

Thermodynamic and quantum bounds on nonlinear dc thermoelectric transport

Robert S. Whitney

Laboratoire de Physique et Modélisation des Milieux Condensés (UMR 5493), Université Grenoble 1 and CNRS, Maison des Magistères, BP 166, 38042 Grenoble, France

(Received 20 November 2012; published 5 March 2013)

I consider the nonequilibrium dc transport of electrons through a quantum system with a thermoelectric response. This system may be any nanostructure or molecule modeled by the nonlinear scattering theory, which includes Hartree-like electrostatic interactions exactly, and certain dynamic interaction effects (decoherence and relaxation) phenomenologically. This theory is believed to be a reasonable model when single-electron charging effects are negligible. I derive three fundamental bounds for such quantum systems coupled to multiple macroscopic reservoirs, one of which may be superconducting. These bounds affect nonlinear heating (such as Joule heating), work and entropy production. Two bounds correspond to the first law and second law of thermodynamics in classical physics. The third bound is *quantum* (wavelength dependent), and is as important as the thermodynamic ones in limiting the capabilities of mesoscopic heat engines and refrigerators. The quantum bound also leads to Nernst's unattainability principle that the quantum system cannot cool a reservoir to absolute zero in a finite time, although it can get exponentially close.

DOI: 10.1103/PhysRevB.87.115404

PACS number(s): 73.63.-b, 05.70.Ln, 72.15.Jf, 84.60.Rb

I. INTRODUCTION

In classical physics, currents in resistive circuits are dissipative—they emit Joule heat that increases the entropy of the environment of the circuit. Devices with thermoelectric responses^{1–3} can be used as heat engines (using heat flows to create electrical power) or heat pumps (using electrical power to create heat flows). These are also dissipative, since they increase the entropy of the environment (at least a little bit) during their operation. The laws of thermodynamics give us strict bounds on the capabilities of such thermoelectric devices.

There is currently great interest in using quantum systems as thermoelectric heat engines or refrigerators, particularly nanostructures^{4–13} and molecules.^{14–19} However, quantum responses are often nonlocal, since thermal equilibration occurs on length scales very much bigger than the size of the system, with equilibrium only being established deep in the reservoirs coupled to the system. The classical models of transport account neither for this nonlocality nor for the wave nature of quantum particles. It is natural to ask what the bounds are for these quantum devices and how they compare to the bounds on classical devices. There are many works asking whether quantum systems are bounded by the laws of thermodynamics,^{20–27} particularly for systems modeled by Markovian or Bloch-Redfield master equations, see Refs. 20,28–30 and references therein. However, the fundamental bounds on *thermoelectric* quantum systems remain an open question.²⁷ Here, I consider the fully nonlinear response of a broad class of thermoelectric quantum systems (see Fig. 1), and show that they obey the bounds imposed by the laws of thermodynamics, while also suffering a quantum bound on their behavior.

The Landauer-Büttiker scattering theory³³ is a widely used theory for modeling such electron flows through quantum systems giving dc and ac conductances^{34,35} and nonlinear effects.^{36–39} It has equally been used to get linear thermal and thermoelectric effects.^{40–45} However, it is a delicate question whether it captures dissipation and the associated laws of thermodynamics (or their quantum equivalent). The standard answer is that the theory accurately models *reversible*

scattering processes, while assuming that equilibration occurs (irreversibly) in the reservoirs via dissipative processes, which the theory does not detail. Hence one might suspect that the theory would not capture how dissipation produces entropy. This suspicion is wrong, the nonlinear scattering theory is sufficient to give information about entropy production, despite the simplistic way in which it treats the physics in the reservoirs. Indeed, Ref. 27 showed the second law of thermodynamics to be a remarkably direct outcome of a nonlinear “dc” scattering theory³¹ for a quantum system of *noninteracting* electrons between two reservoirs.³² Energy conservation leads to the systems also obeying the first law.

Here, I show that the proof in Ref. 27 works equally well for a nonequilibrium scattering theory that includes Hartree-like *electron-electron interactions* (electrostatic charging effects) in a self-consistent and gauge-invariant manner. This theory

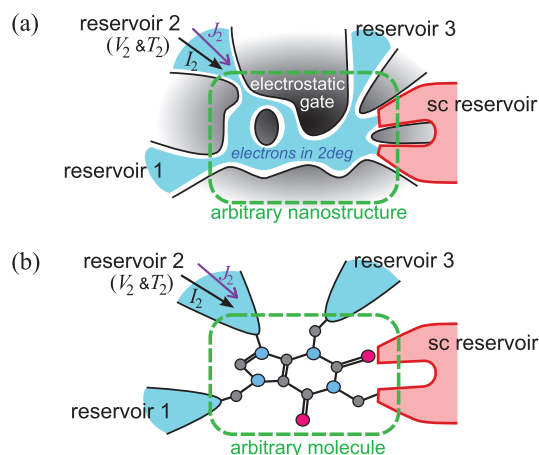


FIG. 1. (Color online) Quantum systems with $K_n = 3$ normal reservoirs and one superconducting (sc) reservoir. Examples include (a) nanostructures such as those defined by electrostatic gates on top of a two-dimensional electron gas (2deg) or (b) molecules. Charge and heat currents, I_i and J_i , are positive if they flow from reservoir i into the quantum system.

is the analog for heat currents¹³ of the nonlinear scattering theory for charge currents;^{36–39} although heat currents are not conserved when charge currents are. Such electrostatic interactions cannot be ignored for the nonlinear response,^{36–39} and entropy production is a purely nonlinear effect (vanishing in the linear-response regime). By keeping only electrostatic interaction effects, this approach is by no means exact, however, it is a reasonable approximation for any system where the single-electron charging energy is small compared to temperature or broadening of the quantum system’s levels due to the coupling to the reservoirs.³⁶ Within this approach, I prove that the dc response of any quantum system coupled to an arbitrary number of reservoirs—one of which may be superconducting—obeys the laws of thermodynamics.

The extension from two²⁷ to many reservoirs requires no new physics, but is complicated by the fact one can no longer use the two-terminal Onsager relations for transmission matrices. However, it extends our understanding of thermodynamics in quantum transport in two ways.

(1) Using the generalization to many reservoirs, one can include dynamic interaction effects (decoherence and relaxation) phenomenologically as additional fictitious reservoirs.^{25,46–48} Performing such an analysis, I conclude that the classical laws of thermodynamics hold for partially coherent (as well as fully coherent) quantum transport.

(2) A superconducting (sc) reservoir has no analog in classical mechanics, because the condensate is a macroscopic quantum state. In addition, charge current can flow into (or out of) this condensate, but heat current cannot. Thus a charge-current can pass into the sc reservoir, I_{sc} , without any change in that reservoir’s entropy, $\dot{S}_{sc} = 0$. Despite this, I show that the laws of thermodynamics hold in the presence of such a reservoir.

There is also a *quantum bound* (qb) on the heat extracted via thermoelectric cooling, identical to Pendry’s bound⁴⁹ for passive cooling of a hot reservoir by a colder one (a fermionic analogue⁵⁰ of the Stefan-Boltzmann law of black-body radiation). No thermoelectric device, supplied with an arbitrary amount of dc power, can ever extract heat from a reservoir faster than the bound $J^{qb} \propto N T^2$, where T is the reservoir temperature and the contact between the device and the reservoir has N transverse modes. This bound is *quantum*; it is only relevant when $N^{-1} \sim \lambda_F^2/A_i \neq 0$ for electron wavelength λ_F and contact cross-section A_i .

For thermoelectric refrigerators, the quantum and thermodynamic bounds *compete*, and the quantum bound can be a stronger constraint than that given by the thermodynamic bounds (the Carnot limit). In contrast, the bounds *combine* to give an upper limit on the power that a thermoelectric heat engine can produce.

I find that the quantum bound means that the system obeys Nernst’s *unattainability principle* (one of the two statements forming the third law of thermodynamics), that states that a reservoir cannot be refrigerated to absolute zero in a finite time. See, for example, Refs. 21,29, and 30 for physical and Refs. 51 and 52 for mathematical overviews. The quantum bound means that the systems considered here have (at best) the critical behavior, i.e., the reservoir *cannot* achieve zero temperature in a finite time, but it can get exponentially close. This rules out such systems as candidates

for violating the unattainability principle in the manner Ref. 30 proposes.

II. EXPLICIT FORM OF THE BOUNDS

In this section, I give the three bounds, before deriving them later in the paper. I consider an arbitrary quantum system coupled to any number of reservoirs, one of which may be superconducting. Normal reservoirs are treated as free-electron gases in thermal equilibrium, while a superconducting reservoir is treated as a condensate of Cooper pairs.⁵³ The heat current flowing out of reservoir i is J_i . The electrical power flowing out of reservoir i is $P_i = V_i I_i$, with V_i being the bias on the reservoir, and I_i being the charge current flowing out of it. The rate of change of entropy in the i th reservoir is defined as $\dot{S}_i = -J_i/T_i$ for reservoir temperature T_i .

I define \dot{E}_{total} and \dot{S}_{total} as the rates of change of the total energy and entropy of the quantum system and all reservoirs averaged over long times. Under dc drive,³¹ the quantum system remains in the same steady state on average over long times, so one can neglect its contribution to \dot{E}_{total} and \dot{S}_{total} . Then scattering theory gives the thermodynamic laws:

$$\dot{E}_{total} = \sum_i (J_i + P_i) = 0 \quad [1 \text{ st law}], \quad (1)$$

$$\dot{S}_{total} = \sum_i -J_i/T_i \geq 0 \quad [2 \text{ nd law}], \quad (2)$$

where the sum is over all reservoirs. The quantum bound (qb) on the heat current out of reservoir i is

$$J_i \leq J_i^{qb} \equiv \frac{\pi^2}{6h} N_i (k_B T_i)^2 \quad [\text{quantum}], \quad (3)$$

where the quantum system couples to reservoir i through N_i transverse modes, and this equation defines J_i^{qb} . Thus the rate of change of entropy in the i th reservoir is $\dot{S}_i \geq -J_i^{qb}/T_i$. Sections IX and X discuss how these bounds act as limits on heat engines and refrigerators.

III. NONLINEAR SCATTERING THEORY FOR HEAT TRANSPORT

The nonlinear Landauer-Büttiker scattering theory, developed for ac^{34,35} and nonlinear-dc^{36,37} charge flows, was recently extended to thermoelectric effects.^{13,38,39} It includes (in a gauge-invariant and self-consistent manner) Hartree-type electron-electron interaction effects, which act as electrostatic charging effects. Here, as in Ref. 13, I apply it to nonlinear heat flows.^{54–56}

One starts with the scattering matrix^{36–39} $S_{ij}^{\mu\nu}$, for a ν particle entering the quantum system from reservoir j to a μ particle leaving via reservoir i , where μ, ν are ± 1 , with $+1$ for electrons with charge e^- or -1 for holes with charge $-e^-$. Here, an electron with energy ϵ is an *occupied* conduction-band state with energy $\epsilon + e^- V_{sc}$, while a hole with energy ϵ is an *empty* conduction-band state with energy $-\epsilon + e^- V_{sc}$, where $e^- V_{sc}$ is the superconductor’s chemical potential. These “holes” are not in a semiconductor’s valence band, unlike those in Ref. 13. Let the lead to reservoir i have N_i modes for all ϵ . The number of *open* modes in this lead can still be ϵ dependent, since a given mode can be closed off at a certain ϵ (purely

reflected in the scattering matrix at ϵ). If a superconducting (sc) reservoir is present, it is modeled by Andreev reflection of electron to hole and vice versa. Then, $\epsilon = 0$ at the sc reservoir's chemical potential e^-V_{sc} (otherwise one can choose $\epsilon = 0$ however is convenient). In the nonlinear regime, $\mathcal{S}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env})$ must include the charging effects self-consistently, because this \mathcal{S} is a function of the charge distribution in the quantum system, which is, in turn, a function of \mathcal{S} as well \mathbf{v}_{env} ,^{36,39} where \mathbf{v}_{env} is the set of all voltages and temperatures, $\{V_k, T_k\}$, in the system's environment (reservoirs and gates).

All charge and heat transport properties are then given by the transmission matrix, $\mathcal{T}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env}) = \text{Tr}[[\mathcal{S}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env})]^\dagger \mathcal{S}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env})]$ where the trace is over all transverse modes of the leads connecting the quantum system to the i and j reservoirs. Any self-consistent analysis must of course respect gauge invariance, i.e., shifting all voltages by the same amount is tantamount to redefining the zero of energy and thus cannot change the physics. I ensure this by taking ϵ and all reservoir and gate voltages (and any screening potentials that depend on them) relative to the superconductor's chemical potential⁵⁷ e^-V_{sc} . If there is no superconductor, one can take these relative to another reservoir voltage. In everything that follows, I will assume that $\mathcal{T}_{ij}^{\mu\nu}$ has this gauge invariance.

The results presented in this paper are all based on only two properties of $\mathcal{T}_{ij}^{\mu\nu}$. The first property is due to the fact that $\mathcal{T}_{ij}^{\mu\nu}$ is the sum of the modulus squared of the elements of $\mathcal{S}_{ij}^{\mu\nu}$. This property is that for all $i, j, \mu, \nu, \epsilon, \mathbf{v}_{env}$,

$$\mathcal{T}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env}) \geq 0. \quad (4)$$

The second property is due to the unitarity of $\mathcal{S}_{ij}^{\mu\nu}$ (particle conservation) and is that for all $\epsilon, \mathbf{v}_{env}$,

$$\begin{aligned} 0 &= \sum_{j=1}^{K_n} \sum_{\nu} [N_i \delta_{ij}^{\mu\nu} - \mathcal{T}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env})] \\ &= \sum_{i=1}^{K_n} \sum_{\mu} [N_i \delta_{ij}^{\mu\nu} - \mathcal{T}_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{env})], \end{aligned} \quad (5)$$

where the i, j sums are over the K_n normal reservoirs, while the μ, ν sums are over ± 1 for electrons or holes.

As Eqs. (4) and (5) are the central results needed for all derivations in this work, let me emphasize that they apply in the Hartree approximation without further approximations. One could self-consistently solve for infinitely many local time-independent Hartree potentials (on a grid of a vanishing cell size). The resulting (very complicated) self-consistent scattering matrix would be unitary, and so it will satisfy Eqs. (4) and (5).

The charge current I_i is the difference between the charge μe^- leaving and entering reservoir i . The heat current J_i is the difference between the excess energy $(\epsilon - \mu e^- V_i)$ leaving and entering reservoir i .⁴² Thus

$$I_i = \sum_{j\mu\nu} \int_0^\infty \frac{d\epsilon}{h} \mu e^- [N_i \delta_{ij}^{\mu\nu} - \mathcal{T}_{ij}^{\mu\nu}(\epsilon)] f_j^\nu(\epsilon), \quad (6)$$

$$J_i = \sum_{j\mu\nu} \int_0^\infty \frac{d\epsilon}{h} (\epsilon - \mu e^- V_i) [N_i \delta_{ij}^{\mu\nu} - \mathcal{T}_{ij}^{\mu\nu}(\epsilon)] f_j^\nu(\epsilon), \quad (7)$$

where the j sum is over the K_n normal reservoirs, while the $\mu\nu$ sums are over electrons (+1) and holes (-1). Here, $\delta_{ij}^{\mu\nu}$ indicates the pair of Kronecker δ functions, $\delta_{ij} \delta_{\mu\nu}$. The Fermi function for ν particles entering from reservoir j is

$$f_j^\nu(\epsilon) = \{1 + \exp[(\epsilon - \nu e^- V_j)/(k_B T_j)]\}^{-1}. \quad (8)$$

Comparing Eqs. (6) and (7), one can easily see that

$$J_i = -V_i I_i + \sum_{j\mu\nu} \int_0^\infty \frac{d\epsilon}{h} \epsilon [N_i \delta_{ij}^{\mu\nu} - \mathcal{T}_{ij}^{\mu\nu}(\epsilon)] f_j^\nu(\epsilon). \quad (9)$$

If a superconductor is present, then the charge current into it (in the form of Cooper pairs), I_{sc} , is given by Kirchoff's law of current conservation. In contrast, heat current is not conserved. However, the heat flow through a boundary at the surface of a superconducting reservoir must be zero, since an electron at energy ϵ is Andreev reflected as a hole with the same energy. Thus

$$I_{sc} = -\sum_j I_j, \quad J_{sc} = 0. \quad (10)$$

Again the j sum is over the K_n normal reservoirs.

The total heat absorbed by the quantum system J_{total} is the sum of Eq. (9) over all reservoirs. Then $J_{total} = -\sum_{i=1}^{K_n} V_i I_i$, since Eq. (5) means that the second term in Eq. (9) cancels. Thus far, voltages are relative to the sc reservoir, if we take them relative to another reference, then

$$J_{total} = -V_{sc} I_{sc} - \sum_{i=1}^{K_n} V_i I_i. \quad (11)$$

Kirchoff's law in Eq. (10) means that changing all voltages by the same amount does not change the total heat flow J_{total} . Thus J_{total} respects gauge invariance whenever I_i does, where one recalls that I_i is a self-consistent function of $(V_1, T_1, V_2, T_2, \dots, V_N, T_N)$.³⁹ Whenever J_{total} is nonzero, heat currents are not conserved in the quantum system; the quantum system is a heat sink for $J_{total} > 0$, or a heat source for $J_{total} < 0$.

IV. ZEROth LAW OF THERMODYNAMICS

The definition of equilibrium is one of the various statements that together form the zeroth law. It is defined as a state for which one can cut the system into parts in any manner, and one will find *no* charge and heat flow between those parts. Thus, if a system in equilibrium consists of multiple reservoirs (evidently in equilibrium with each other) all coupled to each other through a quantum system, then there can not be any charge or heat current through that quantum system. It is trivial to show that any quantum system placed between an arbitrary number of reservoirs all in equilibrium with each other must obey this consequence of the zeroth law; the scattering matrix \mathcal{S} is unitary, this means that the transmission matrix obeys Eq. (5). Substituting this into Eqs. (6) and (7), one can see that charge and heat currents are zero whenever $T_j = T_0$ and $V_j = V_0$ for all j .

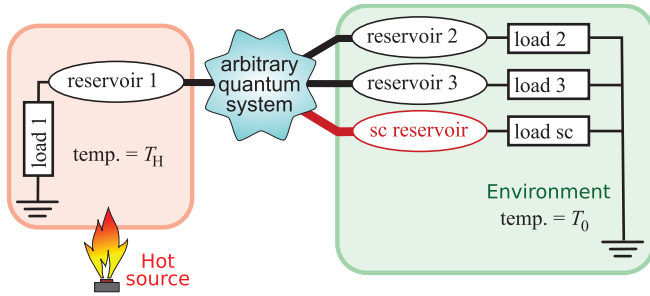


FIG. 2. (Color online) A quantum system with a finite thermoelectric response being used as a heat engine providing power to a set of loads. The sc reservoir is superconducting, but “load sc” is not (its simply the load coupled to the sc reservoir).

V. FIRST LAW OF THERMODYNAMICS AND JOULE HEATING

Equation (11) has the form of a *classical* Joule heating term, i.e., voltage \times current. This is due to the fact that energy conservation ensures that the heat emitted (or absorbed) is equal and opposite to electrical power supplied (or generated). Thus one arrives directly at the first law of thermodynamics, Eq. (1). However, it is important to note that this is only true upon summing over all reservoirs, there is no particular relation between the power flowing out of reservoir i , $P_i = V_i I_i$, and the heat current out of that reservoir, given in Eq. (9).

As a first example, consider a quantum system with two normal reservoirs at the same temperature but different biases, Kirchoff’s law means that $I_2 = -I_1$, and hence $P_{\text{total}} = (V_1 - V_2)I_1$. Here, $P_{\text{total}} > 0$, so the reservoirs supply power to the quantum system, the total heat current into the quantum system, $J_{\text{total}} = -P_{\text{total}} < 0$, which corresponds to Joule heating. If reservoir 1 is superconducting, then all this heat flows into reservoir 2. Thus superconductors filter out the heat flow generated by Joule heating (along with any other heat flow).

As a second example, the quantum system in Fig. 2 is assumed to have a finite thermoelectric response. If one reservoir is heated, the quantum system generates a total electrical power of $P_{\text{gen}} = -P_{\text{total}} = -\sum_i V_i I_i$ at the loads. Here, V_i and I_i have opposite signs, e.g., for $V_i > 0$, the current flows into the i th load, so $I_i < 0$. Then $J_{\text{total}} = -P_{\text{total}} > 0$, so the quantum system absorbs the heat turned into electrical power.

VI. SECOND LAW OF THERMODYNAMICS

A. System coupled to two reservoirs

Here, I reproduce the calculation in Ref. 27 whose outcome is the second law in two-reservoir systems. The Hartree-type interaction effects can be included without any changes to their method. For two reservoirs, the rate of change of entropy is $\dot{S} = -(J_1/T_1 + J_2/T_2)$, one can substitute in Eq. (7) and explicitly write out the sum over $j = 1, 2$. There is no Andreev scattering so $\mathcal{T}_{ij}^{\mu\nu} \propto \delta_{\mu\nu}$, hence, when there are only two reservoirs, Eq. (5) gives us the following two-terminal Onsager relation: $N_1 - \mathcal{T}_{11}^{\mu\mu} = \mathcal{T}_{21}^{\mu\mu} = N_2 - \mathcal{T}_{22}^{\mu\mu} = \mathcal{T}_{12}^{\mu\mu}$. As a

result,

$$\frac{\dot{S}_{\text{total}}}{k_B} = - \sum_{\mu} \int_0^{\infty} \frac{d\epsilon}{h} (\xi_{1\mu} - \xi_{2\mu}) \times \mathcal{T}_{12}^{\mu\mu}(\epsilon, \mathbf{v}_{\text{env}}) [f(\xi_{1\mu}) - f(\xi_{2\mu})], \quad (12)$$

where I define $\xi_{i\mu} = (\epsilon - \mu e^{-V_i}) / (k_B T_i)$, so $f_i^{\mu}(\epsilon) = f(\xi_{i\mu})$ for $f(\xi) = [1 + \exp(\xi)]^{-1}$. Since $f(\xi)$ is a monotonically decaying function of ξ , the product of the two square brackets in Eq. (12) cannot be positive. Taking this together with Eq. (4), one concludes that the second law, $\dot{S}_{\text{total}} \geq 0$, is satisfied for such a two-reservoir system.

B. System coupled to any number of reservoirs

In general for more than two reservoirs, there is no simple relationship between $\mathcal{T}_{ji}^{\nu\mu}$ and $\mathcal{T}_{ij}^{\mu\nu}$. Then the derivation of the second law is more involved. Here, I provide a derivation that uses only the unitarity of $S_{ij}^{\mu\nu}$, in the form of Eqs. (4) and (5). Using Eq. (7), I write $\dot{S}_{\text{total}} = -(k_B/h) \int_0^{\infty} d\epsilon Y(\epsilon)$ with

$$Y(\epsilon) = \sum_{ij\nu\mu} \xi_{i\mu} [N_i \delta_{ij}^{\mu\nu} - \mathcal{T}_{ij}^{\mu\nu}(\epsilon)] f(\xi_{j\nu}), \quad (13)$$

where the i and j sums are over the K_n normal reservoirs. As in Eq. (12), I defined $\xi_{i\mu} = (\epsilon - \mu e^{-V_i}) / (k_B T_i)$ and $f(\xi) = [1 + \exp(\xi)]^{-1}$. I now prove that $Y(\epsilon) \leq 0$ for all ϵ to show that the second law, Eq. (2), is satisfied.

One can relabel the reservoirs in Eq. (13), giving separate labels to the electron and hole states entering the system from a given reservoir. Thus I replace the sum $\sum_{i=1}^{K_n} \sum_{\mu=\pm 1}$ with $\sum_{\tilde{i}=1}^{2K_n}$, where \tilde{i} is related to i and μ as follows. For each i and μ , one calculates $\xi_{i\mu}$, and then orders the elements in ascending order of $\xi_{i\mu}$. I then label these states with superscripts \tilde{i} , running from 1 to $2K_n$, such that $\xi^{(1)} < \xi^{(2)} < \dots < \xi^{(2K_n)}$. Then the quadruple sum over i, j, μ, ν in Eq. (13) can be replaced with a double sum over \tilde{i}, \tilde{j} . I then define the differences

$$\Delta\xi^{(\tilde{n})} = \xi^{(\tilde{n})} - \xi^{(\tilde{n}-1)}, \quad (14)$$

$$\Delta f^{(\tilde{m})} = f(\xi^{(\tilde{m})}) - f(\xi^{(\tilde{m}-1)}), \quad (15)$$

and so I use $\xi^{(\tilde{i})} = \xi^{(0)} + \sum_{\tilde{n}=1}^{\tilde{i}} \Delta\xi^{(\tilde{n})}$ and $f(\xi^{(\tilde{i})}) = f(\xi^{(0)}) + \sum_{\tilde{m}=1}^{\tilde{i}} \Delta f^{(\tilde{m})}$ to get

$$Y(\epsilon) = \sum_{\tilde{i}, \tilde{j}=1}^{2K_n} \left[\xi^{(0)} [N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon)] f(\xi^{(0)}) + \sum_{\tilde{n}=1}^{\tilde{i}} \Delta\xi^{(\tilde{n})} [N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon)] f(\xi^{(0)}) + \sum_{\tilde{m}=1}^{\tilde{j}} \xi^{(0)} [N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon)] \Delta f^{(\tilde{m})} + \sum_{\tilde{n}=1}^{\tilde{i}} \sum_{\tilde{m}=1}^{\tilde{j}} \Delta\xi^{(\tilde{n})} [N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon)] \Delta f^{(\tilde{m})} \right]. \quad (16)$$

Here, $\xi^{(0)}$ is arbitrary, so I take $\xi^{(0)} < \xi^{(1)}$. Then $\Delta\xi^{(\tilde{n})} \geq 0$ for all \tilde{n} and $\Delta f^{(\tilde{m})} \leq 0$ for all \tilde{m} [since $f(\xi)$ decays monotonically with ξ]. From Eq. (5), one sees that the first three lines of Eq. (16) equal to zero when summed over \tilde{i}, \tilde{j} ;

leaving only the term containing the sum over both \tilde{n} and \tilde{m} to evaluate. To do this, I write $\sum_{\tilde{i}=1}^{2K_n} \sum_{\tilde{n}=1}^{\tilde{i}} = \sum_{\tilde{n}=1}^{2K_n} \sum_{\tilde{i}=\tilde{n}}^{2K_n}$ and $\sum_{\tilde{j}=1}^{2K_n} \sum_{\tilde{m}=1}^{\tilde{j}} = \sum_{\tilde{m}=1}^{2K_n} \sum_{\tilde{j}=\tilde{m}}^{2K_n}$, after which,

$$Y(\epsilon) = \sum_{\tilde{n}, \tilde{m}=1}^{2K_n} \Delta \xi^{(\tilde{n})} \Delta f^{(\tilde{m})} \sum_{\tilde{i}=\tilde{n}}^{2K_n} \sum_{\tilde{j}=\tilde{m}}^{2K_n} [N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon)].$$

For $\tilde{n} > \tilde{m}$, one can prove that the sum over \tilde{j} is positive (or zero) for all \tilde{i} . The proof requires noticing that every sum over \tilde{j} contains a positive term for $\tilde{j} = \tilde{i}$ and negative terms for $\tilde{j} \neq \tilde{i}$, and then using Eqs. (4) and (5), showing that the sum over \tilde{j} is not negative. This is not the case if $\tilde{n} < \tilde{m}$, because not all sums over \tilde{j} contain a term with $\tilde{j} = \tilde{i}$. However, for $\tilde{n} < \tilde{m}$, one can do the \tilde{i} sum first, using the same logic as above to find that the sum over \tilde{i} is positive (or zero) for all \tilde{j} . Thus $\sum_{\tilde{i}=\tilde{n}}^{2K_n} \sum_{\tilde{j}=\tilde{m}}^{2K_n} [\mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon) - N_i \delta_{\tilde{i}\tilde{j}}] \geq 0$ for all \tilde{n}, \tilde{m} . Combining this with the fact that $\Delta \xi^{(\tilde{n})} \geq 0$ for all \tilde{n} and $\Delta f^{(\tilde{m})} \leq 0$ for all \tilde{m} , shows that $Y(\epsilon) \leq 0$, and thus the second law, Eq. (2), is obeyed.

On a side note, I want to mention that the above proof of $\sum_{\tilde{i}=\tilde{n}}^{2K_n} \sum_{\tilde{j}=\tilde{m}}^{2K_n} [N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}(\epsilon)] \geq 0$ is most easily seen graphically. First, one can write out the matrix $[N_i \delta_{\tilde{i}\tilde{j}} - \mathcal{T}_{\tilde{i}\tilde{j}}]$ explicitly and draw a rectangle around the elements summed over for given \tilde{n}, \tilde{m} . For $\tilde{n} > \tilde{m}$, every row in this rectangle contains a diagonal ($\tilde{i} = \tilde{j}$) element, so Eqs. (4) and (5) show that summing the elements in each row gives a positive (or zero) result. In contrast, for $\tilde{n} < \tilde{m}$, every column in the rectangle contains a diagonal ($i = j$) element, thus summing over the elements in each column gives a positive (or zero) result.

C. Emission of Joule heat

It is common that all reservoirs have the same temperature, $T_i = T_0$ for all i . Under this circumstance, the above proof of Eq. (2), proves that the quantum system must emit Joule heat, so $J_{\text{total}} \leq 0$.

VII. QUANTUM BOUND ON HEAT FLOWS

Equation (7) has an upper bound on the amount of heat that a thermoelectric quantum system can extract from any given reservoir [see Eq. (3)]. This is simply because no system can extract more heat from a reservoir than if that system is emptying every filled state that comes to it at an energy above the reservoir's chemical potential and filling every empty electron state that comes to it at an energy below the reservoir's chemical potential.⁴⁹ If we can get $\epsilon = 0$ to coincide with the i th reservoir's chemical potential, then the proof is easy (see how the below proof simplifies for $V_i = 0$). However, this may not be possible when there is a superconductor present or if one is interested in heat flows in multiple leads with different chemical potentials. Thus, below, I provide the proof for arbitrary V_i .

To proceed, I split Eq. (7) into two parts: $J_i^{(a)}$ containing only the parts of the integrals with $(\epsilon - \mu e^- V_i) > 0$ and $J_i^{(b)}$ containing the rest. Below, I assume positive $e^- V_i$, the proof for negative $e^- V_i$ follows the same logic (by interchanging electron \leftrightarrow hole). For positive $e^- V_i$, one has $J_i = J_i^{(a)} + J_i^{(b)}$

with

$$\begin{aligned} J_i^{(a)}(e^- V_i > 0) &= \int_{e^- V_i}^{\infty} \frac{d\epsilon}{h} (\epsilon - e^- V_i) \sum_{j,v} [N_i \delta_{ij}^{+1,v} - \mathcal{T}_{ij}^{+1,v}(\epsilon)] f_j^v(\epsilon) \\ &+ \int_0^{\infty} \frac{d\epsilon}{h} (\epsilon + e^- V_i) \sum_{j,v} [N_i \delta_{ij}^{-1,v} - \mathcal{T}_{ij}^{-1,v}(\epsilon)] f_j^v(\epsilon), \\ J_i^{(b)}(e^- V_i > 0) &= \int_0^{e^- V_i} \frac{d\epsilon}{h} (\epsilon - e^- V_i) \sum_{j,v} [N_i \delta_{ij}^{+1,v} - \mathcal{T}_{ij}^{+1,v}(\epsilon)] f_j^v(\epsilon), \end{aligned}$$

where the ± 1 is for an electron and a hole, respectively. Our objective is to find the upper bound on $J_i^{(a)}$ and $J_i^{(b)}$.

For $J_i^{(a)}(e^- V_i > 0)$, the first term in both integrands [the terms of the form $(\epsilon \pm e^- V_i)$] is positive, while Eq. (4) shows that $\mathcal{T}_{ij}^{\mu\nu} > 0$, and the Fermi function satisfies $0 \leq f_j^v(\epsilon) \leq 1$. Thus $J_i^{(b)}(e^- V_i > 0)$ can never be more positive than when $f_j^v(\epsilon) = 0$ for all $j \neq i$ or $v \neq \mu$ (where $\mu = +1$ in the first integral and $\mu = -1$ in the second). The remaining terms—those with $j = i$ and $\mu = \nu$ —can never be more positive than when $\mathcal{T}_{ii}^{\mu\mu} = 0$. Making the substitution $\xi = (\epsilon - \mu e^- V_i)/(k_B T_i)$ for $\mu = +1$ in the first integral and -1 in the second, one arrives at

$$J_i^{(a)}(e^- V_i > 0) \leq \frac{N_i (k_B T_i)^2}{h} \left[P(0) + P\left(\frac{e^- V_i}{k_B T_i}\right) \right], \quad (17)$$

having defined $P(x) \equiv \int_x^{\infty} d\xi \xi / [1 + \exp(\xi)]$.

For $J_i^{(b)}(e^- V_i > 0)$, the first term in the integrand [the term of the form $(\epsilon - e^- V_i)$] is negative. Thus $J_i^{(b)}(e^- V_i > 0)$ is most positive when the j, v sum is as negative as possible, and this is when the Fermi functions $f_j^v(\epsilon) = 1$ for all terms with $j \neq i$ or $v \neq +1$. Then using Eq. (5) to write the sum over $(j, v) \neq (i, \mu)$ in terms of the (i, μ) element of the sum, one sees that $J_i^{(b)} \leq - \int_0^{e^- V_i} \frac{d\epsilon}{h} (\epsilon - e^- V_i) [N_i - \mathcal{T}_{ii}^{+1,+1}(\epsilon)] [1 - f_i^{+1}(\epsilon)]$, which is most positive when $\mathcal{T}_{ii}^{+1,+1} = 0$. Taking this upper bound, one can make the substitution $\xi = (\epsilon - e^- V_i)/(k_B T_i)$, and use the fact that $[1 - f(\xi)] = f(-\xi)$, thus arriving at

$$J_i^{(b)}(e^- V_i > 0) \leq \frac{N_i (k_B T_i)^2}{h} \left[P(0) - P\left(\frac{e^- V_i}{k_B T_i}\right) \right]. \quad (18)$$

Taking the sum of Eqs. (17) and (18) and noting that $P(0) = -\text{Li}_2(-1) = \pi^2/12$, where $\text{Li}_2(z)$ is a dilogarithm function, one arrives at Eq. (3). Redoing the derivation for $e^- V_i < 0$, gives different results for $J_i^{(a)}$ and $J_i^{(b)}$, but their sum is the same as for $e^- V_i > 0$, thus the inequality in Eq. (3) holds for all V_i .

For *passive* cooling, the bound is a fermionic analogue of the Stefan-Boltzmann law of black-body radiation.⁵⁰ To reach the bound J_i^{qb} , one couples reservoir i to a zero-temperature reservoir with the same chemical potential, through a contact containing N_i modes.⁴⁹ To achieve the bound with *active* cooling (thermoelectrically driving heat against a thermal gradient) is more complicated. I will discuss it elsewhere⁵⁸ and show that for coherent two-terminal devices, it cannot exceed $\frac{1}{2} J^{\text{qb}}$.

VIII. PHENOMENOLOGICAL TREATMENT OF DECOHERENCE AND RELAXATION

The scattering theory, used above, includes electrostatic interaction effects but not dynamic interaction effects. This means that neither temperature nor bias induces the decoherence or relaxation (thermalization) of the electrons as they pass through the quantum system. However, one can include these effects in the model in a *phenomenological* manner. The idea is to model a system with such dynamic interaction effects as follows.

Relaxation to a thermal state (and the associated decoherence) is modeled by fictitious reservoirs,^{25,46–48} whose bias and temperature are chosen so that the average charge and heat flows into each such reservoir are zero. “Pure dephasing” (decoherence with no relaxation)⁴⁷ is modeled by a large set of fictitious reservoirs coupled to the system via leads, which only let a given energy pass through them, and by tuning the bias on those reservoirs so that the charge and heat flows into all of them are zero.

A system without dynamic interactions, but with the fictitious reservoirs, obeys the bounds in Eqs. (1)–(3). Since the average charge and heat currents into the fictitious reservoirs are zero, the bounds on flows into the real reservoirs are the same as in the absence of the fictitious reservoirs. Thus it seems reasonable to conclude that Eqs. (1)–(3) are obeyed regardless of whether the electrons decohere and relax within the quantum system (due to electron-electron interactions) or not.

IX. LIMITS ON QUANTUM HEAT ENGINES

Consider a two-terminal thermoelectric device extracting electrical power P_{total} from a heat flow between hot (temperature T_H) and cold (temperature T_C) reservoirs. Then, $J_H > 0$ and $J_C < 0$, while the generated power is $P_{\text{gen}} = -P_{\text{total}} > 0$. The first and second laws, Eqs. (1) and (2), combine to give Carnot’s result that

$$P_{\text{gen}} \leq J_H(1 - T_C/T_H). \quad (19)$$

This places a bound on the efficiency of power extraction, $\eta = P_{\text{gen}}/J_H$, but not on the power itself. Yet, taking Eq. (19) with the quantum bound on J_H in Eq. (3), one gets a bound on the power itself,

$$P_{\text{gen}} \leq \frac{N_H \pi^2 k_B^2 T_H (T_H - T_C)}{6h}. \quad (20)$$

For a heat engine between a hot source at $T_H = 100^\circ\text{C} = 373\text{ K}$ and a cold source at $T_C = 20^\circ\text{C} = 293\text{ K}$, the maximum power per transverse mode is 15 nW.

X. LIMITS ON QUANTUM REFRIGERATORS

Consider a two-terminal device extracting heat from a cold reservoir (to keep it cold or cool it further) when the ambient temperature is T_0 and the cold reservoir’s temperature is $T_C < T_0$. Power is supplied (positive P_{total}) to extract heat from the cold reservoir (positive J_C). Combining the first and second laws, Eqs. (1) and (2), one gets the Carnot bound on refrigeration. Equation (3) gives a second quantum bound.

Together they read

$$J_C \leq \begin{cases} P_{\text{total}} T_C / (T_0 - T_C) & \text{[thermodynamic]}, \\ N_C \pi^2 (k_B T_C)^2 / 6h & \text{[quantum]}. \end{cases} \quad (21)$$

The thermodynamic bound places no limit on the heat that one can extract from the cold reservoir—one can always extract heat if one is able to provide enough electrical power. In stark contrast, the quantum bound places an absolute limit on the heat extracted.

Imagine a kitchen refrigerator consisting of thermoelectric devices, running at 100 W and cooling from room temperature $T_0 = 293\text{ K}$ to $T_C = 0^\circ\text{C} = 273\text{ K}$, then

$$J_C \leq \begin{cases} 1300\text{ W} & \text{[thermodynamic]}, \\ N_C \times 36\text{ nW} & \text{[quantum]}. \end{cases} \quad (22)$$

The quantum bound is stronger than the thermodynamic one if $N_C \lesssim 10^{10}$. A typical thermoelectric semiconductor (Fermi wavelength $\sim 100\text{ nm}$) with a cross-section of $1\text{ cm} \times 1\text{ cm}$ has $N_C \sim 10^{10}$ —the quantum bound dominates for cross-sections smaller than this.

Consider a point contact such as in Ref. 59, where typical powers are picowatts (pW). Suppose such a device is used for cooling, as proposed in Ref. 13, to refrigerate a micrometer-sized island from the cryostat temperature $T_0 \sim 1\text{ K}$ down to $T_C \sim 0.1\text{ K}$. Then

$$J_C \leq \begin{cases} 0.1\text{ pW} & \text{[thermodynamic]}, \\ N_C \times 0.005\text{ pW} & \text{[quantum]}. \end{cases} \quad (23)$$

For a single-mode point contact, the quantum bound is more important. However, the thermodynamic one dominates for 20 or more such point contacts in parallel thermally [as in Fig. 2(b) of Ref. 13].

XI. NERNST’S UNATTAINABILITY PRINCIPLE

Nernst’s unattainability principle is one of the two statements that are together referred to as the third law of thermodynamics. It says that one can never take a finite temperature reservoir down to zero temperature in a finite time. (The other part of the third law is the claim that entropy vanishes at zero temperature.) The textbook result for the heat capacity of a reservoir of free electrons is $C_i \equiv (dQ_i/dT_i) \propto T_i$. If the quantum system is extracting heat out over a long time, then the fastest rate of heat removal is given by the quantum bound, $J_i^{\text{qb}} \propto T_i^2$. Assuming this heat flow is weak enough that the reservoir remains in equilibrium, we have $-J_i^{\text{qb}} = (dQ_i/dt) = C_i(dT_i/dt)$. Thus

$$\frac{dT_i}{dt} \propto -T_i^\zeta \quad \text{with} \quad \zeta = 1. \quad (24)$$

For arbitrary ζ , one sees that $T_i = 0$ is reached in a finite time if $\zeta < 1$, but not if $\zeta > 1$. Equation (24) has the critical value $\zeta = 1$, then the temperature decays exponentially with time t ; thus it gets exponentially close to $T_i = 0$, but never quite reaches it. The point contact in Ref. 13 at large bias has $\zeta = 1$. Scattering matrices with smoother ϵ -dependencies give larger ζ , so the decay goes like $t^{-1/(\zeta-1)}$ for large t . The thermoelectric systems considered here never have $\zeta < 1$, and

so never violates the unattainability principle in the manner proposed in Ref. 30.

XII. CONCLUDING REMARKS

This work is on the fully nonlinear zero-frequency (dc) heat and charge response to time-independent potentials. It applies for any quantum device where single-electron charging effects are not significant (i.e., the single-electron charging energy is much less than the temperature or level broadening due to the coupling to reservoirs). I do not consider heat engines and refrigerators that rely on a classical or quantum pumping cycle, although work in this direction is desirable. One should

also remember that quantum transport is inherently noisy, so the energy and entropy in the quantum system fluctuate randomly on short-time scales. This noise has little effect at low frequency, as it averages out over long time but it will affect finite-frequency responses.

Finally, it is worth recalling that all the results presented here rely on only two ingredients: (i) the formulation of the Schrodinger equation as a scattering theory and (ii) the utilization of the simple *equilibrium* statistical mechanics in the reservoirs. It is remarkable that the thermodynamic laws for *nonequilibrium* transport (far outside the linear-response regime) emerge so naturally from a simple combination of these two ingredients.

- ¹H. J. Goldsmid, *Introduction to Thermoelectricity* (Springer, Heidelberg, 2009).
- ²F. J. DiSalvo, *Science* **285**, 703 (1999).
- ³A. Shakouri and M. Zebarjadi, in *Thermal Nanosystems and Nanomaterials*, edited by S. Volz (Springer, Heidelberg, 2009), Chap. 9; A. Shakouri, *Annu. Rev. Mater. Res.* **41**, 399 (2011).
- ⁴F. Giazotto, T. T. Heikkilä, A. Luukanen, A. M. Savin, and J. P. Pekola, *Rev. Mod. Phys.* **78**, 217 (2006); J. T. Muhonen, M. Meschke, and J. P. Pekola, *Rep. Prog. Phys.* **75**, 046501 (2012).
- ⁵M. Zebarjadi, K. Esfarjani, and A. Shakouri, *Appl. Phys. Lett.* **91**, 122104 (2007); *MRS Proceedings* **1044**, U10-04 (2008).
- ⁶M. Wierzbicki and R. Swirkowicz, *Phys. Rev. B* **84**, 075410 (2011).
- ⁷T. Gunst, T. Markussen, A.-P. Jauho, and M. Brandbyge, *Phys. Rev. B* **84**, 155449 (2011).
- ⁸G. Rajput and K. C. Sharma, *J. Appl. Phys.* **110**, 113723 (2011).
- ⁹A. Glatz, N. M. Chtchelkatchev, I. S. Beloborodov, and V. Vinokur, *Phys. Rev. B* **84**, 235101 (2011).
- ¹⁰B. Sothmann, R. Sánchez, A. N. Jordan, and M. Büttiker, *Phys. Rev. B* **85**, 205301 (2012).
- ¹¹B. Sothmann and M. Büttiker, *Europhys. Lett.* **99**, 27001 (2012).
- ¹²P. Trocha and J. Barnaś, *Phys. Rev. B* **85**, 085408 (2012).
- ¹³R. S. Whitney, *arXiv:1208.6130*.
- ¹⁴G. Casati, C. Mejía-Monasterio, and T. Prosen, *Phys. Rev. Lett.* **101**, 016601 (2008).
- ¹⁵D. Nozaki, H. Sevinçli, W. Li, R. Gutiérrez, and G. Cuniberti, *Phys. Rev. B* **81**, 235406 (2010).
- ¹⁶O. Entin-Wohlman, Y. Imry, and A. Aharony, *Phys. Rev. B* **82**, 115314 (2010).
- ¹⁷K. K. Saha, T. Markussen, K. S. Thygesen, and B. K. Nikolić, *Phys. Rev. B* **84**, 041412(R) (2011).
- ¹⁸O. Karlström, H. Linke, G. Karlström, and A. Wacker, *Phys. Rev. B* **84**, 113415 (2011).
- ¹⁹Y.-S. Liu, B. C. Hsu, and Y.-C. Chen, *J. Phys. Chem. C* **115**, 6111 (2011).
- ²⁰J. Gemmer, M. Michel, and G. Mahler, *Quantum Thermodynamics* (Springer-Verlag, Berlin, 2010).
- ²¹J. C. Wheeler, *Phys. Rev. A* **43**, 5289 (1991).
- ²²S. Abe and A. K. Rajagopal, *Phys. Rev. Lett.* **91**, 120601 (2003).
- ²³F. G. S. L. Brandão and M. B. Plenio, *Nat. Phys.* **4**, 873 (2008).
- ²⁴T. Sagawa and M. Ueda, *Phys. Rev. Lett.* **100**, 080403 (2008); K. Jacobs, *Phys. Rev. A* **80**, 012322 (2009).
- ²⁵P. A. Jacquet, *J. Stat. Phys.* **134**, 709 (2009).
- ²⁶L. del Rio, J. Aberg, R. Renner, O. Dahlsten, and V. Vedral, *Nature (London)* **474**, 61 (2011).
- ²⁷L. Bruneau, V. Jakšić, and C.-A. Pillet, *arXiv:1201.3190*.
- ²⁸K. Maruyama, F. Nori, and V. Vedral, *Rev. Mod. Phys.* **81**, 1 (2009).
- ²⁹A. Levy, R. Alicki, and R. Kosloff, *Phys. Rev. E* **85**, 061126 (2012).
- ³⁰M. Kolar, D. Gelbwaser-Klimovsky, R. Alicki, and G. Kurizki, *Phys. Rev. Lett.* **109**, 090601 (2012).
- ³¹In this work, “dc” is used to mean the zero-frequency heat and charge currents due to time-independent biases and temperature differences. In Sec. XII, I briefly mention the limitations of studying only this dc response.
- ³²Reference 25 discusses the second law within scattering theory but only for $I \propto V$ and without thermoelectric effects.
- ³³Ya. M. Blanter and M. Büttiker, *Phys. Rep.* **336**, 1 (2000).
- ³⁴M. Büttiker, *J. Phys.: Condens. Matter* **5**, 9361 (1993); M. Büttiker, A. Prêtre, and H. Thomas, *Phys. Rev. Lett.* **70**, 4114 (1993); *Z. Phys. B Condens. Matter* **94**, 133 (1994); T. Christen and M. Büttiker, *Phys. Rev. Lett.* **77**, 143 (1996).
- ³⁵C. Petitjean, D. Waltner, J. Kuipers, I. Adagideli, and K. Richter, *Phys. Rev. B* **80**, 115310 (2009).
- ³⁶T. Christen and M. Büttiker, *Europhys. Lett.* **35**, 523 (1996).
- ³⁷D. Sanchez and M. Büttiker, *Phys. Rev. Lett.* **93**, 106802 (2004).
- ³⁸J. Meair and P. Jacquod, *J. Phys.: Condens. Matter* **24**, 272201 (2012).
- ³⁹D. Sanchez and R. Lopez, *Phys. Rev. Lett.* **110**, 026804 (2013).
- ⁴⁰H.-L. Engquist and P. W. Anderson, *Phys. Rev. B* **24**, 1151 (1981).
- ⁴¹U. Sivan and Y. Imry, *Phys. Rev. B* **33**, 551 (1986).
- ⁴²P. N. Butcher, *J. Phys.: Condens. Matter* **2**, 4869 (1990). His Eq. (16c) contains “ $d\varepsilon_\beta$,” it should be “ $d\varepsilon f_\beta$,” there is also some inconsistency in the signs of thermoelectric coefficients, cf. Ref. 45.
- ⁴³N. R. Claughton and C. J. Lambert, *Phys. Rev. B* **53**, 6605 (1996).
- ⁴⁴P. Jacquod and R. S. Whitney, *Europhys. Lett.* **91**, 67009 (2010).
- ⁴⁵P. Jacquod, R. S. Whitney, J. Meair, and M. Büttiker, *Phys. Rev. B* **86**, 155118 (2012).
- ⁴⁶M. Büttiker, *Phys. Rev. B* **33**, 3020 (1986); *IBM J. Res. Dev.* **32**, 63 (1988); H. U. Baranger and P. A. Mello, *Phys. Rev. B* **51**, 4703 (1995).
- ⁴⁷M. J. M. de Jong and C. W. J. Beenakker, *Physica A* **230**, 219 (1996), see particularly Sec. 5.
- ⁴⁸P. A. Jacquet and C.-A. Pillet, *Phys. Rev. B* **85**, 125120 (2012).
- ⁴⁹J. B. Pendry, *J. Phys. A.: Math. Gen.* **16**, 2161 (1983).
- ⁵⁰Stefan-Boltzmann law for black-body radiation (or relativistic fermions⁶⁰ at $k_B T \gg E_F$) has $J \propto T^4$. All such laws take the

form $J \propto N(k_B T)^2$ with $N \sim A/\lambda_{\text{deBr}}^2$ for aperture cross-section A . The de Broglie wavelength is $\lambda_{\text{deBr}} \sim h/\sqrt{2mE_F}$ for nonrelativistic fermions with $E_F \gg k_B T$, while $\lambda_{\text{deBr}} \sim hc/(k_B T)$ for relativistic fermions with $k_B T \gg E_F$ or photons.

⁵¹F. Belgiorno, *J. Phys. A: Math. Gen.* **36**, 8165 (2003).

⁵²P. T. Landsberg, *Rev. Mod. Phys.* **28**, 363 (1956).

⁵³I assume the sc reservoir is a superconducting condensate without quasiparticles, i.e., the sc gap is much larger than the temperatures and biases. Quasiparticles in the superconductor can be treated as a separate electronic reservoir.

⁵⁴After the completion of this work, Refs. 55 and 56 appeared using the same method for the weakly nonlinear heat flow.

⁵⁵J. Meair and P. Jacquod, *J. Phys.: Condens. Matter* **25**, 082201 (2013).

⁵⁶R. López and D. Sánchez (private communication).

⁵⁷Upon measuring the energy ϵ relative to e^-V_{sc} , the condition for gauge invariance³⁶ becomes $\sum_{k'} (dT_{ij}^{\mu\nu}(\epsilon, \mathbf{v}_{\text{env}})/dV_{k'}) = 0$ for all ϵ and \mathbf{v}_{env} , where the sum is over all reservoir and gate voltages (including V_{sc}). This is satisfied by taking all potentials (including the screening potentials) as relative to V_{sc} .

⁵⁸R. S. Whitney (unpublished).

⁵⁹L. P. Kouwenhoven, B. J. van Wees, C. J. P. M. Harmans, J. G. Williamson, H. van Houten, C. W. J. Beenakker, C. T. Foxon, and J. J. Harris, *Phys. Rev. B* **39**, 8040 (1989).

⁶⁰See, e.g., B. Kuchowicz, *Lett. Nuovo Cimento* **8**, 942 (1973).