JETP Letters, Vol. 81, No. 4, 2005, pp. 190–194. From Pis'ma v Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 81, No. 4, 2005, pp. 228–232.
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Low-Temperature Thermal Transport in Nanowires¶

A. V. Zhukov[1, 2], S. Yang[2], and J. Cao[2]
[1] *Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada*
[2] *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA*
e-mail: ozhukov@uwo.ca, jianshu@mit.edu

Received October 27, 2004; in final form, January 27, 2005

We propose a theory of low temperature thermal transport in nanowires in a regime in which competition between a phonon and flexural modes governs the relaxation processes. Starting with the standard kinetic equations for two different types of quasiparticles, we derive a general expression for the coefficient of thermal conductivity. The underlying physics of thermal conductance is completely determined by the corresponding relaxation times, which can be calculated directly for any dispersion of quasiparticles, depending on the size of a system. We show that, if the considered relaxation mechanism is dominant, then at small wire diameters the temperature dependence of thermal conductivity experiences a crossover from $T^{1/2}$ to T^3-dependence. Quantitative analysis shows reasonable agreement with resent experimental results. © *2005 Pleiades Publishing, Inc.*

PACS numbers: 63.20.Kr, 63.22.+m, 65.40.–b

Low-dimension materials have attracted considerable attention in recent years, particularly in view of their potential applications in electronic devices [1, 2]. Many theoretical and experimental studies of nanowires and nanotubes are centered on the properties of electronic transport. However, it is now realized that the thermal properties of nanomaterials are also important for applications [3–5]. It is of special interest to increase thermal conductance in micro- and nanodevices [1, 6, 7]. In this paper, we study thermal transport in nonmetallic systems, in which heat is transported by thermal excitations only. In addition to the practical importance of such studies, thermal transport in nanowires is interesting from the fundamental point of view. Recent theoretical [8] and experimental [9] findings proved the existence of a quantum of thermal conductance in ballistic regime, which is similar to a quantum of electronic conductance. The state of experimental and theoretical understanding of thermal transport in nanoscale systems is comprehensively discussed in review [10]. Recently, D. Li *et al.* [11] reported an accurate measurement of lattice thermal conductivity in silicon nanowires for a wide range of temperatures and wire diameters. They demonstrated a significant influence of the system size not only on the magnitude of the thermal conductivity coefficient, but also on its temperature dependence. It is well known that, for large enough diameters of the wire and diffusive phonon–boundary scattering, the thermal conductivity coefficient at low temperatures is proportional to T^3. But for small values of the wire diameters, experiment [11] shows a clear crossover from cubic to near linear dependence on the temperature. In the present paper, we consider one particular relaxation mechanism that can explain the observed crossover.

Recently, Mingo [12] carried out an accurate numerical study of the thermal conductance of silicon nanowires to explain the decrease of the thermal conductivity coefficient with wire diameter observed in the experiment. He assumed that all the effects can be explained by the reconstruction of the phonon dispersion, where realistic phonon modes obtained from MD simulations were applied to general expression of the thermal conductivity coefficient. His numerical analysis shows excellent quantitative agreement with experiment [11] for large enough diameters at high temperatures. As the system size becomes smaller, the approach fails to describe a sharp decrease of thermal conductance as well as qualitative change of its temperature dependence. This is likely because Matheissen's rule has been used for evaluation of the phonon lifetime, which has rather restricted range of applicability (see, e.g., [13] and references therein).

As was noted in [14], a decrease of the temperature increases the characteristic phonon wavelength and reduces the scattering probability at the boundary surface. This leads to a modification of the phonon spectrum. For ideal wires, this is represented by a set of branches with energies proportional to a one-dimensional (1D) momentum directed along the wire. Thus, the standard theory of thermal conductance in dielectrics and semiconductors has to be modified to account for low dimensionality effects as well as phonon spectrum modification at low temperatures. Thus, to understand thoroughly the physical processes occurring inside the nanowires with decreasing sizes, we need an analytical theory to account for different mechanisms

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¶ This article was submitted by the authors in English.

explicitly, such as dispersion reconstruction and restricted geometry.

To approach the problem, we consider sufficiently low temperatures in which the quasiparticle states of "acoustic" branches are thermally populated ($\epsilon \longrightarrow 0$ when $p \longrightarrow 0$). The corresponding acoustic branches have the following dispersion relations [14, 15]:

$$\epsilon_1 = u_1 p_1, \quad \epsilon_2 = u_2 a p_2^2, \tag{1}$$

where ϵ_i stands for the energy of a quasiparticle, p_i is the corresponding momentum, a is the wire diameter, and u_1 and u_2 are the characteristic velocities. The first expression in Eq. (1) is the phonon dispersion, and the second expression is the dispersion of the flexural mode. The nature of flexural modes comes from the fact they are analogous to the bending modes of classical elasticity theory or to the antisymmetric Lamb waves of a free plate [16]. The appearance of such a mode is just a direct consequence of restricted geometry, and under some conditions it can be considered as the only size effect in thermal transport properties. Strictly speaking, there are two modes for each type of dispersion, but we do not account for them separately since their contributions are qualitatively the same. Consequently, we need to solve the kinetic problem for a two-component gas of quasiparticles. It is well known [13, 17–20] that using a simple Callaway formula to estimate the thermal conductivity coefficient in two-component systems sometimes leads to serious confusions. Simple summation of the relaxation rates, as is done in the majority of theoretical works, is questionable under many physical conditions. The dependence of the kinetic coefficients on different relaxation times is much more complicated in reality. An accurate method for calculation of the diffusion coefficient in a two-component gas of quasiparticles was proposed in [20]. Here, we extend this formalism to the thermal conductance problem. To start with, we consider a system of two types of quasiparticles. Their kinetics is described by equations for corresponding distribution functions f_i:

$$v_i \frac{\partial f_i}{\partial z} = \sum_{j=1}^{2} C_{ij}(f_i, f_j) + C_{i3}(f_i), \quad i = 1, 2, \tag{2}$$

where $C_{ij}(f_i, f_j)$ is the collision integral of thermal excitations and $C_{i3}(f_i)$ is the collision integral describing the scattering processes between quasiparticles and scatterers; $v_i = \partial\epsilon_i/\partial p_i$ is the group velocity of the corresponding thermal excitation. The main purpose of our theory is to obtain analytic expressions of thermal conductance, which are applicable to quasiparticles with arbitrary dispersion relations. In other words, the explicit dispersion relations in Eq. (1) are needed only at the last stage when calculating corresponding relaxation times and thermodynamic quantities. As usual, we seek a pefturbative solution of system (2) in the form

$$f_i = f_i^{(0)} + \delta f_i, \tag{3}$$

where $f_i^{(0)}$ is the local equilibrium Bose-function and $\delta f_i \ll f_i^{(0)}$ represents a small deviation from the equilibrium. The perturbation term can be conveniently chosen to be $\delta f_i = -g_i \partial f_i^{(0)}/\partial\epsilon_i$ with g_i the new target functions. After the standard linearization procedure, Eq. (2) can be written in the following matrix form:

$$|\phi_\kappa\rangle \frac{1}{T}\frac{\partial T}{\partial z} = \hat{\mathcal{C}}|g\rangle, \tag{4}$$

where

$$|\phi_\kappa\rangle = \left|\begin{matrix}\epsilon_1 v_1 \\ \epsilon_2 v_2\end{matrix}\right\rangle, \quad |g\rangle = \left|\begin{matrix}g_1 \\ g_2\end{matrix}\right\rangle.$$

The two-dimensional (2D) collision matrix $\hat{\mathcal{C}}$ can be decomposed into a sum of three terms, corresponding to different relaxation mechanisms—$\hat{\mathcal{C}} = \hat{\mathcal{I}} + \hat{\mathcal{S}} + \hat{\mathcal{U}}$—where $\hat{\mathcal{I}}$, with matrix elements $\mathcal{I}_{ij} = C_{ik}\delta_{ij} + C_{ij}(1-\delta_{ij})$ ($k \neq i$), describes the relaxation due to interaction between quasiparticles of different types; $\hat{\mathcal{S}}$ ($\mathcal{S}_{ij} = C_{ii}\delta_{ij}$) describes collisions between identical quasiparticles; and $\hat{\mathcal{U}}$ ($\mathcal{U}_{ij} = C_{i3}\delta_{ij}$) describes all the other relaxation mechanisms, including scattering on defects, boundaries, umklapp processes, etc. Here, C_{ij} represent *linearized* collision operators [20].

Let us define the scalar product of two-dimensional bra- and ket-vectors as follows [20]:

$$\langle\phi|\chi\rangle = \sum_{k=1,2}(\phi_k|\chi_k) = -\sum_{k=1,2}\int \phi_k^* \chi_k \frac{\partial f_k^{(0)}}{\partial\epsilon_k} d\Gamma_k, \tag{5}$$

where $(\phi_k|$ and $|\chi_k)$ are the correspondent one-component vectors and $d\Gamma$ is the element of phase volume. Under this condition, the collision operator $\hat{\mathcal{C}}$ becomes hermitian. System (4) is a system of nonuniform linear integral equations. According to the general theory of integral equations, the target solution $|g\rangle$ must be orthogonal to the solution of corresponding uniform equations $\hat{\mathcal{C}}\,|\phi_{\mathrm{uni}}\rangle$. It is therefore convenient to write the formal solution of (4) so that the orthogonality condition ($\langle g|\phi_{\mathrm{uni}}\rangle$) is imposed explicitly in the solution. For this purpose we define the projection operator $\hat{\mathcal{P}}_n$ onto the subspace orthogonal to the vector $|\phi_{\mathrm{uni}}\rangle$, $\hat{\mathcal{P}}_n = 1 - \hat{\mathcal{P}}_c$, $\hat{\mathcal{P}}_c = |\phi_{\mathrm{uni}}\rangle\langle\phi_{\mathrm{uni}}|$. As a result, the formal solution of system (4) can be written in the form

$$|g\rangle = \hat{\mathcal{P}}_n(\hat{\mathcal{C}}^{-1})\hat{\mathcal{P}}_n|\phi_\kappa\rangle \frac{1}{T}\frac{\partial T}{\partial z}. \tag{6}$$

The heat flux density due to thermal excitations of different types is given by the expression $Q = \sum_{k=1,2}\int \epsilon_k v_k f_k d\Gamma_k$. Using relation (3) and the definition of scalar product (5), Q can be rewritten as $Q = \langle\phi_\kappa|g\rangle$. On the other hand, the effective thermal conductivity coefficient is defined by the relation $Q = -\kappa_{\rm eff}\partial T/\partial z$. Comparing the above two expressions for Q and using formal solution (6), we obtain

$$\kappa_{\rm eff} = -\frac{1}{T}\langle\phi_\kappa|\hat{\mathscr{C}}^{-1}|\phi_\kappa\rangle. \qquad (7)$$

To derive an exact and analytical expression for thermal conductivity coefficient (7), it is necessary to introduce a complete set of orthonormal 2D vectors $|\psi_n\rangle$ ($n = 1, 2, 3, \ldots$) belonging to an infinite-dimensional Hilbert space with scalar product (5). In principle, the particular choice of the basis is not essential, but for convenience of calculations it is useful to specify at least four of them. It is convenient to chose the first of them as corresponding to the total momentum of quasiparticles and the second as orthogonal, but still linear in momentum [20]:

$$|\psi_1\rangle = \frac{1}{\sqrt{\rho}}\left|\begin{matrix} p_1 \\ p_2 \end{matrix}\right\rangle, \quad |\psi_2\rangle = \frac{1}{\sqrt{\rho\rho_1\rho_2}}\left|\begin{matrix} \rho_2 p_1 \\ -\rho_1 p_2 \end{matrix}\right\rangle, \qquad (8)$$

where $\rho_i = (p_i|p_i)$ is the normal density of the ith component, $\rho = \rho_1 + \rho_2$. The third and the fourth vectors correspond to the energy flux,

$$|\psi_3\rangle = \frac{1}{\mathcal{N}_{\kappa 1}}\left|\begin{matrix} \psi_{\kappa 1} \\ 0 \end{matrix}\right\rangle, \quad |\psi_4\rangle = \frac{1}{\mathcal{N}_{\kappa 2}}\left|\begin{matrix} 0 \\ \psi_{\kappa 2} \end{matrix}\right\rangle, \qquad (9)$$

where

$$\psi_{\kappa j} = \frac{1}{\sqrt{T}}\left(\epsilon_j v_j - \frac{S_j T}{\rho_j}p_j\right), \qquad (10)$$

and $\mathcal{N}_{\kappa j} = \sqrt{(\psi_{\kappa j}|\psi_{\kappa j})}$ is the corresponding normalization coefficient. The partial entropy of quasiparticle subsystem S_j in Eq. (10) is given by the relation

$$S_j = \frac{1}{T}(\epsilon_j v_j|p_j). \qquad (11)$$

Formally, the kinetic problem of a two-component quasiparticles system can be solved in the above basis set. The inversion of the operator matrix $\hat{\mathscr{C}}$ in Eq. (7) is similar to the procedure described in [20]. The final result contains infinite-dimensional nondiagonal matrices. To obtain closed form expressions, we must use some approximations, a correct τ-approximation [19] or Kihara approximation [20–23]. In some physical situations, we are able to obtain closed analytical expressions. It is rigorously proved in [20] that, in the case of quasi-equilibrium within each subsystem of quasiparticles, the corresponding transport coefficient can be obtained in close analytical form. This is a reliable approximation when the low temperature relaxation is mainly governed by defect scattering processes. The approximation formally implies that all the matrix elements of matrix $\hat{\mathscr{S}}$ in Eq. (7) tend to infinity. The thermal conductivity coefficient in this case can be obtained in the form $\kappa_{\rm eff} = \kappa_F + \kappa_D$. Here we separate the flux part of thermal conductivity coefficient $\kappa_F = \tau_F S^2 T/\rho$ with $S = S_1 + S_2$, which approaches infinity when the quasiparticles do not interact with scatterers, and the diffusive part $\kappa_D = \tau_D(S_1T/\rho_1 - S_2T/\rho_2)^2\rho_1\rho_2/T\rho$. The corresponding relaxation times are given by

$$\tau_D = \left\{\frac{\rho_1}{\rho}\tau_{23}^{-1} + \frac{\rho_2}{\rho}\tau_{13}^{-1} + \tau_{12}^{-1} + \tau_{21}^{-1}\right\}^{-1}, \qquad (12)$$

and

$$\tau_F = \tau_D\left(\frac{S_1}{S}\tau_{23}^{-1} + \frac{S_2}{S}\tau_{13}^{-1} + \tau_{12}^{-1} + \tau_{21}^{-1}\right)^2 \times (\tau_{13}^{-1}\tau_{23}^{-1} + \tau_{12}^{-1}\tau_{23}^{-1} + \tau_{21}^{-1}\tau_{13}^{-1})^{-1}. \qquad (13)$$

Relaxation times contained in formulas (12) and (13) are defined by

$$\tau_{kj}^{-1} = \frac{1}{\rho_k}(p_j|C_{kj}|p_j). \qquad (14)$$

We emphasize that these are not actual scattering times, which are momentum dependent, but relaxation times associated with the corresponding scattering mechanisms. Once we obtain the particular scattering rate $\nu_{kj}(p_k)$ from standard scattering theory, we can replace the true collision operator C_k with $\nu_{kj}(p_k)$, so that the corresponding relaxation time can be calculated by

$$\tau_{kj}^{-1} = \rho_k^{-1}\int p_k^2 \nu_{kj}(p_k)\frac{\partial f_k^{(0)}}{\partial\epsilon_k}d\Gamma_k. \qquad (15)$$

As can be seen from the derived formulas, the coefficient of thermal conductivity contains different relaxation times in a rather nontrivial combination. If one component (say set $S_2 = 0$, $\rho_2 = 0$) drops out, we recover the usual result, $\kappa_F^{(1)} = \tau_{13}S_1^2 T/\rho_1$. For phonons with linear dispersion $\epsilon = vp$, κ_F reduces to the well-known result $\kappa_F^{\rm ph} = C_{\rm ph}v^2\tau_{13}/3$, where $C_{\rm ph} = 3S_{\rm ph}$ is the heat capacity of phonon gas.

The main advantage of our approach is its universality. In fact, up to this point we have not restricted ourselves to any particular dimensionality of the system or any quasiparticles dispersion. All the necessary information is contained in the corresponding relaxation times and thermodynamic quantities. This formalism allows us to analyze contributions from different relaxation mechanisms to the total thermal conductivity coefficient. Given the dispersion relations of quasiparticles, we can easily calculate all the quantities contained in (12) and (13).

With Eqs. (12) and (13), we are able to address the competition between relaxation processes of the flexural and phonon modes. Glavin [14] noted that such a competition can be essential at extremely low temperatures if the dominant relaxation mechanism is elastic scattering on defects, where, he argued, the thermal conductivity coefficient would scale as $T^{1/2}$. Our approach allows us to study this competition comprehensively. In particular, we predict a strong dependence of the temperature scaling exponent on the wire diameter. The standard Fermi golden rule approach [14] gives the momentum dependent scattering rates for different modes $\nu_{13} = W_{13}\frac{p^{1/2}}{u_1^3 a^{3/2}}$, $\nu_{23} = W_{23}\frac{1}{p u_2^3 a^3}$, where W_{kj} are the corresponding scattering amplitudes, which depend on the physical properties of particular material. Using Eq. (15), it is easy to show that the corresponding relaxation times scale as

$$\tau_{13}^{-1} \propto a^{-3/2}T^{1/2}, \quad \tau_{23}^{-1} \propto a^{-5/2}T^{-1/2}. \qquad (16)$$

Different temperature dependences of relaxation times lead to a strong competition between two physically different mechanisms of thermal conductivity—flux and diffusive. The dominance of one over the other strongly depends on the wire diameter at a given temperature. To make some specific conclusions, let us summarize the approximations done and specify the range of validity of the proposed theory. We consider a situation in which thermal excitations are multiply scattered elastically while being transferred through the wire, so that other scattering mechanisms are strongly suppressed by interaction with defects. Only for this case were we able to drop relaxation within each subsystem of identical quasiparticles to obtain closed expressions (12) and (13). The influence of the boundary is accounted for in the dispersion of the flexural mode and in the dimensionality of the system. The range of temperature is supposed to satisfy the relation $T < \Delta\epsilon$, where $\Delta\epsilon \sim 1/a$ is the characteristic value of the frequency gap between the adjacent phonon branches. For a larger temperature, we cannot use acoustic modes (1) only, but need to account for higher branches.

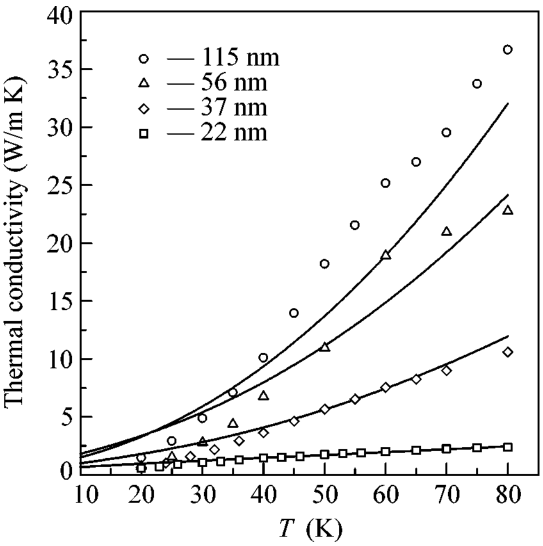

Fig. 1. Thermal conductivity coefficient calculated from Eqs. (12) and (13) for different values of nanowire diameter. Experimented data are from [11].

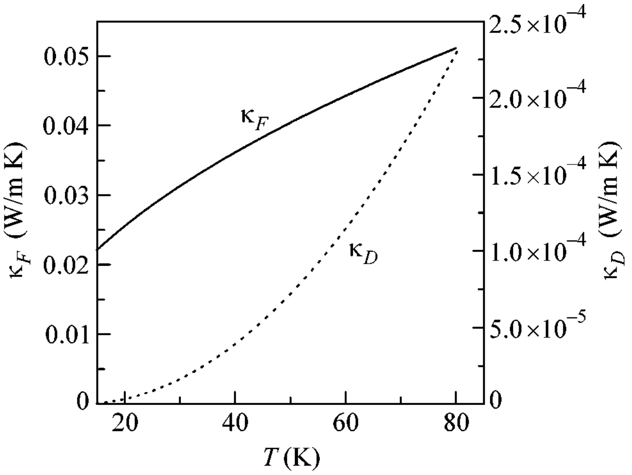

Fig. 2. Comparative contribution from flux and diffusive parts of thermal conductivity for a 2-nm wire.

In Fig. 1, we compare our theoretical results with the experimental data from [11]. We have chosen the unknown parameters $W_{13} = 1.2 \times 10^{-44}$ m^5 s^{-4} and $W_{23} = 0.9 \times 10^{-44}$ m^5 s^{-4} to fit data for a = 22 nm. Deviations from the experimental data for large diameters and temperatures show the restriction of the applicability of our initial approximations. They arise from the Debye approximation and simplified dispersion expression. Additionally, when the diameter of the wire increases, the mechanism we consider becomes less dominant. To be more precise, we need to include higher excitation branches as well as other relaxation mechanisms. However, our approach allows us to understand the physics of the processes in the region under consideration. It is clear that the observed crossover is the result of competition between $\kappa_F \propto T^{1/2}$ and $\kappa_D \propto T^3$. For smaller diameters, κ_F is strongly dominant in a wide range of temperatures as shown on Fig. 2 for wire diameter a = 2 nm. Figure 3 demonstrates a complete crossover from $T^{1/2}$ to T^3 dependence for a nanowire of a = 30 nm. It can be seen that the T dependence between 20 and 40 K is nearly linear, which was observed in experiment [11]. It should be noted that T^3 dependence of κ_D cannot be interpreted by simple analogy with the bulk case. It comes not from a specific heat directly, but from differ-

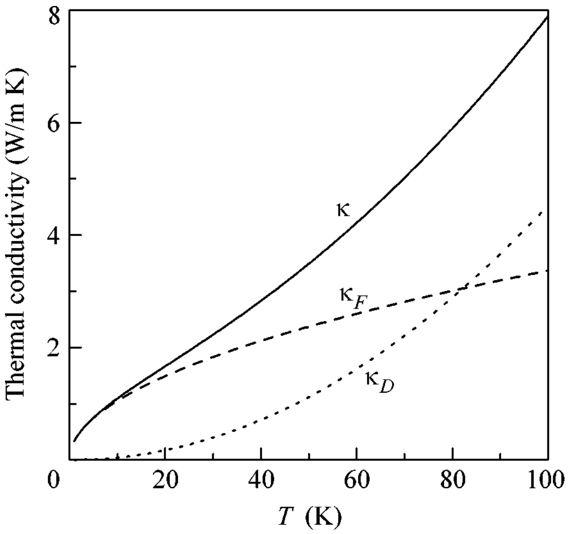

Fig. 3. Crossover from $T^{1/2}$- to T^3-dependence of κ_{eff} for a 30-nm wire.

ent sources, including competition of the relaxation times in Eqs. (12) and (13).

In summary, we derived the general analytical expressions (12) and (13) to explicitly calculate the contributions of different scattering mechanisms to the total relaxation of the system. The simple expressions clarify the essential effects leading to the observed behavior of the thermal conductivity coefficient. It is clear that the particular dispersion laws (and their reconstruction) affect scattering rates and thermodynamic quantities. Restricted geometry and low dimensionality lead to additional scattering mechanisms. Note the information about dimensionality is naturally included in the particular form of phase space element $d\Gamma_i$. Such a formalism helps to distinguish effects from different scattering mechanisms. When applied to a regime in which phonon modes compete with flexural ones, our theory agrees favorably with the available experimental data. Furthermore, we showed that the thermal conductivity coefficient changes from approximately $T^{1/2}$-dependence to T^3-dependence with increasing temperature. In view of our theoretical results, it will be useful to investigate smaller diameters or lower temperatures with fixed diameters in experiment to better reveal the crossover from T^3- to $T^{1/2}$-dependence.

We would like to thank Prof. Peidong Yang and Dr. Deyu Li for providing us with the experimental data. This research is supported by the NSF Career Award, grant no. Che-0093210. J.C. is a recipient of the Camille Dreyfus Teacher-Scholar Award.

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