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Effects of boundary scattering and optic phonon drag on thermal conductivity of a slab of rectangular cross-section

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The lattice thermal conductivity of a slab of the rectangular cross-section is calculated. The approximate kinetic equation for acoustic phonons is derived from the exact kinetic equations for the binary phonon gas in restricted geometry. The approximation covers the effects of boundary phonon scattering and optic phonon drag. It is shown that a proper account for both these effects gives rise to the violation of the Matthiessen's rule. The coefficient of thermal conductivity is calculated in the general form and verified for the particular cases of the Einstein and Debye models. The material-specified examples of the considered effects are presented.

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I. INTRODUCTION

The size limitation of the phonon mean free path affects the transport coefficients of solids significantly.[1] Phonon scattering by specimen boundaries proves to be the main mechanizm of heat resistivity at sufficiently low temperatures.[2–4] This explains why the heat conductivity of a slab is strictly dependent on its particular shape. A similar mechanizm of a phonon transport suppression is recovered in GaAs/AlAs, Si/Ge superlattices at high temperatures.[5–7] A strong decrease in the effective phonon relaxation time, caused by the diffusive scattering at interfaces, explains the observed[8,9] suppression of the perpendicular thermal transport.[5] The comparative by nature effect of reducing the effective phonon group velocity in quasiregular heterostructures have been addressed and exemplified numerically in Ref. 10. These recent works suggest that thermal transport can be affected significantly by material modulation even at finite temperatures owing to the additional internal reflection effects. This claims that special attention in the simultaneous consideration of finite and low-temperature mechanisms of relaxation which used to be treated separately in the conventional approaches.[1,4] Here we address, first of all, the interplay of the effects of optic phonon drag and interface scattering of the acoustic phonons.

Some specific slab geometries can cause unconventional features of heat transport which cannot be derived by simple scaling arguments. This can be exemplified with the logarithmic peculiarities of the thermal conductivity coefficient of a narrow plane-parallel slab.[11–13] For this case, the bulk and boundary phonon scattering are not additive in their effect. The abovementioned peculiarities lead to an effective "mixing" of both scattering mechanisms which can be expressed as a violation of the Matthiessen's rule. In spite of this, the Matthiessen's formula represents the most commonly used tool for the analysis of measurements of thermal conductivity in crystals of the rectangular cross-section.[14] However, this approach disregards the effect of specimen shape completely. In addition, it is not quite clear how the semiempirical Mathiessen's formula agrees with the exact analysis of the size effect near the Casimir limit. It can also be argued that the Mathiessen's decomposition of the collision frequency is valid when considering the processes of normal phonon scattering.

Although being of great interest for microelectronics,[15] the rigorous theory of size effect on the lattice thermal conductivity is still not established finally. Some progress was achieved recently by making use of the equation of phonon radiative transfer.[16–19] This approach, however, employs essentially the relaxation time approximation and does not take into account the normal scattering processes. This also disregards the effects of splitting the phonon spectrum into acoustic and optical branches with different dispersion laws. These effects are especially important when different phonon modes lie closely on the energetic scale. That can be the case for some superconductor[20,21] and semiconductor[22] materials. Given the vicinity of the phonon branches, one cannot treat the optical and acoustical modes separately. The nonequilibrium phonon system should be considered as the binary quasiparticle gas.[23] This requires an essential modernization of the mathematical tools for the problem.

The present paper aims to give theoretical insight into the above described problems. The main purpose of this work is to take into account the effects of optic phonon drag arising due to the normal phonon collisions and boundary scattering of the acoustic phonons. To the best of the author's knowledge these two effects were never treated simultaneously. This motivates the present investigation in view of the following arguments. The contribution of optic phonons to thermal conductivity is usually neglected[18,24] referring to their small group velocity. We will show that this argument does not apply to the optic phonon drag effect caused by the normal collisions. In this case, more accurate treatment reveals a significant contribution of optic phonons to thermal transport. The normal cross collisions of phonons can cause a suppression of the acoustic phonon mean free path (MFP) and considerable drag effect at the same time. The neglectance of this effect causes, in particular, overestimation of the phonon MFP which in turn can result in overestimation of the role of the interface scattering. This latter, however, used to be considered as a dominant mechanizm of relaxation in quantum wires at temperatures up to that of room temperature.[13] The optic phonon drag effect is also significant at these temperatures and the neglectance of this can cause inadequate evaluation of the transport coefficients. The proper understanding of the relation between the different phonon-phonon and phonon-interface relaxation rates is also important for some quantum well[7] and heterostructures.[10] These structures exemplify a variety of systems where both the acoustic and optical phonon branches are activated and the phonon MFP is of the order of the characteristic size of a structure at the same time. For these systems, all three types of phonon scattering (boundary, normal, and nonelastic) must be considered simultaneously.

The effects of both normal and boundary phonon collisions cannot be directly treated in the framework of the relaxation time approximation. We base our speculations on the rigorous analysis of the kinetic boundary value problem in a slab of the rectangular cross-section. The need to simultaneously consider of the acoustic and optic phonons brings another question into focus. To get a reliable picture of lattice heat transport one should account for the effect of mutual phonon drag. The drag effect caused by the nonelastic cross collisions of phonons can be properly taken into consideration by introducing the corresponding collision frequency.[25] As is shown here, this approximation is not sufficient for the account of normal phonon scattering processes. A proper consideration of the effects due to the normal collisions requires a more accurate analysis of the kernels of collision operators.[26–28] This analysis is performed here in the most general form without a reference to any specific model for the collision integrals. The calculated drag effect proves to give a significant contribution to the heat conductivity coefficient. It is shown that this contribution cannot be described by the Matthiessen's formula.

The paper is organized as follows. Section II presents the exact formulation of the kinetic boundary value problem. The kinetic equation derived here makes it possible to take into account the effects of boundary scattering and optic phonon drag on the acoustic phonon system. This equation is solved rigorously in Sec. III. The coefficient of thermal conductivity is calculated and analyzed in Sec. IV. The validity of the Matthiessen's rule is also verified in this section. Conclusions are given in Sec. V.

II. EXACT KINETIC EQUATIONS, KERNELS OF THE COLLISION OPERATORS AND THE BOUNDARY VALUE PROBLEM

We start with the exact formulation of the kinetic problem. A set of kinetic equations describing a nonequilibrium phonon system can be written in the operator form[27]

$$S_{11}|g\rangle + S_{12}|g\rangle + L|g\rangle = |V\rangle. \tag{1}$$

Here S_{11} is the operator of mutual collisions of phonons of the same type, S_{12} the operator of cross collisions of acoustic and optic phonons, and L is the operator describing the scattering of phonons by point defects, dislocations, electrons, etc. We consider that the operators S_{11}, S_{12} preserve the phonon numbers, momenta, and energy in collisions. Contrastingly, we treat the operator L in the Lorentz approximation considering that the phonon momenta are not preserved in the collisions with the above described scatterers. However, the phonon energy remains unchanged in these collisions. It is important to note that the separation of the collision operator into two distinct contributions according to Eq. (1) is of rather conditional character. This can also be interpreted as the separation of all types of collisions into elastic and nonelastic ones, independently on their specific character. For instance, the Umklapp processes in phonon collisions are covered by the operator L while the normal processes belong to the operators S_{11}, S_{12}.

Further we consider that the acoustic phonons make the main contribution to thermal conductivity what is usually the case for sufficiently low temperatures. For the sake of simplicity we restrict ourselves to the consideration of elastic scattering of optic phonons on acoustic ones. We also neglect the interaction of optic phonons with a wall. Under these assumptions, the linearized collision operators and the vectors $|g\rangle = |g_1, g_2\rangle$, $|V\rangle = |V_1, V_2\rangle$ in Eq. (1) are defined by

$$S_{11} = \begin{pmatrix} \hat{S}_{11} & 0 \\ 0 & \hat{S}_{22} \end{pmatrix}, \quad S_{12} = \begin{pmatrix} \hat{S}_{12}^{(1)} & \hat{S}_{12}^{(2)} \\ \hat{S}_{21}^{(1)} & \hat{S}_{21}^{(2)} \end{pmatrix},$$

$$L = \begin{pmatrix} -\hat{\nu}(\epsilon_1) & 0 \\ 0 & 0 \end{pmatrix}, \quad |V\rangle = \left| \begin{matrix} \dfrac{\partial \epsilon_1}{\partial \vec{p}_1} \nabla_{\vec{r}} \left(\dfrac{\epsilon_1}{T} + g_1 \right) \\ \dfrac{\partial \epsilon_2}{\partial \vec{p}_2} \nabla_{\vec{r}} \left(\dfrac{\epsilon_2}{T} \right) \end{matrix} \right\rangle,$$

$$\begin{aligned} \hat{S}_{ii} g_i = \int & W_{ii}(\vec{p}_i, \vec{p}_{i_1} | \vec{p}_{i_2}, \vec{p}_{i_3}) [1 + f_0^{(i)}(p_i)]^{-1} \\ & \times [1 + f_0^{(i)}(p_{i_2})] f_0^{(i)}(p_{i_1}) [1 + f_0^{(i)}(p_{i_3})] [g_i(\vec{p}_{i_2}) \\ & + g_i(\vec{p}_{i_3}) - g_i(\vec{p}_i) - g_i(\vec{p}_{i_1})] d\Gamma_{i_1} d\Gamma_{i_2} d\Gamma_{i_3}, \end{aligned} \tag{2}$$

$$\begin{aligned} \hat{S}_{ij}^{(i)} g_i = \int & W_{12}(\vec{p}_i, \vec{p}_j | \vec{p}_{i_1}, \vec{p}_{j_1}) [1 + f_0^{(i)}(p_i)]^{-1} \\ & \times [1 + f_0^{(i)}(p_{i_1})] f_0^{(j)}(p_j) [1 + f_0^{(j)}(p_{j_1})] \\ & \times [g_i(\vec{p}_{i_1}) - g_i(\vec{p}_i)] d\Gamma_{i_1} d\Gamma_j d\Gamma_{j_1}, \end{aligned} \tag{3}$$

$$\begin{aligned} \hat{S}_{ij}^{(j)} g_j = \int & W_{12}(\vec{p}_i, \vec{p}_j | \vec{p}_{i_1}, \vec{p}_{j_1}) [1 + f_0^{(i)}(p_i)]^{-1} \\ & \times [1 + f_0^{(i)}(p_{i_1})] f_0^{(j)}(p_j) [1 + f_0^{(j)}(p_{j_1})] \\ & \times [g_j(\vec{p}_{j_1}) - g_j(\vec{p}_j)] d\Gamma_{i_1} d\Gamma_j d\Gamma_{j_1}. \end{aligned} \tag{4}$$

Hereafter, the index $i=1$ ($i=2$) corresponds to acoustic (optic) phonons, T is the temperature, $\vec{p}_i$ and $\varepsilon_i(|\vec{p}_i|)$ the phonon momentum and energy, respectively, $d\Gamma_i$ the volume element of the momentum phase space, f_i the true distribution functions, $g_i = [f_0^{(i)\prime}(\varepsilon_i/T)]^{-1}(f_i - f_0^{(i)})$ the small corrections to the equilibrium distribution functions $f_0^{(i)}$, and $\hat{\nu}$ is the frequency describing the nonelastic collisions of acoustic phonons with the abovementioned external scatterers. The gradients are directed along the z axis, the prime denotes differentiation with respect to the argument, the Boltzmann and Planck constants are set equal to 1.

We aim to derive the Callaway-like formula for thermal conductivity with the correct inclusion of the contributions due to both boundary effects and optic phonons. For this purpose we consider that the operator L plays a dominant role in the collision integral. The artless way to treat this case is to completely neglect the operators S_{11}, S_{12} in the leading approximation when constructing the perturbation expansion. This would lead to the splitting Eq. (1) into the independent equations for the acoustic and optic components. However, this approach is not appropriate to the case for both physical and mathematical reasons. First of all, it does not make it possible to take into account the relaxation process due to the normal cross collisions of acoustic and optic phonons. This process is responsible for the mutual influence of the components of the binary phonon gas and should be treated more accurately. Let us note that even a comparatively small contribution of the elastic phonon scattering can affect the phonon system significantly. The normal collisions produce the "dissipationless" mutual drag of acoustic and optic components. Therefore, these two components cannot be treated separately, even in the considered limit $L|g\rangle \gg S_{12}|g\rangle$. Formally, we refer to that the operators S_{11}, S_{12} have the nontrivial kernels constituted by the collision invariants. These kernels should be taken into account by correct perturbation approach.

The above effect of mutual drag can be taken into account by the proper inclusion of the collision invariants into the perturbation expansion. Further we focus on the momentum conservation law in the cross collisions of acoustic and optic phonons. This law can be expressed in the following equivalent forms:

$$P_i S_{12} = S_{12} P_i = 0, \quad (E-P_i) S_{12} (E-P_i) = S_{12}. \tag{5}$$

Here we introduced the unity operator E and the projector P_i to the subspace associated with the i components of the vector $|\vec{p}_1, \vec{p}_2\rangle$ so that $P_i|p_{1i}, p_{2i}\rangle = 0$ and $P_i P_i = P_i$. The projections of Eq. (1) onto the subspaces associated with P_i and the subspace orthogonal to them can be written as

$$P_i L|g\rangle = P_i|V\rangle, \tag{6}$$

$$\left(E - \sum_{i=x,y,z} P_i\right)(S_{11}+S_{12})\left(E - \sum_{i=x,y,z} P_i\right)|g\rangle + \left(E - \sum_{i=x,y,z} P_i\right) L|g\rangle = \left(E - \sum_{i=x,y,z} P_i\right)|V\rangle, \tag{7}$$

correspondingly. Please note that the first operator in the left hand side of Eq. (7) has the trivial kernel. Thus this equation is subject to the ordinary perturbation expansion procedure. Also note that $P_{x,y}|V\rangle = 0$.

The nontrivial z component of Eq. (6) for the correction g_1 can be rewritten in the explicit form as follows:

$$\langle p_{1z}|\hat{\nu} g_1\rangle + \langle p_{1z}|V_1\rangle + \langle p_{2z}|V_2\rangle = 0, \tag{8}$$

where the inner product is introduced by the definition

$$\langle h(\vec{p}_1), g(\vec{p}_1)\rangle = -\int f_0^{(1)\prime}\left(\frac{\varepsilon_1}{T}\right) h^*(\vec{p}_1) g(\vec{p}_1) d\Gamma_1. \tag{9}$$

It should be stressed that Eq. (8) is exact and it does not contain the operators S_{11}, S_{12}. This proves that the true moment $\langle p_{1z}|\hat{\nu} g_1\rangle$ differs from that expected in the leading order of the perturbation series obtained when S_{11}, S_{12} are neglected either. The exact expression (8) for the above moment takes into account the effect of optic phonon drag and describes the limiting case $\hat{\nu}=0$ correctly.[29]

In order to proceed with Eq. (7) it is instructive to introduce the orthonormal basis $\{|e_i\rangle\}_{i=1}^{\infty}$ in the Hilbert space of functions of momentum $\vec{p}_1$ with the first vector[30] $|e_1\rangle = |p_{1z}\rangle/\sqrt{\langle p_{1z}|p_{1z}\rangle}$. Then Eqs. (6) and (7) can be rewritten in the projections onto the orthogonal subspaces associated with the vectors $|e_i\rangle$. Formally we define the function

$$G(x,y,\vec{p}_1) = \hat{\nu} g_1 + \frac{\partial \epsilon_1}{\partial \vec{p}_1} \nabla_{\vec{r}} \left(\frac{\epsilon_1}{T} + g_1\right) \tag{10}$$

and neglect the operator $(E-P_z)(S_{11}+S_{12})(E-P_z)$ in Eq. (7). Then Eqs. (6),(7) are equivalent to

$$\langle e_i|G\rangle = \delta_i^1 \frac{\langle p_{2z}|V_2\rangle}{\sqrt{\langle p_{1z}|p_{1z}\rangle}} \quad (i=1,\ldots), \tag{11}$$

where δ_i^l is the Kronecker delta.

Equations (11) can be interpreted as the definitions of the components of the function G in the basis $\{|e_i\rangle\}_{i=1}^{\infty}$. This makes it possible to obtain the equation for g_1 in the closed form. The formal derivation is rather trivial. From Eq. (11) we have

$$G = \sum_{i=1}^{\infty} |e_i\rangle\langle e_i|G\rangle = |e_1\rangle \frac{\langle p_{2z}|V_2\rangle}{\sqrt{\langle p_{1z}|p_{1z}\rangle}}. \tag{12}$$

Using the definition (10) we rewrite Eq. (12) in the form

$$\frac{\partial \epsilon_1}{\partial p_{1x}} \partial_x g_1 + \frac{\partial \epsilon_1}{\partial p_{1y}} \partial_y g_1 + \hat{\nu} g_1 = \Lambda(\vec{p}_1), \tag{13}$$

where

$$\Lambda(\vec{p}_1) = \left(\frac{\partial \epsilon_1}{\partial p_{1z}} \frac{\epsilon_1}{T} + p_{1z} \frac{\left\langle p_{2z} \middle| \frac{\partial \epsilon_2}{\partial p_{2z}} \frac{\epsilon_2}{T}\right\rangle}{\langle p_{1z}|p_{1z}\rangle}\right) \frac{\partial_z T}{T}. \tag{14}$$

Equalities (13), (14) present the partial differential equation for the nonequilibrium correction g_1 to the equilibrium distribution function of acoustic phonons. The second term in Eq. (14) stands for the contribution of the optic phonon drag due to the elastic phonon collisions. Note that the effect of the momentum dissipation in the system of acoustic phonons due to the inelastic scattering is described by the collision frequency $\hat{\nu}$. Dissipation of the momentum of the acoustic component on specimen boundaries should be taken into account separately, by employing an appropriate boundary condition. Here we restrict ourselves to the consideration of the diffuse boundary condition taken in its simplest form

$$g\left(\vec{r}\in B,\frac{\partial\epsilon_1}{\partial\vec{p}_1}\vec{n}\geqslant 0\right)=0, \tag{15}$$

where B are the points of a slab surface and $\vec{n}$ is a positive normal to B. Kinetic equations (13), (14) completed with the boundary condition (15) will be solved in the next section.

III. SOLUTION OF THE KINETIC EQUATION

The general solution of Eq. (13) can be written in the form[31]

$$g_1=(1-e^{-\Omega})\hat{\nu}^{-1}\Lambda. \tag{16}$$

Function Ω should be specified for the particular geometry of a slab. For a slab of the rectangular cross-section with the lengths of sides $2a$ and $2b$ this function is found to be given by

$$\Omega=\min\left(\frac{x}{s_x}+\frac{a}{|s_x|},\frac{y}{s_y}+\frac{b}{|s_y|}\right) \tag{17}$$

where $\vec{s}=\hat{\nu}^{-1}(\partial\epsilon_1/\partial\vec{p}_1)$. For the sake of definiteness we set $b\leqslant a$.

To be used in the calculation of thermal conductivity of a slab, expression (16) should be averaged over the cross-section area. After some straightforward algebra one finds

$$\frac{1}{ab}\int_S g_1=\Lambda\tilde{g}\left(\frac{s_x}{2a},\frac{s_y}{2b}\right), \tag{18}$$

where

$$\tilde{g}\left(\frac{s_x}{2a},\frac{s_y}{2b}\right)=1-\frac{1}{\sigma}(1+e^{-\omega})-\frac{1}{\omega}(1-e^{-\omega})\left(1-\frac{2}{\sigma}\right), \tag{19}$$

$\sigma=\max(2a/|s_x|,2b/|s_y|)$, $\omega=\min(2a/|s_x|,2b/|s_y|)$.

We facilitate further derivation by calculating the average over the angle coordinates of the spherical system with the polar axis taken in the direction of the temperature gradient, defined as follows:

$$\hat{g}(\hat{a},\hat{b})=\frac{3}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}\tilde{g}\left(\frac{\sin\theta\cos\phi}{\hat{a}},\frac{\sin\theta\sin\phi}{\hat{b}}\right)\times\cos^2\theta\sin\theta d\theta, \tag{20}$$

where we introduced the reduced lengths $\hat{a}=2a/|\vec{s}|$, $\hat{b}=2b/|\vec{s}|$. Note that $\hat{g}=1$ for $\tilde{g}=1$.

The direct calculation gives

$$\hat{g}=1-\frac{2}{\pi}[H(\hat{a},\hat{b})+H(\hat{b},\hat{a})], \tag{21}$$

where

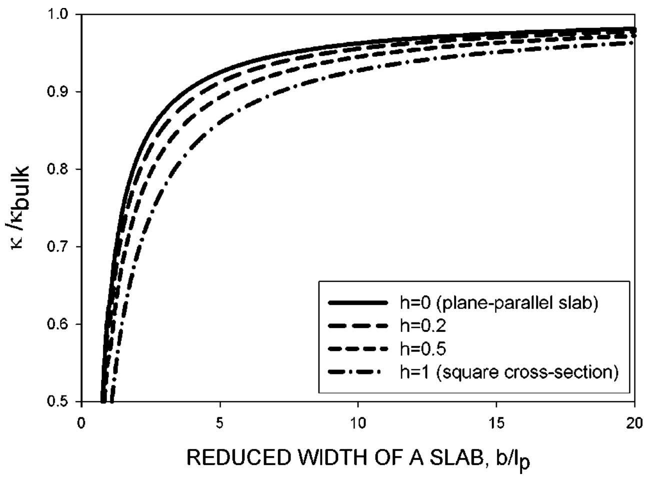

FIG. 1. Size effect on thermal conductivity for different values of aspect ratio $h=b/a$ of a slab cross-section. The ratio of the thermal conductivity of a slab to the bulk thermal conductivity is plotted against the reduced width of a slab. The solid line presents thermal conductivity of the plane-parallel slab.

$$H(\hat{a},\hat{b})=\frac{\hat{a}}{\hat{b}}(F(\hat{a})-F(\hat{c}))+\frac{3}{\hat{a}}Q(\hat{a},\hat{b}),$$

$$F(x)=\frac{3\pi}{16x}+\frac{3}{x^2}\left(S_6(x)-\frac{2}{15}\right), \tag{22}$$

$$Q(\hat{a},\hat{b})=\frac{\pi}{16}\{1+4[E_5(\hat{a})-E_3(\hat{a})]\}+\frac{\pi\hat{a}^2\hat{b}}{32\hat{c}^3}\left(1-\frac{16}{\pi}S_5(\hat{c})\right)-\frac{1}{2}\int_{\hat{c}/\hat{a}}^{\infty}\frac{y^2-1}{y^5}\times(1-e^{-\hat{a}y})\arccos\frac{\hat{b}}{\hat{a}\sqrt{y^2-1}}dy, \tag{23}$$

$E_n(x)=\int_1^{\infty}y^{-n}e^{-xy}dy$ is the exponential integral, $S_n(x)=\int_1^{\infty}\sqrt{y^2-1}y^{-n}e^{-xy}dy$ is the special function introduced in Refs. 12, 13, and $\hat{c}=\sqrt{\hat{a}^2+\hat{b}^2}$. The value $\hat{g}$ plays an important role in further speculations. Although it is expressed in terms of special functions, the numerical evaluation of this value can be more convenient for the practical use. The results of such an evaluation are presented in Fig. 1. We postpone the detailed discussion of these results to the next section.

Equality (21) presents the solution of Eq. (13) averaged over the slab cross-section area and the azimuthal and polar angles of the phonon momentum vector. This solution can be used for calculations of transport coefficients of a binary phonon gas in a slab of the rectangular cross-section. In particular, Eq. (21) makes it possible to express the coefficient of thermal conductivity in a slab via its value in the bulk.

IV. COEFFICIENT OF THERMAL CONDUCTIVITY AND THE MATTHIESSEN'S RULE

First we focus on the investigation of the optic phonon drag effect on the coefficient of thermal conductivity κ_{bulk} in the bulk. This coefficient can be derived from Eq. (21) for any given energy-momentum relation of acoustic phonons. In case of the simplest phonon dispersion law of the form $\epsilon_1 = v|\vec{p}_1|$, κ_{bulk} is found to be written as

$$\kappa_{\text{bulk}} = [1+\eta(T)]\frac{T^3}{2v\pi^2}\int_0^{\theta_D/T}\frac{y^4 e^y}{(e^y-1)^2}\hat{\nu}^{-1}(yT)dy, \tag{24}$$

where $\eta = S_2/S_1$ and

$$S_i = \left\langle p_{iz}\left|\frac{\epsilon_i}{T^2}\frac{\partial\epsilon_i}{\partial p_{iz}}\right.\right\rangle \tag{25}$$

is the entropy of the ith component of the phonon gas, v is the sound velocity. In the gray media (constant relaxation time) approximation the coefficient of thermal conductivity can be expressed as

$$\kappa_{\text{bulk}} = [1+\eta(T)]\frac{\hat{\nu}^{-1}v^2 C_V}{3},$$

where C_V is the specific heat.

The coefficient η describes the above effect of optic phonon drag on the thermal conductivity caused by acoustic phonons. This value can be easily evaluated in the framework of the Einstein approximation[25] for optic phonons $\epsilon_2 = \theta_E$. This reads

$$\eta(\tau,t) = (t\tau)^3\left(\frac{\tau}{e^\tau - 1} - \ln(1-e^{-\tau})\right)\left(\int_0^{t\tau}\frac{y^4 e^y}{(e^y-1)^2}dy\right)^{-1}, \tag{26}$$

where $\tau = \theta_E/T$, $t = \theta_D/\theta_E$, and θ_D is the Debye temperature.

As should be expected, the above drag effect increases with the temperature. To better estimate this effect at high temperatures we fitted the coefficient $\eta(t^{-1},t)$ with the function $\eta_{\text{fit}}(t^{-1},t) = -0.58 + 3.99t$ within the accuracy $|\eta - \eta_{\text{fit}}| < 0.03$ in the interval $0.25 < t < 0.95$. The good agreement of η with the fit function of a linear shape allows one to conclude that the contribution of optic phonon drag is directly proportional to the ratio θ_D/θ_E. Therefore, the closer the acoustical and optical phonon brunches lie on the energetic scale, the larger contribution comes from the mutual drag of different species of the phonon gas. At sufficiently high temperatures and large values of t this contribution can even exceed the main term in Eq. (27) describing the thermal conductivity of the pure system of acoustic phonons.

In order to illustrate the above evaluations we presented the coefficient η for several selected materials (GaAs, Si, Ge, and MgB_2) in Fig. 2 . All these materials are characterized by the relatively close values of the Debye (acoustic phonon) and Einstein (optic phonon) temperatures. Thus, according to the previous arguments one should expect a considerable drag effect. As can be seen, the contribution to thermal conductivity due to the optic phonon drag is several times larger than the main term describing the drift of acoustic phonons. This causes 75% correction to the thermal conductivity of GaAs at room temperature. The situation here is of resemblance to the acoustic phonon drag effect on the electron conductivity and thermopower in metals. As is well known,[1] this effect produces an increase of several orders of magnitude in transport coefficients.

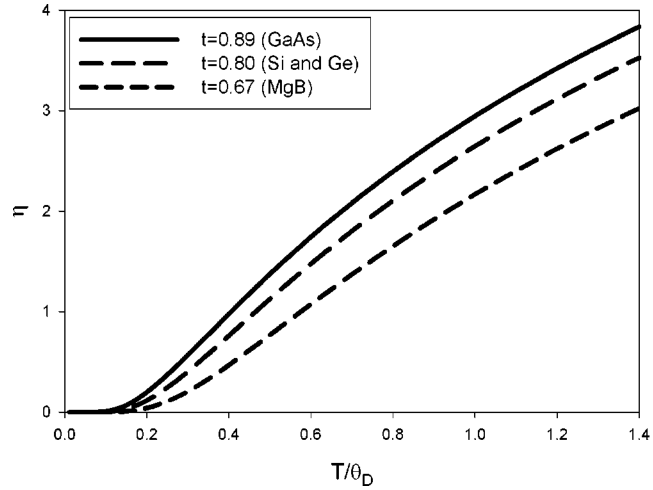

FIG. 2. Effect of optic phonon drag on thermal conductivity for several selected materials. Coefficient η defined by Eq. (26) is plotted against the reduced temperature.

In view of the above, the use of the classical kinetic formula $\kappa = C_V l_p v/3$ when evaluating the phonon MFP l_p can also be argued. This point is illustrated in Fig. 3 for GaAs. According to this figure, overestimation of the acoustic phonon MFP (Ref. 7) caused by the neglectance of the optic phonon drag effect reaches 75% at room temperature. This can also bring significant corrections to the understanding of

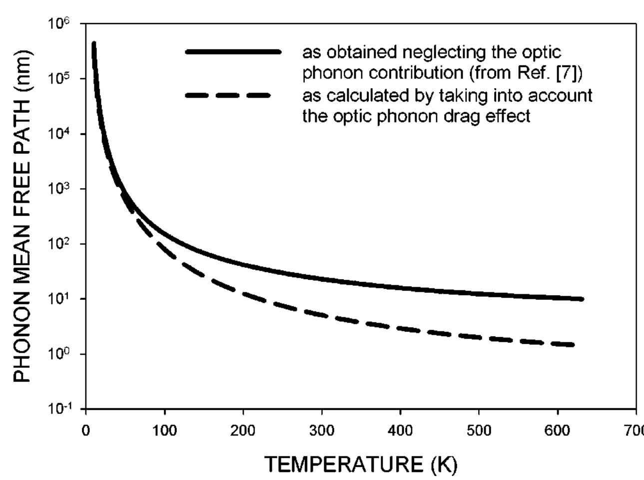

FIG. 3. Estimation of the phonon mean free path by taking into account the effect of optic phonon drag. The solid line is reproduced from Ref. 7. The dashed line demonstrates the result of the presented theory.

mutual role of the bulk and interface scattering in thermal conductivity of superlattices and quantum wells.

We now turn to the investigation of the size effect on thermal conductivity. Given that $|\vec{s}|$ does not depend on the phonon momentum, the ratio of the thermal conductivity coefficient κ to its value in the bulk can be found particularly simply. This is the case for the above simplest energy-momentum relation for the acoustic phonons of the form $\epsilon_1 = v|\vec{p}_1|$. We merely have $|\vec{s}| = \hat{\nu}^{-1} v$. Therefore, the coefficient of thermal conductivity caused by the acoustic phonons reads

$$\kappa = \hat{g}(\hat{a},\hat{b})\kappa_{\text{bulk}}. \tag{27}$$

First, we verify result (27) in the simple limiting cases. For the plane-parallel slab ($a \to \infty$), Eq. (27) goes over into the result derived independently by Kaganov, Podd'yakova[11] for thermal conductivity of HeII in capillaries and by Hyldgaard, Mahan[12] for semiconductor heterostructures. This reads

$$\hat{g} = 1 - \frac{3}{8\hat{b}} + \frac{3}{2\hat{b}}[E_3(\hat{b}) - E_5(\hat{b})]. \tag{28}$$

In the Casimir limit $\hat{a},\hat{b} \ll 1$ one finds

$$\hat{g}_C = \frac{3}{4}\left[\hat{a}\ln\left(\frac{\hat{c}+\hat{b}}{\hat{a}}\right) + \hat{b}\ln\left(\frac{\hat{c}+\hat{a}}{\hat{b}}\right)\right] + \frac{1}{2\hat{a}\hat{b}}(\hat{a}^3 + \hat{b}^3 - \hat{c}^3). \tag{29}$$

For a slab of the square cross-section ($\hat{a} = \hat{b}$) the result of MacDonald and Sarginson[32] is recovered from Eq. (29)

$$\hat{g}_C(\hat{a},\hat{a}) = \frac{3\hat{a}}{4}\ln\left(\frac{\sqrt{2}+1}{\sqrt{2}-1}\right) + \hat{a}(1-\sqrt{2}). \tag{30}$$

Now we will discuss the possibility to describe the boundary phonon scattering by means of the properly defined collision frequency. This trick is commonly used in a variety of evaluations of the size effect in the framework of the Matthiessen's approximation. The typically used phonon-wall collision rate is $\nu_w = v/H$ where H is the characteristic size of a slab. This crude scale estimation is to be compared with the results of the exact approach developed here. The presence of the logarithmic terms in the rigorous results (29), and (30) put under question the possibility of correct introduction of the above collision frequency. Evidently, such a frequency cannot be used in the Casimir limit $H \ll v/\hat{\nu}$ for the above reason. In the opposite limit $H \gg v/\hat{\nu}$ the effective phonon-wall collision rate can be defined properly. Asymptotic expression for the function $\hat{g}$ in the limit $\hat{a},\hat{b} \ll 1$ reads

$$\hat{g} = 1 - \frac{3}{8}\left(\frac{1}{\hat{a}} + \frac{1}{\hat{b}}\right). \tag{31}$$

By introducing the collision frequency

$$\nu_w = \frac{3v}{4}\frac{a+b}{ab}, \tag{32}$$

one can rewrite Eqs. (27),(24) in the form

$$\kappa = [1+\eta(T)]\frac{T^3}{6v\pi^2}\int_0^{\theta_D/T}\frac{y^4 e^y}{(e^y-1)^2}\nu_{\text{eff}}^{-1}(yT)dy, \tag{33}$$

where the effective frequency ν_{eff} is defined by the Matthiessen's rule $\nu_{\text{eff}} = \hat{\nu} + \nu_w$. According to Eqs. (27), and (24) the above introduced value H should be taken equal to $\frac{4}{3}[ab/(a+b)]$. As is expected, this value does not depend on the size of a slab in the direction of applied gradient.

Figure 1 demonstrates the contribution of phonon-boundary scattering to the thermal conductivity coefficient ($\hat{g}$) against reduced width of a slab ($\hat{b}$) for several values of the cross-section aspect ratio. In agreement with the above calculation, the square shape of a cross-section ($a=b$) produces the maximal effect of suppression of thermal transport in a slab. It is also clearly indicated that the value of the size effect decreases exponentially as the reduced width increases.

V. CONCLUSIONS

The size effect on thermal conductivity of a slab of the rectangular cross-section was investigated. The kinetic boundary value problem describing the binary phonon gas in restricted geometry is considered. We focused on the case where the effect of normal phonon scattering is much smaller than that due to nonelastic phonon collisions. In this limit, the rigorous analysis of the true collision operators made it possible to construct the correct perturbation expansion. The approximate kinetic equation (13) for acoustic phonons was derived in the leading order of this expansion. The accurate treatment of the kernels of the operators describing the mutual and cross phonon collisions allowed one to take into account the effect of optic phonon drag. This drag effect proves to give rise to a significant contribution to the thermal conductivity caused by the acoustic phonons.

Exact solution (16) of kinetic equation (13) completed with diffuse boundary condition (15) was found. This solution made it possible to calculate the coefficient of thermal conductivity (27) of a slab of the rectangular cross-section. Both effects of the optic phonon drag and the boundary scattering of acoustic phonons were taken into account. The results indicate an agreement with the well known limiting cases. Material-specified examples of the optic phonon drag effect on thermal transport are presented. It is found that in some cases this effect can cause an increase of several orders of magnitude in thermal conductivity.

The validity of the Mathiessen's rule was reexamined for different ratios of the characteristic size of a slab to the phonon mean free path. The violation of the Mathiessen's rule was indicated near the Casimir limit (in a "narrow" slab). The exact value of the collision frequency (32) describing the boundary phonon scattering is calculated in the opposite limit to be used in the refined Mathiessen's formula. The introduced frequency does not depend on the slab size in the direction of an applied temperature gradient. Its value found to be strictly dependent on the aspect ratio of the cross section of a slab normal to the direction of the gradient. The effect of boundary scattering on the thermal conductivity is evaluated numerically for several selected materials.

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