Hopping thermoelectric transport in finite systems: boundary effects

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I. INTRODUCTION

Achieving large thermopowers is a challenge to our understanding of electronic transport. At the same time, it is a crucial ingredient for many energy-conversion devices. In good, wide band, conductors the thermopower, S, is typically very small, due to the approximate electron-hole symmetry. Breaking this symmetry is therefore important for obtaining large values of S. This happens in various poor or narrow band conductors/semiconductors, near the metal-insulator transition and in the hopping regime.1–10

Recent experiments addressed thermoelectric transport in mesoscopic systems.11–13 Besides their general interest, they may be relevant for small-scale thermoelectric devices.1,2,12,13 Especially in the hopping regime, where the electronic states are localized and discrete, electron-hole symmetry is usually broken in a given sample, even if it is restored by averaging over many realizations. This should result in relatively large, sample-specific, thermopower. In addition, the parasitic phonon heat conductivity can be reduced due to interfaces and sample shape and geometry effects.14–15

Most of the studies on the thermoelectric effects in the hopping regime were devoted to bulk systems.1,9,10 Recently, we discussed the thermoelectric transport properties in finite one-dimensional (1D) systems, where the boundary effect was found to be very important for the thermopower. In this work we follow up, substantiate and generalize that study. The importance of edge effects on the thermopowers will be highlighted. We shall consider both 1D and 2D finite systems, which can be arbitrarily large. Since the conduction electrons have to exchange energy with a reservoir, the “three-terminal geometry” naturally appears. In addition to the two electronic terminals which exchange charge and energy/heat, the third terminal is purely thermal and mainly exchanges energy with the conduction electrons. The three-terminal setup for 1D finite systems is shown in Fig. 1. The system, bridging two electronic terminals (leads) consists of a number of localized states (LSs) with random energies. The system is connected to the leads by (dominantly elastic) tunnel couplings. Electronic conduction through the system is achieved via tunneling and phonon-assisted hopping. The setup can be realized, e.g., when the two electronic leads are suspended and the system is mounted on a (boson bath) substrate.10 The complete description of the thermoelectric transport in the linear-response regime is a 3 × 3 transport matrix relating the three currents to three “forces” (or “affinities”).16–18

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In this paper we consider a noninteracting localized system with constant density of states and localization length, in an energy window (−Ec,Ec).20 We start with a short review of the three-terminal thermoelectric transport (Sec. II). We show that the boundary effect dominates the thermopower in nearest-neighbor hopping (NNH) 1D systems (Sec. III). The simple underlying physics is illustrated via the solution of a simple 3-site model (Sec. IIIA and Appendix C). Then, longer NNH1D systems are considered (Sec. IIIB). In Sec. IV simplified types of 2D systems are treated. Because of incomplete averaging at the boundaries there can be a finite and fluctuating thermopower even for a very large system. The situation for variable-range hopping (VRH)
is discussed in Sec. VI. In Sec. VII we shall first focus on the 1D case and then consider small 2D systems, whose width and length are comparable. In these cases the bulk effect plays a limited role, which will tend to disappear when the system size increases. When the system size is increased further, one would expect both the thermopower and its fluctuations to eventually go to zero in the macroscopic limit as a consequence of the particle-hole symmetry being restored with averaging. We find however that the fluctuations remain finite for an arbitrarily long system, as long as its transverse size is finite. Finally, we discuss special effects of “non-spanning electronic paths” (that do not transport charge) to the thermal conductances (Sec. VIII). Our statements are backed up numerically. The numerical scheme is explained in Appendix A, and the contributions of various conducting paths are compared in Appendix B. Finally, Sec. VII includes a short summary and conclusions.

II. THERMOELECTRIC TRANSPORT THROUGH LOCALIZED STATES IN THE THREE-TERMINAL GEOMETRY

The study of hopping thermoelectric transport in three-terminal geometry was done in Refs. 16 and 17. For completeness we summarize here the basic formulation of the problem. The hopping transitions between the LSs are assisted by phonons. We focus on the situation when the on-site Coulomb interaction is so strong that each LS can only be occupied by at most one electron. The inter-site Coulomb interaction may lead to interesting effects but these will not be discussed here.21 The hopping rate from LS $i$ to LS $j$ for, say, $\varepsilon_j > \varepsilon_i$, is given by the Fermi golden-rule as

$$\Gamma_{i\rightarrow j} = 2\pi \sum_q |\alpha_{iq}|^2 \delta(\varepsilon_j - \varepsilon_i - \omega_q) f_i(1 - f_j) N_{ij},$$

$$= \gamma_{ij} f_i(1 - f_j) N_{ij}. \quad (1)$$

Here, $\alpha_{ijq}$ is the electron-phonon interaction matrix element between the two LSs, $\varepsilon_j$ and $\varepsilon_i$ are the energy of the LSs $j$ and $i$, respectively, $\omega_q$ is the phonon energy, $f_j$ and $f_i$ are the occupation probability on the LSs $j$ and $i$, respectively, and $N_{ij}$ is the phonon distribution at the energy $\omega_j$. The phonon distribution in the system is determined by the phonon bath, $N_{ij} = \exp([\varepsilon_j - \varepsilon_i]/(k_B T_P)) - 1^{-1}$. At large distances the overlap of the wavefunctions of the two LSs is exponentially small. The asymptotic behavior of $\gamma_{ij}$ is thus $\gamma_{ij} \sim \rho_e \exp(-2r_{ij}/\xi)$ where $r_{ij} = |r_j - r_i|$ is the distance between the LSs with $r_j$ and $r_i$ denoting their position vectors, $\xi$ is the localization length, and $\gamma_{ij}$ is proportional to the electron-phonon coupling and the phonon density of states. The hopping rate from LS $i$ to the left lead is

$$\Gamma_{i\rightarrow L} = \gamma_{iL} f_i(1 - f_L(\varepsilon_i)),$$  

where $\gamma_{iL} = 2\pi |\alpha_{iL}|^2 \rho_L$ with $\alpha_{iL}$ standing for the coupling between the LS $i$ and the extended states in the left lead of which $\rho_L$ is the density of states. We focus on the situation where $\gamma_{iL}$ does not depend on the energy $\varepsilon_i$ (i.e., no particle-hole asymmetry). $f_L$ stands for the distribution in the left lead, $f_L(\varepsilon) = \exp(\varepsilon - \mu_L)/(k_B T_L) + 1^{-1}$. The transition rate from $i$ to the right lead can be written down similarly. The asymptotic behavior of $\gamma_{iL}$ and $\gamma_{iR}$ at large distances is also exponential, $\gamma_{iL} \sim \gamma_e \exp(-2r_{iL}/\xi)$ $\gamma_{iR} \sim \gamma_e \exp(-2r_{iR}/\xi)$ where $r_{iL}$ $r_{iR}$ is the distance between LS $i$ and the left (right) lead and $\gamma_e$ scales with the tunnel coupling strength between LSs and the leads. The electric current flowing from $i$ to $j$ is

$$I_{i\rightarrow j} = e(\Gamma_{i\rightarrow j} - \Gamma_{j\rightarrow i}), \quad (3)$$

with $e$ being the charge of the carrier. The electric current flowing from $i$ to the left (right) lead is calculated similarly. At steady state, according to Kirchhoff’s current law,

$$\sum_j I_{i\rightarrow j} + I_{i\rightarrow L} + I_{i\rightarrow R} = 0. \quad (4)$$

which is also a statement of probability conservation. The steady-state distribution on each LS is obtained by solving Eqs. (1), (2), (3), and (4).

Before formulating the currents among the three terminals in terms of the transition rates, we present a thermodynamic analysis in the linear-response regime. There are three heat currents flowing into each terminal, $\dot{Q}_L$, $\dot{Q}_R$, and $\dot{Q}_P$, as well as two particle currents flowing into the electronic terminals, $\dot{N}_L$ and $\dot{N}_R$. The heat currents are related to the energy and particle currents according to the thermodynamic relation

$$\dot{Q}_i = \dot{E}_i - \mu_i \dot{N}_i \quad (i = L, R)$$

for the phononic terminal with $\dot{E}_i$ being the energy current flowing into terminal $i$. Particle and energy conservation renders

$$\sum_{i=L,R} \dot{N}_i = 0, \quad \sum_{i=L,R,P} \dot{E}_i = 0.$$  

Hence there are only three independent currents which are the electric...
current \( I_e = e\dot{N}_L = -e\dot{N}_R \) and two heat currents. For the latter one can choose \( Q_L \) and \( Q_R \), or any two linear independent combinations of them. We shall adopt the convention introduced in our previous work\(^{16,18} \) and choose the following heat currents\(^{9,10} \):

\[
I_Q^0 = \frac{1}{2}(\dot{Q}_R - \dot{Q}_L), \quad I_Q^{pe} = -\dot{Q}_P = \dot{Q}_L + \dot{Q}_R . \tag{5}
\]

In the linear-response regime the entropy production rate \( S \) is given by \( T S = T[\langle \dot{Q}_L/T_L \rangle + \langle \dot{Q}_R/T_R \rangle + \dot{Q}_P/T_P] \) = \( I_e(\delta\mu/e) + I_Q^0(\delta T/T) + I_Q^{pe}(\Delta T/T) \), where \( T \) is the common (equilibrium) temperature of the setup. This relation identifies the three “forces” (affinities) conjugated to the three currents, \( \delta\mu = \mu_L - \mu_R, \delta T = T_L - T_R, \) and \( \Delta T = T_P - (T_L + T_R)/2 \). The phenomenological linear-transport equation which satisfies the Onsager reciprocity relations is then\(^{16} \):

\[
\begin{pmatrix}
I_e \\
I_Q^0 \\
I_Q^{pe}
\end{pmatrix} =
\begin{pmatrix}
G & L_1 & L_2 \\
L_1 & K_0 & L_3 \\
L_2 & L_3 & K_{pe}
\end{pmatrix}
\begin{pmatrix}
\delta\mu/e \\
\delta T/T \\
\Delta T/T
\end{pmatrix}, \tag{6}
\]

In the three-terminal geometry, besides the normal thermopower \( S = L_1/(TG) \) there is the three-terminal thermopower \( S_p = L_2/(TG) \) which converts the temperature difference \( \Delta T \) to voltage (and vice versa)\(^{16,18} \).

We now formulate the currents \( I_e, I_Q^0, \) and \( I_Q^{pe} \) in terms of microscopic quantities. The electric current is given by

\[
I_e = -\sum_i I_{i \rightarrow L} = \sum_i I_{i \rightarrow R} . \tag{7}
\]

The heat currents \( I_Q^0 \) and \( I_Q^{pe} \) can be obtained from \( \dot{Q}_L \) and \( \dot{Q}_R \),

\[
\dot{Q}_L = \sum_i \left( \frac{E_i - \mu}{e} \right) I_{i \rightarrow L}, \quad \dot{Q}_R = \sum_i \left( \frac{E_i - \mu}{e} \right) I_{i \rightarrow R} \tag{8}
\]

where \( \mu \) is the equilibrium chemical potential.

In the linear-response regime the current between two LS can be written as

\[
I_{i \rightarrow j} = G_{ij}(U_i - U_j \pm \epsilon_{ij}) , \tag{9}
\]

where the signs + and − are for \( \epsilon_j > \epsilon_i \) and \( \epsilon_j < \epsilon_i \), respectively, and the conductance of the bond \( (ij) \) is

\[
G_{ij} = (e^2/(k_BT))^\gamma_{ij}f_0(1-f_0)(N_{ij}^0 + 1/2 \pm 1/2) \] (the superscript 0 is used to denote an equilibrium distribution function). In Eq. \( U_j = (k_BT/e)(f_j - f_0)/(f_0^2(1-f_0)) \) and \( U_i = (k_BT/e)(N_i - N_0^0)/(N_0^0(N_j^0 + 1)) \). To complete the description of the resistor network we also write down the current between the leads and the LSs

\[
I_{i \rightarrow L} = e(\Gamma_{i \rightarrow L} - \Gamma_{L \rightarrow i}) = G_{iL}[U_i - U_L(\epsilon_i)] , \tag{10}
\]

where \( G_{iL} = (e^2/(k_BT))^\gamma_{iL}f_0(1-f_0) \) and \( U_L(\epsilon_i) = (k_BT/e)[f_L(\epsilon_i) - f_0^2(1-f_0)]/(f_0^2(1-f_0)) \). We shall adopt the widely-used approximation, valid in the rather broad regimes discussed in Refs. \( 22,24 \), which yields

\[
G_{ij} \approx G_0 \exp\left( \frac{-2\tau_{ij}}{\xi} - \frac{|\epsilon_i - \mu| + |\epsilon_j - \mu| + |\epsilon_i - \epsilon_j|}{2k_BT} \right),
\]

\[
G_{iL} \approx G_0 \exp\left( \frac{-2\tau_{iL}}{\xi} - \frac{|\epsilon_i - \mu|}{k_BT} \right), \tag{11}
\]

where \( G_0 \sim e^2\gamma_{ep}/(k_BT) \sim e^2\gamma_{ei}/(k_BT) \) has been introduced. This coefficient sets the scale of the whole conductance and will not play a role in the subsequent discussions. The resistor network described above has been investigated for the case \( \Delta T = 0 \) a long time ago\(^{25} \).

We have recently considered the effect of the term \( U_{ij} \), which arises due to a finite small \( \Delta T \). We have recently considered the effect of the term \( U_{ij} \), which arises due to a finite small \( \Delta T \).

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### III. BOUNDARY EFFECT IN 1D NNH SYSTEMS

#### A. A simple three-site 1D NNH system

To demonstrate the boundary effect in the NNH regime we study a simple model system which consists of just three LSs. Consider the situation where LSs 1 and 3 are strongly coupled, by elastic transitions, to the lead continua on the left and on the right, respectively so that \( f_1 = f_L(\epsilon_1) \) and \( f_3 = f_R(\epsilon_3) \). That is, the conductances \( G_{1L} \) and \( G_{3R} \) are much larger than the other conductances. It is also assumed that the tunneling conductances between LS2 and the leads are so small that the transport through the system is dominated by the hopping path illustrated in Fig. 2(a). The condition for this to be true is analyzed in detail in Appendix [B]. This model system can be realized in experiments by, say, a serially coupled three-quantum-dots. For concreteness, consider the situation when \( \epsilon_1, \epsilon_3 < \epsilon_2 \). \( U_2 \) is then determined by \( I_{1 \rightarrow 2} = I_{2 \rightarrow 3} \) where

\[
I_{1 \rightarrow 2} = G_{12}(U_1 - U_2 + U_{12}) ,
\]

\[
I_{2 \rightarrow 3} = G_{23}(U_2 - U_3 - U_{23}) , \tag{12}
\]

and consequently

\[
U_2 = \frac{G_{12}(U_1 + U_{12}) + G_{23}(U_3 + U_{23})}{G_{12} + G_{23}} , \tag{13}
\]

and

\[
I_e = \frac{G_{12}G_{23}}{G_{12} + G_{23}} [U_3 + U_{23} - U_1 - U_{12}] , \tag{14}
\]

where \( I_e = I_{1 \rightarrow 2} \) is the total electric current. Expressing the \( U's \) as functions of the chemical potential and temperature differences gives

\[
I_e = \frac{G_{12}G_{23}(\delta\mu)}{G_{12} + G_{23}} e + \frac{\tau_{12}}{e} \frac{\delta T}{T} + \frac{\omega_{12}}{e} \frac{\Delta T}{T} , \tag{15}
\]
where we have denoted $\varepsilon_{31} = (\varepsilon_1 + \varepsilon_3)/2 - \mu$ and $\omega_{31} = \varepsilon_3 - \varepsilon_1$. Using Eqs. (4) and (5) one finds

$$Q_L = -\frac{\varepsilon_1 - \mu}{e} I_e, \quad Q_R = \frac{\varepsilon_3 - \mu}{e} I_e .$$

Inserting these results into Eq. (3) yields the transport coefficients in the linear-response regime,

$$L_1 = G \left( \frac{\varepsilon_{31}}{e} \right), \quad L_2 = G \left( \frac{\omega_{31}}{e} \right), \quad K_0^0 = G \left( \frac{\varepsilon_{31}}{e} \right)^2 ,$$

$$L_3 = G \left( \frac{\varepsilon_{31}}{e} \right) \left( \frac{\omega_{31}}{e} \right), \quad K_{pc} = G \left( \frac{\omega_{31}}{e} \right)^2 ,$$

with

$$G = \frac{G_{12} G_{23}}{G_{12} + G_{23}} ,$$

and confirms the Onsager reciprocity relations. In Appendix C we reproduce these results by a probabilistic analysis.

Remarkably, the thermopower $S = L_1/(T G)$ as well as the coefficients $L_2/G$, $L_3/G$, $K_0^0/G$, and $K_{pc}/G$ depend all only on $\varepsilon_1$ and $\varepsilon_3$, i.e., the energies of the LSs at the boundaries. The site energy of the central level does not affect these quantities. The thermoelectric properties are completely determined at the boundaries. On the contrary, the bulk (in this simple example, the central level) can affect the conductance of the system. Clearly, we can replace the middle site by a more complicated construction. As long as it is coupled to the boundary sites in the same way, the properties of this mid-system do not matter for the above-mentioned transport coefficients!

To illustrate the 3-site case, we have numerically computed the conductance $G$ and the thermopower $S$ of a three-site system as a function of the decrease of the conductance of the bonds (1,2) and (2,3). Namely, we have determined the conductance and the thermopower of the system when $G_{12} \rightarrow G_{12}/r_g$ and $G_{23} \rightarrow G_{23}/r_g$. We plot the ratio of the new conductance $G'$ to the original one $G$ as well as the ratio $S'/S$ as functions of the scale factor $r_g$ in Fig. (b). It is seen that although the conductance decreases significantly with increasing $r_g$, the thermopower remains unchanged, $S'/S = 1$. More complicated models will be discussed below.

## B. Longer 1D NNH systems

We now extend the discussion to longer 1D hopping systems. Nearest-neighbor hopping in a chain of LSs is accomplished via electron transits into the left (right) lead only through the leftmost (rightmost) LS, having energies $\varepsilon_\ell$ ($\varepsilon_r$). Therefore from Eqs. (4) and (5)

$$\dot{Q}_L = -\frac{\varepsilon_\ell - \mu}{e} I_e , \quad \dot{Q}_R = \frac{\varepsilon_r - \mu}{e} I_e ,$$

and one readily finds

$$I_e^c = \frac{\varepsilon_\ell \varepsilon_r}{e} I_e , \quad I_Q^c = \frac{\omega_\ell \varepsilon_r}{e} I_e ,$$

with $\varepsilon_r = (\varepsilon_\ell + \varepsilon_r)/2 - \mu$ and $\omega_\ell r = \varepsilon_r - \varepsilon_\ell$. Interestingly enough, the thermoelectric properties can be deduced without solving the resistor network. For example,
when \( \delta \mu \neq 0 \) and \( \delta T = \Delta T = 0 \), one has \( I_c = G \delta \mu / e \) and then by Eq. \( 20 \) \( I_Q^0 = (\tau_{r\ell} / e) I_c = G \tau_{r\ell} \delta \mu / e^2 \) and \( I_Q^{pe} = (\omega_{r\ell} / e) I_c = G \omega_{r\ell} \delta \mu / e^2 \). Therefore

\[
L_1 = G \left( \frac{\tau_{r\ell}}{e} \right), \quad L_2 = G \left( \frac{\omega_{r\ell}}{e} \right).
\]

Analyzing the situations when \( \delta T \neq 0 \) and \( \delta \mu = \Delta T = 0 \) and when \( \Delta T \neq 0 \) and \( \delta \mu = \delta T = 0 \) and exploiting the Onsager reciprocity relations one obtains

\[
K^0_c = G \left( \frac{\tau_{r\ell}}{e} \right)^2, \quad K_{pe} = G \left( \frac{\omega_{r\ell}}{e} \right)^2.
\]

Again the thermoelectric properties are completely determined at the boundaries. This is clearly manifested in Fig. \( 2 \)\( b \) for a NNH system with 31 LSs. It is seen that the thermopower is immune to the change in the middle part of the system while the conductance is considerably affected. Remarkably, this also implies that the thermopower (and other thermoelectric coefficients) is finite and random (as long as \( \varepsilon_L \) and \( \varepsilon_R \) are finite and random) regardless of the bulk properties. This even persists, in general, for very long systems where the particle-hole asymmetry is negligible, as long as the edge sites have definite energies (and their sum does not happen to vanish exactly). Therefore the particle-hole symmetry may no longer dictate a zero sample-specific thermopower in the macroscopic limit in 1D NNH systems.

IV. SIMPLIFIED 2D NNH SYSTEMS

We start by studying a situation where the boundary effect fully dominates thermoelectric properties: When the electronic leads are geometrically sharp (as with a high resolution STM configuration) and each of them is coupled strongly only with a single LS as illustrated in Fig. \( 3 \)\( a \). Specifically the left lead is coupled with a LS of energy \( \varepsilon_L \) while the right one with a LS of energy \( \varepsilon_R \). In this way the relation between the two heat currents \( (I_Q^0 \text{ and } I_Q^{pe}) \) and the electric current \( I_e \) is given again by Eqs. \( 20 \). Following the same logic as that applied for 1D NNH systems one again obtains Eqs. \( 22 \). Therefore the thermoelectric properties are completely determined by the boundary LSs (i.e., the LSs coupled strongly with the two electronic leads) in this case as well.

Next we consider another special type of 2D systems that consist of parallel 1D hopping chains where there is no transport between different chains as sketched in Fig. \( 3 \)\( b \). The heat and electric currents are given by

\[
I_e = \sum_k I_e^{(k)}, \quad I_Q^0 = \sum_k \left( \frac{\tau_{r\ell}}{e} \right)^{(k)} I_e^{(k)}, \quad I_Q^{pe} = \sum_k \left( \frac{\omega_{r\ell}}{e} \right)^{(k)} I_e^{(k)},
\]

where the superscript \( k \) denotes the \( k \)-th chain. One then has

\[
L_1 = G \left( \frac{\tau_{r\ell}}{e} \right), \quad L_2 = G \left( \frac{\omega_{r\ell}}{e} \right), \quad K^0_c = G \left( \frac{\tau_{r\ell}}{e} \right)^2, \quad K_{pe} = G \left( \frac{\omega_{r\ell}}{e} \right)^2,
\]

where \( G = \sum_k G_k \) with \( G_k \) being the conductance of the \( k \)-th chain and

\[
\langle \ldots \rangle = \frac{\sum_k G_k \ldots}{\sum_k G_k}.
\]

Altering the central region will modify the conductances \( G_k \). Due to the random nature of the system this modification varies among different chains and changes the averaging in Eq. \( 24 \). Although \( \tau_{r\ell} \) and \( \omega_{r\ell} \) for each chain do not change, the averaged values in Eqs. \( 20 \) do. Therefore the thermoelectric properties also depend on the bulk in this type of 2D systems. This is also true for other types of 2D NNH systems where the backbone consists of parallel hopping paths. Even when there are connections between those parallel paths, if the current distribution at the boundaries can be considerably affected by the bulk, the bulk effect cannot be ignored. However for sufficiently long 2D systems the current distribution at the boundaries should not be affected by the far away bulk. In general there is a correlation length \( L_{co} \) in hopping systems beyond which the spatial current distributions are uncorrelated. In 1D NNH systems \( L_{co} \) is on the order of the distance between the adjacent LSs. In 2D NNH \( L_{co} \) can be much larger but still finite. In Fig. 4 we show how the conductance and the thermopower are affected by changes in the middle part of a long and a short 2D NNH system. In the long system the thermopower is almost unchanged whereas in the short one it is significantly modified (but, possibly much less than the conductance, which can be, for example, affected exponentially). \( L_{co} \) for the chosen parameters is estimated as \( \sim 6 \) times the distance between the adjacent LSs.
version asymmetry in the sense that 

tances in the middle of the system by a factor of 

When the density of states is symmetric with respect to 

symmetry is broken, such that 

limit. In deriving Eqs. (26) we have used 

conductance and thermopower, for a 2D NNH single realiza-

mopower, and 

value. The curves with 

distribution as the bulk ones, then 

ξ/̂ &= 3 

for the conductance or the ther-

denotes the ratio of the conductance 

\[ r \] and 

\[ \frac{\Delta}{X} \]

V. BOUNDARY EFFECT IN 1D VRH SYSTEMS 

Here we will not assume that only a single LS is strongly coupled to each lead. Quite generally, all LSs located within a distance from the lead smaller than or comparable to the Mott hopping distance \( R_M \) can be considerably coupled to that lead, with the conductance of the connection given by Eq. (11). Other LSs, which are not coupled directly with the leads have much lower conductances, due to the exponential decay of \( G_{iL} \) and \( G_{iR} \) with the distance \( r_{iL} \) and \( r_{iR} \). This implies that the boundary effect is somewhat weakened. To study this situation, we consider sufficiently long 1D VRH systems whose length \( L \) is much larger than \( R_M \) and denote by “boundaries” the regions that are within a distance of a few \( R_M \)’s from the leads. We shall find that the boundary effect on the VRH thermopower is still important.

Specifically for VRH systems the current flowing into each lead comes mainly from the LSs in the boundary regions. The summations in Eqs. (7) and (5) are then reduced to summations over those LSs. Accordingly, the thermopowers can be written as

\[ S = \frac{1}{eT} \left( \frac{\langle \varepsilon_r \rangle + \langle \varepsilon_L \rangle}{2} - \mu \right), \quad S_p = \frac{1}{eT} \left( (\langle \varepsilon_r \rangle - \langle \varepsilon_L \rangle) \right) \]  

where

\[ \langle \varepsilon_r \rangle = \frac{\sum_i \varepsilon_i I_i \rightarrow R}{\sum_i I_i \rightarrow R}, \quad \langle \varepsilon_L \rangle = \frac{\sum_i'' \varepsilon_i I_i \rightarrow L}{\sum_i'' I_i \rightarrow L} \]  

with \( \sum_i \) (\( \sum_i'' \)) being restricted to the LSs in the right (left) boundary region. In 1D NNH systems the summation is restricted to a single LS that is coupled strongly with each lead, while in 1D VRH systems there are more than one such LSs. Nevertheless, whenever the number of LSs involved in each summation is not too large the thermopowers will be finite and will fluctuate regardless of the particle-hole symmetry in the bulk. The boundary part of the backbone picture is drawn in Fig. (a). Similar to NNH 2D systems, the weights of the various \( i \)’s in Eqs. (25) (e.g, \( I_i \rightarrow L \)) does depend on the bulk. Therefore in a given sample, there will again exist some limited dependence of the thermopowers on the bulk. However, this will be averaged out in an ensemble of many realizations of the sample.

A. Thermopowers

We now turn to the thermoelectric properties of VRH systems in 1D. The conductance of a 1D system is mainly suppressed by the “breaks” rendering the Mott VRH picture not entirely applicable. At low temperatures the characteristic conductance of a 1D VRH system of length \( 2L \) is

\[ G_{1D} = G_0 e^{-\gamma} \]  

with
where
\[ \eta = \left( \frac{T_M}{T} \right)^{1/2}, \quad T_M = 2T_0 \ln \left( \frac{2\sqrt{\delta L}}{\xi} \right), \] (30)
with \( k_B T_0 = (\rho \xi)^{-1} \) and \( \rho \) denoting the density of (localized) states. \( \nu \) is the solution of Eq.\( \text{28,29} \)
\[ \nu = \frac{2T}{T_0} \ln \left( \frac{2\sqrt{\delta L}}{\xi} \right). \] (31)

The current mainly flows in the backbone of the resistor network which mostly consists of connections with conductance higher than or comparable with \( G_{1D} \text{28,29} \). The typical hopping length and energy are \( R_M = \eta \xi / 2 \) and \( E_M = \eta k_B T \). Below we use the energy scale
\[ E_0 = k_B \sqrt{T_0 T}, \] (32)
which does not depend on the system length \( 2L \). For example, \( T \) in units of this scale will be seen to be relevant for the thermopower fluctuations, see Fig.\( \text{7(b).} \)

The boundary effect is detected by comparing the thermopower \( S \) (and other thermoelectric coefficients) of a random system and that of the same configuration but with the central region modified, \( S' \). Specifically, we apply the following modification: \( G_{ij} \to 10^{-2} G_{ij} \), if both \( i \) and \( j \) are in the central part. The boundary effect is monitored by \( |\ln((S'/S))| \). Concomitantly we compute the conductance of the original and the modified systems, \( G \) and \( G' \), and monitor the change via \( |\ln(G'/G)| \). If \( |\ln((S'/S))| \) is very small (i.e., \( S' \) is almost the same as \( S \)) then the thermopower is insensitive to the bulk and the boundary effect dominates. We model the localized electron system by a number of LSs located at random positions and having energies which are uniformly distributed in the ranges \((-L, L)\) and \((-E_c, E_c)\), respectively. The central region is taken as \( x \in (-R_M, R_M) \). The linear-response transport coefficients are computed using the method described in Appendix\( \text{A} \). Note that for the numerics we use dimensionless energy and temperature, with \( k_B = 1 \). For a given system, the appropriate energy unit can be introduced.

The averages of the two quantities over \( 10^6 \) random configurations are plotted in Fig.\( \text{7(b, c).} \). It is seen that the conductance is considerably modified, \( |\ln(G')/G| > 1 \). In contrast the change in thermopower is much smaller, especially when the distance between the central region and the boundary \( L - R_M \) exceeds the hopping length \( R_M \). \( |\ln((S'/S))| \) decays rapidly with the distance \( L - R_M \) and soon becomes negligible.

For the choice of the central region adopted in the figure (from \(-R_M \) to \( R_M \)), the change of the conductance is not dramatic, e.g., \( G'/G \approx 1/4 \) for the last point (\( N=120 \)). But if the central region is taken to be from \(-2R_M \) to \( 2R_M \) then \( G'/G \approx 1/22 \). The relative changes in thermopower in the former and latter cases are, however, no larger than \( 8 \times 10^{-4} \) and \( 2 \times 10^{-2} \) respectively.

The three-terminal thermopower \( S_p \), shown in Fig.\( \text{4(c),} \) behaves similarly. Therefore the probability that the LSs far away from the boundaries can affect the average thermopowers is very small. This also indicates that the correlation length, \( L_{co} \), giving the scale over which a local change in the network influences the conducting path, in 1D VRH system is only a few hopping lengths.

The question naturally arises, what happens in a specific sample? We find that there again the boundary effect can be dominant. In Fig.\( \text{6(a),} \) we plot the change of the thermopower and the conductance for two systems as a function of the increase of the resistance in the middle part of the sample. For the longer system it is seen that the thermopower is unaffected while the conductance decreases by almost three orders of magnitude. This is the situation when the distance between the boundary and the middle exceeds the correlation length \( L_{co} \) so that the bulk affects the thermopower negligibly. However for a shorter system a change in the central part can affect both the thermopower and the conductance. Nevertheless the change in the conductance is still much more significant than that in the thermopower.

Interestingly enough, our analysis points out that the thermopower has unexpectedly large sample-to-sample fluctuations even for very large samples. This is very different from the vanishing of the VRH conductance fluctuations for increasing-length samples. No matter whether the bulk effect is important or not, as long as the number of the LSs involved in the summation in Eqs.\( \text{23} \) is finite, the thermopowers have a finite and fluctuating value due to insufficient averaging. For 1D VRH, the LSs involved in the averaging, i.e., those with \( r_{iL} < R_M \) (or \( r_{iR} < R_M \)) and \( E_i < E_M \) are typically just a few. Thus the fluctuations of the thermopower can be rather large. To check this, we computed the variance of the thermopower as a function of the length of the system. The results are shown in Fig.\( \text{7(a).} \) Indeed the variance of the thermopower remains considerably large and attains a constant value for very long systems. The variance of the thermopower in very long systems increases with increasing temperature (decreasing \( R_M \)). The appearance of a “break” (whose probability is exponentially small anyway) should not modify the hopping energy window considerably. If the break is sufficiently far from the boundary it should not affect the current distribution among the boundary LSs. Hence the break mechanism has negligible effect on hopping thermopower although it greatly modifies the hopping conductance. As a result, the variance of the thermopower \( \text{Var}(eST) = (\text{eST} - (eST)^2)^2 \) does not depend on the length of the system in the limit \( 2L \to \infty \). That is, it becomes a constant although \( (S) = 0 \) for systems with particle-hole symmetry when \( 2L \to \infty \). In contrast, for the conductance, \( (\ln G) \to -\infty \) and \( \text{Var}(\ln G) = (\ln G - (\ln G)^2)^2 \to 0 \) when \( 2L \to \infty \), as the conductance is determined by the bulk and is significantly affected by the break mechanism.

We also computed the probability distribution function of the thermopower for a specific set of parameters and plotted it in Fig.\( \text{7(b).} \) It is seen that the ther-
The thermopower is mostly distributed in the range of $-E_0 < eST < E_0$. The probability distribution function is not a normal distribution. Rather, it has exponential tails, $\sim \exp[-C|eS/T/E_0|]$, at large $|S|$ with $C$ being a constant depending on the parameters of the system. The exponential tails should come from the fact that LSs with high energies have exponentially small probabilities to be part of the backbone at the boundaries because the resistance between such sites and the lead is exponentially large. In the inset of Fig. 7(b) we also show how the thermopower evolves as a function of the system length for two random configurations. By increasing the system length there is an increasing probability to have, for example, a poorly conducting piece in the bulk of the system. It is seen that the thermopower saturates with large system length since the boundary effect is dominant. Meanwhile, the different thermopowers for the two configurations vividly indicate the fluctuations of the thermopower even in very long systems. Relatively large mesoscopic (sample to sample) fluctuations in the low-temperature thermopower have been found also in the weak-disorder regime.

**B. Special contributions to the heat conductances**

In deriving Eqs. (21) and (22) we have assumed that the heat current is carried by the percolating (spanning) paths which transport the charge current as well. Therefore, the heat conductances $K_e^0$, $L_3$, and $K_{pc}$ were all proportional to the conductance $G$. However, non-spanning paths can also contribute to the heat conduction. This mechanism becomes especially important when the conductance $G$ is sufficiently small. As the non-spanning paths do not conduct charge between the two leads, they have no contribution to $G$, $L_1$, and $L_2$. A non-spanning hopping path is schematically shown in Fig. 8(a). It is seen that by hopping back and forth between a lead and the nearby LSs having different energies, the associated phonon energy is transferred between the lead and the phonon bath. Therefore, whenever $T_L \neq T_P$, $T_R \neq T_P$ there will be heat flowing between the left (right) lead and the phonon terminal. Even when there is no spanning hopping path this scenario can lead to a finite heat conduction. Denoting the heat conductances due to non-spanning paths on the left and on the right sides by $K_L$ and $K_R$, respectively, the corresponding heat currents are $Q_L = K_L(T_P - T_L)/T$ and $Q_R = K_R(T_P - T_R)/T$. Hence, when the non-spanning paths determine the heat conduction, we find using the definitions of currents and affinities in and below Eqs. (5) and the transport coefficients of Eq. (3)

$$K_e^0 = (K_L + K_R)/4, \quad L_3 = (K_R - K_L)/2, \quad K_{pc} = K_L + K_R = 4K_e^0. \quad (33)$$

In Fig. 8(b) we show the numerically-computed averages of $K_e^0/(GE^2 e^{-2})$ (curves with $\bullet$), $|L_3|/(GE^2 e^{-2})$ (curves with $\triangle$), and $K_{pc}/(GE^2 e^{-2})$ (curves with $\square$). It is seen that the heat conductances are too large to be explained by the contributions from the spanning paths, for which the upper bound is $GE^2 e^{-2}$. This becomes more significant at lower temperatures or for longer lengths $L$, where the conductance is $G$ is reduced but the non-spanning paths are only marginally affected. Clearly, the Wiedemann-Franz law totally breaks down here. These results confirm that the non-spanning paths can have much larger contributions to the heat conductances than the spanning ones, when the conductance $G$ is suppressed. Most of the non-spanning paths are also close to the boundary since the sites there are much more strongly coupled to the leads and the conductance and the number of long paths are substantially reduced.

The boundary effect is demonstrated in Fig. 8(c). One notes that the distance dependencies in this case are different from those of the changes in $S$ and $R_p$ due to the different conduction mechanisms. Finally, this scenario is not important in 1D NNH systems when the tunneling conductance between the left (right) lead and the LSs other than the leftmost (rightmost) LS is small enough. It can, however, play a role in 2D NNH systems when more than one LSs is strongly coupled to each of the leads.

**VI. CONCLUSIONS AND DISCUSSION**

The study of the thermopower in the hopping regime is augmented in this paper in two ways: 1. by considering the appropriate three-terminal case; and 2. by studying the possibly-all-important effect of the edges on the thermoelectric transport. We emphasize that the three-terminal picture is dictated by the fact that hopping conductance necessitates energy-exchange with a (usually bosonic) thermal bath.

We studied the boundary effect on the thermoelectric properties of finite 1D and 2D hopping systems. We find that the boundary effect may play a crucial role for the thermopowers. This is first shown for a simple three-site hopping model and then for 1D NNH systems via analytical and numerical discussions. For 1D VRH systems qualitative arguments and numerical results indicate that only the LSs with a distance from the boundaries smaller than or comparable to the Mott distance $R_M$ can affect the thermoelectric properties considerably. As a consequence, the thermopowers of a specific sample of a very long 1D hopping system where the particle-hole asymmetry is negligible on average is still finite and fluctuating due to the insufficient averaging at the boundaries. This is confirmed by numerical calculations in 1D VRH systems where a nonzero variance of the thermopower persists and eventually becomes a constant at very large system size. At the same time the average of the thermopower over many samples does vanish. We emphasize that the sample-dependent changes in the thermopower due to modifying the middle of the sample do exist, but they can be much smaller than the corresponding changes in the conductance.
For 2D systems we first found a situation which resembles the NNH 1D cases: when the electronic leads are geometrically sharp and each of them is coupled with a single LS (as with a high-resolution STM probe). In this type of systems the boundary effect completely determines the thermoelectric properties. However, in other types of 2D hopping systems the bulk effect can also be important, but much less so than for the conductance. This is manifested by a simplified type of 2D hopping systems which are made up of parallel 1D hopping chains where there is no hopping between different chains. The total thermopower is an average of the thermopower in each chain weighted by the conductance in that chain. Changing the central part of the system will alter the electric current in each chain differently. Although the thermopower in each chain does not change, the weights of the various chains does change. Therefore the total thermopower is modified by changing the central part. This modification can again be much smaller than that for the conductance (for example, when the latter is changed by many orders of magnitude by changing the bulk conductance that much) and it disappears upon ensemble averaging. In general the sample-specific thermoelectric properties depend mostly on the boundaries and in a limited fashion on the bulk whenever the current distribution at the boundaries can be affected by the bulk. This includes 1D VRH systems, realistic 2D ones (for which some numerical results are presented) and we propose also 3D ones.

For the thermal conductances sector of the linear-transport matrix [see Eq. (3)] for the three-terminal geometry considered here we find new contributions. These are not due to the usual percolating paths, and will become important whenever the electrical conductance, due to the latter, is small enough. This implies a very serious breakdown of the Wiedemann-Franz law.

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**Appendix A: Numerical scheme for solving the resistor network in three-terminal geometries**

Here we present the numerical scheme for solving the resistor network in three-terminal geometries, in the linear-response regime,

\[ U_{ij} = \frac{|\varepsilon_j - \varepsilon_i| \delta T_i}{T}, \]

\[ U_{L,R}(\varepsilon_i) = \frac{\delta \mu L,R}{e} + \frac{\varepsilon_i - \mu}{T}. \]  \hspace{1cm} (A1)

Here \( \delta \mu_i = \mu_i - \mu \) and \( \delta T_i = T_i - T \) with \( i = L, R, P \). To simplify the calculation one may choose \( \mu = (\mu_L + \mu_R)/2 \) and \( T = (T_L + T_R)/2 \), so that \( \delta \mu_L = -\delta \mu_R = \delta \mu/2, \delta T_L = -\delta T_R = \delta T/2 \), and \( \delta T_p = \Delta T \). According to the sign convention in Eq. (A2), \( \pm U_{ij} = (\varepsilon_j - \varepsilon_i) \delta T_p/eT \). The final form of the equations to be solved is thus

\[ \sum_j A_{ij} U_j = z_i, \]  \hspace{1cm} (A2)

with

\[ A_{ii} = \sum_{k \neq i} G_{ik} + G_{iL} + G_{iR}, \]

\[ A_{ij} = -G_{ij} \quad \text{(for } i \neq j), \]

\[ z_i = G_{iL} \left( \frac{\delta \mu_L}{e} + \frac{\varepsilon_i - \mu}{e} \frac{\delta T_L}{T} \right) + G_{iR} \left( \frac{\delta \mu_R}{e} + \frac{\varepsilon_i - \mu}{e} \frac{\delta T_R}{T} \right) + \sum_{k \neq i} G_{ik} \left( \frac{\varepsilon_i - \varepsilon_k}{e} \frac{\delta T_p}{T} \right). \]  \hspace{1cm} (A3)

Once the \( U_i \)'s are obtained by solving Eqs. (A2), the three currents are found straightforwardly,

\[ I_e = \frac{1}{2} \sum_i (I_{i \rightarrow R} - I_{i \rightarrow L}), \]

\[ I_{p} = \frac{1}{2} \sum_i (I_{i \rightarrow R} - I_{i \rightarrow L}) \frac{\varepsilon_i - \mu}{e}, \]

\[ I_{pe} = \sum_i (I_{i \rightarrow R} + I_{i \rightarrow L}) \frac{\varepsilon_i - \mu}{e}, \]  \hspace{1cm} (A4)

where

\[ I_{i \rightarrow L} = G_{iL} \left[ U_i - \left( \frac{\delta \mu_L}{e} + \frac{\varepsilon_i - \mu}{e} \frac{\delta T_L}{T} \right) \right], \]

\[ I_{i \rightarrow R} = G_{iR} \left[ U_i - \left( \frac{\delta \mu_R}{e} + \frac{\varepsilon_i - \mu}{e} \frac{\delta T_R}{T} \right) \right]. \]  \hspace{1cm} (A5)

The transport coefficients are obtained by computing the currents for three different cases: (i) \( \delta \mu \neq 0 \) but \( \delta T = \Delta T = 0 \), (ii) \( \delta T \neq 0 \) but \( \delta \mu = \Delta T = 0 \), and (iii) \( \Delta T \neq 0 \) but \( \delta \mu = \delta T = 0 \). Using Eqs. (A5) in case (i) one obtains \( G, L_1, \) and \( L_2 \). In case (ii) one finds \( L_1, K_0^0, \) and \( L_3 \), and case (iii) yields \( L_2, L_3, \) and \( K_{pe} \). The Onsager reciprocity relationships can then be verified from the numerical computation explicitly.
Appendix B: Comparing the conductance in the dominant hopping path with other conductances in the three-site NNH model

Besides the dominant hopping path demonstrated in Fig. 2(a), there are the following transport processes: (A) elastic tunneling through the whole system; (B) tunneling from the left lead to LS1, hopping from LS1 to LS2 and then tunneling into the right lead; (C) tunneling from the left lead to LS2, hopping to LS3 and then tunneling into the right lead; (D) tunneling from the left lead to LS1, hopping from LS1 to LS3, and then tunneling into the right lead. One must keep in mind the assumption that \( G_{1L} \) and \( G_{3R} \) are much larger than all other conductances. The conductance of (B) and (C) are

\[
G_B = G_{12}G_{2R}/(G_{12} + G_{2R})
\]

and

\[
G_C = G_{2L}G_{23}/(G_{2L} + G_{23}).
\]

If \( G_{12} \sim G_{23} \), then such contributions can be negligible. According to Eq. (11), this condition is fulfilled since

\[
G_{2L}/G_{12} \approx \exp[-2r_{1L}/\xi] \ll 1
\]

and

\[
G_{2R}/G_{23} \approx \exp[-2r_{1R}/\xi] \ll 1.
\]

The conductance in process (D) can be considered similarly.

It remains to consider the conductance of process (A). The following analysis generalizes the one of Ref. 16 which discusses only the two-LS assisted tunneling [see Eq. (B3) below]. The tunneling conduction consists of several contributions. It can be assisted by one, two, or three of the three LSs. For example, the tunneling conductance through LS1 = (1, 2, 3) can be written as

\[
ge_i \sim e^{2\varepsilon_i^2/|\alpha_{iL}|^2|\alpha_{iR}|^2 \rho_L \rho_R},
\]

with \( \rho_L \) and \( \rho_R \) being the density of states in the left and right leads, respectively, \( |\alpha_{iL}| \approx |\alpha_e| \exp(-r_{iL}/\xi) \) and \( |\alpha_{iR}| \approx |\alpha_e| \exp(-r_{iR}/\xi) \) where \( |\alpha_e| \) measures the tunnel coupling strength between the electronic states. The asymptotic behavior of \( g_i \) is thus

\[
ge_i \sim e^{2\varepsilon_i^{-2}|\alpha_e|^4 \rho_L \rho_R \exp} \left( -\frac{4L}{\xi} \right),
\]

where \( 2L = r_{iL} + r_{iR} \) is the length of the system. Similarly one can find the tunneling conductance through two LSs \( i \neq j = (1, 2, 3) \) as

\[
ge_{ij} \sim e^{2\varepsilon_i^{-2}\varepsilon_j^{-2}|\alpha_e|^4 \rho_L \rho_R \exp} \left( -\frac{4L}{\xi} \right).
\]

Similar exponential dependence is also found for the tunneling through three LSs. The asymptotic behavior of the total tunnel conductance \( G_{tun} \) is then

\[
G_{tun} \sim e^{2\varepsilon_{tun}^2} |\alpha_e|^4 \rho_L \rho_R \exp} \left( -\frac{4L}{\xi} \right),
\]

with \( \varepsilon_{tun}^2 = \sum_i \varepsilon_i^{-2} + \sum_{i \neq j} \varepsilon_i^{-2}\varepsilon_j^{-2}|\alpha_e|^2 + .... \). In comparison, the conductance of the hopping channel is given by

\[
G \sim \frac{1}{2} G_{12} \sim e^{2 \varepsilon_{ep}^2 \rho_L \rho_R} \exp} \left( -\frac{|\varepsilon_1 - \mu| + |\varepsilon_2 - \mu| + |\varepsilon_1 - \varepsilon_2|}{2k_BT} - \frac{2r_{12}}{\xi} \right).
\]

It is seen that the hopping conductance is limited by the exponential factor at very low temperatures. Therefore the hopping conduction dominates at relatively high temperatures while the tunneling is more important at low ones. Ignoring the difference in the tunnel coupling and electron-phonon coupling, i.e. to a logarithmic accuracy, the crossover temperature between the two types of conductance, \( T_x \), is given by

\[
k_BT_x \approx \frac{\Delta T}{4(2L-r_{12})}.
\]

Appendix C: A probability analysis of thermoelectric transport in the NNH three-site model

Denoting the probability for an electron at LS 1 to be transferred to LS 2 per unit time by \( P_{1 \rightarrow 2} \), and that of the transfer from LS 2 to LS 3 by \( P_{2 \rightarrow 3} \), the entire probability per unit time for an electron to be transferred from LS 1 to LS 3 by passing LS 2 is

\[
P_{1 \rightarrow 3} = P_{1 \rightarrow 2} P_{2 \rightarrow 3}.
\]

\( P_{2 \rightarrow 3} \) is the probability for the transfer from LS 2 to LS 3 when the electron is already at LS 2. In that case there are two possibilities: the electron can either hop to LS 1 or to LS 3. Hence \( P_{2 \rightarrow 3} \) is given by the ratio

\[
P_{2 \rightarrow 3} = \frac{P_{2 \rightarrow 1} P_{2 \rightarrow 3}}{P_{2 \rightarrow 1} + P_{2 \rightarrow 3}},
\]

and consequently

\[
P_{1 \rightarrow 3} = \frac{P_{1 \rightarrow 2} P_{2 \rightarrow 3}}{P_{2 \rightarrow 1} + P_{2 \rightarrow 3}}.
\]

The probability per unit time for the reversed process is

\[
P_{3 \rightarrow 1} = \frac{P_{3 \rightarrow 2} P_{2 \rightarrow 1}}{P_{2 \rightarrow 1} + P_{2 \rightarrow 3}}.
\]

The Fermi golden-rule [see Eq. (11)] implies that \( P_{1 \rightarrow 2} = \gamma_{12}f_1(1-f_2)N_{21}, P_{2 \rightarrow 1} = \gamma_{12}f_2(1-f_1)(N_{21}+1), P_{2 \rightarrow 3} = \gamma_{23}f_3(1-f_2)(N_{23}+1), \) and \( P_{3 \rightarrow 2} = \gamma_{23}f_3(1-f_2)N_{23} \). At equilibrium \( P_{1 \rightarrow 3} = P_{3 \rightarrow 1} \). When the system is out of equilibrium, in the linear-response regime, one has

\[
I = P_{1 \rightarrow 3} - P_{3 \rightarrow 1} = P_{1 \rightarrow 2} P_{2 \rightarrow 3} - P_{2 \rightarrow 3} P_{2 \rightarrow 1} = \frac{G_{12}G_{23}}{G_{12} + G_{23}} [-U_1 - U_{12} + U_3 + U_{23}]
\]

\[
\approx \frac{G_{12}G_{23}}{G_{12} + G_{23}} \left[ \frac{\delta \mu}{k_BT} + \frac{\varepsilon_{31}}{k_BT} \frac{\Delta T}{T} + \frac{\omega_{31}}{k_BT} \frac{\Delta T}{T} \right].
\]

This confirms the results obtained from the rate equation method, i.e., Eq. (13).
T. C. Harman and J. M. Honig, *Thermoelectric and Thermomagnetic Effects and Applications*, (McGraw-Hill, New York, 1967); H. J. Goldsmid, *Introduction to Thermoelectricity* (Springer, Heidelberg, 2009); G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics: Basic Principles and New Materials Development* (Springer, Berlin, 2001).

1. J. T. Muhonen, M. Meschke, and J. P. Pekola, Rep. Prog. Phys. 181, 1336 (1969); N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979).

2. A. Shakouri, Annu. Rev. Mater. Res. 41, 399 (2011).

3. G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. 93, 7436 (1996). Here, in addition to the possibly large thermopowers, very low values of the electronic thermal conductivity are possible.

4. M. Cutler and N. F. Mott, Phys. Rev. 181, 1336 (1969); N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979).

5. U. Sivan and Y. Imry, Phys. Rev. B 33, 551 (1986).

6. Y. Imry and A. Amir, 50 Years of Anderson Localization, E. Abrahams, ed., chapter 9, pp 191, World Scientific, 2010.

7. Z. Ovadyahu, J. Phys. C: Solid State Phys. 19, 5187 (1986); M. Lakner and H. v. Loehneysen, Phys. Rev. Lett. 70, 4745 (1993).

8. See, e.g., R. Fletcher, V. M. Pudalov, A. D. B. Radcliffe, and C. Pozzanzini, Semicon. Sci. Technol. 16, 386 (2001); A. Makash, S. Li, B. Wen, S. V. Kravchenko, A. A. Shashkin, V. T. Dolgopolov, and M. P. Sarachik, Phys. Rev. Lett. 109, 096405 (2012).

9. I. P. Zvyagin, Phys. Stat. Sol. (b) 58, 443 (1973).

10. I. P. Zvyagin, *The Hopping Thermopower*, in *Hopping Transport in Solids*, ed. M. Pollak and B. I. Shklovskii (North-Holland, Amsterdam, 1991).

11. K. Schwab, E. A. Henriksen, J. M. Worlock, and M. L. Roukes, Nature 404, 974 (2000); P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, Phys. Rev. Lett. 87, 215502 (2001); *Thermal nanosystems and nanomaterials*, S. Volz (Ed.) (Springer, Heidelberg, 2009).

12. F. Giazotto, T. T. Heikkilä, A. Luukanen, A. M. Savin, and J. P. Pekola, Rev. Mod. Phys. 78, 217 (2006).

13. J. T. Muhonen, M. Meschke, and J. P. Pekola, Rep. Prog. Phys. 75, 046501 (2012).

14. L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993); ibid., 16631 (1993).

15. R. Venkatadruman, Phys. Rev. B 61, 3091 (2000); K. R. Patton and M. R. Geller, Phys. Rev. B 64, 155320 (2001); M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J.-P. Fleurel, and P. Gogna, Adv. Mater. 19, 1043 (2007); J.-K. Yu, S. Mitrovic, D. Tham, J. Varghese, and J. R. Heath, Nature Nanotech. 5, 718 (2010).

16. J.-H. Jiang, O. Entin-Wohlman, and Y. Imry, Phys. Rev. B 85, 075412 (2012).

17. B. Rutten, M. Esposito, and B. Cleuren, Phys. Rev. B 80, 235122 (2009); O. Entin-Wohlman, Y. Imry, and A. Aharonov, Phys. Rev. B 82, 115314 (2010); R. Sánchez and M. Büttiker, Phys. Rev. B 83, 085428 (2011); B. Sothmann, R. Sánchez, A. N. Jordan, and M. Büttiker, Phys. Rev. B 85, 205301 (2012); B. Cleuren, B. Rutten, and C. Van den Broeck, Phys. Rev. Lett. 108, 120603 (2012); B. Sothmann and M. Büttiker, arXiv:1206.1259.

18. J. H. Jiang, O. Entin-Wohlman, and Y. Imry, “Three-terminal semiconductor junction thermoelectric devices: improving performance”, to be submitted for publication.

19. The thermal terminal is also coupled to the *phonons* in the system and will determine their temperature if that coupling is strong enough.

20. The cut-off energy $E_c$ is assumed to be sufficiently higher than the Mott hopping energy $E_M$ relevant for one dimension [see discussion around Eqs. (60), (61), and (62)].

21. The polaron effect is also not considered in this work.

22. A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960).

23. A. Mokashi, S. Li, B. Wen, S. V. Kravchenko, A. A. Shashkin, V. T. Dolgopolov, and M. P. Sarachik, Phys. Rev. Lett. 109, 096405 (2012).

24. A. Amir, Y. Oreg, and Y. Imry, Phys. Rev. B 80, 245214 (2009).

25. Efforts have been devoted to extend the Miller-Abrahams resistor network to include the temperature difference in the two-terminal geometry (i.e., $\delta T \neq 0$ but $\Delta T = 0$), see e.g., K. I. Wysokinski and W. Brenig, Z. Phys. B 59, 127 (1985) and Refs. 4 and 11. In those works a local temperature is defined and associated with each LS. In contrast, we do not define such local thermodynamic quantities. Rather, the temperatures and chemical potentials are only defined for the reservoirs.

26. Hopping thermoelectric transport in quantum dot systems has been recently studied, see e.g., T. Ruokola and T. Ojsn, Phys. Rev. B 86, 035454 (2012); P. Li and B. Jia, Phys. Rev. E 83, 062104 (2011); J. Ren, J.-X. Zhu, J. E. Gubernatis, C. Wang, and B. Li, Phys. Rev. B 85, 155443 (2012); L. Sinine and D. Segal, Phys. Chem. Chem. Phys. 14, 13820 (2012).

27. A. S. Skal and B. I. Shklovskii, Fiz. Tekh. Poluprov. 8, 1586 (1974) [Semicond. Phys.-Semicond. 8, 1029 (1975)]; B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors*, p.126, (Springer, New York, 1984).

28. P. A. Lee, Phys. Rev. Lett. 53, 2042 (1984); R. A. Serota, R. K. Kalia, and P. A. Lee, Phys. Rev. B 33, 8441 (1986).

29. M. E. Raikh and I. M. Ruzin, Zh. Eksp. Teor. Fiz. 95, 1113 (1989) [Sov. Phys. JETP 68, 642 (1989)].

30. A. S. Rodin and M. M. Fogler, Phys. Rev. B 39, 155435 (2009); ibid. 84, 125447 (2011).

31. Figure 5 shows in fact that the thermopower is insensitive to the “break” created artificially in the middle of the system.

32. A small narrow peak around zero is seen in the probability distribution. We are not certain whether it represents interesting physics or is an artifact of the numerical procedure. This is outside of our main topic, and its study will be continued in a subsequent work.

33. V. Anisovich, B. L. Al'tshuler, A. G. Aronov and A. V. Zvyuzin, Sov. Phys. JETP Lett. 45, 295 (1987).
FIG. 5. (Color online) 1D VRH. (a): The boundary part of the hopping backbone, generalizing Fig. 2a. The gray region depicts the main part of the backbone. The connections (arrows) to the leads are through the LSs (red dots) near the boundaries. (b) and (c): Length $(L - R_M)/R_M$ dependence of the average $\langle |\ln(\frac{|X'|}{X}|)\rangle$. In (b): the conductance $X = G$ (dashed curves) and the thermopower $X = S$ (solid curves); In (c): the three-terminal thermopower $X = S_p$. Results given for three different temperatures $k_B T$ =15 (●), 30 (△), and 60 (□). $\gamma = 100$, $\mu = 0$, $\xi = 0.1$, and $\rho = 0.03$, $k_B T_0 = 333$, $E_c = 424$, 600, and 849 for the three temperatures respectively. Along each curve from left to right the number of LSs for the first, second, ..., fifth data point are $N = 30$, 50, 70, 100, and 120 respectively. The Mott distances are $R_M = 0.4, 0.49, 0.54, 0.58, 0.60(0.28, 0.35, 0.38, 0.41, 0.42)$ and the corresponding Mott energies are $E_M = 120, 147, 161, 174, 180(170, 208, 227, 246, 254)$ for the five points at $k_B T = 15(30)$ respectively. $R_M$ ($E_M$) at $k_B T = 60$ is half (two times) of that at $k_B T = 15$ for the five points respectively. The average nearest neighbor distances $2L/N$ for the three $T$’s are 0.039, 0.028, and 0.02 respectively. The results are averaged over $10^6$ random configurations. The curves in (b) and (c) are guide to the eye.
FIG. 6. (Color online) The effect of decreasing the conductances in the middle part of a random 1D VRH system, by a factor of $r_g$, on the conductance and the thermopower. $X = G$ or $S$, with $X'/X$ denoting the ratio of the conductance or thermopower after changing the middle, to the original value. The curves with $\triangle$ depict the thermopower while the ones with $\bullet$ depict the conductance. The parameters are: $k_B T = 15$, $\mu = 0$, $\xi = 0.1$, $\rho = 0.03$, $k_B T_0 = 333$ and $E_c = 424$. The average distance between adjacent LSs is 0.039. For the longer (a) system ($N = 400$, $2L = 22R_M$) the resistances in the region ($-2R_M, 2R_M$) are increased by a factor of $r_g$. For the shorter (b) system ($N = 40$, $2L = 3.5R_M$) the resistances in the region ($-R_M, R_M$) are increased in the same way.

FIG. 7. (Color online) Thermopower in 1D VRH. (a): The variance of the thermopower $\text{Var}(eST) = \langle (eST - \langle eST \rangle)^2 \rangle$ as a function of the length of the system $2L/R_M$ at $k_B T = 15$ ($\bullet$), 30 ($\triangle$), and 60 ($\square$). Along each curve from left to right the number of LSs for the first, second, ..., seventh data point are $N = 30$, 50, 70, 100, 120, 200, and 400 respectively. The other parameters are the same as in Fig. 5. (b): Probability distribution function (PDF) of the thermopower for 1D VRH systems, where $k_B T = 15$, $\mu = 0$, $\xi = 0.1$, $\rho = 0.03$, $E_c = 424$, and $N = 120$. The average distance is $2L/N = 0.039$. The results are obtained from $10^6$ random configurations. The straight red line is an exponential fit to the tail, $\sim \exp(-C|eS|T/E_0)$ with $C \approx 5.5$. In the inset we show how the thermopower evolves as a function of the system length for two random configurations. The parameters are: $k_B T = 30$, $\mu = 0$, $\xi = 0.1$, $\rho = 0.03$, and $E_c = 600$. The average distance between adjacent LSs is 0.028. In figure (a) the curves are guide to the eye.
FIG. 8. (Color online) (a): Schematic of the non-spanning hopping paths which may contribute significantly to the heat conductances. The wavy lines denote the phonons involved in the processes. (b) and (c): Distance \((L-R_M)/R_M\) dependence of the average of (b) \(|X|/(GE_c^2 e^{-2})\) with \(X = K_0^0\) (●), \(X = L_3\) (△), and \(X = K_{pe}\) (□) for \(k_B T = 15\) (solid curves) and 30 (dashed curves). (c) \(|\ln(|X'/X|)|\) for \(X = K_{pe}\) (solid curves), \(X = K_0^0\) (dashed curves), and \(X = L_3\) (dot-dashed curves) for three different temperatures with \(k_B T = 15\) (●), 30 (△), and 60 (□). The other parameters are the same as those in Fig. 5. The results are obtained by averaging over 10^6 random configurations. Note that in figure (c) the curves for \(K_0^0\) are quite indistinguishable from those of \(K_{pe}\), since \(K_{pe} = 4K_0^0\) when the non-spanning paths determine the heat conduction. The curves in figures (b) and (c) are guide to the eye.