The effect of dephasing on the thermoelectric efficiency of molecular junctions

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Abstract
In this work we report the results of theoretical analysis of the effect of the thermal environment on the thermoelectric efficiency of molecular junctions. The environment is represented by two thermal phonon baths associated with the electrodes, which are kept at different temperatures. The analysis is carried out using the Buttiker model within the scattering matrix formalism to compute electron transmission through the system. This approach is further developed so that the dephasing parameters are expressed in terms of relevant energies, including the thermal energy, strengths of coupling between the molecular bridge and the electrodes and characteristic energies of electron–phonon interactions. It is shown that the latter significantly affect thermoelectric efficiency by destroying the coherency of electron transport through the considered system.

Keywords: electron transport, molecular junctions, thermoelectric efficiency

(Some figures may appear in colour only in the online journal)
associated with random nuclear motions in the environment. In the present work we aim at theoretical analysis of the effect of thermal phonons on the thermoelectric characteristics of molecules and other similar systems. To carry out this analysis we combine NEGF with the approach first suggested by Buttiker to describe quantum transport through molecules [39]. An important advantage of this approach is that it could be easily adapted to analyze various aspects of incoherent/inelastic transport through molecules (and some other mesoscopic systems), avoiding complicated and time-consuming methods based on more advanced formalisms.

2. Main equations

For simplicity, in the following computations we simulate a molecule/quantum dot by a single level with the energy $E_0$. We assume that this single-level bridge is coupled to the pair of dissipative reservoirs, as shown in figure 1. While on the bridge, an electron could be scattered into one of the reservoirs through channels 3 and 4 (or 5 and 6) with a certain probability. In the reservoir, it undergoes inelastic scattering accompanied by phase breaking, and afterwards returns to the bridge with the same probability. In the present analysis, the reservoirs are treated as phonon baths representing thermal phonons associated with the left and right electrodes. Within the accepted model we imply that there is no phonon thermal conductance through the junction. This seems a reasonable assumption, for experiments give low values of phonon thermal conductance in several thermoelectric molecular junctions [40, 41]. This may be attributed to the fact that in many molecules the majority of vibrational transitions lie above the range determined by thermal energy when temperature takes on values of the order of or lower than the room temperature [14, 29]. Within the Buttiker model, the electron transport through a thermoelectric junction is considered as a combination of tunnellings through potential barriers separating the electrodes from the molecule/quantum dot and interaction with the reservoirs coupled to the bridge site.

The Buttiker approach has been applied to describe and analyze electron transport through molecules in several works (see, e.g., [42–44]). Following this approach, one can present particle fluxes $J'_i$, outgoing from the system as linear combinations of incoming fluxes $J_k$, where the indices $i, k$ label the channels for transport. For the adopted model $1 \leq i, k \leq 6$.

$$J' = \sum T_{ik}J_k$$

(1)

In these equations, the coefficients $T_{ik}$ are related to matrix elements of the scattering matrix $M$, namely $T_{ik} = iM_{ik}$. The scattering matrix expresses outgoing wave amplitudes $b_1', b_R', a_3', a_4', a_5', a_6'$ in terms of incident ones $b_1, b_R, a_3, a_4, a_5, a_6$. To provide charge conservation in the system, zero net current should flow in the channels linking the bridge site with the dephasing reservoirs, so we may write the following equations:

$$J_1 + J_4 - J_1' - J_4' = 0, \quad J_5 + J_6 - J_5' - J_6' = 0.$$  

(2)

To find the expressions for the matrix elements $M_{ik}$, we first consider a subsystem including the left electrode with the associated dephasing reservoir and the bridge site. The expression for the matrix $s^{(1)}$ relating the wave amplitudes $a_1'$, $a_2'$, $a_3'$, $a_4'$ to the wave amplitudes $a_1, a_2, a_3, a_4$ has the form [39]

$$s^{(1)} = \begin{pmatrix}
0 & \sqrt{1-t_1} & \sqrt{\sqrt{t_1}} & 0 \\
\sqrt{1-t_1} & 0 & 0 & \sqrt{\sqrt{t_1}} \\
\sqrt{\sqrt{t_1}} & 0 & 0 & -\sqrt{1-t_1} \\
0 & -\sqrt{1-t_1} & 0 & 0
\end{pmatrix}$$

(3)

where the phenomenological scattering probability $t_1$ corresponds to the reservoir associated with the left electrode. Also, an electron tunneling through a single potential barrier separating this electrode from the molecule/quantum dot is characterized by the transmission and reflection amplitudes ($t_1$ and $r_1$, respectively). These are the matrix elements of a $2 \times 2$ matrix:

$$M_{ik} = \left( \begin{array}{c}
t_i & r_i \\
r_i & t_i\end{array} \right).$$

(4)

Combining equations (3) and (4) one obtains the expression for the scattering matrix $M^{(1)}$ relating $b_1', a_1', a_2', a_3', a_4'$ to $b_1, a_2, a_3, a_4$:

$$M^{(1)} = \begin{pmatrix}
t_1 & a_{1L} & \beta_{L1} & 0 \\
a_{1L} & t_2 & a_{2L} & \beta_{L2} \\
\beta_{L1} & a_{2L} & t_3 & \beta_{L3} \\
0 & \beta_{L2} & \beta_{L3} & t_4
\end{pmatrix}.$$  

(5)

Here, $t_i = \sqrt{1-t_1}$, $\beta_L = \sqrt{t_1}$. Now, we take into consideration the remaining elements of the original system. The matrix $M^{(2)}$, which relates $a_2', b_R', a_5', a_6'$ to $a_2, b_R, a_5, a_6$ is [43, 44]

$$M^{(2)} = \begin{pmatrix}
a_{aL} & a_{bL} & \beta_r & a_{aL} & a_{bL} \\
a_{aL} & \beta_r & 0 & a_{bL} & \beta_r \\
a_{bL} & \beta_r & 0 & \beta_r & 0 \\
a_{aL} & \beta_r & \beta_r & 0 & \beta_r
\end{pmatrix}.$$  

(6)

where $a_{aL} = \sqrt{1-t_1}$, $\beta_r = \sqrt{t_1}$, the scattering probability $t_1$ is associated with the right reservoir, and the transmission ($t_r$) and reflection ($t_r$) amplitudes characterize electron tunneling through the potential barrier between the molecule (bridge) and the right electrode. Using equations (5) and (6) and excluding the wave amplitudes $a_2, a_2'$, which correspond to the transport inside the system, we get the following expression for the scattering matrix:
Here, \( Z = 1 - \alpha_2^2 \delta \tilde{R}_0 \).

Solving the system of linear equations (1) and (2) one obtains the following expression for the electron transmission \( T(E) \), which coincides with the corresponding result reported by D’Amato and Pastawski [42]:

\[
T(E) = \frac{J_f}{J_i} = T_{12} + \sum_{i,j} K_{ij}^{(2)} (W^{-1})_{ji} K_{ji}^{(1)}. \tag{8}
\]

Within the considered model, \( 1 \leq i, j \leq 2 \),

\[
K_{ij}^{(1)} = T_{2i+1,1} + T_{2i+2,1} \quad K_{ij}^{(2)} = T_{2i+2,1} + T_{2i+2,2} \tag{9}
\]

and \( W^{-1} \) is the inverse matrix with respect to the \( 2 \times 2 \) matrix \( W \), whose matrix elements are given by

\[
W_{ij} = (2 - R_{ij}) \delta_{ij} - \tilde{R}_{ij} (1 - \delta_{ij}). \tag{10}
\]

In this expression, the following denotations are used:

\[
R_{ij} = T_{2i+1,2j+1} + T_{2i+2,2j+1} + T_{2i+2,2j+2} + T_{2i+1,2j+2} \tag{11}
\]

Assuming that both dephasing reservoirs are detached from the bridge (\( \epsilon_L = \epsilon_R = 0 \)), the transport through the system becomes coherent and elastic. In this case, the electron transmission given by equations (8)–(11) is reduced to a simple form:

\[
T(E) = \frac{i \Gamma_{ph}^2}{(1 + n_{ph})^2}. \tag{12}
\]

As known, the expression for the electron transmission in the case of coherent transport may be presented as follows:

\[
T(E) \equiv q^2(E) = \text{Trace} \left[ \left( \Gamma_{ph} G_0(E) \Gamma_{ph} \right) G_0(E) G_0(E) \right] \tag{13}
\]

where \( G_0^\alpha (E) \) are the retarded and advanced Green's functions associated with the molecule/quantum dot bridging the electrodes, and self-energy terms \( \Gamma_{ph} \) describe the coupling between the electron of a certain spin orientation on the bridge and the corresponding electrode. For a symmetrically coupled system (\( \Gamma_{ph} = \Gamma_{ph} = \Gamma \)), the expression for electron transmission may be reduced to the form

\[
T(E) = \frac{i}{2} \Gamma(E) \sum_\sigma [G^\alpha_\sigma (E) - G^{\alpha \dagger}_\sigma (E)]. \tag{14}
\]

Provided that electron transport through the system is undisturbed by electron–phonon interactions, and disregarding spin-flip processes, the retarded Green's function \( G_\alpha^\alpha (E) \) may be approximated as [45]

\[
G_\alpha^\alpha (E) = \frac{E - E_0 - \Sigma_\alpha^\alpha - U (1 - \langle n_{ph} \rangle)}{(E - E_0 - \Sigma_0) (E - E_0 - U - \Sigma_\alpha^\alpha) + U \Sigma_\sigma}. \tag{15}
\]

Here, \( U \) is the charging energy associated with Coulomb repulsion between the electrons on the molecular bridge/ quantum dot and \( \langle n_{ph} \rangle \) are one-particle occupation numbers:

\[
\langle n_{ph} \rangle = \frac{1}{2\pi} \int dE \text{Im} [G_\sigma^\alpha (E)] \tag{16}
\]

where \( G_\sigma^\alpha (E) \) is the lesser Green's function for electrons on the bridge. Self-energy corrections \( \Sigma_{0\sigma}, \Sigma_{1\sigma}, \Sigma_{2\sigma} \) appear in the expression for \( G_\sigma^\alpha \) due to the coupling of the bridge to the electrodes. For example,

\[
\Sigma_{0\sigma} = \sum_{\eta} \left[ \frac{\Gamma_{ph}^\eta}{E - E_{\alpha \sigma} + i\eta} \right] \equiv \Sigma^\eta_{0\sigma} + \Sigma^R_{0\sigma}. \tag{17}
\]

In this expression, \( \epsilon_{ph} \) are single-electron energies on the electrode \( \beta (\beta \in \{L, R\}) \). \( \Gamma_{ph} \) are coupling parameters characterizing the coupling of the electron states on the bridge to the electrodes and \( \eta \) is an infinitesimal positive parameter. These self-energy terms are closely related to the previously introduced coupling strengths \( \Gamma_{ph} \), namely \( \Gamma_{ph} (E) = -2 \text{Im} \Sigma^R_{0\sigma} \).

Expressions (14)–(16) have been repeatedly employed in studies of thermal transport through quantum dots (see, e.g., [26, 46]).

For a symmetrically coupled system, one may assume that the potential barriers separating the electrodes from the bridge are identical: \( t_L = t_R = t \), \( n_L = n_R = n \). Then the transmission amplitude could be easily expressed in terms of the corresponding Green's functions:

\[
\Gamma^2 = \frac{2g}{1 + g}. \tag{18}
\]

Within the Buttiker approach, the scattering probabilities \( \epsilon_{L,R} \) are introduced as phenomenological parameters. However, these parameters may be given an explicit physical meaning by expressing them in terms of the relevant energies. In the considered system, dissipation and loss of coherence appear due to the interaction of charge carriers with thermal phonons associated with the electrodes and represented by the dephasing reservoirs. Therefore, as was suggested in an earlier work [47], one can approximate these parameters as follows:

\[
\epsilon_{L,R} = \frac{\Gamma^\eta_{ph}}{2(\Gamma_{ph} + \Gamma_{ph}^R)} + \Gamma^\eta_{ph}. \tag{19}
\]

Here, \( \Gamma^\eta_{ph} \) represents the self-energy term originating from electron–phonon interactions occurring in the reservoir associated with the left/right electrode. Using NEGF and computing the relevant electron and phonon Green's functions.
within the self-consistent Born approximation, one can arrive at a relatively simple expression for $\Gamma_{ph}^{e}$ [30]:

$$\Gamma_{ph}^{e}(E) = 2\pi\lambda^{2} \int_{0}^{\infty} d\omega \rho_{ph}^{e}(\omega) \times \left\{ N(\omega)[\rho_{e}(E - \hbar\omega) + \rho_{e}(E + \hbar\omega)] + [1 - n(E - \hbar\omega)]\rho_{e}(E - \hbar\omega) + n(E + \hbar\omega)\rho_{e}(E + \hbar\omega) \right\}.$$  \hspace{1cm} (20)

In this expression, $\rho_{e}(E)$ and $n(E)$ are respectively the electron density of states associated with the bridge level and its steady state occupation, and $\rho_{ph}^{e}(\omega)$ is the phonon spectral function for the corresponding reservoir. We assume that the electrodes may be kept at different temperatures $T_{\mu}$, so we introduce phonon distribution functions $n_{ph}(\omega) = \exp\left[\hbar\omega/k_{B}T_{\mu}\right] - 1$ where $k_{B}$ is the Boltzmann constant. Finally, the constant $\lambda_{\beta}$ characterizes the coupling strength for electron interactions with the thermal phonons belonging to the bath $\beta$.

The particular form of the phonon spectral functions $\rho_{ph}^{e}(\omega)$ may be found based on the molecular dynamic simulations. However, to qualitatively analyze the effect of dephasing on the thermoelectric transport, one may employ the approximation [48]

$$\rho_{ph}^{e}(\omega) = \rho_{0}^{e}(\omega_{\omega_{ph}} \omega): \exp\left[ - \frac{\omega}{\omega_{ph}} \right]$$  \hspace{1cm} (21)

where the parameter $\rho_{0}^{e}$ is related to the electron–phonon coupling strength, and $\omega_{ph}$ characterizes the relaxation time for the thermal phonons.

The electron density of states includes self-energy corrections which appear due to electron–phonon interactions. Therefore, equation (20) is an integral equation for $\Gamma_{ph}^{e}$. Substituting the approximation (17) into this equation, one may see that the major contribution to the integral over $\omega$ originates from the region where $\omega \ll \omega_{ph}$. Omitting the terms $\hbar\omega$ from the arguments of all slowly varying terms in the integrand, we may reduce equation (20) to the form

$$\Gamma_{ph}^{e}(E, \Gamma_{L}, \Gamma_{R}, \Gamma_{ph}, \Gamma_{ph}) \propto \mathcal{Q}(\lambda_{\beta}, \omega_{ph}, T_{\beta}) \times$$  \hspace{1cm} (22)

where

$$\mathcal{Q}(\lambda_{\beta}, \omega_{ph}, T_{\beta}) = \frac{4\pi\lambda_{\beta}^{2} k_{B}T_{\beta}}{\hbar\omega_{ph}} \left( 2/1 + \frac{k_{B}T_{\beta}}{\hbar\omega_{ph}} \right)$$  \hspace{1cm} (23)

and $\zeta(x;q)$ is the Riemann $\zeta$ function.

The suggested approach gives a means to theoretically analyze the effect of thermal phonons on the thermoelectric properties of thermoelectric junctions. Using the results given by equations (7)–(21), one may compute electron transmission, implying that the difference in the temperatures $T_{L}$ and $T_{R}$ can take on an arbitrary value. Therefore, these results may be employed to study thermoelectric properties of the considered systems beyond the linear regime. As known, nonlinear thermoelectric properties of molecular junctions and similar systems currently attract significant interest [33, 37, 46, 49, 50].

However, in studies of thermoelectric characteristics of such systems beyond the linear regime, one inevitably encounters a nontrivial task of introducing and defining the local temperature for the bridge, which differs from temperatures $T_{L,R}$ associated with the electrodes. The definition of local temperature and related problems are thoroughly discussed in the recent review [49].

In the present work we avoid these difficulties by restricting further analysis with the linear temperature and bias regime. Also, we remark again that within the considered model the thermal conductivity associated with phonons is omitted, for we do not include in our consideration vibrational modes coupled to the bridge. Therefore, we may employ the following commonly used expressions for measurable thermoelectric characteristics:

$$S = \frac{1}{eT} \frac{L_{1}}{L_{0}},$$  \hspace{1cm} (24)

$$ZT = \frac{S^{2}GT}{\kappa} = \frac{L_{1}^{2}}{L_{0}L_{2} - L_{1}^{2}}.$$  \hspace{1cm} (25)

Here, $G$ and $\kappa$ are electron electrical and thermal conductances, $S$ is the thermopower (Seebeck coefficient) and $ZT$ is the dimensionless thermoelectric figure of merit characterizing the efficiency of charge-driven cooling devices and/or heat-driven current generators. In deriving these expressions, it is assumed that $T_{L} = T$ and $T_{R} = T + \Delta T$ ($\Delta T \ll T$). The integrals $L_{n}$ included in equations (24) and (25) are given by

$$L_{n} = \int_{-\infty}^{\infty} (E - \mu)^{n} T(E) \frac{\partial f}{\partial E} dE$$  \hspace{1cm} (26)

where $f$ is the Fermi distribution function for the energy $E$, and the chemical potential $\mu$ characterizes the electrodes at zero bias. Coulomb interactions between electrons on the molecule/quantum dot may be accounted for by using appropriate expressions for the electron Green's functions incorporated into the expression for the coherent transmission (13) as well as into the expression for the electron density of states $\rho_{e}$.

3. Results and discussion

Specific thermoelectric properties of the considered systems depend on the relation of four relevant energies. These are the strength of coupling of the bridge to the electrodes $\Gamma$, the electron–phonon coupling strength $\lambda$, the charging energy $U$ characterizing Coulomb interactions of electrons on the bridge, and the thermal energy $k_{B}T$. It was established that greater values of $ZT$ could be achieved in weakly coupled systems where the condition $\Gamma \ll k_{B}T$ may be satisfied at reasonably low temperatures (see, e.g., [21]), so in further analysis we assume that the considered system complies with this condition.

Also, we assume that the considered quantum dot/molecule is symmetrically coupled to the electrodes ($\Gamma_{L} = \Gamma_{R} = \Gamma$) and the two thermal baths are identical ($\omega_{ph} = \omega_{ph} = \omega_{ph} = \lambda_{L} = \lambda_{R} = \lambda$). Omitting for a while Coulomb interactions, one may derive a simple Lorentzian expression for the electron density of states:

$$\rho_{0} = \frac{1}{2\pi} \frac{\Gamma}{(E - E_{0})^{2} + (\Gamma + \Gamma_{ph})^{2}}$$  \hspace{1cm} (27)
where $f_{ph} = f_{ph} \Gamma + f_{ph} \Gamma$. Substituting this expression into equation (22), we may solve this equation and arrive at a reasonable asymptotic expression for $f_{ph}$:

$$f_{ph} = \frac{\Gamma \delta^2 \left( 1 + \sqrt{1 + \delta^2} \right)}{(E-E_0)^2 + \left( 1 + \sqrt{1 + \delta^2} \right)^2},$$

(28)

where $\delta^2 = 2Q(\lambda, \omega, T) / \Gamma$. Using this result and the expression (19) for the scattering probabilities, we obtain

$$\epsilon_L = \epsilon_R = \epsilon = \frac{\delta^2}{2} \left( 1 + \sqrt{1 + \delta^2} \right).$$

(29)

The parameter $\epsilon$ values vary between 0 and 1. When $\epsilon = 0$, the bridge is detached from the reservoirs, and the electron transport is completely coherent and elastic. Within the opposite limit ($\epsilon = 1$) the transport is characterized by the overall phase randomization typical for inelastic sequential hopping. Within the adopted approach, the scattering probabilities depend on tunnel energy $E$. As well as the electron transmission function $T(E)$, they reach their maximum values ($\epsilon_{max}$ and $T_{max}$, respectively) at $E = E_0$. This is shown in the left panels of figure 2.

As follows from equation (29), the character of the electron transport is determined by the value of the dimensionless parameter $\delta$. Transport remains nearly coherent when $\delta \ll 1$. In contrast, the strong dephasing/dissipation occurs when $\delta$ takes on values significantly greater than 1. To find a suitable estimate for $\delta$, one needs to approximate the Riemann $\zeta$ function included in expression (23). The approximation depends on the relation between the energies $\hbar \omega_c$ and $k_B T$. As discussed in an earlier work [43], the effect of the thermal bath on the electron transport is significantly more pronounced when the lifetime of thermal excitations is sufficiently long ($\hbar \omega_c \ll k_B T$). Under this condition, one may apply the estimation $Q \approx 4k_B T/\delta^2$. Correspondingly, $\delta^2 \approx 4k_B T/\Gamma^2$. This shows that the maximum value of the scattering probabilities $\epsilon_{max}$ is determined with two parameters, namely, $T$ and $\lambda$. We remark that in the absence of electron–phonon interactions ($\lambda = 0$), $\epsilon \equiv \epsilon_m = 0$ regardless of the value of energy $E$, and $T_{max} = 1$. In general, $\epsilon_{max}$ increases when the temperature rises, and it takes on greater values when the electron–phonon interactions are getting stronger, as illustrated in figure 2. The enhancement of $\epsilon_{max}$ is accompanied by a decrease of the maximum value of electron transmission $T_{max}$. These results have an obvious physical sense, because in the considered situation the phase randomization is inseparable from inelastic scattering of electrons by thermal phonons hindering electron transport through the system.

It was first shown by Sofo and Mahan [51] and then confirmed in several later works (see, e.g., [21]) that the figure of merit diverges when $\Gamma$ approaches zero, provided that the system is characterized by zero phonon contribution to the thermal conductance, and the effects of Coulomb interactions between electrons on the bridge are disregarded. The results obtained in the present work agree with this conclusion. In the bottom right panel of figure 3, the divergence of $ZT$ within

![Figure 2](image-url)

**Figure 2.** Left panels: scattering probability (top) and electron transmission (bottom) as functions of tunnel energy $E$. Right panels: temperature dependences of peak values of $\epsilon$ (top) and the electron transmission (bottom). All curves are plotted for a symmetrically coupled system ($T_L = T_R = \Gamma$) with identical dephasing reservoirs, assuming that $T_L = T_R = \Gamma = 1$ meV, $E_0 = 0$, $\lambda = 1.5$ meV (dotted line), $\lambda = 3$ meV (dash–dotted line), $\lambda = 6$ meV (dashed line), $\lambda = 9$ meV (solid line). In the left panels $k_B T = 2.6$ meV. The parameter $\epsilon$ values vary between 0 and 1. When $\epsilon = 0$, the bridge is detached from the reservoirs, and the electron transport is completely coherent and elastic. Within the opposite limit ($\epsilon = 1$) the transport is characterized by the overall phase randomization typical for inelastic sequential hopping. Within the adopted approach, the scattering probabilities depend on tunnel energy $E$. As well as the electron transmission function $T(E)$, they reach their maximum values ($\epsilon_{max}$ and $T_{max}$, respectively) at $E = E_0$. This is shown in the left panels of figure 2. The enhancement of $\epsilon_{max}$ is accompanied by a decrease of the maximum value of electron transmission $T_{max}$. These results have an obvious physical sense, because in the considered situation the phase randomization is inseparable from inelastic scattering of electrons by thermal phonons hindering electron transport through the system.

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the limit $\Gamma \to 0$ in the absence of the electron–phonon interactions is clearly illustrated. The junction figure of merit is limited due to the effect of thermal phonons associated with the electrodes. The stronger these interactions are, the lower in magnitude the maximum values of both $ZT$ and thermopower become. Comparing the present results with those reported in [21], one may presume that the thermal phonons take the part of phonon thermal conductance (which is equal to zero for the considered system) in limiting the maximum value of $ZT$ and removing the divergence. Unlike $ZT$, the thermopower remains finite at small values of $\Gamma$, even when the electron–phonon interactions are disregarded, as illustrated in figure 3 (see top right panel). This means that the divergence of $ZT$ originates from extremely strong violation of the Wiedemann–Franz law, resulting in divergence of the Lorentz ratio.

In analyzing the temperature dependences of thermoelectric characteristics of systems consisting of a molecule/quantum dot linking two electrodes, it was established that usually the figure of merit $ZT$ is a nonmonotonic function of temperature (see, e.g., [9], [19–21], [25], [46]). Also, the present results show that at low temperatures $ZT$ increases as the temperature increases, and it reaches a maximum value at a certain temperature $T_0$. As $T$ further rises, the figure of merit decreases, approaching zero when the temperature significantly exceeds $T_0$. This is illustrated in figure 4. The value of the optimal temperature $T_0$ as well as the corresponding value of $ZT_{\text{max}}$ is determined by the relation between the coupling energies $\lambda$ and $\Gamma$. Assuming that $\lambda$ is fixed, one observes that $ZT_{\text{max}}$ takes on greater values and the optimal temperature $T_0$ becomes higher as $\Gamma$ increases. In contrast, enhancement of $\lambda$ at fixed $\Gamma$ leads to a significant decrease of $ZT_{\text{max}}$, and shifts $T_0$ to a lower value. Thus the electron interactions with the thermal baths suppress $ZT$ values. Molecular vibrations may affect the thermoelectric efficiency of the considered nanoscale systems in a similar way, as discussed in several works (see, e.g., [13, 21, 30]).

The character of the temperature dependence of $ZT$ displayed in figure 4 indicates that, while the transition from coherent and elastic tunneling to the dissipative transport significantly reduces $ZT$ values, the general character of the temperature dependence of the figure of merit remains unchanged. At low temperatures, erosion of the sharp step in the Fermi distribution functions for the electrodes occurring at $E = \mu$ creates better opportunities for electron tunneling through the system. However, when the temperature exceeds a certain value, the same process starts to hinder electron transport. Also, at sufficiently strong electron–phonon interactions, the peak value of the electron transmission decreases, bringing further reduction of the thermoelectric efficiency.

Although considerable efforts are being applied to reach understanding of the combined effects of electron–electron and electron–phonon interactions on the thermoelectric transport, this subject has not been fully investigated so far. Now, we reconsider the above results, taking into account previously
disregarded Coulomb interactions between electrons on the bridge of a thermoelectric junction. Then the expression (15) for the electron Green’s function may be employed to compute the scattering probabilities and, ultimately, the electron transmission $T(E)$ and measurable characteristics of thermoelectric transport. In further analysis we assume that the linker (molecule/quantum dot) is weakly coupled to the electrodes, so the charging energy $U$ significantly exceeds the coupling parameter $\Gamma$. The results of these computations are displayed in figures 5 and 6.

As shown in figure 5, the dependence of $ZT$ on $E_0$ undergoes significant changes as the temperature increases. At low temperatures, $ZT$ exhibits two pairs of peaks of unequal height situated near $E_0 = \mu$ and $E_0 = \mu - U$, respectively. At higher temperatures two peaks making a pair cling together, so each pair is transformed to a single peak. At sufficiently high temperatures, these peaks become nearly equal in height, and their tops are shifted farther away from each other. The curves displayed in the left panel of figure 5 are plotted assuming that temperature is noticeably lower than the temperature $T_0$ providing the maximum value of $ZT$, as shown in figure 4. We cannot explicitly compare the results represented in these figures because the curves shown in figure 4 are plotted disregarding electron–electron interactions. However, we may conjecture that further increase of temperature accompanied by intensification of scattering processes will bring a further rise of $ZT$ peaks, as also happens in the case when one neglects electron–electron interactions. Also, we may expect that the increase in the heights of the peaks will be replaced by their reduction as the temperature exceeds a certain value. An explicit effect of electron–phonon interactions on the figure of merit is shown in the right panel of figure 5. Again, one may observe the suppression of $ZT$ originating from these interactions.

Further illustration of the influence of thermal phonons on the figure of merit is presented in figure 6. The curves shown in the left panel of this figure are plotted at a moderately high temperature ($k_B T = 2.6$ meV), when the adjacent peaks are already merged, so that $ZT$ exhibits only two maxima. Omitting electron–phonon interactions, one observes a significant difference in the peak heights. This difference originates from the characteristic features of the electron density of states on the bridge level, which are manifested in the characteristics of coherent electron transport. As the electrons’ interaction with thermal phonons strengthens, the peak heights become leveled. At fixed temperature, the maximum value of $ZT$ is determined by the relation between the charging energy $U$ and coupling strengths $\lambda$ and $\Gamma$. We remark that the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Maximum value of $ZT$ as a function of temperature. The curves shown in the left panel are plotted assuming $\lambda = 0.25$ meV, $\Gamma = 0.3$ meV (solid line), $\Gamma = 0.7$ meV (dashed line), $\Gamma = 1.25$ meV (dash–dotted line). In the right panel, the curves are plotted at $\Gamma = 0.7$ meV, $\lambda = 0$ (dash–dotted line), $\lambda = 0.25$ meV (dashed line), and $\lambda = 1$ meV (solid line).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Combined effect of electron–electron and electron–phonon interactions on the dependence of $ZT$ of the bridge level position. The curves are plotted at $U = 10$ meV. Left panel: $\Gamma = 1, 2.5$ meV, $\lambda = 0.25$ meV, $k_B T = 2.6$ meV (dash–dotted line), $k_B T = 1.3$ meV (dashed line), $k_B T = 0.7$ meV (solid line). Right panel: $\Gamma = 1.25$ meV, $k_B T = 0.7$ meV, $\lambda = 0$ (dash–dotted line), $\lambda = 0.25$ meV (dashed line), $\lambda = 1$ meV (solid line).}
\end{figure}
suppression of $ZT$ due to electron–phonon interactions may be replaced by its promotion, which occurs due to a combined effect of electron–electron and electron–phonon interactions [33]. However, this increase of thermoelectric efficiency is expected to appear when electron–phonon interactions and Coulomb repulsion between electrons are comparable in strength. These conditions are different from those considered in the present work. Disregarding for a while the effect of photons, one observes that $ZT$ takes on greater values within the limits of low ($U \ll k_B T$) and high ($U \gg k_B T$) values of charging energy, and it drops at intermediate values of $U$. This behavior was previously described and explained within the sequential hopping approximation for the electron transmission through a thermoelectric junction [21]. Electron–phonon interactions promote washing out of these features.

4. Conclusion

In conclusion, we remark that thorough studies of thermoelectric properties of nanoscale systems taking into account both electron and phonon transport as well as diverse effects arising due to electron–electron and electron–phonon–phonon interactions have not been completed so far. In several earlier works this theoretical research was carried out employing the single-particle scattering approach pioneered by Landauer in the context of charge transport in mesoscopic and nanoscale systems. These ideas were generalized to phonon transport through nanoscale junctions [30, 32, 42, 52, 53]. Within this approach, transport characteristics of a considered nanoscale system are expressed in terms of electron and phonon transmission functions. The latter were computed employing several methods, including some based on scattering matrix formalism [42, 54]. Later, these methods were mostly abandoned in favor of more advanced formalisms such as NEGF and/or various modifications of quantum rate equations. However, the potential usefulness of the approaches based on scattering theory has not been exhausted so far.

These approaches have the advantage of being computationally simple and less time and effort consuming than advanced formalisms. At the same time, their shortcomings could be largely removed by incorporating some NEGF based results into a computational scheme. In the present work we suggest such an approach, and we employ it to theoretically analyze some effects of electron–phonon interactions on the efficiency of nanoscale thermoelectric junctions. Currently, various manifestations of electron–phonon interactions in thermoelectric transport characteristics of nanoscale molecular junctions have already been explored, and the research is still going on. However, the research efforts were and still are mostly concentrated on the effects arising from vibrational modes on the molecules linking the electrodes. Less attention has been paid to the influence of thermal phonons associated with random nuclear motions in the ambiences. Here, we focus on the analysis of thermal phonons in the electron transport.

We show that direct interaction of electrons with thermal phonons, assuming that these phonons are assembled in two baths associated with the electrodes, may significantly affect the thermoelectric efficiency of molecular junctions and similar nanoscale systems. Specifically, we show that electron–phonon interactions assist the increase of the scattering probabilities, thus destroying the coherence of electron transport and promoting energy dissipation. When the electron–phonon coupling becomes sufficiently strong, this brings a significant suppression of both thermopower and thermoelectric figure of merit, thus worsening the thermoelectric efficiency of a considered system. This effect is illustrated in figures 3 and 4. We remark that $\lambda$ and thermal energy $k_B T$ appear as cofactors in the expression for the scattering probability $\epsilon$ (see equation (29)), so they affect it in a similar way. When either $\lambda$ or $k_B T$ increases, this results in strengthening of dephasing in the electron transport. However, the entire effects of these two parameters on the thermoelectric properties of the considered systems are unidentical. While the strengthening of electron–phonon interactions always leads to reduction of $ZT$, the rise of temperature can promote the figure of merit increase provided that the temperature does not exceed a certain value. This may be explained by the fact that, besides affecting the intensity of scattering, the temperature influences distributions of electrons in the electrodes, and it may either assist or hinder their transport through the system. Also, we analyzed
the combined effect of electron–electron and electron–phonon interactions on thermoelectric properties. Obtained results agree with those reported in earlier works [21, 33]. In particular, it was confirmed that $ZT$ exhibits a minimum at a certain value of the charging energy $U$, which becomes less distinct at stronger values of $\lambda$.

The suggested computational scheme may be generalized to include vibrational modes. For this purpose, one may add to the adopted model simulating a thermoelectric junction an extra reservoir representing vibrons. Also, one may mimic the molecular bridge by a set of energy levels, thus opening the way to studies of interference effects. For a realistic molecular junction, relevant energies may be computed using either density functional theory or other method of electronic structure calculation. Finally, the proposed scheme may be helpful in studies of thermoelectric transport beyond linear regime in temperature. On these grounds, we believe that the presented method and results could help to reach a better understanding of some important aspects of thermal transport in molecular junctions and similar nanoscale systems.

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