Theory of non-equilibrium thermoelectric effects in nanoscale junctions

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Despite its intrinsic non-equilibrium origin, thermoelectricity in nanoscale systems is usually described within a static scattering approach which disregards the dynamical interaction with the thermal baths that maintain energy flow. Using the theory of open quantum systems we show instead that unexpected properties, such as a resonant structure and large sign sensitivity, emerge if the non-equilibrium nature of this problem is considered. Our approach also allows us to define and study a local temperature, which shows hot spots and oscillations along the system according to the coupling of the latter to the electrodes. This demonstrates that Fourier’s law – a paradigm of statistical mechanics – is violated at the nanoscale.

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Non-equilibrium (NE) processes at the nanoscale are receiving a great deal of attention due in large part to the advancements in fabrication and manipulation of these systems. [1] An especially interesting class of NE phenomena pertain to energy transport and the conversion of thermal to electrical energy. When a thermal gradient $\Delta T$ is applied to a finite system, electrons respond by departing from their ground state to partially accumulate at one end of the system, thus creating a measurable voltage difference $\Delta V$. The ratio $S = -\frac{\Delta V}{\Delta T}$ is called thermopower [2], and has been measured in a variety of nano-scale systems such as quantum point contacts [3], atomic-size metallic wires [4], quantum dots [5], Si nanowires [6] and recently in molecular junctions [7]. In a bulk material, when $S < 0$ the transient current is carried by electrons; when $S > 0$ it is carried by holes.

In nanoscale systems this NE problem is generally described within the single-particle scattering formalism [8], which relates the thermopower to single-particle transmission probabilities. This approach, however, does not take into account the dynamical formation of the thermopower, and completely neglects the fact that even at steady state, when the charge current is zero, an energy current is still present. [10] In addition, local density variations across the system induce local temperature variations, an effect which is also not taken into account in the above theories, and which is now within reach of experimental verification [11]. In order to study all these effects one needs to describe a nanoscale system interacting with an environment that maintains the thermal gradient, namely one needs to resort to a theory of NE open quantum systems.

In this letter we introduce such a theory, based on a generalization of quantum master equations, and use it to study the dynamical formation of thermo-electric effects in nanojunctions. We show that the thermopower is a highly non-linear function of the thermal gradient and it is very sensitive to the junction geometry, even in the simplest case of non-interacting electrons. This precludes an easy interpretation of its sign in terms of electrons or holes as it has been argued in some literature [3, 12–15].

In addition, the theory allows us to define the local electron temperature by means of a temperature floating probe that is locally coupled to the system, and whose temperature is adjusted so that the system dynamics is minimally perturbed. This temperature, which can be measured experimentally, shows important features such as hot spots in the cold lead at small coupling between the nanowire and the bulk electrodes, and temperature oscillations in the wire at intermediate coupling. These findings clearly show that Fourier’s law, which is considered a paradigm of thermodynamics, is violated for electronic systems at the nanoscale [16].

**Method.** – Since we consider non-interacting electrons coupled to an environment, we employ a quantum master equation of the Lindblad type [17] which describes the dynamical evolution of the many-body density matrix (DM) $\rho_M$ of a quantum system in the presence of a markovian bath, via the introduction of a super-operator $\mathcal{L}$. The quantum master equation is then

$$\dot{\rho}_M = -i[H, \rho_M] + \mathcal{L}[\rho_M] \ , \quad (1)$$

where $\{ \cdot, \cdot \}$ denotes the commutator. The super-operator $\mathcal{L}$ is defined via a set $V_{n'n}$ of operators via

$$\mathcal{L}[\rho_M] = \sum_{nn'} \left( -\frac{1}{2} \{ V_{nn'}, \rho_M \} + V_{nn'} \rho_M V_{nn'}^\dagger \right) , \quad (2)$$

with $\{ \cdot, \cdot \}$ being the anti-commutator. The sums over $n$ and $n'$ ($n \neq n'$) are performed over all many-particle levels of the system, and the $V$-operators are conveniently selected in the form $V_{nn'} = \sqrt{\gamma_{nn'}} |\Psi_n\rangle \langle \Psi_{n'}|$, describing a transition from the many-body state $|\Psi_n\rangle$ into the state $|\Psi_{n'}\rangle$ with the transition rate $\gamma_{nn'}$.

This problem scales exponentially with the number of particles, but recently a mapping of the many-body super-operator to a single-particle form has been introduced [19]. This results in a quantum master equation for the single-particle DM, $\rho = \sum_{kk'} \rho_{kk'} |k\rangle \langle k'|$ which provides excellent agreement with the many-body solution. Here, $|k\rangle$ are the single-particle states, and the matrix elements are derived from the many-body DM by $\rho_{kk'} = \text{Tr} \left( c^\dagger_k c_{k'} \rho_M \right)$. 
We now consider a finite nano-junction (i.e., with a fixed number of electrons and ions) which is composed of two identical quasi-two-dimensional leads connected via a one-dimensional wire (see upper panel of Fig. 1). The far edges of the leads are coupled to two different baths kept at different temperatures. The Hamiltonian of the system is given by $H = H_L + H_R + H_d + H_c$, where $H_{L,R,d} = -t \sum_{\langle i,j \rangle} c_{i}^\dagger c_{j} + h.c.$ are the tight-binding Hamiltonians of the left lead, right lead and wire, respectively ($t$ is the hopping integral, which serves as the energy scale hereafter), and $H_c = g \left( c_L^\dagger c_d^\dagger,0 + c_{R}^\dagger c_{d,L} + h.c. \right)$ describes the coupling between the left (right) lead to the wire, with $c_L^\dagger$ ($c_R^\dagger$) being the creation operator for an electron at the point of contact between the left (right) lead and the wire, and $c_{d,L}^\dagger$ ($c_{d,R}$) destroys an electron at the left-most (right-most) sites of the wire. We consider here spinless electrons. The master equation now takes the form

$$\dot{\rho} = -i[H, \rho] + \mathcal{L}_L[\rho] + \mathcal{L}_R[\rho]$$

(3)

where $\mathcal{L}_L(R)$ describes relaxation processes due to the contact between the left (right) lead with its respective bath at temperature $T_L(R)$. The $V$-operators are generalized to account for the different baths, and are given by [19]

$$V_{kk'}^{(L,R)} = \sqrt{\gamma_{kk'}^{(L,R)} f^{(L,R)}(\epsilon_k)} |k\rangle\langle k'|,$$

(4)

where $f^{(L,R)}(\epsilon_k) = 1/\left(\exp\left(\frac{\epsilon_k - \mu^{(L,R)}}{k_b T^{(L,R)}}\right) + 1\right)$ are the Fermi distributions of the left and right leads, with $\mu$ the chemical potential. The coefficients

$$\gamma_{kk'}^{(L,R)} = \sum_{\mathbf{r}_i \in S_{L,R}} \psi_i^\ast (\mathbf{r}_i) \gamma_0 \psi_i (\mathbf{r}_i)$$

(5)

describe the overlap between the single-particle states $|k\rangle$ and $|k'|$ over the region of contact $S_{L,R}$ between the left (right) baths and the corresponding junction leads, shown by the solid lines in the upper panel of Fig. 1. The quantity $\gamma_0$ is a constant describing the strength of interactions between the bath and electrons. The form (5) can be derived from first principles by tracing out the bath degrees of freedom, with the latter formed by a dense spectrum of boson excitations (e.g., phonons), which interact locally with electrons at the edges of the system. The operators (4) guarantee that the system evolves to a global equilibrium if $T_L = T_R$, or equilibrate each lead at its own temperature if $g = 0$, i.e., the leads and the wire are completely decoupled (and hence no voltage drop can form).

We now solve equation (3) numerically for several temperature gradients. From the obtained charge density distribution we derive the electrical potential via the Poisson equation. The potential is averaged along the transverse direction (see example in Fig. 1(b)), and the voltage drop is calculated from the center of the leads [20]. The off-diagonal elements of the DM decay fast (on a time-scale $\sim \gamma_0^{-1} \sim 10$ in our calculations) and hence do not contribute to the density in the long-time limit. This allows us to neglect them completely, a fact which significantly simplifies the calculation [21].

**Numerical results.** – In Fig. 1(a) the voltage drop $\Delta V$ across the junction is plotted as a function of the temperature difference $\Delta T$ between the contacts. The leads are of dimensions $12 \times 11$ and the wire is of length $L_d = 6$. The lead-wire coupling is $g = 0.001$ and the number of electrons is $n_E = 90$, which corresponds to 1/3 filling. The initial temperatures are set to $T_L = T_R = 0.05$. From Fig. 1 one notices three regimes in the range of $\Delta T$. At small $\Delta T$, a linear-response regime can be identified. This is followed by a regime of rapid rise in $\Delta V$, eventually reaching a saturation at large $\Delta T$, due to the finite size of the system. The solid line is a fit to an exponential rise. Although the parameters of the exponential fit depend on sample parameters, we found that the exponential form is an excellent fit for all non-interacting junctions. In the inset of Fig. 1(a) we plot the generalized thermopower, $S = -\frac{\partial (\Delta V)}{\partial (\Delta T)}$, which reduces to the regular thermopower in the linear regime. As seen, $S$ exhibits a resonance at $\Delta T \approx 0.25$ (this value is not universal and depends on junction parameters), which means that at this value the response of the system to a change in the temperature gradient is maximal; a fact that can be checked experimentally and may be used in actual devices.

**Nonequilibrium distributions.** – The formalism presented here allows us to calculate various NE properties. As an example, we plot in Fig. 2(a) the distribution function $f(E_k) = \rho_k$. In the inset the distribution function is calculated at $\Delta T = 0$, showing a regular Fermi distribution. On the other hand, for $\Delta T = 1.5$ (same parameters as in Fig. 1) we find an unusual distribution, composed of two branches, corresponding to “Fermi distributions” for the low- and high-temperature limits. This means that out of equilibrium a situation may develop in which states which are very close in energy will have very different occupation probabilities, which will depend on, e.g., the spatial form of the corresponding wave-functions. This cannot happen at equilibrium, where two states with close energies would have similar occupations. A way of detecting such a double-branched distribution experimentally is to probe the noise of a measurement that couples to the distribution (e.g., measurements of tunneling into the system). For such a distribution, one expects a telegraph noise to appear, due to the coupling to the two different branches of the distribution function.

**Geometrical effects.** – Due to the local variations of the density at the junction and hence local variations
of kinetic energy, the thermo-electric response strongly depends on junction geometry, as it was anticipated experimentally [4]. As an example, we have calculated the charge-imbalance \( \Delta Q \), across a junction (leads size 6 \times 7, wire length \( L_d = 6 \), density at one third filling) with an asymmetric coupling between the leads and the wire. The coupling to the left lead was kept at \( g_L = 0.001 \) and the coupling to the right lead, \( g_R \), was changed. In Fig. 2(b) we plot the charge imbalance as a function of \( g_R \) at a fixed temperature difference \( \Delta T = 1 \). Strong and narrow oscillations can be seen, and for certain values of coupling asymmetry, \( \Delta Q \) may even change sign. This is consistent with the experiments in [4] and may account for the sign change of the thermo-power observed in some experiments in molecular junctions [4, 7].

Local temperature. – The concept of a local temperature is generally not unique out of equilibrium [22]. Here we provide an operational definition, which is both physically transparent and can (in principle) be directly probed experimentally [11]. In order to do so, we add an additional relaxation operator \( \mathcal{L}_{\text{tip}} \rho_M \) to the master equation (1). This corresponds to applying a local bath at a temperature \( T_{\text{tip}} \) in contact with a single site of the system (see upper panel of Fig. 3). Due to energy flow between the probe and the coupled site, the system dynamics is generally modified. However, one can “float” the temperature \( T_{\text{tip}} \), such that the change in local (and hence global, e.g., thermopower) properties of the system is minimal. We define this temperature as the local temperature of our system at the probe position. We choose to monitor the change in the local density from its value in the absence of the probe, but any other quantity would be equally valid and lead to the same local temperature.

The latter is plotted in Fig. 3 at steady state for three different values of the lead-wire coupling, \( g = 0.001, 0.1, 0.8 \) and a junction with lead dimensions 4 \times 3, wire length \( L_d = 21 \), temperatures \( T_L = 0.05 \) and \( T_R = 1.55 \), and electron density at third filling. For weak coupling (\( g = 0.001 \)), it is found that the temperature inside the wire is very low, but a “hot spot” develops in the cold lead. As the coupling increases the hot spot vanishes, and temperature oscillations develop in the wire. As expected, at high coupling, the wire equilibrates at a temperature that is roughly the average between \( T_L \) and \( T_R \). For large lead-wire coupling the temperature in the wire is uniform, and most of the temperature drop occurs at the contacts, similar to what has been argued for the phenomenon of local ionic heating [23]. We note
and the electrodes, in violation of Fourier’s law.

We conclude by pointing that the results presented here may be relevant to other systems of present interest (e.g. graphene nano-ribbons, nanotubes etc.). Studies of these effects that include electron interactions represent another important research direction, and are underway using stochastic time-dependent current density-functional theory [24].

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[21] Note that in a driven system the off-diagonal elements of the DM do not decay at all, and hence it is crucial to calculate them fully, as is done in Ref. [19]. However, in a currentless steady state they vanish identically.
