Hierarchy of models for calculating the thermal conductivity in nanostructures

V I Khvesyuk¹ and A A Barinov²
¹,² Bauman Moscow State Technical University, Moscow, Russia
¹2636623@gmail.com, ²barinovE6@bmstu.ru

Abstract. This work is devoted to the problem of the thermal conductivity calculation in nanostructures. Various models for thermal conductivity determination are discussed, including the original one. The results of calculations are presented.

1. Introduction
The thermal physics of solid-state nanostructures is one of the fundamental basics of technologies. The ensuring of optimal temperature regimes is very relevant for nanotechnology development in almost all areas, such as energy, electronics, medicine, optics, etc. The searches for a solution to thermal problems of nanostructures are carried by the research groups of many leading universities, for example MIT [1, 2] and Stanford [3, 4].

The thermal conductivity in nanostructures is based on the thermal conductivity theory of macroscopic samples. However, heat transfer in nanostructures has a number of important features, which require the development of new methods for heat transfer analysis. Here we take into consideration semiconductor and dielectric materials, where the heat is transferred by phonons – the gas of quasi-particles with zero mass. Phonons represent the quanta of the elastic waves propagating in solids [5, 6]. Due to significant features of heat transfer the corresponding property for nanostructures is called the effective thermal conductivity [7] and denoted as \( \kappa_{\text{eff}} \).

The paper presents an attempt to systematize existing methods of the effective thermal conductivity determination in nanostructures with dimensions of order or less than the mean free path of the phonons in macroscopic samples, \( l_{\text{bulk}} \). Unique features of heat transfer in nanostructures are caused by the following conditions. At first, the classical theory of thermal conductivity in solids, based on use of Fourier law, is not applicable for nanostructures. At second, heat transfer process in nanostructures strongly depends on the parameters that do not affect the thermal properties in macroscopic systems (such as the size and shape of samples, direction of heat flow, surface roughness and etc.).

Dimensionless quantity that describes transport in nanostructures is the ratio \( l_{\text{bulk}} / h \), where \( h \) is the minimum size of the nanostructure (e.g., thickness for nanofilms, diameter for nanowires). This parameter is called the Knudsen number, \( Kn \).

The nature of heat propagation in nanostructures has significant physical features. Firstly, for macroscopic bodies the regime of heat transfer is diffusive, \( Kn << 1 \). While in nanostructures the regime can be ballistic, \( Kn \gg 1 \), which is often called the Casimir limit [8], or diffusion–ballistic for intermediate values of Knudsen number. Secondly, in the case of nanostructures it is necessary to take into account the phonon interactions with the boundaries of solid bodies. This problem is far from the precise solution.
2. Phonon interactions
Phonons are the quanta of elastic waves propagating in discrete lattices of solids. Parameters of these waves are frequency $\omega$ and wave vector that defines the direction of wave propagation $\vec{k}$, in absolute value equal to $|\vec{k}| = 2\pi / \lambda$, where $\lambda$ is the wavelength. These characteristics are connected by dispersion relations $\omega = \omega(k)$. In the three-dimensional samples, there are two types of elastic waves – one longitudinal and two transverse. Energy and momentum of phonons are determined from the de Broglie’s relations: $E = h\omega$ and $\vec{p} = h\vec{k}$. The speed of phonon can be derived from the dispersion relations and the definition of the group velocity $\vec{v} = \partial \omega / \partial \vec{k}$.

Unlike photons, the frequency of phonons cannot be more than a certain value $\omega_{\text{max}}$, which is different for various materials. Therefore a parameter characterizing the thermal properties of materials is introduced – $\theta = h\omega_{\text{max}} / k_B$ – the Debye temperature. The value $\omega_{\text{max}}$ corresponds to the minimum rate $\lambda_{\text{min}}$ of wavelengths and the maximum value $k_{\text{max}}$ of the wave vectors of the phonons that can exist in the solid lattice. In the case of a one-dimensional lattice with the equilibrium distance $a$ between identical atoms, the magnitude of possible values $k$ is in the range $-\pi / a \leq k \leq \pi / a$. This interval is called the first Brillouin zone. Similar relations can be defined for 2D and 3D lattices with different geometries.

The features of interactions of phonons with each other are as follows. First, the main contribution to the thermal conductivity is made by internal interactions involving three phonons. Second, the number of particles in a phonon gas is changed due to interaction processes. Third, there are two types of phonon-phonon interactions: N - processes and U - processes.

For N - processes the following equations of momentum conservation are performed (Planck’s constant $h$ is omitted):

$$\vec{k}_1 = \vec{k}_2 + \vec{k}_3, \quad \vec{k}_1 + \vec{k}_2 = \vec{k}_3.$$  

U - processes arise, for example, when the amount $|\vec{k}_1 + \vec{k}_2|$ is more than $\pi / a$. In these cases, the equation of momentum conservation looks like:

$$\vec{k}_1 = \vec{k}_2 + \vec{k}_1 + \vec{G}, \quad \vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{G}.$$  

The magnitude $\vec{G}$ of the momentum transferred to the lattice is determined from the law of energy conservation due to phonons interactions, and equals to $|\vec{G}| = 2\pi / a$. For all processes the relation of energy conservation is written as:

$$\omega_1 = \omega_2 + \omega_3, \quad \omega_1 + \omega_2 = \omega_4.$$  

3. Thermal conductivity in nanostructures
Determination of the thermal conductivity in nanostructures involves the following fundamental problems.

The first one is the study of lattice dynamics in solids. It allows to determine the dispersion relations $\omega(k)$, and hence the speed of phonons [7]. From the analysis of lattice dynamics in bulk body the average time between phonon interactions can be determined [9]. The problem of phonon interaction with the lattice irregularities is solved separately [10].

The second problem is the development of various methods for determining thermal conductivity in nanostructures. Firstly, it’s a kinetic analysis of phonon interactions with each other and with irregularities of the lattice inside the structure. Such calculations coincide with the models developed in
the thermal conductivity theory for macroscopic solids. Secondly, there are specific processes caused by the comparability of nanostructure size with the mean free path of phonons. Phonon interactions with the boundary surface influence on the effective thermal conductivity. Moreover, it includes the issue of the impact of surface roughness on the nature of phonon scattering at the boundaries.

Kinetic analysis of heat transfer processes in nanostructures often is carried out using the Boltzmann transport equation in the relaxation time approximation (RTA). This equation has the form:

\[ \tilde{v} \cdot \frac{\partial f}{\partial \tau} = \frac{f_0 - f}{\tau}, \quad (1) \]

Here \( \tilde{v} \) is the speed of phonon, \( f_0 \) is the equilibrium Bose-Einstein distribution function, \( f = [\exp(h\omega/k_B T) - 1]^{-1} \). The relaxation time \( \tau \) includes the time between two consecutive interactions of phonons with each other, \( \tau_{ph} \), the time between interactions with the irregularities of the lattice, \( \tau_I \), and the time \( \tau_B \) between phonon interactions with the boundaries of the structure. The values \( \tau_{bulk} \) and \( \tau_{nano} \) are determined from the Mattissen rule [11]:

\[ \tau_{bulk}^{-1} = \tau_{ph}^{-1} + \tau_I^{-1}, \quad \tau_{nano}^{-1} = \tau_{ph}^{-1} + \tau_I^{-1} + \tau_B^{-1}, \quad (2) \]

where all the times dependent on \( \omega \), \( T \) and the type of waves (polarization). As will be seen further, consideration of phonon scattering on the boundaries in solids is not only due to introduction of \( \tau_B \) but also in other ways.

The general solution of the Boltzmann equation (1) gives the following expression for the thermal conductivity in nanostructures:

\[ \kappa_{eff} = \frac{1}{6\pi^2} \sum_P \int_0^{\frac{\omega_{max}(P)}{k_B T}} \frac{k_B \langle \omega \rangle^2 \exp(\hbar \omega / k_B T)}{(k_B T)^2[\exp(\hbar \omega / k_B T) - 1]^2} \cdot \tau_{nano}(\omega, j) \cdot \frac{\omega^2}{v^3(\omega, j)} d\omega. \quad (3) \]

For the calculations of bulk thermal conductivity \( \kappa_{bulk} \), \( \tau_{bulk} \) is substituted in (3). The summation in (3) is performed according to the waves types (one longitudinal and two transverse). The first factor under the integral is the capacity of the system, the fourth – density of energy states for phonons. The integration in this expression is over the first Brillouin zone.

Then let us present a several ways to calculate the time between phonon interactions with the boundaries in nanostructures.

1. The most common is the model [11]. In its framework for thin films \( \tau_B \) is written as [11]:

\[ \tau_B^{-1} = v / (\Gamma d_s), \quad (4) \]

where \( d_s \) is the film thickness, \( \Gamma \) – the correction factor depending on Knudsen number. The possible dependence \( \Gamma \) on the corresponding properties is not discussed in [11]. Let us discuss this question. The value \( \Gamma \) should take into consideration the scattering of phonons at the boundaries and the nature of the phonon transfer between two consecutive interactions with the walls. Therefore we will divide this value in two factors: \( \Gamma = \Gamma_1 \cdot \Gamma_2 \).

Let \( \Gamma_1 \) takes into account the nature of the phonon scattering on a rough surface, which depends on the ratio between the size of the roughness, \( \delta \), and the phonon wavelength, \( \lambda \). Long-wavelength phonons, for which \( \delta / \lambda << 1 \), are scattered specularly, and their mean free path remains equal to mean free path in the macroscopic sample, \( l_{bulk} \). In the opposite limit \( \delta / \lambda >> 1 \), diffusion scattering is implemented, which significantly reduces the effective mean free path of phonons and the thermal
conconductivity. A modern approach to the nature of phonon scattering at the boundaries is to introduce the integral parameter of the probability of specular reflection for phonons on the boundary, $p$. The value $p=1$ corresponds to the specular reflection only, and $p=0$ is for purely diffuse reflection. However, there is no way to calculate this value. Experimental evaluation also does not exist. There are only estimations of the $p$ influence on the thermal conductivity. The calculations show that the $p$ variation from 0 to 0.9 leads to the five times increase in thermal conductivity for the silicon film with thickness of 10 nm [1].

In fact, there is a formula that establishes the dependence $p(\delta/\lambda)$ [12]:

$$p(\delta/\lambda) = \exp(-16\pi^2\delta^2/\lambda^2).$$

However, serious physical justification for this dependence is absent. Obviously, the value $p$ depends on the temperature, since the mean free path of phonons influence on it. Simple estimations show that already at a temperature of 30 K the roughness of about 0.5 nm has a significant effect on the thermal conductivity [13]. Therefore, there exists an interest of the experimental study on the influence of surface roughness on the thermal conductivity in nanostructures. Currently there is no such data, only results that presents the temperature dependence of thermal conductivity. As for calculation methods, currently the only way of considering the roughness is to set some integral value $p$, and then substitute it into the form $\Gamma_1 = (1+p)/(1-p)$.

The second problem regards to the proper relation for the time between consecutive scatterings of phonons at the boundaries. For assessments in a first approximation it is necessary to determine the average distance in a straight line, which separates the points of the beginning and the end of phonons propagation from one boundary to the other. It is equal to $\pi \cdot d_s / 2$. The time between the interactions of phonons with the boundaries depends on the values of the Knudsen number, $Kn = l_{bulk} / d_s$, here

$$l_{bulk} = v \cdot \tau_{bulk}.$$

Summarize the mentioned factors we obtain the following expression for $\Gamma_2$:

$$\Gamma_2 = \pi / 2 \cdot (1+Kn) / Kn, \quad Kn = Kn(\omega, T, j)$$

This relation ensures the correct behavior $\tau_B$ from the $Kn$ parameter. While the Knudsen number approaches zero (diffusion regime), the time $\tau_u$ tends to infinity. And on the contrary, when Knudsen seeks to infinity (ballistic regime), the time tends to a constant value $\tau_B^{-1} = 2v / \pi d_s$. Thus a smooth transition from the diffusion regime of heat transfer through the diffusive-ballistic to the ballistic regime is ensured. Finally, we obtain:

$$\tau_B^{-1} = \frac{(1-p)}{(1+p)} \cdot \frac{2}{\pi} \cdot \frac{Kn}{1 + Kn} \frac{v}{d_s}.$$  \hspace{1cm} (5)

It takes into account the dependencies $Kn(\omega, j, p)$ and $v(\omega, j)$.

2. Another way to consider the interactions of phonons with the boundaries is the model [14, 15]. In [14] an analytical expression to account the boundary effects on electrical conductivity in thin films is obtained from the solution of Boltzmann transport equation. Then this method was adapted for the phonon gas and thermal conductivity of films and wires [15]. In [15], while neglecting the dependency of Knudsen number and velocity from the frequency and wave types, this model allows to receive the following expression [3]:

$$\frac{\kappa_{eff}}{\kappa_{bulk}} = F(Kn, p) = 1 - \frac{3}{2} (1-p)Kn \int_0^\infty \left( \frac{1}{t^3} - \frac{1}{(t+\delta)^3} \right) \left( 1 - \exp\left( -t / Kn \right) \right) \frac{1}{1 - p \exp\left( -t / Kn \right)} dt.$$  \hspace{1cm} (6)

Here is $t = 1 / \cos \theta$, and $\theta$ is angle between film surface and normal to one.

There is an alternative way of using the function $F$ to calculate $\kappa_{eff}$, which is more accurate and involves consideration of depending $F$ on $\omega, j, p$. According to this method, the relation
\( \tau_{\text{nano}} = F(\omega, j, p) \cdot \tau_{\text{bulk}} \) is used in equation (3) for \( \kappa_{\text{eff}} \) calculations [3, 4, 16]. According to the data presented in [3], it allows to improve significantly the agreement between theory and experiment data. Moreover, the work [16] shows the importance of detailed description of phonons propagation to calculate the thermal conductivity in a wide range of temperatures (from 10 K to 450 K) and film thickness (from 10 nm to 100 µm).

3. In papers [1, 2] the equation (3) for the thermal conductivity is written as:

\[
\kappa = \frac{1}{(2\pi)^3} \sum_j \int \frac{k_B \left( \frac{\hbar \omega_j}{k_B T} \right)^2}{\exp(\frac{\hbar \omega_j}{k_B T}) - 1} v_j(\bar{k}) \cos \theta \cdot l_j(\bar{k}) \cos \theta d\bar{k} .
\] (7)

Here the influence of the boundary in nanoﬁlms is taken into account through the function \( l_j(\bar{k}) \), as in the previous case parameter \( F(Kn, p) \) is used. Moreover, the function includes all the processes of interaction of phonons within the film. This model is actually close to the second model of the previous study.

4. Quasi-hydrodynamic solution of the Boltzmann equation [5, 17, 18] gives the following relationship between heat flux, \( \bar{q} \), thermal conductivity, \( \kappa_{\text{bulk}} \), and mean free path, \( l_{\text{bulk}} \):

\[
\bar{q} = -\kappa_{\text{bulk}} \nabla T + l_{\text{bulk}} \nabla^2 \bar{q} .
\] (8)

In this model the phonon gas is represented as a classical rareﬁed gas that ﬂows between the boundaries of the film according with the laws of hydrodynamics (in the general case described by the Navier - Stokes equation for compressible ﬂuids [7]). Equation (8) is determined not the thermal conductivity, but heat ﬂux. From (8) it is clearly that the heat ﬂow at the nanoscale (e.g. thin ﬁlms) is lower than in macroscopic structures. This is due to the deceleration of the ﬂow of phonons, on the boundaries of the ﬁlm and inside it. A detailed discussion of this model is given in [5, 7, 19]. The comparison of the calculation by this model with experimental data shows good agreement [18].

Finally, let’s present the calculations using the presented models. Figure 1 shows the dependence of the thermal conductivity in the silicon ﬁlm from its thickness. Curve 1 on the plot corresponds to the relation (4) with \( \Gamma = 1 \). Curve 2 shows the behavior of \( \tau_{\text{eff}} = (1 - p) \frac{2}{(1 + p) \pi d_s} \). Curve 3 corresponds to the equation (5). For temperature 300 K and 77 K parameter \( p \) equal to zero, for the temperature of 30 Kelvin \( p = 0.3 \). This is consistent with the concept that in low temperature limit the value \( p \) should be different from zero and grow with temperature decrease. Curve 4 represents the calculations from [16] using equation (6). Curve 5 shows another variation of model (6) from [20]. Experimental data is taken from [20].

In conclusion it should be noted the following issues. First, it is necessary to develop rigorous methods of analysis of the phonon scattering on the boundary surfaces of the nanostructures. Secondly, the dependences of the mean free path from \( \bar{k} \) and \( \omega \) used in the presented models for estimation of Knudsen number are quite rude. The fact is that in the diffusion and diffusive-ballistic regimes interactions occur to phonons during the transition from one boundary to another, which change the propagation direction and energy (frequency) of phonons. For this reason, the most reliable method for determining the effective thermal conductivity of nanostructures can be the numerical Monte Carlo method [21].
Figure 1. The dependence of the in-plane thermal conductivity of Si films for different models of boundary scattering: 1 – equation (4) with $\Gamma=1$; 2 – (4) with var. $p$; 3 – relation (5); 4 – results from [16], using (6); 5 – theoretical model [20], variation of (6); ‘+’ – experimental data [20].

Acknowledgment
Work was supported by Russian Ministry of Science and Education, project 16.8107.2017/6.7.

References
[1] Maldovan M 2011 J. Appl. Phys. 110 034308
[2] Maldovan M 2012 Appl. Phys. Lett. 101 113110
[3] Marconnet A, Asheghi M and Goodson K 2013 ASME J. Heat Transfer 135 061601
[4] Liu W and Asheghi M 2006 ASME J. Heat Transfer 128 75
[5] Lifshitz E and Pitaevskii L 1981 Physical Kinetics (New York: Pergamon Press)
[6] Dove M 2004 Introduction to Lattice Dynamics (Cambridge: Cambridge University Press)
[7] Khvesyuk V and Scryabin A 2017 High Temperature 55 428
[8] Casimir H 1938 Physica 5 495
[9] Chernatynski A and Philpott S 2010 Phys Rev B 82 134301
[10] Klemens P 1958 The Solid State 7
[11] Holland M 1963 Phys. Rev. 132 2461
[12] Soffer S 1967 J. Appl. Phys. 38 1710
[13] Asheghi M, Kurbayashi K, Kasnavi R and Goodson K 2002 J. Appl. Phys. 91 5079
[14] Sondheimer E 1952 Adv. in Phys. 1 297
[15] Zhang Z 2007 Nano/Micro Heat Transport (New York: Mc Grow Hill)
[16] Barinov A., Liu B, Zhang K and Khvesyuk V 2017 Science and Education: Scientific Publication of BMSTU 6 1
[17] Guyer R and Krumhonsl J 1966 Phys. Rev. 148 766
Guyer R and Krumhonsl J 1966 Phys. Rev. 148 778
[18] Ma Y 2012 Appl Phys. Lett. 101 211905
[19] Alvarez F, Jou D and Sellito A 2009 J. Appl. Phys. 105 014317
[20] Asheghi M et al. 1997 J. Appl. Phys. 71 1798
[21] Mazumder S and Majumdar A 2001 ASME J. Heat Transfer 123 749