Nonlinear thermoelectric transport in single-molecule junctions: the effect of electron–phonon interactions

Natalya A Zimbovskaya

Department of Physics and Electronics, University of Puerto Rico-Humacao, CUH Station, Humacao, PR 00791, USA
E-mail: natalya.zimbovskaya@upr.edu

Received 20 February 2016, revised 5 May 2016
Accepted for publication 6 May 2016
Published 1 June 2016

Abstract
In this paper, we theoretically analyze steady-state thermoelectric transport through a single-molecule junction with a vibrating bridge. The thermally induced charge current in the system is explored using a nonequilibrium Green function formalism. We study the combined effects of Coulomb interactions between charge carriers on the bridge and electron–phonon interactions on the thermocurrent beyond the linear response regime. It is shown that electron–vibron interactions may significantly affect both the magnitude and the direction of the thermocurrent, and vibrational signatures may appear.

Keywords: nonlinear thermoelectric transport, molecular junctions, effect of phonons

1. Introduction

Thermoelectric transport in nanoscale systems is currently attracting much interest. This was triggered in the early 1990s by the pioneering works of Hicks and Dresselhaus [1, 2]. They predicted that heat-to-electricity conversion efficiency, which is known to be rather low in conventional bulk materials, may be significantly enhanced in nanoscale systems. Correspondingly, the thermoelectric properties of tailored nanoscale systems such as carbon-based nanostructures and quantum dots (QD) and/or molecules put into contact with macroscopic leads, were explored both theoretically and experimentally [3–6].

The key to the transport properties of single-molecule junctions is a combination of a discrete electron energy spectrum of a molecular bridge and nearly continuous energy spectra that are typical for charge carriers on the leads. Owing to this combination, sharp features appear in the electron transmission spectra that determine various transport characteristics. In particular, these features may give rise to a considerable enhancement of the heat-to-electricity conversion efficiency in single-molecule junctions and similar nanoscale systems [5, 6].

Transport through molecular junctions is controlled by several factors, including the strength of the molecular bridge coupling to the leads and Coulomb interactions between traveling electrons. In addition, interactions between electrons and molecular vibrations may strongly affect electron transport through molecules. Over the past two decades, theoretical studies of vibrationally induced electron transport through QDs and single-molecule junctions have been carried out by many authors. For the most part, they used master equations [7–11], functional renormalization group-based approaches [12, 13], scattering theory [14–17], and the nonequilibrium Green function formalism (NEGF) [18–26]. Signatures of electron–vibron interactions were observed in experiments [27–31].

In this paper we focus on the Seebeck effect in molecular junctions. It is known that a difference in the temperatures of the leads induces a charge current $I_{th}$ to flow through the system. The Seebeck effect is measured by recording the voltage $V_{th}$, which completely stops this current, provided that the difference in temperatures $\Delta T$ remain fixed. When $\Delta T \ll T_{LR}$ ($T_{LR}$ being the temperatures of the left and right electrodes, respectively), the system operates within a linear response regime, and both the thermally excited current $I_{th}$
Here, \(= \Lambda\) are substitutions of electron-electron interactions, with \(\Lambda\) being the relevant coupling parameter. The terms \(H_j (\beta = L, R)\) correspond to the noninteracting electrons on the leads with energies \(\epsilon_{r \beta}\).

\[
H_j = \sum_{r \beta} \epsilon_{r \beta} c_{r \beta}^\dagger c_{r \beta},
\]

where \(c_{r \beta}^\dagger\) and \(c_{r \beta}\) are the creation and annihilation operators for these electrons. The transport term

\[
H_T = \sum_{r \beta} \tau_{r \beta} c_{r \beta}^\dagger d_{\sigma} + \text{H.C.}
\]

represents the tunneling effects between the bridge and the leads, with the factors \(\tau_{r \beta}\) characterizing the coupling of the electron states on the bridge to those on the leads. Below we consider a symmetrically coupled system, so \(\tau_{L \sigma} = \tau_{R \sigma} = \tau_{\sigma}\). Finally, the term \(H_{\phi}\) describes the phonon bath coupled to the vibrational mode. We assume that the bath is kept at the temperature \(T = \frac{1}{2} (T_L + T_R)\), and that its coupling to the vibrational mode far exceeds the electron–phonon coupling strength. Then the phonon population on the bridge is given by the Bose–Einstein distribution \(N_\phi\) [24].

To eliminate the electron–phonon coupling term from the Hamiltonian (1), a small polaron transformation is commonly applied to convert the Hamiltonian \(H_{\text{as}} \hat{H} = \exp (s) H \exp (-s)\), where

\[
s = \frac{\Lambda}{\hbar \Omega} \sum_{\sigma} \epsilon_{r \sigma} d_{\sigma}^\dagger d_{\sigma} (a^\dagger - a).
\]

As a result, the term that describes electron–phonon interactions disappears from the transformed bridge Hamiltonian (1), and the energies \(E_0\) and \(U\) acquire corrections that originate from electron–phonon interactions and should be replaced by renormalized energies:

\[
E_0 = E = \frac{\Lambda^2}{\hbar \Omega}, \quad \tilde{U} = U - \frac{2 \Lambda^2}{\hbar \Omega}.
\]

The transfer Hamiltonian (3) also undergoes a transformation, so that the renormalized coupling parameters \(\tau_{r \sigma}\) are substituted for \(\tau_{r \sigma}\):

\[
\tau_{r \sigma} = \tau_{r \sigma} X \equiv \tau_{r \sigma} \exp \left[ -\frac{\Lambda}{\hbar \Omega} (a^\dagger - a) \right].
\]

The expectation value of the operator \(X\) in the considered case of thermal equilibrium is given by:

\[
\langle X \rangle = \exp \left[ -\left(\frac{\Lambda}{\hbar \Omega}\right)^2 \left(N_{\phi} + \frac{1}{2}\right) \right].
\]
Following [21], one may approximate the expression for \( \tilde{\tau}_\sigma \) by substituting (X) instead of X into equation (6), thus decoupling the electron and phonon subsystems.

The transformed Hamiltonian \( \tilde{\mathcal{H}} \) is the sum of the electron part \( \tilde{\mathcal{H}}_\text{el} \) and the phonon part \( \tilde{\mathcal{H}}_\text{ph} \). Since the electron and phonon subsystems are decoupled, these Hamiltonians may be applied independently to compute relevant average values. The Hamiltonian \( \tilde{\mathcal{H}}_\text{el} \) has a form that is similar to the one that describes a single-level bridge attached to the leads via transfer terms. However, the key parameters of the model \( E_0, U, \) and \( \tau_\sigma \) are now replaced by renormalized values given by equations (5)–(7). Using this Hamiltonian, one can derive expressions for renormalized electron Green functions. Disregarding spin-flip processes, one arrives at separate equations for the retarded and advanced Green functions that correspond to different spin orientations. The expressions for the retarded Green function can be presented in the form first derived in [40]:

\[
\tilde{G}^>_{\sigma}(E) = \frac{E - E_0 - \Sigma_{02}^{\sigma} - \bar{U}(1 - \langle n_{-\sigma} \rangle)}{(E - E_0 - \Sigma_{02}^{\sigma}) - \bar{U} + \Sigma_{12}^{\sigma}}.
\] (8)

Here, \( \langle n_{-\sigma} \rangle \) are one-particle occupation numbers on the bridge level:

\[
\langle n_{\sigma} \rangle = \int \frac{dE}{2\pi} \text{Im}[\tilde{G}^<_{\sigma}(E)]
\] (9)

and \( \Sigma_{02}^{\sigma}, \Sigma_{12}^{\sigma}, \) and \( \Sigma_{22}^{\sigma} \) are self-energy corrections. These self-energy terms are described by the usual expressions (see e.g. [40–42]), where the characteristic energies \( E_0, U, \) and \( \tau_\sigma \) are replaced by the renormalized values.

The lesser Green function \( \tilde{G}^<_{\sigma}(E) \) is related to the retarded and advanced Green functions by the Keldysh equation:

\[
\tilde{G}^<_{\sigma}(E) = \tilde{G}^<_{\sigma}(E) \tilde{\Sigma}_{\sigma}(E) \tilde{G}_{\sigma}(E).\]
(10)

A similar expression may be written out for the greater Green function \( \tilde{G}^>_{\sigma}(E) \) by substituting a self-energy \( \tilde{\Sigma}_{\sigma}(E) \) for \( \tilde{\Sigma}_{\sigma}(E) \). These self-energy terms may be presented in the form [41]:

\[
\tilde{\Sigma}_{\sigma}(E) = i \sum_{\beta} f^\beta_{\sigma}(E) \Delta^\beta_{\sigma}(E),
\]
(11)

\[
\tilde{\Sigma}_{\sigma}(E) = -i \sum_{\beta} [1 - f^\beta_{\sigma}(E)] \Delta^\beta_{\sigma}(E).
\]
(12)

Here, \( f^\beta_{\sigma}(E) \) are the Fermi distribution functions for the leads, and the factors \( \Delta^\beta_{\sigma}(E) \) differ from \( \Gamma^\beta_{\sigma}(E) \equiv -2\text{Im}[\tilde{\Sigma}_{02}^{\sigma}] \) due to renormalization originating from electron–phonon interactions between electrons on the bridge. When these interactions are omitted from consideration, the difference between \( \Delta^\sigma_{\sigma}(E) \) and \( \Gamma^\sigma_{\sigma}(E) \) vanishes. The terms \( \Gamma^\sigma_{\sigma}(E) \) describe the coupling of the bridge to the leads. Renormalization of these terms due to Coulomb interactions may bring about noticeable changes to the values of the occupation numbers when the considered system is shifted from the equilibrium position. In this paper, we assume that this occurs due to the temperature gradient applied across the system. It was shown [39] that for moderate values of \( \Delta T (\Delta T / T < 1) \) one may disregard the renormalization of the coupling parameters, because it causes very small corrections to the \( \langle n_{\sigma} \rangle \) values. Therefore, in further calculations we employ equations (11) and (12), where \( \Delta^\sigma_{\sigma}(E) \) are replaced by \( \Gamma^\sigma_{\sigma}(E) \), and the latter parameters are computed using the wide band approximation.

True Green functions for the electrons on the bridge are related to those given before. For instance, one may approximate the lesser and greater Green functions as follows [21]:

\[
G^\sigma_{\sigma}(E) = \sum_{r = -\infty}^{\infty} L_r \tilde{G}^\sigma_{\sigma}(E + r\hbar \Omega),
\]
(13)

\[
G^\sigma_{\sigma}(E) = \sum_{r = -\infty}^{\infty} L_r \tilde{G}^\sigma_{\sigma}(E - r\hbar \Omega),
\]
(14)

with the coefficients \( L_r \) of the form:

\[
L_r = \exp \left( -\frac{\Lambda}{\hbar \Omega} \right) \left( 2N_{\text{ph}} + 1 \right) \int \frac{d\Omega}{2\pi} \times \int \frac{d\Omega}{2\pi} \left( N_{\text{ph}}(N_{\text{ph}} + 1) \right).
\]
(15)

Here, the Bose–Einstein distribution function \( N_{\text{ph}} \) is taken for the phonon frequency \( \Omega \) and the temperature \( T, k \) is the Boltzmann constant, and \( I_\nu(z) \) is the modified Bessel function of the order \( \nu \).

Assuming that \( f^\beta_{\sigma}(E) \equiv f^\beta( E ) \), we may present the charge current flowing through a symmetrically coupled junctions as the Landauer expression:

\[
I = \frac{e}{\hbar} \int \tau(E)[f^L(E) - f^R(E)]dE,
\]
(16)

where the electron transmission function is given by:

\[
\tau(E) = \frac{1}{4} \sum_{\sigma} \left[ G^\sigma_{\sigma}(E) - G^{\sigma \sigma}(E) \right].
\]
(17)

We remark that in this expression the prefactor \( \Gamma \) that characterizes the coupling of the leads to the bridge (\( \Gamma^\sigma_{\sigma} = \Gamma^R_{\sigma} \equiv \Gamma \)) is computed omitting renormalization due to electron–phonon interactions. Strictly speaking, equations (16) and (17) remain valid only when electron–phonon interactions are sufficiently weak (\( \Lambda \lesssim \hbar \Omega \)). This conclusion results from the procedure used to obtain expressions (13)–(15). In deriving these expressions, only terms of the lowest order in (\( \Lambda^2 / \hbar \Omega \)) were taken into account. Better approximations for the relevant Green functions were obtained in several works (see e.g. [20, 26]). However, in these works, the effects of Coulomb interactions between electrons on the bridge were not considered. Keeping in mind the above-mentioned limitations, we employ equations (13)–(17) to study steady-state thermoelectric transport through a molecular junction with a vibrating bridge.

3. Numerical results

In this section, we consider some numerical results obtained by applying the formalism outlined above. The effect of electron–vibron interactions on the transport characteristics of a molecular junction depends strongly on the relationships between the energies \( \Gamma, \hbar \Omega, \) and \( \Delta \). It was argued that when the bridge is weakly coupled to the leads (\( \Gamma \lesssim \hbar \Omega, \Delta \)) the ‘mobility’ of the traveling electrons remains low and the
local oscillator (the vibrational mode) is fast enough to individually adjust to them [4, 26]. This creates the most favorable conditions for manifestations of electron–vibron interactions in the transport characteristics of single-molecule junctions, so we assume this condition to be satisfied. We also assume that electron–phonon interactions are moderate ($\Lambda < \hbar \Omega$) and electron–electron interactions sufficiently strong ($U > \hbar \Omega$). Reasonable values for these energies may be taken based on the fact that the frequencies of the vibrational modes range between 10 meV and several hundreds of meV [28, 31]. In further calculations we accept $\hbar \Omega = 10$ meV, which is typical for small molecules.

While on the bridge, electrons participate in events that occur due to their interactions with vibrational phonons. These events involve virtual phonon emission and absorption, which results in the appearance of metastable electron states. These events involve virtual phonon emission and absorption, as shown in figure 1. In the presence of electron–vibron interactions, each of the two unequally high peaks corresponding to electron transmission through a junction with a single-state bridge within the Coulomb blockade regime is replaced by a set of narrower peaks associated with the metastable states. All of these peaks are arranged as two subsets, including the peaks centered at energies $E_0$ and $E = \tilde{E}_0 + \tilde{U}$, respectively. One observes that the subsets become closer to each other as the electron–phonon coupling strengths. This happens because the effective charging energy $\tilde{U}$ is renormalized due to electron–phonon interactions. As follows from equations (6) and (7), electron–phonon interactions significantly reduce the effective coupling of the bridge to the leads. Therefore, one may expect the considered junction to remain within the Coulomb blockade regime even at low temperatures. Nevertheless, it was shown that phonon-induced sidebands may accompany the Kondo maximum in electron transmission [12, 21].

Figure 2. Thermally excited current $I_{th}$ in an unbiased junction as a function of the bridge level energy $E_0$ at a fixed value of $\Delta T$ (left) and as a function of $\Delta T$ at several values of $E_0$ (right). The curves are plotted for $kT_R = 0.6$ meV, $U = 60$ meV, $\hbar \Omega = 10$ meV, $\Gamma = 2.5$ meV, $\Delta T_0 = 0.8T_R$, $\Delta T = 0.8T_R$ (left), and $\Lambda = 7.5$ meV (right).

Figure 3. Top: thermally excited current $I_{th}$ versus $\Delta T$ and $U$ plotted assuming $kT_R = 0.6$ meV, $E_0 = -10$ meV, $\Lambda = 7.5$ meV, $\Gamma = 2.5$ meV, and $\hbar \Omega = 10$ meV. Bottom: cross-sections of the surface shown on the top at several fixed values of $T_L$ (left) and $U$ (right).

Thermally excited current starts to flow through an unbiased molecular junction when the leads are kept at different temperatures. For certainty, we assume below that the right lead is cooler than the left one ($T_R < T_L$). We also assume that $T_R$ remains constant, whereas $T_L$ varies. The difference of the Fermi distributions in the expression (16) for the thermally excited charge current takes on nonzero values only when the tunnel energy values belong to the close vicinity of the chemical potential of the leads $\mu$. For simplicity, we assume that $\mu = 0$, and thus the thermally excited current $I_{th}$ flows through the system, provided that the energy level on the bridge is shifted to a position where the renormalized energy $E_0$ (or $E_0 + \tilde{U}$) is close to zero. This corresponds to opening transport channels for charge carriers. As $\tilde{E}_0$ approaches zero from above, electrons start to flow from the left (hot) electrode to the right (cold) one, and $I_{th}$ accepts negative values, as shown in figure 2. However, when $E_0$ becomes very close to zero, holes start to participate in transport along with electrons. At a certain value of $E_0$ the hole flow counterbalances the electron flow, and $I_{th}$ becomes zero. At a further shift of $E_0$ to a position below zero, the hole flow predominates, and $I_{th}$

\[
\begin{align*}
\text{Figure 2. Thermally excited current } I_{th} \text{ in an unbiased junction as a function of the bridge level energy } E_0 \text{ at a fixed value of } \Delta T \text{ (left) and as a function of } \Delta T \text{ at several values of } E_0 \text{ (right). The curves are plotted for } kT_R = 0.6 \text{ meV, } U = 60 \text{ meV, } \hbar \Omega = 10 \text{ meV, } \\
\Gamma = 2.5 \text{ meV, } \Delta T_0 = 0.8T_R, \Delta T = 0.8T_R \text{ (left), and } \Lambda = 7.5 \text{ meV (right).}
\end{align*}
\]
accepts positive values. The same explanation may be given for \( I_{th} \) behavior at \( E_0 \) close to \(-\tilde{U}\).

The interactions of charge carriers on the bridge with the vibrational mode bring about noticeable changes to the \( I_{th} \) behavior. Renormalization of the bridge level energy \( E_0 \) and the charging energy \( U \) due to these interactions changes the positions of the derivative-like features that correspond to the opening up of channels for charge carrier transport. One observes that the stronger the electron–vibron interactions become, the smaller the separation between these features is. In addition, the \( I_{th} \) magnitude largely depends on the electron–vibron interaction strength. However, at fixed \( \Lambda \), peaks in electron transmission that correspond to metastable states \( E_m \) and \( E_n \) (\( n, m = 0 \)) do not leave explicit signatures in the \( I_{th}(E_0) \) lineshape shown in the figure. This agrees with the results reported in earlier works [18, 20, 26].

Thermally excited current depends strongly on the temperature difference \( \Delta T \). As demonstrated in figure 2, \( I_{th} \) accepts a distinctly nonlinear lineshape when \( \Delta T \) is not too small. To a considerable degree, \( I_{th} \) temperature dependence is controlled by the bridge energy level position. For each considered value of \( E_0 \), \( I_{th}(\Delta T) \) reaches its minimum at certain value of \( \Delta T \). In addition, some of these curves show maxima at small values of \( \Delta T \) followed by the change of sign. As discussed in [38, 39], the variety of \( I_{th}(\Delta T) \) lineshapes originates partly from the relationship between the characteristic energies \( E_0 \) and \( U \). The third controlling factor is the electron–vibron coupling strength \( \Lambda \).

The effect of Coulomb interactions is further elucidated in figure 3. One observes that the value of the charging energy \( U \) affects the positions of the minima at the \( I_{th}(\Delta T) \) curves as well as the thermocurrent magnitudes. The effect of electron–phonon coupling at comparatively high temperatures is illustrated in figure 4. The presented surface reveals several ridges separated by ravines, which means that electron–vibron coupling may influence \( I_{th} \) in more than one way. This may be observed by studying the surface profiles corresponding to several fixed \( E_0 \) values. A rather complex shape of the \( I_{th}(E_0, \Lambda) \) surface may be explained as follows. It was demonstrated previously that \( I_{th} \) takes on nonzero values when the renormalized energies \( \tilde{E}_0 \) and \( \tilde{E}_0 + \tilde{U} \) are close to the chemical potential of the electrodes. The width of the ‘conduction window’ centered at \( E = \mu = 0 \) is determined by the temperature difference \( \Delta T \).

By simultaneously varying \( E_0 \) and \( \Lambda \), one may put either \( \tilde{E}_0 \) or \( \tilde{E}_0 + \tilde{U} \) inside this window, thus providing favorable conditions for thermally excited current to flow. In this way, one can manipulate both the magnitude and the direction of \( I_{th} \). In addition, the surface presented in figure 4 is built with the
assumption that the temperatures of the leads are rather high, and the thermal energies $kT_{L,R}$ and $k\Delta T$ accept values comparable to $h\Omega$. Under these conditions, signatures of metastable transport channels may appear in $I_{th}(E_0, \Lambda)$ alongside (or even instead of) those of the original channels existing in a molecular junction with a rigid (nonvibrating) bridge. This may happen because the suppression of metastable state contributions that occurs at low lead temperatures [18, 26] becomes less effective when $T_{L,R}$ and $\Delta T$ are moderately high. In principle, one may similarly control $I_{th}$ by varying $E_0$ and $U$ at a certain fixed value of $\Lambda$. Again, $I_{th}$ will flow through the system when the renormalized bridge level energy $\tilde{E}_0$ (or $\tilde{E}_0 + \tilde{U}$) is moved into the conduction window. In addition, one may expect phonon sideband signatures to appear when $kT_{th}$, $k\Delta T$, and $\Lambda$ accept values of the order of $h\Omega$. As is known, polaron formation on the bridge may cause the reversal of the renormalized charging energy sign, so that electron repulsion is replaced by effective attraction. The crossover occurs when $U = 2\Delta/h\Omega$ ($U = 0$). One observes that two ridges on the surface $I_{th}(E_0, U)$ displayed in figure 5 approach each other in the vicinity of the crossover, and they merge into a single peak at a certain value of the bridge level energy.

4. Conclusion

In this paper, we theoretically studied the steady thermoelectric transport in a single-molecule junction with a vibrating bridge. We employed a simple model for the bridge, simulating it by a single spin degenerated energy level coupled to a single vibrational mode. We concentrated on analyzing the diverse properties of the thermally excited charge current that appears when a temperature gradient is applied across the system. This quantity is especially interesting, because it is available for direct measurement in experiments on nanoscale systems.

In the studies, we took into account Coulomb repulsion between electrons on the bridge and their interactions with the vibrational mode. The adopted computational method was based on the nonequilibrium Green function formalism. To simplify the calculations, only terms of the lowest order in $\Delta/h\Omega$ were kept in the expressions for the relevant Green functions. In addition, rather simple approximations were used for electron Green functions $\tilde{G}^-(E)$ and $\tilde{G}^-\Lambda(E)$, We are aware of the limitations of the computational scheme employed in this paper. However, we remark that the approximations for the electron Green functions that we used bring reasonably good results for the characteristics of electron transport through QDs and single-molecule junctions, as shown in [42] and several other works. These approximations remain appropriate when the considered system is not too strongly coupled, so that $\Gamma$ is smaller than $U$.

The effect of the vibrational mode on the thermally excited current flowing through a single-molecule junction is twofold. Firstly, electron–vibron interactions bring about renormalizations of the bridge energy level (polaronic shift) and charging energy $U$ and effectively reduce the bridge coupling to the leads. Secondly, extra channels for electron transport associated with metastable states $E_{\sigma}$, $E_{\tau}$ may open up. Signatures of these states may appear as extra peaks in the electron transmission and extra steps in the current–voltage curves in biased junctions.

At low temperatures, signatures of these extra peaks do not explicitly appear in $I_{th}(E_0)$ lineshapes because of the ‘floating’ condition of the phonon bands, as was first discussed in the context of studies on linear electric transport through molecules [18]. Thus the electron–vibron interactions mostly affect the $I_{th}$ magnitude and direction through the polaron shift of $E_0$ and the renormalization of $U$. This renormalization may move $\tilde{E}_0$ and $\tilde{E}_0 + \tilde{U}$ inside/outside the ‘conduction window’ that occurs about the leads’ chemical potential when the temperature gradient is applied across the system. Thus electron–phonon interactions may affect both the magnitude and the direction of the thermally induced current at fixed $E_0$ value. The $I_{th}$ dependence of $\Delta T$ appears to be nonlinear and nonmonotonic. The magnitude and direction of the thermally induced current are very sensitive to the values of the relevant energies $E_0, U, \Lambda$, and $k\Delta T$. At moderately high temperatures of the leads when $k\Delta T$ accepts values comparable to the energy of the vibrational phonon $h\Omega$, signatures of metastable states may appear in $I_{th}(E_{\sigma}, \Lambda)$, bringing additional features into this surface shape.

It was established in previous studies that Coulomb interactions between electrons on the bridge strongly influence the thermolectric properties of molecular junctions [7, 12, 21, 35, 41, 42]. Here, we analyzed the combined effects of Coulomb repulsion between electrons on the bridge and electron–phonon interactions on the thermally induced current through the system. The most interesting effects may appear when strong electron–phonon interactions cause the change of sign of the renormalized charging energy $\tilde{U}$. It had already been shown that one may expect a significant enhancement of the linear response thermopower in a strongly coupled system described by an Anderson model with negative charging energy [43]. Therefore, it would be interesting to generalize the present analysis to strongly coupled systems that can be moved from the Coulomb blockade regime to the Kondo regime and consider the effects that may occur when the renormalized charging energy $\tilde{U}$ becomes negative due to electron–phonon interactions.

Finally, in this paper we used a simple Anderson–Holstein model for a molecular junction, and a rather simple computational method was applied to derive approximations for the relevant Green functions. Nevertheless, the presented analysis captures some essential physics associated with thermolectric transport through vibrating molecules. We believe that the reported results may be useful to better understand the nonlinear Seebeck effect in nanoscale systems.

Acknowledgments

The author thanks G M Zimbovsky for help with the manuscript. This work was supported by NSF-DMR-PREM 1523463.
References

[1] Hicks L D and Dresselhaus M S 1993 Phys. Rev. B 47 12727
[2] Hicks L D and Dresselhaus M S 1993 Phys. Rev. B 47 16631
[3] Giazotto F, Heikkil T T, Luukanen A, Savin A M and Pekola J P 2006 Rev. Mod. Phys. 78 217
[4] Galperin M, Ratner M A and Nitzan A 2007 J. Phys.: Condens. Matter 19 103201
[5] Dubi Y and Di Ventra M 2011 Rev. Mod. Phys. 83 131
[6] Zimbovskaya N A and Pederson M R 2011 Phys. Rep. 509 1
[7] Koch J, von Oppen F, Oreg Y and Sela E 2004 Phys. Rev. B 70 195107
[8] Leitjse M, Wegewijs M R and Flensberg K 2010 Phys. Rev. B 82 045412
[9] Sanchez R and Buttiker M 2011 Phys. Rev. B 83 085428
[10] Schaller G, Krause T, Brandes T and Esposito M 2013 New J. Phys. 15 033032
[11] Hartle R and Thoss M 2011 Phys. Rev. B 83 115414
[12] Paaske J and Flensberg K 2005 Phys. Rev. Lett. 94 176801
[13] Jovchev A and Anders F B 2013 Phys. Rev. B 87 195112
[14] Cizek M, Thoss M and Domcke W 2004 Phys. Rev. B 770 125406
[15] Benesch C, Cizek M, Klimes J, Kondov I, Thoss M and Domcke W 2008 J. Phys. Chem. C 112 9880
[16] Zimbovskaya N A and Kuklij M M 2009 J. Chem. Phys. 131 114703
[17] Arguello-Luengo J, Sanchez D and Lopez R 2015 Phys. Rev. B 91 165431
[18] Mitra A, Aleiner I and Millis A J 2004 Phys. Rev. B 69 245302
[19] Galperin M, Nitzan A and Ratner M A 2006 Phys. Rev. B 73 045314
[20] Galperin M, Ratner M A and Nitzan A 2008 Mol. Phys. 106 397
[21] Swirkowicz R, Wilczynski M and Barnas J 2008 J. Phys.: Condens. Matter 20 255219
[22] Frederiksen T, Paulsson M, Brandbyge M and Jauho A-P 2007 Phys. Rev. B 75 205413
[23] Bergfield J P and Stafford C A 2009 Phys. Rev. B 79 245125
[24] Entin-Wohlman O, Imry Y and Aharony A 2010 Phys. Rev. B 81 113408
[25] Azema J, Dare A M, Schafer S and Lombardo P 2012 Phys. Rev. B 86 075303
[26] Koch T, Loos J and Fejeske H 2014 Phys. Rev. B 89 155133
[27] Park H, Park J, Lim A K L, Anderson E H, Alivisatos A P and McEuen P L 2000 Nature 407 57
[28] Zhitenyev N B, Meng H and Bao Z 2002 Phys. Rev. Lett. 88 226801
[29] LeRoy B J, Lemay S G, Kong J and Dekker C 2004 Nature 432 371
[30] Yu L H and Natelson D 2004 Nano Lett. 4 79
[31] Franke K J and Ignacio Pascual J 2012 J. Phys.: Condens. Matter 24 394002
[32] Reddy R, Jang S-Y, Segalman R A, Majumdar A 2007 Science 315 1568
[33] Svensson S F, Hoffmann E A, Nakpathomkun N, Wu P M, Xu H Q, Nilsson H A, Sanchez D, Kashcheyevs V and Linke H 2013 New J. Phys. 15 105011
[34] Lin W, Hehn M, Chaput L, Negulescu B, Andrieu S, Montaigne F and Mangin S 2012 Nat. Commun. 3 744
[35] Dubi Y and Di Ventra M 2009 Nano Lett. 9 97
[36] Muralidharan B and Grifoni M 2012 Phys. Rev. B 85 155423
[37] Lopez R and Sanchez D 2013 Phys. Rev. B 88 045129
[38] Sierra M A and Sanchez D 2014 Phys. Rev. B 90 115313
[39] Zimbovskaya N A 2015 J. Chem. Phys. 142 244310
[40] Meir Y, Wingreen N S and Lee P A 1991 Phys. Rev. Lett. 66 3048
[41] Swirkowcz R S, Barnas J and Wilczynski M 2003 Phys. Rev. B 68 195318
[42] Zimbovskaya N A 2014 J. Chem. Phys. 140 104706
[43] Andergassen S, Costi T A and Zlatic V 2011 Phys. Rev. B 84 241107