Universal Limits of Thermopower and Figure of Merit from Transport Energy Statistics

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Abstract

The search for new thermoelectric materials aims at improving their power and efficiency, as expressed by thermopower $S$ and figure of merit $ZT$. By considering a very general transport spectral function $W(E)$, expressions for $S$ and $ZT$ can be derived, which contain the statistical weights of an effective distribution function only, see Refs.1–3.

We assumption of a Lorentzian shape with width $k_B T$ resulting from the electron-phonon coupling allows to estimate an upper limit of $S$ and $ZT$ independent on the microscopic mechanisms of the transport process. A simple estimate for an upper limit of the thermopower $S$ is derived from formula. It is given by 3 times the unit of the thermopower $k_b/e$ which is about 250 $\mu V/K$.

We consider different systems which represent the general features of the electronic structure of thermoelectric relevant materials very well. The transport integrals were evaluated varying the band gap size and the chemical potential position. For all cases upper limits for both, the thermopower and the figure of merit, are obtained. The universal limit of $|S|$ is given by 1.88 in units of $k_B/e$, which is about 160 $\mu V/K$. The universal limit for $ZT$ is obtained by about 1.11, which is in good agreement with available thermoelectric systems and devices.

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I. INTRODUCTION

Limitations of TE applications and efficiency is given by the Figure of Merit $ZT$. Ref.\textsuperscript{4} pointed to the limit range of obtained $ZT$ values, but no reasons were given for the pessimistic view that a $ZT$ of 2 is 'eventually plausible', and a $ZT$ of 4 'is ambitious'. Some reports on $ZT$ values larger than 2 are available, e.g. 3.5 in quantum dot superlattices\textsuperscript{5}, 2.4 and 2.9 in bismuth telluride and antimonide superlattices\textsuperscript{6}, and 2.2 in antimony silver telluride materials\textsuperscript{7}.

Here we give a simple explanation for the limitations of achievable $ZT$ values. We assume the presence of electron-phonon coupling which broadens the width of all electronic states by $k_B T$. This broadening along the real energy axis is besides the limits in the electron life time which gives a shift of the electron density resonances along the imaginary energy axis.

To study the transport properties we consider the transport spectral function as a superposition of Lorentzian peaks. So, we assume that all features of the transport spectral function are broadened by $k_B T$.

II. METHODS AND ASSUMPTIONS

A. Thermoelectric Transport Coefficients

Following Refs.\textsuperscript{1,2,8} we write the linear transport formalism using a general transport spectral function $w(E)$. This is not restricted to diffusive transport and solving a quasiclassical Boltzmann equation. A similar approach was discussed by\textsuperscript{2} generalizing it to multi-terminal geometries. The transport spectral function $w(E)$ quantifies the contribution of the electronic states at energy $E$ to the electrical current if different occupations in the terminals drive a current through the device.

Longitudinal transport with electric field $\mathcal{E}$, temperature gradient $\nabla T$, and electrical and thermal currents $j$ and $Q$, respectively, in the same direction will be considered in the following:

\begin{equation}
    j = e^2 I_0 \mathcal{E} - \frac{e}{T} I_1 \nabla T = \sigma \mathcal{E} - \sigma S \nabla T
\end{equation}

\begin{equation}
    Q = e I_1 \mathcal{E} - \frac{1}{T} I_2 \nabla T = \Pi j - \kappa \nabla T
\end{equation}
The integrals $I_n$ over the transport spectral function $w(E)$ depend explicitly on the chemical potential $\mu$ and the temperature $T$, and are given by

$$I_n(\mu, T) = \int_{-\infty}^{+\infty} dE W(E) \left[-\frac{\partial f_{FD}(\mu, T)}{\partial E}\right] (E - \mu)^n$$  \hspace{1cm} (3)

$$I_n = (k_B T)^n \int_{-\infty}^{+\infty} dE W(\epsilon) \frac{e^\epsilon}{(1 + e^\epsilon)^2} \epsilon^n \quad \text{with} \quad \epsilon = \frac{E - \mu}{k_B T}.$$  \hspace{1cm} (4)

Using the conductivity $\sigma = e^2 I_0$, the thermopower $S = -\frac{1}{|e|T} I_0 = -\frac{k_B}{|e| k_B T}$, the Peltier coefficient $\Pi = ST = -\frac{<\epsilon>}{|e|}$, and the electron thermal conductivity $\kappa/\sigma = \frac{1}{T \sigma} - TS^2 = \frac{1}{\epsilon_T} (\epsilon^2 - <\epsilon^2>)$, we arrive at the main result:

$$ZT = \frac{\sigma S^2}{\kappa T} = \frac{<\epsilon^2>}{<\epsilon^2> - <\epsilon^2>}.$$  \hspace{1cm} (5)

Here we neglected the contribution of the lattice thermal conductivity $\kappa_L$, so we derive an upper limit for the figure of merit $ZT$. To simplify the discussion and the calculations in the following, we consider all energies in units of $k_B T$. So, $\epsilon$ is given in units of 1 and measures the energy relative to the chemical potential. The FERMI-DIRAC occupation function reads like $1/(1 + \exp(x))$ in these units.

**B. Electron-Phonon Coupling**

Now, the general properties of the transport spectral function should be introduced as the Main Assumption:

All features of the transport spectral function $W(E)$ are broadened by electron-phonon coupling with a Lorentzian line shape. This results in a superposition of Lorentzian peaks of width $\Gamma = k_B T$. The most important consequence with respect to the thermoelectric performance is the smooth behavior of the transport spectral function on the scale of the thermal energy $k_B T$. As we will show, this limits the thermopower and the figure of merit to certain values independent on the transport mechanism and the dimensionality of the system.

**C. Systems under Consideration**

Assuming the above mentioned level broadening all transport spectral functions can be formed by a superposition of Lorentzian peaks at different energetic positions and with
different weights.

1/ The first system to consider is a single level system. It might be a quantum dot with one energy level $E_0$ coupled to two electrodes

$$W(E) = \frac{1}{1 + (E - E_0)^2}.$$  (6)

All energies are given in units of $k_B T$. This is illustrated in fig. 1.

2/ The next system under consideration contains 2 levels with spacing $E_1 - E_0$ to mimic a band gap material. For simplicity the peak position $E_0 = 0$ will define the zero of the energy scale. Both peaks have equal weight $W_0 = W_1 = 1$: 

$$W(E) = \frac{1}{1 + (E)^2} + \frac{1}{1 + (E - E_1)^2}.$$  (7)

3/ To mimic more sophisticated spectral functions the 2 level system with different peak weights $W_0$ and $W_1$ will be considered. For simplicity peak width $W_0 = 1$ is set to one.

$$W(E) = \frac{1}{1 + (E)^2} + \frac{W_1}{1 + (E - E_1)^2}.$$  (8)

By considering different separations $E_1$ and peak weight ratios $W_1$ a wide range of functional behaviors can be simulated. As under the defined circumstances every transport spectral function is a linear superposition of Lorentzian peaks, this investigate clearly shows that by superposition no larger values for thermopower and figure of merit can be obtained.

4/ This case studies the behavior for a reduced peak width $\Gamma = N \times k_B T$ with $N < 1$. It is not considered by which means this could be realized in materials. To our opinion this is just to complete the discussion, but without striking relevance for real systems. As expected an increase of thermopower and figure of merit is obtained. The behavior of $ZT$ will be discussed in detail in fig. 12.

D. Simple estimate for $S$ using Mott’s Formula

A very rough estimate for the Maximum Thermopower can be obtained using MOTT’s formula:

$$S \approx -\frac{k_B}{|e|} 3k_B T \frac{W'}{W} \bigg|_{E=\mu}.$$  (9)

Assuming a smooth behavior of $W(E)$ on a scale of $k_B T$ restricts the logarithmic derivative $|W'/W|$ to about $1/k_B T$. This limits the thermopower $|S|$ to $3\frac{k_B}{|e|}$, which is about $250 \mu V/K$. 
So, by assuming a smooth behavior of the transport spectral function, the thermopower has a universal upper limit, which does not depend on the character of the transport mechanism.

In the following we will calculate the thermopower in parallel to the figure of merit using mainly $\langle \epsilon \rangle$. Assuming a broadening of the transport spectral function features by the thermal energy scale $k_B T$ with a Lorentzian line shape, an upper limit of 1.88 is obtained. Together with the thermopower quantum of $k_B/|e|$ the upper limit is reduced to about 160 $\mu$V/K.

III. RESULTS AND DISCUSSION

A. Quantum-Dot System

![Transport spectrum: N_p = 1, E_0 = 0 (quantum dot system)](image)

FIG. 1: Quantum dot system: Transport spectral function $W(E)$, derivative of Fermi occupation function $-f'_{FD}$ for $\mu = 4.8$, the effective distribution function $p(\epsilon)$, and the product $p(\epsilon) \times \epsilon$ to visualize the contributions to $\langle \epsilon \rangle$. The energy $E$ and the relative energy $\epsilon = E - \mu$ are given in units of the thermal energy $k_B T$. 
FIG. 2: Quantum dot system: Thermopower $|S|$ as function of chemical Potential, The maximum $ZT$ for $\Gamma = 1 \times k_B T$ is 1.11.

The main messages from these figures are: The maximum of the thermopower $-S-$ is obtained with $1.88 \ k_B |e|$ at a chemical of about $4.8 \ k_B T$. This is somewhat smaller than the estimate obtained from the Mott formula.

The maximum figure of merit $ZT$ is obtained with about 1.11 at a chemical potential of $3.2 \ k_B T$. This universal value does not depend on the character of the transport mechanism, nor the character of the current as electron or hole.
FIG. 3: Quantum dot system: The figure of merit $ZT$ as function of chemical Potential. The maximum $|S|$ for $\Gamma = 1 \times k_B T$ is 1.88.
B. 2-level System

Now we consider a 2-level system with symmetric peak weights, see fig. 4. The additional lines in figs. 5 and 6 show:
- lower black solid line: position of the 2nd Lorentzian peak at energy $E_1$
- upper black solid line: middle of the "band gap" at $E_1/2$: all results depending on energy $E$ are symmetric with respect to this line $E_1/2$,
- red line: position of $ZT$ maximum depending on the 'band gap' $E_1$, for this, only values of $\mu$ inside the 'band gap' were considered, so between 0 and $E_1/2$. The behavior of the maximum $ZT$ value and the corresponding chemical potential is analyzed in more detail in fig. 7.

![Transport spectrum: $N_p = 2, E_1 - E_0 = 7$ (2-level system)](image)

**FIG. 4:** 2-level system system: Transport spectral function $W(E)$ for $E_1 = 7$, derivative of Fermi occupation function $-f'_{FD}$ for $\mu = 4.8$, the effective distribution function $p(\epsilon)$, and the product $p(\epsilon) \times \epsilon$ to visualize the contributions to $<\epsilon>$. The energy $E$ and the relative energy $\epsilon = E - \mu$ are given in units of the thermal energy $k_B T$.

The behavior of $ZT$ as function of the peak position (the effective band gap) shows 2 regions: For small peak separations, $ZT$ is very small and the optimum is obtained for
FIG. 5: 2-level system: The thermopower $|S|$ as function of peak distance $E_1$ and chemical Potential $\mu$.

chemical potential positions very close to one of the peak centers - here shown for the left peak. For larger separations, ZT tends to it’s maximum value and the optimum $\mu$ is about 3.2 in units of $k_B T$. This transition occurs for peak separations between 8 and 16 $k_B T$. 
FIG. 6: 2-level system: The figure of merit $ZT$ as function of peak distance $E_1$ and chemical potential $\mu$. 
FIG. 7: 2-level system: Maximum figure of merit $ZT$ and position of chemical potential $\mu_{\text{max}}$ as function of peak distance $E_1$. 
C. Asymmetric 2-level system

Now, the asymmetric 2-level system will be analyzed:
- the maximum values for $|S|$ and $ZT$ for systems with different peak heights do not exceed the values found for the quantum dot and the symmetric 2-level system,
- the largest values are obtained for small distances - close to the single peak case /1/, and for large peak separations - similar to case /2/, the case for large separations $E_1$ is not shown in the figures.

![Transport spectrum: $N_p=2$, $E_1-E_0=7$, $W_1=0.5$ (2-level system)](image)

FIG. 8: Asymmetric 2-level system: Transport spectral function $W(E)$ for $E_1 = 7$, $W_0 = 1$, and $W_1 = .5$, derivative of Fermi occupation function $-f'_{FD}$ for $\mu = 4.8$, the effective distribution function $p(\epsilon)$ and the product $p(\epsilon) \times \epsilon$ to visualize the contributions to $< \epsilon >$. The energy $E$ and the relative energy $\epsilon = E - \mu$ are given in units of the thermal energy $k_B T$. 

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FIG. 9: Asymmetric 2-level system: $S$ depending on $E_1$, $W_0 = 1$, and $W_1 = .5$, derivative of Fermi occupation function $-f_{FD}'$ for $\mu = 4.8$, the effective distribution function $p(\epsilon)$ and the product $p(\epsilon) \times \epsilon$ to visualize the contributions to $<\epsilon>$. The energy $E$ and the relative energy $\epsilon = E - \mu$ are given in units of the thermal energy $k_B T$.

FIG. 10: Asymmetric 2-level system: $ZT$ as function of $E_1$, and relative peak width $W_1$. 

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D. Scaled Electron-Phonon Coupling

Here the case of smaller peak width than the thermal energy is considered. As expected a strong increase of the maximum $ZT$ is obtained.

![Graph showing $ZT$ for different $\Gamma$ values](image)

**FIG. 11:** Quantum dot system: $ZT$ as function of chemical potential $\mu$ for different effective coupling strengths $\Gamma$. The maximum of $ZT$ is marked by dots. The maximum values are summarized in Fig. 12.

Assuming a weaker broadening than $\Gamma = k_B T$, $ZT$ increases stronger than inverse proportional, A $\Gamma^{-5/4}$ behavior is roughly obtained.
FIG. 12: Quantum dot system: Maximum $ZT$ as function of coupling strength $\Gamma$. For small $\Gamma$ the increase of $ZT$ is roughly $\Gamma^{-5/4}$. 
IV. CONCLUSIONS

To conclude these considerations we state that for a large $ZT$ the following three conditions have to be met by the transport mechanism in the thermoelectric material:

1. The band gap has to be quite large, at least larger than $8\times k_B T$.
2. To suppress the lattice thermal conductivity a phonon glass like behavior should be present.
3. The electron-phonon interaction should be smallest as possible. To our understanding, a minimum peak width in the transport spectral function of $k_B T$ can be realized.

Independent on the transport mechanisms the following universal limits are obtained:

The absolute value of the thermopower $|S|$ is limited by about $160\, \mu V/K$.

The figure of merit $ZT$ is limited by about $1.11$.

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