Thermoelectric efficiency of heterogeneous media at low temperatures

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A quantum limit of the thermoelectric efficiency for heterogeneous media with weak links is established with a use of the Landauer-type formulae.

I. INTRODUCTION

As is well known, the kinetic parameters of semiconductors and metals such as conductivity $\sigma$, thermoelectric power $S$ and thermoconductivity $\kappa$ are determined by a crystallographic and atomic structure of the material and are, therefore, very specific for an every given material [1]. However, there is a class of conductors that have low-temperature kinetic properties, which are not specifically related to a concrete scattering mechanism and to other nonuniversal factors. We will show here that the thermoelectric efficiency $zT = \frac{S^2 \sigma}{\kappa}$ of these structures at low enough temperatures can be expressed in terms of the fundamental constants and of the system geometry.

II. CONDUCTING STRUCTURES WITH WEAK LINKS

Let us consider a polycrystal with point contacts between crystallites. These point contacts are really small bridges or weak links between the crystallites. We assume that within the actual temperature range, all quasiparticles (carrier charges, phonons, etc) are almost thermalized in crystallites and their distribution functions insignificantly differ from the equilibrium ones. Large volume of crystallites in comparison with bridges connecting them ensure effective thermalization. Notice, that by our opinion, it is not even necessary for strong inequality $D \gg l$ (with $l$ being the mean free path) to be fulfilled because nonspherical crystallites can play a role of three-dimensional Sinai’s billiards [2] for most of the quasiparticles. In other words, large time delay in propagation of quasiparticles in result of multiple reflections on the crystallite boundary leads to effective thermalization, if the total path through the crystallite including multiple reflections by the crystallite boundaries exceeds the mean free path. Similar processes can occur in conducting composites based on opals, porous glasses etc. Rather narrow windows in the spectrum are formed by excitations, which avoided multiple reflections because of a spatial coherence resonance. Such windows of coherence can be actual only at very low temperatures. Large cross section of a crystallite makes the electric current and heat flux densities extremely small there. Thus, we can consider the system as a network of electric and thermal resistors and thermoelements (weak links) connecting nodes (crystallites), which can be characterized by their electric potentials and temperatures. Then the transport problem is reduced to the following two steps: (i) calculation of the electric and thermal resistance and of the thermoelectric power of a single weak link; (ii) calculation of integral characteristics of the network. The latter is extremely simple in the case of a regular network, but can be rather complicated in the irregular case. In the case of a strong irregularity (severed connections, in particular), the percolation theory can be applied.

III. TRANSPORT PROPERTIES OF A WEAK LINK

Let us consider a bridge connecting two crystallites as a figure of revolution only slightly different from a cylinder. Phonon and electronic contributions have to be considered separately.

Long wavelength excitations propagate without feeling of possible disorder that allows us to use the quasiparticle picture at low temperatures. Size quantization of excitation spectra in the weak link permits us to consider it as a waveguide for excitations that establishes a lower limit for propagating waves using the relation:

$$\beta_n = \sqrt{k^2 - \kappa_n^2},$$

(1)

where $k$ is the wave vector value, $\beta_n$ is the wave vector component along the waveguide axis, $\kappa_n$ is the membrane eigenvalue, the lowest one is of order $d^{-1}$. Simple estimates show that these wavelengths are related for acoustic phonons and electrons, respectively, to energies of order $1 \: K$ and $10 \: K$. Therefore, only a few waveguide modes participate in transport processes within this temperature range, but their number fast increases with energy. This conclusion is valid if we assume that actual excitations feel the weak link as a regular waveguide that can be correct
only for the most low-lying excitations with large wave length. When the energy of an excitation increases, the bridge becomes more irregular for waves. The transmission coefficient decreases catastrophically except for a few (if they exist) special energy values related to possible resonances in irregular interfaces. Besides, there exist gapless surface modes.

The one-dimensional electronic ballistic transport in the presence of the temperature and electrochemical potential is described by the equation [3]:

$$J = \frac{2e^2}{2\pi \hbar} \sum_\nu \int_0^\infty dE \frac{dn_{\nu}(E)}{dE} \epsilon_{\nu}(E) \left[ \frac{E - \mu}{T} \Delta T + \Delta \mu \right], \quad (2)$$

where $J$ is the electric current through the link, $n_{\nu}$ is the Fermi-Dirac distribution, $\epsilon_{\nu}$ is the electron transmission coefficient, $\mu$ and $\Delta \mu$ are respectively the electrochemical potential and its drop across the weak link, $\Delta T$ is the temperature difference between the adjacent grains. The energy flow $Q = Q^{ph} + Q^{el}$ comprises contributions both from the electronic and phonon subsystems

$$Q^{ph} = \sum_\nu \int_0^\infty \frac{dk}{2\pi} \omega_{\nu} \frac{\partial \omega_{\nu}}{\partial k} \epsilon_{\nu}^{ph} (n_R^{ph} - n_L^{ph}), \quad \text{(3)}$$

$$Q^{el} = \sum_\nu \int_0^\infty \frac{dk}{2\pi} \epsilon_{\nu}(k) \frac{\partial \epsilon_{\nu}}{\partial k} \epsilon_{\nu}(n_R^{el} - n_L^{el}) \quad \text{(4)}$$

where $\omega_{\nu}(k)$ is the $\nu$-th acoustic phonon branch frequency, $n_R^{ph}$ and $n_L^{ph}$ are respectively the quasiequilibrium phonon distribution functions in the bulk of the right and left crystallites; $\epsilon_{\nu}(k)$ is the $\nu$-th branch of the electronic spectrum in the link, $n_R^{el}$ and $n_L^{el}$ are corresponding electronic distribution functions.

**IV. KINETIC PROPERTIES OF THE NETWORK**

Within the approximation of locally equilibrium crystallites, the electric potential and temperature distributions are governed by a finite-difference equations. In the steady state, the electric potential and temperature distributions satisfy the time-independent finite-difference electric and heat transport equations: the "Kirhoffs law" for currents entering into the $n$-th site

$$\sum_{\langle m \rangle} J_{nm} = 0, \quad \text{(5)}$$

$$\sum_{\langle m \rangle} Q_{nm} = 0 \quad \text{(6)}$$

and the Ohm-Fourier-Peltier-Zeebeck law for the electric $J_{nm}$ and heat $Q_{nm}$ currents between the sites $m$ and $n$

$$Q_{nm} = -G_{nm}(T_n - T_m) + \Pi_{nm} J_{nm}$$

$$-(V_n - V_m) = R_{nm} J_{nm} + S_{nm}(T_n - T_m), \quad \text{(7)}$$

where $n$ stands for the crystallite number vector with components $n_x$, $n_y$, $n_z$; $G_{nm}$ is the thermal conductance of the weak link connecting crystallites $m$ and $n$, $G_{nn} \neq 0$ if and only if $m$ and $n$ differ by a unit superlattice vector $e$; $\langle m \rangle$ means summing over the nearest neighbours of the given node $n$; $R_{nm}$ is the electric resistance of the link, $V_n$ is the potential of the $n$-th crystallite, the thermopower $S_{nm}$ and the Peltier coefficient $\Pi_{nm}$ are related by the Kelvin-Onsager symmetry law $\Pi_{nm} = S_{nm}(T_n + T_m)/2$, $Q_{nm}$ is the energy flow through the link, $J_{nm}$ is the electric current through the link. Now the theoretical analysis of the heat transport problem for the polycrystal is reduced to two different ones: the first problem is to study the electric and heat transport through the weak link and the second is to solve the network equations for a given distribution of links parameters. The former can be considered using different methods depending on the temperature range, the weak link geometry, and the microscopic properties of the material, while the latter is determined exclusively by the system geometry and a distribution of parameters. For a regular superlattice we have $G_{n,n+e} = G$ for all $n$ and $m$, and the effective thermoconductivity of the sample reads
\[ \kappa_{\text{eff}} = \frac{G}{A} \quad (8) \]

where \( A \) is the superlattice spatial period. A calculation of the effective thermoconductivity in the case of a random distribution of \( G_{mn} \) can be very sophisticated problem mathematically similar to the electron transport in irregular conductors, but we concentrate our attention here on the weak link thermal resistance assuming that the superlattice is regular.

V. EFFICIENCY

Assuming the structure to be regular, we calculate the thermoelectric efficiency of a single link. The thermoelectric efficiency can be expressed in terms of the single link transport coefficients:

\[ zT = \frac{S^2 G_{el} T}{G_{th}} \quad (9) \]

where \( S, G_{el}, \) and \( G_{th} \) are respectively the thermopower, the electric and thermal conductances of the single link, which are given by the formulae following from [2]:

\[ S = \frac{k_B}{e} \sum_\nu \int_0^\infty dE \cdot t^el_\nu \frac{dn_{el}}{dE} \frac{E - \mu}{k_B T} \left[ \int_0^\infty dE \cdot t^el_\nu \frac{dn_{el}}{dE} \right]^{-1}, \quad (10) \]

\[ G^{el} = \frac{2e^2}{2\pi\hbar} \sum_\nu \int_0^\infty dE \frac{dn_{el}(E)}{dE} t^el_\nu(E), \quad (11) \]

\[ G^{ph} = \frac{\pi k_B^2 T}{6\hbar} \sum_\nu \int_0^\infty dx \frac{3x \exp(x)}{[\exp(x) - 1]^2} t^{ph}_\nu(x) \quad (12) \]

Notice that the group velocity \( \frac{\partial \epsilon}{\partial k} \) and the one-dimensional density of states \( 1/(\frac{\partial \epsilon}{\partial k}) \) cancel one another in the one-dimensional transport. Thermal conductance is extremely sensitive to the real geometry of the link that can be seen from the effective dimension of the transport and the behaviour of the transmission coefficient. In the three-dimensional diffraction regime it reads:

\[ G^{ph} = \frac{\pi^2 a T^3}{30\hbar^3} \quad (13) \]

In the one-dimensional case it can be written as

\[ G^{ph} = \frac{k_B^2 \pi^2}{6\pi\hbar} T N^{ph}, \quad (14) \]

where \( a \) is the link cross-section area, \( N^{ph} \) is the number of the gapless phonon modes.

We can write within this approximation for the electric conductance:

\[ G^{el} = \frac{e^2}{\pi\hbar} N^{el}, \quad (15) \]

While the conductance and the thermoconductance have a universal form, which is very not sensitive to details of the weak link geometry,

\[ S = \frac{k_B}{e} \frac{\ln 2}{N^{el} + \frac{1}{2}}. \quad (16) \]
Substituting these formulae into (16) we obtain for the thermoelectric efficiency quantum limit at the low-temperature regime

\[ zT = \frac{6 (\ln 2)^2}{\pi \left( N^{cl} + \frac{1}{2} \right)^2 \left( 1 + \frac{N^{ph}}{N^{el}} \right)} \]  

(17)

This means that one has to minimize the number of modes involved into the transport through the weak link in order to raise the thermoelectric efficiency.

[1] A.I. Anselm, *Introduction to the semiconductor theory*, Nauka, Moscow, 1978.
[2] G.M. Zaslavskii, *Stochasticity of dynamic systems*, Nauka, Moscow, 1984.
[3] R. Landauer, IBM J. Res. Dev. 1, 223 (1957).