low-temperature region are found. The behaviour of quantum dot's specific heat with temperature is compared to that of corresponding bulk structures, as well as those of thin films, superlattices, and quantum wires. It has been shown that at extremely low temperatures thermal capacitance of the quantum dot is significantly lower than the thermal capacitance listed for above structures. Consequences of this fact are discussed in detail and its influence on kinetic and thermodynamic properties of materials are estimated.

1. Introduction

Determining the basic physical properties underlying the nanostructures is essential for their implementation. As a consequence of several various factors, nanostructures are characterized by a variety of diverse features, such as superconductivity, transport of carriers, heat-insulation, acoustic properties, and many other. Most, if not all of these factors, are directly related to the existence of the boundaries of the structure. The main goal of this paper, which can be considered as a continuation of our previous research, is to investigate how dimensional phonon confinement in low-dimensional structures (quantum dots) influences its thermodynamic properties, which forms the basis for the concept of phonon engineering (nanophononics) [1–5]. Research of this type has become extremely important in recent years, due to the great commercializing potential of novel two-dimensional materials such as graphene, being the lightest, strongest, and most conductive material known today. Examining the influence of the phonon subsystem on the properties of the graphene is mandatory in order to tailor graphene's mechanical properties [6–10]. Phonons are collective excitations of atoms (molecules) and represent the most important subsystem in condensed matter. Without them, it is almost impossible to examine and describe the acoustical characteristics, as well as the thermal, conductive, and superconductive properties of solids. Thermal properties of nanostructures have attracted a lot of attention lately: the influence of size effects on thermal conductivity is becoming extremely important for heat removal and device design and reliability. It is also foreseen that the use of nanostructured components may increase the sensitivity of measuring instruments, which in turn leads to new experimental results.

Quantum dots are confined crystalline structures [11–13] in which conditions on boundary surfaces differ from those inside the dots, i.e. translational symmetry is disrupted alongside all three crystallographic directions (x, y, and z, Fig. 1). Providing that there is no disturbance of the crystalline structure inside the dot (between its boundary surfaces), we assume that the quantum dot is ideal. On the contrary, if there are impurities, vacancies, and the like in the crystalline lattice, the quantum dot is deformed. The scope of our study in this paper is the ideal quantum dot

Fig. 1. Quantum dot model.

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of a simple cubic crystalline structure consisting of identical atoms, with one atom per elementary cell. At first glance, this fact may seem like a big limitation in terms of the applicability of the described model, but this is not the case: in accordance with the method of achievement, statistical and dynamical equivalence between rectangular and structures with lower symmetry [5], it is applicable to a large number of crystalline structures. In the case of monoclinic structures, for instance, the method of equivalence is applicable with no restrictions.

The basic crystallographic parameters of the chosen model structure, in the nearest neighbours approximation, are

$$a_x = a_y = a_z = a, \quad N_{x,y,z} \sim 10,$$

$$C_{\boldsymbol{n,m}}^{\alpha,\alpha} = C_{\boldsymbol{n,n\pm\lambda}}^{\alpha} \equiv C_{n_x n_y n_z; n_x \pm 1, n_y n_z}^{\alpha} =$$

$$C_{n_x n_y n_z; n_x n_y \pm 1, n_z}^{\alpha} = C_{n_x n_y n_z; n_x n_y n_z \pm 1}^{\alpha} \equiv C^{\alpha},$$

$$C_{n_x, n_y, 0; n_x, n_y, -1}^{\alpha} = C_{n_x, n_y, -1; n_x, n_y, 0}^{\alpha} = (1+\varepsilon)C^{\alpha},$$

$$C_{n_x, n_y, N_z; n_x, n_y, N_z+1}^{\alpha} = C_{n_x, n_y, N_z+1; n_x, n_y, N_z}^{\alpha} = (1+\gamma)C^{\alpha},$$

$$C_{n_x, 0, n_z; n_x, -1, n_z}^{\alpha} = C_{n_x, -1, n_z; n_x, 0, n_z}^{\alpha} = (1+\sigma)C^{\alpha},$$

$$C_{n_x, N_y, n_z; n_x, N_y+1, n_z}^{\alpha} = C_{n_x, N_y+1, n_z; n_x, N_y, n_z}^{\alpha} = (1+\varphi)C^{\alpha},$$

$$C_{0, n_y, n_z; -1, n_y, n_z}^{\alpha} = C_{-1, n_y, n_z; 0, n_y, n_z}^{\alpha} = (1+\vartheta)C^{\alpha},$$

$$C_{N_x, n_y, n_z; N_x+1, n_y, n_z}^{\alpha} = C_{N_x+1, n_y, n_z; N_x, n_y, n_z}^{\alpha} = (1+\phi)C^{\alpha},$$

$$(\varepsilon, \gamma, \sigma, \varphi, \vartheta, \phi) \geq -1, \tag{1}$$

where a is the lattice constant, $N_{x,y,z}$ are the numbers of atoms along x, y, and z directions, C^{α} is the straining Hooke elastic constant in direction α, $n_{x,y,z} \in (0, 1, 2, \cdots, N_{x,y,z})$ is the atom site counter along x, y, and z directions, and vector $\boldsymbol{\lambda}$ associates atom in place $\boldsymbol{n}$ with its nearest neighbors.

Respecting above facts, we are able to say the following about the described model structure:

1. Quantum dots have six boundary surfaces: two of them are parallel to the xy planes (for $z = 0$ and $z = L_z = N_z a$), two to xz planes (for $y = 0$ and $y = L_y = N_y a$), and two to yz planes (for $x = 0$ and $x = L_x = N_x a$). Thus, these structures are confined along x, y, and z directions. Along x-axis, there are $N_x + 1$ atoms, along y-axis, $N_y + 1$ atoms, and along z-axis, $N_z + 1$ atoms.

2. Torsion Hooke's elastic constants $C^{\alpha\beta}$ are negligible relative to the straining constants C^{α}. Besides that, it is considered that there is an interaction

between atoms in boundary layers of the quantum dot and external areas, disregarding that along x, y, and z directions outside boundary surfaces there are no atoms belonging to the quantum dot. However, boundary atoms are coupled through changed Hooke's forces with the atoms of the external environment [14–16]. In accordance with these conditions, elastic constants which describe interactions between atoms of boundary surfaces and external environment are modified with appropriate coefficients $\varepsilon, \gamma, \sigma, \varphi, \vartheta,$ and ϕ. These perturbations of boundary surfaces do not disturb the macroscopic geometry of the structure and only redefine the small movements of atoms. A simpler but more pragmatic approach implies that the quantum dot atoms are surrounded by atoms/molecules belonging to only two different environments ($\sigma, \varphi, \vartheta, \phi \mapsto \varepsilon$).

With respect to described model and regarding the fact that layers with $n_x \leq -1$ and $n_x \geq N_x + 1$, $n_y \leq -1$ and $n_y \geq N_y + 1$ and also $n_z \leq -1$, and $n_z \geq N_z + 1$ are not present, we have to take into account the following:

$$u_{\alpha; n_x, n_y, n_z} = 0, \quad -1 \geq n_{x,y,z} \wedge n_{x,y,z} \geq N_{x,y,z} + 1,$$

$$(n_{x,y,z} \notin [0, N_{x,y,z}]).$$

These boundary conditions are in accordance with the free surface model, but at this point, it should be noted that there are also other approaches. One of them, which is often found in literature, is the rigid walls model (or frozen surfaces model), where boundary conditions with zero atomic displacements are required at the boundary surfaces. In this paper we have chosen flexible boundary surfaces, considering that this is closer to the real situation in which the quantum dot can "breathe". On the other hand, the rigid walls model presumes the appearance of phonon standing waves with nodes at the boundaries.

2. Theoretical analysis

Starting point of our theoretical approach is the standard Hamiltonian of the phonon subsystem for bulk structures [16–18], written in the harmonic as well as in the nearest neighbors approximations, which is adapted to the model-structure of quantum dot presented in Fig. 1

$$H = T + V_{eff}, \quad T = \sum_{\alpha; \boldsymbol{n}} \frac{p_{\alpha; \boldsymbol{n}}^2}{2M}, \tag{2}$$

$$V_{eff} = \sum_{\alpha; n_x, n_y, n_z} \frac{C_\alpha}{4} \Bigg[\left(u_{\alpha; n_x+1, n_y, n_z} - u_{\alpha; n_x, n_y, n_z}\right)^2 + \left(u_{\alpha; n_x-1, n_y, n_z} - u_{\alpha; n_x, n_y, n_z}\right)^2 + \left(u_{\alpha; n_x, n_y+1, n_z} - u_{\alpha; n_x, n_y, n_z}\right)^2$$

$$+ \left(u_{\alpha; n_x, n_y-1, n_z} - u_{\alpha; n_x, n_y, n_z}\right)^2 + \left(u_{\alpha; n_x, n_y, n_z+1} - u_{\alpha; n_x, n_y, n_z}\right)^2 + \left(u_{\alpha; n_x, n_y, n_z-1} - u_{\alpha; n_x, n_y, n_z}\right)^2 \Bigg], \tag{3}$$

where $u_{\alpha;\boldsymbol{n}}$ are the small movements of atom in position $\boldsymbol{n} \equiv (n_x, n_y, n_z)$ from its equilibrium position in direction α, and $p_{\alpha;\boldsymbol{n}}$ are the corresponding momentum, and M is the mass of the atoms.

We are looking for the phonon dispersion law with the help of the phonon two-time commutator Green's function [18–20]:

$$G_{\boldsymbol{n},\boldsymbol{m}}^{\alpha}(t - t') \equiv \langle\langle u_{\alpha;\boldsymbol{n}}(t)|u_{\alpha;\boldsymbol{m}}(t')\rangle\rangle =$$

$$\Theta(t - t')\langle[u_{\alpha;\boldsymbol{n}}(t), u_{\alpha;\boldsymbol{m}}(t')]\rangle_0, \tag{4}$$

which satisfies the equation of motion

$$-M\omega^2 G_{\boldsymbol{n},\boldsymbol{m}}^{\alpha}(\omega) =$$

$$-\frac{\mathrm{i}\hbar}{2\pi}\delta_{\boldsymbol{n},\boldsymbol{m}} + \frac{1}{\mathrm{i}\hbar}\langle\langle[p_{\alpha;\boldsymbol{n}}, H]|u_{\alpha;\boldsymbol{m}}\rangle\rangle_\omega. \tag{5}$$

By calculating corresponding commutators in the Green function which appears in Eq. (5), we obtain the system of $(N_x + 1) \times (N_y + 1) \times (N_z + 1)$ nonhomogeneous algebraic-difference equations with the same number of undetermined Green's functions [10–13]:

$$G_{n_x-1,n_y,n_z} + G_{n_x,n_y-1,n_z} + G_{n_x,n_y,n_z-1}$$

$$+\wp G_{n_x,n_y,n_z} + G_{n_x,n_y,n_z+1} + G_{n_x,n_y+1,n_z}$$

$$+G_{n_x+1,n_y,n_z} = \mathcal{K}_{n_x n_y n_z}, \tag{6}$$

where

$$\wp = \Big[\varrho - \varepsilon\left(\delta_{n_x,0} + \delta_{n_x,N_x} + \delta_{n_y,0} + \delta_{n_y,N_y} + \delta_{n_z,0}\right)$$

$$-\gamma\delta_{n_z,N_z}\Big], \qquad \varrho = \frac{\omega^2}{\Omega_\alpha^2} - 6, \qquad \Omega_\alpha^2 = \frac{C_\alpha}{M},$$

$$\mathcal{K}_{n_x,n_y n_z} = \frac{\mathrm{i}\hbar}{2\pi C_\alpha}\delta_{n_x,n_y n_z,m_x m_y m_z}. \tag{7}$$

In order to find the spectra of the allowed phonon energies amounts, we must determine the zeroes of the determinant of the system of Eq. (6). This task, in general, is not analytically solvable (it can be solved numerically with given parameters $\varepsilon, \gamma, N_x, N_y$, and N_z). Hereafter, we will give our attention to the model of the loose surfaces [16, 17], when surface perturbations are negligible, i.e. $\varepsilon = \gamma = 0$. In this model, an elastic interaction of the quantum dot surface atoms with atoms/molecules of surrounding environments is of the same nature and strength. We call it "a model of the ideal quantum dot with free surfaces". The reason for choosing this model is that there is an analytical solution for the phonon dispersion law and other physical properties. Besides that, in determining the micro- and macroscopic physical properties of the sample this choice favours the quantum size effect [1,9], while the contributions of all other confinement effects (shape, etc.) are negligible and can only slightly affect changes caused by the size effect [2, 3, 11–13]. In that case, the system of Eq. (6) reduces to

$$G_{n_x-1,n_y,n_z} + G_{n_x,n_y-1,n_z} + G_{n_x,n_y,n_z-1}$$

$$+\varrho G_{n_x,n_y,n_z} + G_{n_x,n_y,n_z+1} + G_{n_x,n_y+1,n_z}$$

$$+G_{n_x+1,n_y,n_z} = \mathcal{K}_{n_x,n_y n_z}, \tag{8}$$

and undetermined Green's functions from Eq. (3) can be expressed as follows:

$$G_{n_x,n_y,n_z} = \frac{\mathcal{D}_{n_x,n_y,n_z}}{\mathcal{D}_{N_x+1,N_y+1,N_z+1}}, \tag{9}$$

where $\mathcal{D}_{n_x,n_y,n_z}$ is the determinant of the variable and $\mathcal{D}_{N_x+1,N_y+1,N_z+1}$ is the three-dimensional determinant of the system. Poles of Green's functions by which the phonon dispersion law is determined can be obtained on condition that the determinant of the system is equal to zero

$$\mathcal{D}_{N_x+1,N_y+1,N_z+1}(\varrho) = 0. \tag{10}$$

Determinant $\mathcal{D}_{N_x+1,N_y+1,N_z+1}$ can be expressed through Chebyshev's polynomials of second order, by which the phonon dispersion law can be obtained in form

$$\mathcal{E}_{\boldsymbol{k}}^{\alpha} = 2\sqrt{\sin^2\frac{ak_x(\chi)}{2} + \sin^2\frac{ak_y(\mu)}{2} + \sin^2\frac{ak_z(\nu)}{2}},$$

$$\big(\chi = 1, 2, \ldots N_x + 1, \quad \mu = 1, 2, \ldots N_y + 1,$$

$$\nu = 1, 2, \ldots N_z + 1\big), \tag{11}$$

similar to that of the bulk structures. The main difference is, however, that phonon quasimomentum in quantum dots takes discrete values in all three directions. It can also be seen that minimum phonon energy in quantum dots differs from zero, and is given by

$$\Delta_{\min} = \mathcal{E}_{k_x^{\min}, k_y^{\min}, k_z^{\min}}^{\alpha} =$$

$$2\sqrt{\sin^2\frac{ak_x^{\min}(\chi)}{2} + \sin^2\frac{ak_y^{\min}(\mu)}{2} + \sin^2\frac{ak_z^{\min}(\nu)}{2}},$$

$$k_x^{\min}(\chi = 1) = \frac{\pi}{a}\frac{1}{N_x + 2}, \quad k_y^{\min}(\mu = 1) = \frac{\pi}{a}\frac{1}{N_y + 2},$$

$$k_z^{min}(\nu = 1) = \frac{\pi}{a}\frac{1}{N_z + 2}, \tag{12}$$

while the corresponding minimum phonon frequency is

$$\omega_\alpha^{\min} = 2\frac{v}{a}\bigg[\sin^2\frac{\pi}{2(N_x + 2)} + \sin^2\frac{\pi}{2(N_y + 2)}$$

$$+ \sin^2\frac{\pi}{2(N_z + 2)}\bigg]^{1/2}. \tag{13}$$

Although in crystals with a simple elementary cell only acoustic phonon branches can occur, the previous analysis has shown that due to the influence of the quantum size effect there is an energy gap, which is a characteristic of optical phonon modes. It can, therefore, be concluded that in quantum dots, as in other nanostructures, acoustic phonons of the optical type appear.

3. Phonon thermodynamics of quantum dots

In order to determine thermodynamic properties of quantum dots, it is necessary to find corresponding values for Debye's wave vector k_{D} and Debye frequency ω_{D}. We assume that phonon wave vectors of quantum dot lie in the sphere of radius k_{D}. Since the translational symmetry of the quantum dot is interrupted alongside

all three directions, possible values of wave vectors along x, y, and z directions are:

$$k_{x/y/z} \in \left[\frac{1}{N_{x/y/z}+2} \frac{\pi}{a}, \frac{N_{x/y/z}+1}{N_{x/y/z}+2} \frac{\pi}{a} \right]$$

$$\Rightarrow \Delta k_{x/y/z} = \frac{N_{x/y/z}}{N_{x/y/z}+2} \frac{\pi}{a},$$

and we obtain

$$V = \begin{cases} \frac{4}{3}\pi \left(a k_D^d \right)^3 \\ a^3 \Delta k_x \Delta k_y \Delta k_z \end{cases} \Rightarrow$$

$$k_D^d = \sqrt[3]{\frac{3\pi^2}{4a^3}} \sqrt[3]{\frac{N_x}{N_x+2}\frac{N_y}{N_y+2}\frac{N_z}{N_z+2}} \Rightarrow$$

$$k_D^d = k_D^b \sqrt[3]{\frac{N_x}{2\left(N_x+2\right)}\frac{N_y}{2\left(N_y+2\right)}\frac{N_z}{2\left(N_z+2\right)}},$$

where $k_D^b = \sqrt[3]{6\pi^2}/a$ is the Debye wave vector in corresponding unbounded (bulk) structure. For the number of allowed values of $\boldsymbol{k}$ per volume unit of $\boldsymbol{k}$-space, next adjusted general expression is applicable

$$\mathcal{D}(\omega) = \frac{3N_x N_y N_z a^3}{(2\pi)^3} \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi \int_{k_{min}}^{k_D} k^2\, dk\, \delta(\omega - vk) =$$

$$\frac{N_x N_y N_z a^3}{2\pi^2} \frac{\omega^2}{v^3} \tag{14}$$

and by applying the normalization condition (according to fact that the total number of phonon states is equal to the number of atoms)

$$\int_{\omega_{min}}^{\omega_D} \mathcal{D}(\omega)\, d\omega = N \Rightarrow$$

$$\frac{N_x N_y N_z a^3}{2\pi^2 v^3} \int_{\omega_{min}}^{\omega_D} \omega^2\, d\omega = (N_x+1)(N_y+1)(N_z+1),$$

we obtain an expression for Debye frequency in quantum dot in the forms

$$\omega_D = \omega_D^b \left\{ \frac{N_x+1}{N_x}\frac{N_y+1}{N_y}\frac{N_z+1}{N_z} + \frac{4}{3\pi^2} \left[\sin^2 \frac{\pi}{2(N_x+2)} \right. \right.$$

$$\left. \left. + \sin^2 \frac{\pi}{2(N_y+2)} + \sin^2 \frac{\pi}{2(N_z+2)} \right]^{3/2} \right\}^{1/3}, \tag{15}$$

where $\omega_D^b = k_D^b v$ is the Debye frequency in the corresponding bulk-structure. It can be seen that the Debye frequency has somewhat greater value in the quantum dot than in an unbounded structure.

Internal energy of the quantum dot is calculated in terms of standard definition form [18, 20]:

$$U = \int_{\omega_{min}}^{\omega_D} d\omega\, \mathcal{D}(\omega) \langle n(\omega,T)\rangle \hbar\omega = \int_{\omega_{min}}^{\omega_D} d\omega \left(\frac{\omega^2 V}{2\pi^2 v^3} \right)$$

$$\times \left(\frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right) = 9Nk_B T \left(\frac{T}{T_D} \right)^3 \int_{x_{min}}^{x_D} \frac{x^3}{e^x-1}\, dx, \tag{16}$$

where $V = Na^3 = (N_x+1)(N_y+1)(N_z+1)a^3$, $x = \frac{\hbar\omega}{k_B T}$, $x_{min} = \frac{\hbar\omega_{min}}{k_B T}$, and $x_D = \frac{\hbar\omega_D}{k_B T} = \frac{T_D}{T}$. In a low temperature region, when $x_D \to \infty$, the last expression becomes

$$U = 9Nk_B T \left(\frac{T}{T_D} \right)^3 \int_{x_{min}}^\infty \frac{x^3}{e^x-1}\, dx =$$

$$9Nk_B T \left(\frac{T}{T_D} \right)^3 \left(\int_0^\infty \frac{x^3}{e^x-1}\, dx - \int_0^{x_{min}} \frac{x^3}{e^x-1}\, dx \right) =$$

$$9Nk_B T \left(\frac{T}{T_D} \right)^3 \left(\frac{\pi^4}{15} - \int_0^{x_{min}} \frac{x^3}{e^x-1}\, dx \right). \tag{17}$$

On the basis of expansion $(e^t-1)^{-1} = \sum_{j=1}^\infty e^{-jt}$ the last equation becomes

$$U = 9Nk_B T \left(\frac{T}{T_D} \right)^3 \left(\frac{\pi^4}{15} - \sum_{j=1}^\infty \int_0^{x_{min}} x^3 e^{-jx}\, dx \right).$$

Integral from this expression is analyzed by multiple partial integration

$$U = 9Nk_B \frac{T^4}{T_D^3} \left[\frac{\pi^4}{15} + \sum_{j=1}^\infty \frac{1}{j} e^{-jx_{min}} \right.$$

$$\left. \times \left(x_{min}^3 + \frac{3}{j}x_{min}^2 + \frac{6}{j^2}x_{min} + \frac{6}{j^3} \right) - \sum_{j=1}^\infty \frac{6}{j^4} \right]. \tag{18}$$

To find the expression for the thermal capacitance per a unit cell (here: per atom), the standard definitional [18, 20] form is used: $C^* = \frac{1}{N}\frac{\partial U}{\partial T}$. In accordance with that we obtain

$$C^* = \frac{12\pi^4}{5}k_B \left(\frac{T}{T_D} \right)^3 + 9k_B \left(\frac{T}{T_D} \right)^3$$

$$\times \sum_{j=1}^\infty \frac{1}{j} e^{-jx_{min}} \left[\frac{1}{j}x_{min}^4 + \left(1 + \frac{3}{j^2} \right) x_{min}^3 \right.$$

$$\left. + \frac{6}{j}\left(1 + \frac{1}{j^2}\right) x_{min}^2 + \frac{6}{j^2}\left(3 + \frac{1}{j^2}\right) x_{min} + \frac{24}{j^3} \right],$$

or

$$C^* = \frac{12\pi^4}{5}k_B \frac{\mathcal{T}^3}{f^3(N_x,N_y,N_z)} + 9k_B \frac{1}{f^3(N_x,N_y,N_z)}$$

$$\times \sum_{j=1}^\infty \frac{1}{j} e^{-j\frac{\Delta}{\mathcal{T}}} \left[\frac{1}{j}\frac{\Delta^4}{\mathcal{T}} + \left(1 + \frac{3}{j^2}\right)\Delta^3 + \frac{6}{j}\left(1 + \frac{1}{j^2}\right)\Delta^2\mathcal{T} \right.$$

$$\left. + \frac{6}{j^2}\left(3 + \frac{1}{j^2}\right)\Delta\mathcal{T}^2 + \frac{24}{j^3}\mathcal{T}^3 \right], \tag{19}$$

where $\mathcal{T} \equiv T/T_D^b$, $\Delta \equiv \omega_{min}/\omega_D^b$, ($T_D^b$, and ω_D^b are the Debye temperature and frequency for bulk structure, respectively) and relative Debye's frequency related to bulk ones is

$$\frac{\omega_{\mathrm{D}}}{\omega_{\mathrm{D}}^{b}} = \left\{ \frac{N_x+1}{N_x} \frac{N_y+1}{N_y} \frac{N_z+1}{N_z} + \frac{4}{3\pi^2} \left[\sin^2 \frac{\pi}{2\left(N_x+2\right)} \right. \right.$$

$$\left. \left. + \sin^2 \frac{\pi}{2\left(N_y+2\right)} + \sin^2 \frac{\pi}{2\left(N_z+2\right)} \right]^{3/2} \right\}^{1/3}$$

$$\equiv f(N_x, N_y, N_z).$$

It is well known that the phonon part in the thermal capacitance of the system is described with cubic temperature dependence. For comparison of these dependences for the bulk-structure and the quantum dot, the last expression is divided by the constant $C_0 = \frac{12\pi^4 k_{\mathrm{B}}}{5}$, whose dimension is equal to the dimension of thermal capacitance

$$\mathcal{C} = \frac{\mathcal{T}^3}{f^3\left(N_x, N_y, N_z\right)} + \frac{15}{4\pi^4} \frac{1}{f^3\left(N_x, N_y, N_z\right)}$$

$$\times \sum_{j=1}^{\infty} \frac{1}{j} e^{-j\frac{\Delta}{\mathcal{T}}} \left[\frac{1}{j} \frac{\Delta^4}{\mathcal{T}} + \left(1+\frac{3}{j^2}\right) \Delta^3 + \frac{6}{j}\left(1+\frac{1}{j^2}\right) \Delta^2 \mathcal{T} \right.$$

$$\left. + \frac{6}{j^2}\left(3+\frac{1}{j^2}\right) \Delta \mathcal{T}^2 + \frac{24}{j^3} \mathcal{T}^3 \right]. \qquad (20)$$

Figure 2 shows the relative (non-dimensional) thermal capacitances of bulk structure, superlattice, ultrathin film, quantum wire, and quantum dot subject to the relative temperature $\mathcal{T}$ in the low-temperature region.
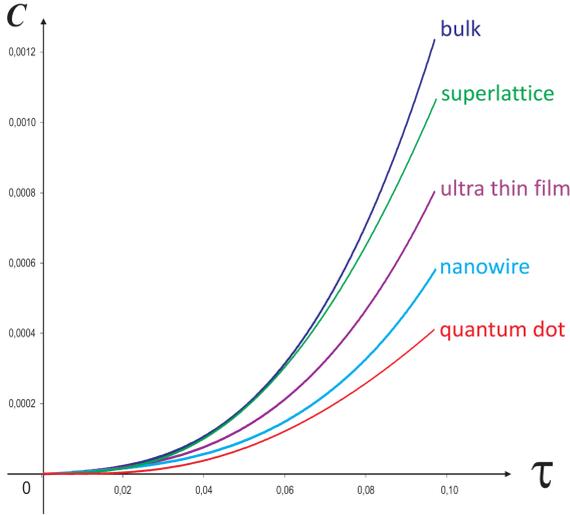
Fig. 2. Low-temperature behavior of thermal capacitance for bulk and quantum dot.

Determining the phonon impact on the physical, and primarily thermodynamic properties of low-dimensional structures (ultrathin films, superlattices, and ultranarrow wires) has been the subject of research of our team for many years and the results of these studies have been published [4–6, 16, 17, 21–26] in the previous period. Here, we will use some of these results in order to compare them with the results obtained in this paper for quantum dots.

It can be seen that phonon contribution to the thermal capacitance of crystalline quantum dot is lowest, compared to that of more massive specimens. On this basis, it can be concluded that the quantum dots are the weakest thermal as well as electrical conductors.

4. Conclusions

Application of nanostructures requires a knowledge of their fundamental physical properties. Lately, a great interest has been induced by the thermodynamic aspect associated with phonon movements through the nanometer-sized samples. Spatial confinement of acoustic and optical phonons in nanostructures unavoidably changes their properties in comparison with bulk materials. Their interactions are altered by the effects of dimensional constraint on the phonon modes in nanostructures. Phonon confinement in low-dimensional structures leads to the emergence of the quantized energy sub-bands with the corresponding alteration of the phonon density of states. The changes in the phonon dispersion law lead to a modification in the electron–phonon scattering rates, optical properties of the nanostructured materials, and phonon scattering on defects, boundaries, and other phonons. In this paper, we applied a strict theoretical approach in order to examine the influence of the quantum size effect on the thermodynamic properties of a quantum dot that is surrounded by different materials from every side. In this respect, desirable properties of the structure can be modified by changing the lattice constant, i.e. dimensions of the quantum dot, by inserting atoms of different kinds and by changing the parameters $\varepsilon, \gamma, \sigma, \varphi, \vartheta$, and ϕ. However, considering the technology of fabricating quantum dots, there is no reason to assume that it will be on all sides surrounded by different materials. A simpler but more pragmatic approach implies that the quantum dot atoms are surrounded by atoms/molecules belonging to only two different environments $(\sigma, \varphi, \vartheta, \phi \mapsto \varepsilon)$.

With respect to all of the above we come to the following conclusions: since phonons with the Debye frequencies are responsible for electrically and thermally induced transport properties of materials, it follows that the quantum dot will be inferior electrical and thermal conductor in contrast to the relative massive structures, providing there are no chemical and structural differences between them. On the other hand, it is a well known fact that the more inferior electrical conductor material is (under normal conditions), the better superconductor it becomes. Due to that, the experimental fact can be concluded and justified, that in very spatially confined structures more qualitative superconductive properties have been achieved.

These facts point out that the key role in high T_C superconductors comes from the low dimension of the observed structure. More detailed answer to this question will be obtained by examination of the electronic subsystem in quantum dots.

The results obtained, however, cannot be considered final, since the analyses were carried out on ideal samples of perfectly correct shapes and with ideally smooth surfaces. Real samples, on the other hand, cannot be devoid of defects and irregularities, and in structures of such small dimensions, as quantum dots are, this irregularity can significantly affect their physical (thermodynamic) properties. It is well known that the thermal behaviour of materials is influenced by many different factors: the density of the sample, its thermal expansion, the share of impurities, surface absorption, dimensions, etc. whereby for each particular material the different effect is predominant. Only with thorough theoretical and experimental analysis of individual properties of nanostructures and all essential influences on them, can the thermodynamic behaviour of materials be completely examined. To that end, it is necessary to implement much more theoretical calculations and develop different methods for solving them.

Acknowledgments

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