Colloquium: Fundamental aspects of steady state heat to work conversion

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We review theoretical approaches to analyzing efficiency of steady state heat to work conversion which is crucial in the timely problem of optimizing efficiency of small-scale heat engines and refrigerators. A rather abstract perspective of non-equilibrium statistical mechanics and dynamical system’s theory is taken to view at this very practical problem. Several recently discovered general mechanisms of optimizing the figure of merit of thermoelectric efficiency are discussed, also in connection to breaking time-reversal symmetry of the microscopic equations of motion. Applications of these theoretical and mathematical ideas to practically relevant models are pointed out.

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I. INTRODUCTION

The need of providing a sustainable energy to the world population is becoming increasingly important. It is likely that in the following decades the efforts of the scientific community will be increasingly addressed to this direction and in particular to the heat to work transformation. An important possibility under investigation is the thermoelectric power generation and refrigeration. In spite of relevant progress made in the last years the efficiency of thermoelectric technology remains too low (Dresselhaus et al., 2007; Dubi and Di Ventra, 2011; Goldsmid, 2010; Shakouri, 2011; Snyder and Toberer, 2008; Sootsman et al., 2009; Vineis et al., 2010). Indeed such efficiency depends on physical properties of a given material namely the electrical conductivity $\sigma$, the thermal conductivity $\kappa$, and the Seebeck coefficient $S$, and is expressed by a non-dimensional quantity, often called figure of merit, $ZT = (\sigma S^2/\kappa) T$ (Ioffe, 1957). High efficiency requires high $ZT$ values which seem difficult to achieve. After more than 50 years from Ioffe’s discovery that doped semiconductors exhibit a relatively large thermoelectric effect (Ioffe, 1957; Ioffe and Stil’bans, 1959), and in spite of recent achievements, the most efficient
actual devices still operate at $ZT$ around 1. Certainly, in consideration of the importance of the problem, even a small improvement would be most welcome. However, it is generally accepted that $ZT \approx 3$ is a target value for efficient competing thermoelectric technology and, so far, no clear paths exist which may lead to reach that target.

In such a situation it is probably useful to investigate a different approach namely an approach which starts from first principles i.e. from the fundamental microscopic dynamical mechanisms which determine the phenomenological laws of heat and particles transport. In this connection, as it is well known, the enormous achievements in nonlinear dynamical systems and the new tools developed have led to a much better understanding of the statistical behavior of dynamical systems. For example, the question of the derivation of the phenomenological Fourier law of heat conduction from the dynamical equations of motion has been studied in great detail (Dhar, 2008; Lepri, Livi, and Politi, 2003). Theoretical work in this direction even led to the possibility to control the heat current and devise heat diodes, transistors, and thermal logic gates (Li et al., 2012). Preliminary experimental results have also been obtained (Chang et al., 2006; Kobayashi, Teraoka, and Terasaki, 2009). We are confident that this theoretical approach, combined with the present sophisticated numerical techniques, may lead to substantial progress on the way of improving the long standing problem of thermoelectric efficiency. An additional motivation in favor of this approach is that thermoelectric technology, at small sizes (e.g. at micro or nano-scale), is expected to be more efficient than traditional conversion systems. Indeed the efficiency of mechanical engines decrease very rapidly at low power level. The recent progress in engineering nanostructured materials opens now new possibilities. The study of dynamical complexity of these structures may lead to the design of new strategies for developing materials with high thermoelectric efficiency. Nanostructures may allow to control the thermal and electrical conductivity e.g. with appropriate scattering mechanisms (Dresselhaus et al., 2007; Shakouri, 2011; Vineis et al., 2010).

In summary, what is required is a better understanding of the fundamental dynamical mechanisms which control heat and particles transport. The combined efforts of physicists and mathematicians working in nonlinear dynamical systems and statistical mechanics, condensed matter physicists, and material scientists may prove useful to contribute substantially to the progress in this field of great importance for both energy supply and the environmental concern.

The purpose of the present Colloquium is to introduce the basic tools and fundamental results on steady state heat to work conversion, mainly from a rather abstract, statistical physics and dynamical system’s perspective, yet with a clear focus toward potential applications. We hope our paper might help bridging the gap among rather diverse communities and research fields, such as non-equilibrium statistical mechanics, mathematical physics and dynamical systems, mesoscopic physics, and strongly correlated many-body systems of condensed matter. Our line of presentation is going from more abstract to more phenomenological. We start with a short overview of non-equilibrium thermodynamics in section II where fundamental results on linear response theory and Onsager reciprocity relations are discussed. In section III we then explain basic abstract definitions of thermoelectric heat to work conversion efficiency. In section IV we review the microscopic Landauer-Buttiker framework for non-interacting systems and discuss the main non-interacting concepts for controlling thermodynamic efficiency: energy filtering, external noise and probe reservoirs. We believe that most of exciting future investigations on heat to work conversion will be devoted to strongly interacting systems, therefore we set the stage in section V by reviewing state of the art on understanding thermalization in equilibrium and local-thermalization near-equilibrium in closed and open interacting systems. As the analysis of strongly interacting systems is mainly relying on numerical simulations, we outline in section VI some of the key ideas and methods for efficient simulation of non-equilibrium steady states of classical and quantum open many-body systems. In section VII we then discuss some simple models of thermoelectric engines and stress their importance from either exact-solvability or practical-relevance perspective. In section VIII we outline some phenomenological and empirical laws governing thermoelectric phenomena, with the emphasis on open theoretical problems. We conclude in Sec. IX with some remarks on future prospects of the field.

II. OVERVIEW OF BASIC CONCEPTS OF NON-EQUILIBRIUM THERMODYNAMICS

Non-equilibrium thermodynamics (Callen, 1985; de Groot and Mazur, 1984) describes processes on the basis of two types of parameters: thermodynamic forces $X_i$ (also known as generalized forces or affinities) driving irreversible processes, and the fluxes $J_i$ characterizing the response of the system to the applied forces. More specifically, we will consider a generic setup for the extraction of work from a heat flow. The system performs work $W = -Fx$ against an external force $F$, with thermodynamically conjugate variable $x$. The force can be of mechanical, chemical, or electrical nature. The thermodynamic force is $X_1 = F/T$, with $T$ being the temperature of the system. The thermodynamic flux is $J_1 = \dot{x}$, where the dot denotes the time derivative. The output power reads $P = W = -J_1 X_1 T$. We are considering heat to work conversion, that is, the work is performed by converting a part of the amount of heat $Q_1$ flowing from the hot reservoir at temperature $T_1$ (we assume $T_1 > T_2$). The thermodynamic force is $X_2 = 1/T_2 - 1/T_1$, and the heat current reads $J_2 = \dot{Q}_1$.

For instance, in thermoelectric power generation (see
Assuming the property of time-reversal invariance of the equations of motion, [Onsager, 1931] derived fundamental relations, known as Onsager reciprocal relations for the cross coefficients of the Onsager matrix: $L_{a,b} = L_{b,a}$. When an external magnetic field $B$ is applied to the system, the laws of physics remain unchanged if time $t$ is replaced by $-t$, provided that simultaneously the magnetic field $B$ is replaced by $-B$. In this case the Onsager-Casimir relations [Casimir, 1945; Onsager, 1931] read

$$L_{a,b}(B) = L_{b,a}(-B).$$

At zero magnetic field, we recover the Onsager reciprocal relations $L_{a,b} = L_{b,a}$. Note that only the diagonal coefficients are bound to be even functions of the magnetic field: $L_{a,a}(B) = L_{a,a}(-B)$, while in general, for $a \neq b$, $L_{a,b}(B) \neq L_{a,b}(-B)$.

The Onsager coefficients are related to the familiar transport coefficients. In the case of thermoelectricity we have

$$G = \left( \frac{J_1}{\Delta V} \right)_{T=0} = \frac{L_{11}}{T},$$

$$\Xi = \left( \frac{J_2}{\Delta T} \right)_{J_1=0} = \frac{1}{T^2} \det L_{11},$$

$$S = -\left( \frac{\Delta V}{\Delta T} \right)_{J_1=0} = \frac{1}{T} \frac{L_{12}}{L_{11}},$$

where $G$ is the (isothermal) electric conductance, $\Xi$ the thermal conductance, $S$ the thermopower (or Seebeck coefficient), and $L$ denotes the Onsager matrix with matrix elements $L_{a,b}$ $(a, b = 1, 2)$. The Peltier coefficient

$$\Pi = \left( \frac{J_2}{J_1} \right)_{T=0} = \frac{L_{21}}{L_{11}}$$

is related to the thermopower via the Onsager reciprocal relation: $\Pi(B) = TS(-B)$. Note that the Onsager-Casimir relations imply $G(-B) = G(B)$ and $\Xi(-B) = \Xi(B)$, but in general do not impose the symmetry of the Seebeck coefficient under the exchange $B \rightarrow -B$.

We can eliminate in the phenomenological equations the Onsager matrix elements in favor of the transport coefficients $G, \Xi, S, \Pi$, thus obtaining

$$\begin{cases} J_1 = G \Delta V + GS \Delta T, \\ J_2 = G \Pi \Delta V + (\Xi + GS \Pi) \Delta T. \end{cases}$$

By eliminating $\Delta V$ from these two equations we obtain an interesting interpretation of the Peltier coefficient. Indeed, the entropy current reads

$$J_s = \frac{J_2}{T} = \frac{\Pi}{T} J_1 + \frac{\Xi}{T} \Delta T.$$
Hence, $\Pi/T$ can be understood as the entropy transported by the electron flow $J_1$. Since $J_1 = eJ_p$, each electron carries an entropy of $e\Pi/T$. This contribution to the entropy current adds to the last term in (10), which is independent of the electric current. For time-reversal symmetric systems, the same interpretation applies to the Seebeck coefficient, since in this case $S = \Pi/T$. The heat flow $J_2 = Tj_2$ is the sum of two terms, $\Pi J_1$ and $\Xi \Delta T$. While the last term is irreversible, the first one is reversible, that is, it changes sign when reversing the direction of the current. It can be intuitively understood that efficient energy conversion requires to minimize irreversible, dissipative processes with respect to reversible processes. Hence, it is desirable to have a large Peltier coefficient and a small heat conductance.

The heat dissipation rate $\dot{Q}$ can be computed from the entropy production rate (2):

$$\dot{Q} = T\dot{S} = \frac{J_1^2}{G} + \frac{\Xi}{T}(\Delta T)^2 + J_1(\Pi - TS)\frac{\Delta T}{T},$$  \hspace{1cm} (11)

where the first term is the Joule heating, the second term is the heat lost by thermal resistance and the last term, which disappears for time-reversal symmetric systems, can be negative when $J_1(\Pi - TS) < 0$, thus reducing the dissipated heat. It is clear from (11) that to minimize dissipative effects for a given electric current and thermal gradient, we need a large electric conductance and low thermal conductance.

Under the assumption of local equilibrium, we can write coupled equations like (1), connecting local fluxes to local forces, expressed in terms of gradients $\nabla \mu$, $\nabla T$ rather than $\Delta \mu$, $\Delta T$ (see, for instance, Callen (1985)). In this case, Eqs. (3) and (6) can be written with on the left-hand side the electric conductivity $\sigma$ and the thermal conductivity $\kappa$ rather than the conductances $G$ and $\Xi$.

### III. THERMODYNAMIC EFFICIENCIES

#### A. Finite-time thermodynamics

A cornerstone result goes back to Carnot (1824). In a cycle between two reservoirs at temperatures $T_1$ and $T_2$ ($T_1 > T_2$), the efficiency $\eta$, defined as the ratio of the performed work $W$ over the heat $Q_1$ extracted from the high temperature reservoir, is bounded by the Carnot efficiency $\eta_C$:

$$\eta = \frac{W}{Q_1} \leq \eta_C = 1 - \frac{T_2}{T_1}. \hspace{1cm} (12)$$

The Carnot efficiency is obtained for a quasi-static transformation which requires infinite time and therefore the extracted power, in this limit, reduces to zero. An important question is how much the efficiency deteriorates when the cycle is operated in a finite time. This is the central question in the field of finite-time thermodynamics (for a recent review, see Andersen (2011)). In particular, endoreversible thermodynamics views a thermodynamic system as a collection of reversible subsystems which interact in an irreversible manner.

A very important concept is that of efficiency at maximum power. An upper bound for the output power $W$ of a heat engine can be deduced for the endoreversible Carnot-Ahborn (CA) engine depicted in Fig. 1. The CA engine consists of two heat baths at temperatures $T_1$ and $T_2$ and a reversible Carnot engine operating between internal temperatures $T_{1i}$ and $T_{2i}$ ($T_1 > T_{1i} > T_{2i} > T_2$). The two processes of heat transfer, from the hot reservoir to the system and from the system to the cold reservoir, are the only irreversible processes in the CA engine. The output work $W$ is the difference between the heat $Q_1$ absorbed from the hot reservoir and the heat $-Q_2$ ($Q_1 > 0$, $Q_2 < 0$) evacuated to the cold reservoir ($W = Q_1 - Q_2$). Heat transfers take place during the isothermal strokes of the Carnot cycle, with the working fluid (the system) at internal temperatures $T_{1i}$ and $T_{2i}$. We further assume that the rate of heat flow $Q_k(\dot{Q}_k)$ is proportional to the temperature difference $T_1 - T_{1i}$ ($T_2 - T_{2i}$) between the hot (cold) reservoir and the working fluid, the proportionality factor being the heat conductance $\Xi_k(\Xi)$.

Finally, we need a time $t_1(t_2)$ to transfer an amount $Q_1(Q_2)$ of heat, so that

$$Q_1 = \Xi_1 t_1(T_1 - T_{1i}), \hspace{1cm} (13)$$

$$-Q_2 = \Xi_2 t_2(T_{2i} - T_2). \hspace{1cm} (14)$$

Taking into account that the internal Carnot engine operating between temperatures $T_{1i}$ and $T_{2i}$ has efficiency $\eta_{C_i} = 1 - T_{2i}/T_{1i} = 1 + Q_2/Q_1$ and using the relations $Q_1 + Q_2 = W$ and $t_j = Q_j/\Xi_j(T_j - T_{ji})$, $(j = 1, 2)$, we can express the power as

$$P = \frac{W}{t} = \frac{Q_1 + Q_2}{t} = \frac{k_1 t_1(T_1 - T_{1i}) + k_2 t_2(T_2 - T_{2i})}{t_1 + t_2}. \hspace{1cm} (15)$$

By maximizing the power with respect to the internal temperatures $T_{1i}$ and $T_{2i}$ we obtain

$$P_{\text{max}} = \Xi_1 \Xi_2 \left(\frac{\sqrt{T_1} - \sqrt{T_2}}{\sqrt{\Xi_1 + \Xi_2}}\right)^2. \hspace{1cm} (17)$$

The efficiency at the maximum power $P_{\text{max}}$, commonly referred to as Curzon-Ahborn upper bound (Chambadal, 1974; Rubik, 1979; Hoffmann, Burzler, and Schubert, 1997).
and therefore the range of validity of the Curzon-Ahlborn cycle. The two heat baths at temperatures $T_1$ and $T_2$ are coupled for times $t_1$ and $t_2$ to the system $S$ (the working fluid, with output work per cycle equal to $W$) by heat conductances $\Xi_1$ and $\Xi_2$. The system $S$ is considered as a Carnot engine operating between the internal temperatures $T_{1i}$ and $T_{2i}$ ($T_1 > T_{1i} > T_{2i} > T_2$).

Figure 2: Schematic drawing of the endoreversible engine for the Curzon-Ahlborn cycle. The two heat baths at temperatures $T_1$ and $T_2$ are coupled for times $t_1$ and $t_2$ to the system $S$ (the working fluid, with output work per cycle equal to $W$) by heat conductances $\Xi_1$ and $\Xi_2$. The system $S$ is considered as a Carnot engine operating between the internal temperatures $T_{1i}$ and $T_{2i}$ ($T_1 > T_{1i} > T_{2i} > T_2$).

The CA efficiency was derived for the Carnot cycle in the limit of low and symmetric dissipation by Esposito et al. (2010a). They considered a Carnot engine which operates under reversible conditions at the Carnot efficiency when the cycle duration becomes infinitely long. In that limit, the system entropy increase $\Delta S = Q_1/T_1$ during the isothermal transformation at the hot temperature $T_1$ is equal to the system entropy decrease $-\Delta S = Q_2/T_2$ during the isothermal transformation at the cold temperature $T_2$. Hence, there is no overall entropy production and the Carnot efficiency $\eta_C = 1 + Q_2/Q_1 = 1 - T_2/T_1$ is achieved. Esposito et al. (2010a) consider the weak dissipation regime and assume that the system relaxation is much faster than the times $t_1$ and $t_2$ spent in the isothermal strokes, so that the overall cycle duration is a good approximation given by $t_1 + t_2$. In the low dissipation regime the entropy production is proportional to $1/t_1$ and $1/t_2$, so that it vanishes in the limit of infinite-time cycle where it is supposed that the Carnot efficiency is recovered. Therefore the amount of heat entering the system from the hot (cold) reservoir is, to first order in $1/t_1$ and $1/t_2$,

$$Q_1 = T_1 \left( \Delta S - \frac{\Sigma_1}{t_1} \right), \quad Q_2 = T_2 \left( -\Delta S - \frac{\Sigma_2}{t_2} \right),$$

(20) with $\Sigma_1$ and $\Sigma_2$ coefficients depending on the specific implementation. The maximum of the output power

$$P = \frac{Q_1 + Q_2}{t_1 + t_2} = \frac{(T_1 - T_2) \Delta S - T_1 \Sigma_1/t_1 - T_2 \Sigma_2/t_2}{t_1 + t_2},$$

(21) is obtained when $\partial P/\partial t_1 = \partial P/\partial t_2 = 0$. This leads to the efficiency at the maximum output power

$$\eta(P_{\text{max}}) = \frac{\eta_C \left( 1 + \sqrt{\frac{T_2 \Sigma_2}{T_1 \Sigma_1}} \right)}{1 + \sqrt{\frac{T_2 \Sigma_2}{T_1 \Sigma_1}} + \frac{T_1}{T_2} \left( 1 - \frac{T_2}{T_1} \right)}.$$

(22)

Note that this result was also obtained in the context of stochastic thermodynamics by Schmiedl and Seifert (2008). Within linear response, the Curzon-Ahlborn efficiency is recovered for symmetric dissipation, $\Sigma_1 = \Sigma_2$. From (22) we obtain

$$\eta_+ = \frac{\eta_C}{2} \leq \eta(P_{\text{max}}) \leq \eta_+ = \frac{\eta_C}{2} - \eta_C.$$
with the lower and upper bound reached in the limits of completely asymmetric dissipation, for $\Sigma_2/\Sigma_1 \to \infty$ and $\Sigma_2/\Sigma_1 \to 0$, respectively. The lower and upper bound coincide in the linear response regime where $\eta_\text{L} = \eta_\text{U} = \eta_{\text{CA}} = \eta_C/2$. The same upper bound as in [20] was obtained with a different approach by Gaveau, Moreau, and Schulman (2010).

B. Figure of merit for thermodynamic efficiency

Within the linear response, the efficiency of steady state heat to work conversion reads

$$\eta = \frac{\dot{W}}{Q_1} = -\frac{T X_1 J_1}{J_2} = -\frac{T X_1 (L_{11} X_1 + L_{12} X_2)}{L_{21} X_1 + L_{22} X_2}, \quad (24)$$

where $J_2 = \dot{Q}_1 > 0$ and the power $P = \dot{W} > 0$. The maximum of $\eta$ over $X_1$, for fixed $X_2$, is achieved for

$$X_1 = \frac{L_{22}}{L_{21}} \left(-1 + \sqrt{\frac{\det L}{L_{11} L_{22}}} \right) X_2. \quad (25)$$

For systems with time-reversal symmetry (so that $L_{12} = L_{21}$), the maximum efficiency is given by

$$\eta_{\text{max}} = \eta_C \frac{\sqrt{ZT + 1} - 1}{\sqrt{ZT + 1} + 1}, \quad (26)$$

where the figure of merit

$$ZT = \frac{L_{12}^2}{\det L} \quad (27)$$

is a dimensionless parameter. In the case of thermoelectricity, $ZT$, expressed in terms of the electric conductance $G$, the thermal conductance $\Xi$ and the thermopower $S$, reads

$$ZT = \frac{G S^2}{\Xi} T. \quad (28)$$

For systems with local equilibrium, the figure of merit can be expressed in terms of the material constants, the electric conductivity $\sigma$ and the thermal conductivity $\kappa$, rather than $G$ and $\Xi$: $ZT = (\sigma S^2/\kappa) T$. The only restriction imposed by thermodynamics (more precisely, by the positivity of the entropy production rate) is $ZT \geq 0$ and $\eta_{\text{max}}$ is a monotonous growing function of $ZT$, with $\eta_{\text{max}} = 0$ when $ZT = 0$ and $\eta_{\text{max}} \to \eta_C$ when $ZT \to \infty$ (full curve in Fig. 3).

Note that $ZT$ diverges (thus leading to Carnot efficiency) if and only if the the Onsager matrix $L$ is ill-conditioned, namely the condition number

$$\text{cond}(L) = \frac{\text{Tr}(L)^2}{\det L} \quad (29)$$

diverges and therefore the system (1) becomes singular.

That is, $J_2 = c J_1$, the proportionality factor $c$ being independent of the values of the applied thermodynamic forces. In short, within linear response (and without external magnetic fields or other effects breaking time-reversal symmetry) the Carnot efficiency is obtained if and only if charge and energy flows are proportional (tight coupling condition, also known as strong coupling in the literature).

The output power

$$P = -T X_1 J_1 = -T X_1 (L_{11} X_1 + L_{12} X_2) \quad (30)$$

is maximal when

$$X_1 = -\frac{L_{12}}{2 L_{11}} X_2 \quad (31)$$

and is given by

$$P_{\text{max}} = \frac{T L_{12}^2}{4 L_{11}} X_2^2 = \frac{\eta_C L_{12}^2}{4 L_{11}} X_2. \quad (32)$$

Using Eqs. (5) and (7) we can also write

$$P_{\text{max}} = \frac{1}{4} S^2 G (\Delta T)^2. \quad (33)$$

We can see from this last equation that the maximum power is directly set by the combination $S^2 G$, known for this reason as power factor. Note that $P$ is a quadratic function of $X_1$ and the maximum is obtained for the value $X_{\text{max}}$ corresponding to half of the stopping force,

$$X_{\text{stop}} = \frac{L_{12}}{L_{11}} X_2, \quad (34)$$

that is, to the value for which the motion halts, $J_1 = 0$. For systems with time reversal symmetry, the efficiency at maximum power reads [Van den Broeck 2003]

$$\eta(P_{\text{max}}) = \frac{\eta_C}{2} \frac{ZT}{ZT + 2}. \quad (35)$$
This quantity also is a monotonous growing function of $ZT$, with $\eta(P_{\max}) = 0$ when $ZT = 0$ and $\eta(P_{\max}) \rightarrow \eta_C/2$ when $ZT \rightarrow \infty$ (dashed curve in Fig. 3). Note that for small $ZT$ we have $\eta(P_{\max}) \approx \eta_{\text{max}} \approx (\eta_C/4)ZT$. The difference between $\eta(P_{\max})$ and $\eta_{\text{max}}$ becomes relevant only for $ZT > 1$.

Note that we can establish an efficiency versus power plot. We can express the ratio between the power at a given value of $X_1$ and the maximum power as a function of the force ratio $r = X_1/X_{1\text{stop}}$:

$$\frac{P}{P_{\max}} = 4r(1-r). \quad (36)$$

This relation can be inverted:

$$r = \frac{1}{2} \left[ 1 \pm \sqrt{1 - \frac{P}{P_{\max}}} \right], \quad (37)$$

with the plus sign for $r \geq 1/2$ and the minus sign for $r \leq 1/2$. Inserting this latter relation into Eq. (21) we can express the efficiency (normalized to the Carnot efficiency) as

$$\frac{\eta}{\eta_C} = \frac{P}{2 \left( 1 + \frac{2}{ZT} \sqrt{1 - \frac{P}{P_{\max}}} \right)}, \quad (38)$$

where the minus sign corresponds to $r \geq 1/2$, the plus sign to $r \leq 1/2$. Plots of the normalized efficiency versus the normalized power are shown in Fig. 4, for several values of the figure of merit $ZT$. Note that, while for low values of $ZT$ the maximum efficiency is close to the efficiency at maximum power, for large $ZT$ the difference becomes relevant (see also Fig. 3). For $ZT = \infty$ the Carnot efficiency is achieved at the stopping power $X_1 = X_{1\text{stop}} (r = 1)$.

When the force ratio exceeds one, $r > 1$, the thermoelectric device works as a refrigerator. In this case the most important benchmark is the efficiency of an ideal, dissipationless refrigerator. Since the ratio $\eta^{(r)}_{\text{max}}/\eta^{(r)}_C$ for refrigeration is equal to the ratio $\eta_{\text{max}}/\eta_C$ for thermoelectric power generation, $ZT$ is the figure of merit for both regimes.

C. Systems with broken time-reversal symmetry

The same analysis as above can be repeated when time-reversal symmetry is broken, say by a magnetic field $B$ (or by other effects such as the Coriolis force). In this case the maximum efficiency and the efficiency at maximum power are both determined by two parameters (Benenti, Saito, and Casati, 2011): the asymmetry parameter

$$x = \frac{L_{12}}{L_{21}} = \frac{S(B)}{S(-B)} \quad (40)$$

and the “figure of merit”

$$y = \frac{L_{12}L_{21}}{\det L} = \frac{G(B)S(B)S(-B)}{\Xi(B)} T. \quad (41)$$

The maximum efficiency reads

$$\eta_{\text{max}} = \eta_C x \sqrt{y + 1} \left( \frac{1}{y + 1} - 1 \right), \quad (42)$$

while the efficiency at maximum power is

$$\eta(P_{\max}) = \frac{\eta_C xy}{2 + 2 y}. \quad (43)$$

In the particular case $x = 1$, $y$ reduces to the $ZT$ figure of merit of the time-symmetric case, Eq. (12) reduces to Eq. (20), and Eq. (43) to Eq. (35). While thermodynamics does not impose any restriction on the attainable values of the asymmetry parameter $x$, the positivity of entropy production implies $h(x) \leq y \leq 0$ if $x \leq 0$ and $0 \leq y \leq h(x)$ if $x \geq 0$, where the function $h(x) = 4x/(x - 1)^2$. Note that $\lim_{x \rightarrow 1} h(x) = \infty$ and therefore there is no upper bound on $y(x = 1) = ZT$. For a given value of the asymmetry $x$, the maximum (over $y$) $\bar{\eta}(P_{\max})$ of $\eta(P_{\max})$ and the maximum $\bar{\eta}_{\text{max}}$ of $\eta_{\text{max}}$ are obtained for $y = h(x)$:

$$\bar{\eta}(P_{\max}) = \eta_C \frac{x^2}{x^2 + 1}, \quad (44)$$

This relation can be inverted:

$$x = \frac{1}{2} \left[ 1 \pm \sqrt{1 - \frac{P}{P_{\max}}} \right], \quad (37)$$

with the plus sign for $r \geq 1/2$ and the minus sign for $r \leq 1/2$. Plots of the normalized efficiency versus the normalized power are shown in Fig. 4, for several values of the figure of merit $ZT$. Note that, while for low values of $ZT$ the maximum efficiency is close to the efficiency at maximum power, for large $ZT$ the difference becomes relevant (see also Fig. 3). For $ZT = \infty$ the Carnot efficiency is achieved at the stopping power $X_1 = X_{1\text{stop}} (r = 1)$.

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$$y = \frac{L_{12}L_{21}}{\det L} = \frac{G(B)S(B)S(-B)}{\Xi(B)} T. \quad (41)$$

The maximum efficiency reads

$$\eta_{\text{max}} = \eta_C x \sqrt{y + 1} \left( \frac{1}{y + 1} - 1 \right), \quad (42)$$

while the efficiency at maximum power is

$$\eta(P_{\max}) = \frac{\eta_C xy}{2 + 2 y}. \quad (43)$$

In the particular case $x = 1$, $y$ reduces to the $ZT$ figure of merit of the time-symmetric case, Eq. (12) reduces to Eq. (20), and Eq. (43) to Eq. (35). While thermodynamics does not impose any restriction on the attainable values of the asymmetry parameter $x$, the positivity of entropy production implies $h(x) \leq y \leq 0$ if $x \leq 0$ and $0 \leq y \leq h(x)$ if $x \geq 0$, where the function $h(x) = 4x/(x - 1)^2$. Note that $\lim_{x \rightarrow 1} h(x) = \infty$ and therefore there is no upper bound on $y(x = 1) = ZT$. For a given value of the asymmetry $x$, the maximum (over $y$) $\bar{\eta}(P_{\max})$ of $\eta(P_{\max})$ and the maximum $\bar{\eta}_{\text{max}}$ of $\eta_{\text{max}}$ are obtained for $y = h(x)$:

$$\bar{\eta}(P_{\max}) = \eta_C \frac{x^2}{x^2 + 1}, \quad (44)$$
The functions \( \bar{\eta}(P_{\text{max}})(x) \) and \( \bar{\eta}_{\text{max}}(x) \) are drawn in Fig. 5. In the case \( |x| > 1 \), it is in principle possible to overcome the CA limit within linear response and to reach the Carnot efficiency, for increasingly smaller and smaller figure of merit \( y \) as the asymmetry parameter \( x \) increases. The Carnot efficiency is obtained for \( \det L = (L_{12} - L_{21})^2/4 > 0 \) when \( |x| > 1 \), that is, the tight coupling condition is not fulfilled.

The output power at maximum efficiency reads

\[
P(\bar{\eta}_{\text{max}}) = \frac{\bar{\eta}_{\text{max}}}{4} \left| \frac{L_{12}^2 - L_{21}^2}{L_{11}} \right| X_2.
\]  

Therefore, always within linear response, it is allowed from thermodynamics to have Carnot efficiency and nonzero power simultaneously when \( |x| > 1 \). Such a possibility can be understood on the basis of the following argument (Brandner, Saito, and Seifert, 2013; Brandner and Seifert, 2013). We first split each current \( J_i \) into a reversible and an irreversible part, defined by

\[
J_i^{\text{rev}} = \sum_{j=1}^{2} \frac{L_{ij} - L_{ji}}{2} X_j, \quad J_i^{\text{irr}} = \sum_{j=1}^{2} \frac{L_{ij} + L_{ji}}{2} X_j.
\]  

It is readily seen from Eq. 2 and 47 that only the irreversible part of the currents contributes to the entropy production:

\[
\mathcal{S} = J_1^{\text{irr}} X_1 + J_2^{\text{irr}} X_2.
\]

The reversible currents \( J_i^{\text{rev}} \) vanish for \( B = 0 \). On the other hand, for broken time-reversal symmetry the reversible currents can in principle become arbitrarily large, giving rise to the possibility of dissipationless transport.

While in the time-reversal case the linear response normalized maximum efficiency \( \bar{\eta}_{\text{max}}/\eta_C \) and coefficient of performance \( \bar{\eta}^{(r)}_{\text{max}}/\eta_C^{(r)} \) for power generation and refrigeration coincide, this is no longer the case with broken time-reversal symmetry. For refrigeration the maximum value of the coefficient of performance reads

\[
\eta^{(r)}_{\text{max}} = \eta_C^{(r)} \frac{1}{x} \frac{\sqrt{y + 1} - 1}{\sqrt{y + 1} + 1}.
\]

For small fields, \( x \) is in general a linear function of the magnetic field, while \( y \) is by construction an even function of the field. As a consequence, a small external magnetic field either improves power generation and worsens refrigeration or vice-versa, while the average efficiency

\[
\frac{1}{2} \left[ \frac{\eta_{\text{max}}(B)}{\eta_C} + \frac{\eta_{\text{max}}^{(r)}(B)}{\eta_C^{(r)}} \right] = \frac{\eta_{\text{max}}(0)}{\eta_C} = \frac{\eta_{\text{max}}^{(r)}(0)}{\eta_C^{(r)}}.
\]  

FIG. 5 Ratio \( \eta/\eta_C \) as a function of the asymmetry parameter \( x \), with \( \eta = \bar{\eta}(P_{\text{max}}) \) (dashed curve) and \( \bar{\eta} = \bar{\eta}_{\text{max}} \) (full curve). For \( x = 1 \), \( \bar{\eta}(P_{\text{max}}) = \eta_C/2 \) and \( \bar{\eta}_{\text{max}} = \eta_C \) are obtained for \( y(x = 1) = ZT = \infty \).

Onsager relations do not impose the symmetry \( x = 1 \), i.e., we can have \( S(B) \neq S(-B) \). However, as discussed in Sec. IV.B below, in the non-interacting case \( S(-B) = S(B) \) as a consequence of the symmetry properties of the scattering matrix (Datta, 1997). On the other hand, this symmetry may be violated when electron-phonon and electron-electron interactions are taken into account. While the Seebeck coefficient has always been found to be an even function of the magnetic field in two-terminal purely metallic mesoscopic systems (Godijn et al., 1999; van Langen, Silvestrov, andBeenakker, 1998), measurements for certain orientations of a bismuth crystal (Wolfe, Smith, and Haszko, 1963), Andreev interferometer experiments (Eom, Chien, and Chandrasekhar, 1998) and recent theoretical studies (Jacquod and Whitney, 2010; Saito et al., 2013; Sánchez and Serra, 2011) have shown that systems in contact with a superconductor or subject to inelastic scattering can exhibit non-symmetric thermopower, i.e., \( S(-B) \neq S(B) \). So far, investigations of various classical (Horvat et al., 2012) and quantum (Saito et al., 2011) dynamical models have shown arbitrarily large values of the asymmetry \( x \), but correspondingly with low efficiency. However, efficiency at maximum power beyond the CA limit for \( x > 1 \) has been recently shown in (Balachandran, Benenti, and Casati, 2013; Brandner, Saito, and Seifert, 2013; Brandner and Seifert, 2013) (see Sec. IV.B below).
IV. NON-INTERACTING SYSTEMS.
LANDAUER-BÜTTIKER FORMALISM

Exact calculation of thermodynamic efficiencies is possible for non-interacting models by means of the Landauer-Büttiker approach. This approach describes the coherent flow of electrons through a channel. All dissipative and phase-breaking processes are limited to the contacts (reservoirs). The electric and thermal currents are expressed in terms of the scattering (transmission) properties of the system (Datta, 1995; Imry, 1997):

\[ J_1 = \frac{e}{h} \int_{-\infty}^{\infty} dE \tau(E) [f_1(E) - f_2(E)], \]

\[ J_2 = \frac{1}{h} \int_{-\infty}^{\infty} dE (E - \mu_1) \tau(E) [f_1(E) - f_2(E)]. \]

Here, \( e \) is the electron charge, \( h \) the Planck’s constant, \( \tau(E) \) the transmission probability for a particle with energy \( E \) to transit from terminal (reservoir) 1 to terminal 2 \((0 \leq \tau(E) \leq 1)\), and \( f_i(E) = \frac{\exp[(E - \mu_i)/k_BT]}{[\exp[(E - \mu_i)/k_BT] + 1]^{-1}} \) is the Fermi distribution of the particles injected from reservoir \( i \). Note that \( J_2 = \dot{Q}_1 \) is the heat current from the hot reservoir \((T_1 > T_2)\).

The Onsager coefficients \( L_{a,b} \) can be derived from the linear expansion of the currents \( (51) \) and \( (52) \). We obtain

\[ L_{11} = e^2 T I_0, \quad L_{12} = L_{21} = e^2 T I_1, \quad L_{22} = T I_2. \]

Here, the integrals \( I_n \) have been defined as

\[ I_n = \frac{1}{h} \int_{-\infty}^{\infty} dE (E - \mu)^n \tau(E) \left( -\frac{\partial f}{\partial E} \right), \]

where the derivative of the Fermi function, \( -\partial f/\partial E = 1/4k_BT \cosh^2[(E - \mu)/k_BT] \), is a bell-shaped function centered at \( \mu \) and has a width of the order of \( k_BT \). It immediately follows that conductances and the thermopower can be expressed in terms of the integrals \( I_n \):

\[ G = e^2 I_0, \quad \Xi = \frac{1}{T} \left( I_2 - \frac{I_1^2}{I_0} \right), \quad S = \frac{1}{eT} \frac{I_1}{I_0}. \]

While Landauer-Büttiker approach describes coherent quantum transport, semiclassical transport can be described by means of the Boltzmann equation. Here we consider transport processes that occur much slower than the relaxation to local equilibrium and treat collisions within the relaxation-time approximation (Ashcroft and Mermin, 1978). That is, collisions drive the electronic system to local thermodynamic equilibrium under the assumption that the distribution of electrons emerging from collisions does not depend on the structure of their non-equilibrium distribution prior to the collision and that collisions do not alter local equilibrium. We can then express conductivities and the thermopower in terms of the integrals

\[ K_n = \int_{-\infty}^{\infty} dE (E - \mu)^n \Sigma(E) \left( -\frac{\partial f}{\partial E} \right). \]

Here \( \Sigma(E) \approx D(E)\nu(E)^2/E \) is the transport distribution function, where \( D(E) \) is the density of states, \( \nu(E) \) is the electron relaxation time, and \( \nu(E) \) is the electron group velocity. We obtain (Mahan and Söf, 1996)

\[ \sigma = e^2 K_0, \quad \kappa = 1 \left( \frac{K_2 - \frac{K_1^2}{K_0}}{I_1} \right) = 1 \left( \frac{I_1}{I_1 - I_2} \right) \to \infty. \]

A. Energy filtering

An interesting question is what transmission function \( \tau(E) \) (or transport distribution function \( \Sigma(E) \)) in the Boltzmann approach provides the largest thermodynamic efficiencies (Mahan and Söf, 1996). While Landauer-Büttiker approach describes coherence, the Boltzmann approach can provide the largest thermodynamic efficiency. As discussed in Sec. III.B, ZT diverges if and only if the Onsager matrix \( L \) is ill-conditioned, that is, in the tight coupling limit \( J_2 = cJ_1 \), with \( c \) independent of the applied forces. The tight coupling condition is achieved when the transmission is possible only within a tiny energy window around \( E = E^* \) (energy filtering). In this case from Eq. \( (54) \), we obtain

\[ I_n \approx (E^* - \mu)^n I_0, \]

and therefore

\[ ZT = \frac{GS^2}{\Xi} T = \frac{I_1^2}{I_0 I_2 - I_1^2} \to \infty. \]

The energy filtering mechanism allows us to achieve the Carnot efficiency also beyond linear response (Humphrey et al., 2002; Humphrey and Linke, 2005). In this case, assuming \( T_1 > T_2, \mu_1 < \mu_2, J_1 > 0 \) and \( J_2 > 0 \), the efficiency for power generation is given by

\[ \eta = \frac{(\mu_2 - \mu_1)/e}{J_1/J_2} \]

\[ = \frac{\int_{-\infty}^{\infty} dE \tau(E) |f_1(E) - f_2(E)|}{\int_{-\infty}^{\infty} dE (E - \mu_1) \tau(E)|f_1(E) - f_2(E)|}. \]

When the transmission is possible only within a tiny energy window around \( E = E^* \), the efficiency reads

\[ \eta = \frac{\mu_2 - \mu_1}{E^* - \mu_1}. \]

We have \( f_1(E^*) = f_2(E^*) \), namely the occupation of states is the same in the two reservoirs at different temperatures and electrochemical potentials, when

\[ \frac{E^* - \mu_1}{T_1} = \frac{E^* - \mu_2}{T_2} \Rightarrow E^* = \frac{\mu_2 T_1 - \mu_1 T_2}{T_1 - T_2}. \]

Substituting such \( E^* \) into Eq. \( (60) \), we obtain the Carnot efficiency \( \eta = \eta_C = 1 - T_2/T_1 \). Note that Carnot efficiency is obtained in the limit \( J_1 \to 0 \), corresponding to reversible transport (zero entropy production) and zero output power.

High values of ZT can still be achieved if rather than delta-shaped transmission function one considers...
sharply rising transmission functions (O’Dwyer et al., 2003; Vashaee and Shakouri, 2004). The advantage of step over narrow transmission functions is that good efficiencies can be obtained without greatly reducing power.

B. Noise and probe reservoirs

The Landauer-Büttiker approach provides a rigorous framework for the description of coherent quantum transport. The transport can be only partially coherent when inelastic scattering, due to the interactions of the electrons with phonons, photons, and other electrons, is taken into account. A very convenient way to introduce inelastic scattering is by means of a third terminal (or conceptual probe), whose parameters (temperature and chemical potential) are chosen self-consistently so that there is no net average flux of particles and heat between this terminal and the system (see Fig. 6). In mesoscopic physics, probe reservoirs are commonly used to simulate phase-breaking processes in partially coherent quantum transport, since they introduce phase-relaxation without energy damping (Büttiker, 1988). The advantage of such approach lies in its simplicity and independence from microscopic details of inelastic processes. Probe terminals have been widely used in the literature and proved to be useful to unveil nontrivial aspects of phase-breaking processes (Bandyopadhyay and Segal, 2011; Bolsterli, Rich, and Visscher, 1978; Bonetto, Lebowitz, and Lukkarinen, 2004; Bonetto et al., 2009; Dhar, 2008; Pereira, 2010; Rov and Dhar, 2007; Segal and Nitzan, 2005), and thermo-electric transport (Bedikian, Bandyopadhyay, and Meister, 2013; Entin-Wohlman and Aharony, 2012; Entin-Wohlman, Imry, and Aharony, 2010; Entin-Wohlman, Imry, and Aharony, 2010; Hershfield, Mutalib, and Pekola, 2013; Horvat et al., 2012; Jacquod, 2009; Jiang, Entin-Wohlman, and Imry, 2012; Jordan et al., 2013; Ruokola and Ojane, 2013; Saito et al., 2011; Sánchez and Büttiker, 2011; Sothmann et al., 2011, 2013). Note that some of the above models consider the third terminal as a bosonic (phonons, photons, or magnons) rather than a fermionic bath and cannot be treated within the Landauer-Büttiker approach for non-interacting particles. In that case one has to use other methods such as the Keldysh technique (Entin-Wohlman and Aharony, 2012; Entin-Wohlman, Imry, and Aharony, 2010).

The approach can be generalized to any number of probes. We call $J_{1,k}$ and $J_{2,k}$ the charge and heat currents from the $k$th terminal (at temperature $T_k$ and electrochemical potential $\mu_k$), with $k = 3, \ldots, n$ denoting the $n_p = n - 2$ probes. Due to the steady-state constraints of charge and energy conservation, $\sum_k J_{1,k} = 0$ and $\sum_k (J_{2,k} + \mu_k J_{1,k}) = 0$, we can express, for instance, the currents from the second reservoir as a function of the remaining $2(n-1)$ currents. The corresponding generalized forces are given by $J_{1,k} = \mu_k (eT)$ and $J_{2,k} = \Delta T_k/\tau_k$, with $\Delta \mu_k = \mu_k - \mu$, $\Delta T_k = T_k - T$, $\mu = \mu_3$, and $T = T_2$. The linear response relations between currents and thermodynamic forces, are expressed in terms of an Onsager matrix $L$ of size $2(n-1)$. We then impose the condition of zero average currents through the probes, $J_{1,k} = J_{2,k} = 0$ for $k = 3, \ldots, n$ to reduce the Onsager matrix to a $2 \times 2$ matrix $L'$ connecting the fluxes $J_{1,1}$ through the first reservoir and the conjugated forces $X_{1,1}$:

$$
J_{1,1} = \sum_{j=1}^{2} \sum_{l=1}^{n} L_{1j:k} X_{j,l},
$$

The reduced matrix $L'$ fulfills the Onsager-Casimir relations and represents the Onsager matrix for two-terminal inelastic transport modeled by means of self-consistent reservoirs. Details of the reduction from $L$ to $L'$ for $n = 3$ reservoirs are provided in Saito et al. (2011). Note that, if the average flow of particles and heat through the probe reservoirs is zero, then thermodynamic efficiencies can be computed by means of the standard two-terminal formulas (12) and (13), with the parameters $x = L'_{12}/L'_{21}$ and $y = L'_{21}/L'_{12}/\text{det}L'$. However, the transport between these two terminals is no longer fully coherent, since the electrons can be absorbed and emitted by the probe terminals.

Electric and heat currents can be conveniently computed, for any number of probes, by means of the multi-terminal Landauer-Büttiker formula (Datta, 1995):

$$
J_{1,k} = \frac{e}{h} \int_{-\infty}^{\infty} dE \sum_{t} \left[ \tau_{t-k}(E) f_k(E) - \tau_{k-t}(E) f_t(E) \right],
$$

FIG. 6 Schematic drawing of partially-coherent thermoelectric transport, with the third terminal acting as a probe reservoir mimicking inelastic scattering. The temperature $T_3$ and the chemical potential $\mu_3$ of the third reservoir are such that the net average electric and heat currents through this reservoir vanish: $J_{1,3} = J_{2,3} = 0$. This setup can be generalized to any number of probe reservoirs, $k = 3, \ldots, n$, by setting $J_{1,k} = J_{2,k} = 0$ for all probes.
\[ J_{2,k} = \frac{1}{h} \int_{-\infty}^{\infty} dE (E - \mu_k) \sum_l (\tau_{l \to k}(E) f_k(E) - \tau_{k \to l}(E) f_l(E)), \]

where \( \tau_{l \to k}(E) \) is the transmission probability from terminal \( k \) to terminal \( l \) at the energy \( E \). Charge conservation and the requirement of zero current at zero bias impose

\[ \sum_k \tau_{k \to l} = \sum_l \tau_{l \to k} = M_l, \tag{66} \]

with \( M_l \) being the number of modes in the lead \( l \). Moreover, in the presence of a magnetic field \( B \) we have

\[ \tau_{k \to l}(B) = \tau_{l \to k}(-B). \tag{67} \]

The last relation is a consequence of the unitarity of the scattering matrix \( S(B) \) that relates the outgoing wave amplitudes to the incoming wave amplitudes at the different leads. The time reversal invariance of unitary dynamics leads to \( S(B) = S(-B) \), which in turn implies \( \tau_{l \to k} = \tau_{k \to l} \). Hence, we can conclude from this relation and Eq. \( \tau_{l \to k}(B) = \tau_{l \to k}(-B) \), thus implying that the Seebeck coefficient is a symmetric function of the magnetic field.

The third (probe) terminal can break the symmetry of the Seebeck coefficient. We can have \( S(-B) \neq S(B) \), that is, \( L_{12} \neq L_{21} \) in the reduced Onsager matrix \( L' \). Arbitrarily large values of the asymmetry parameter \( x = S(B)/S(-B) = L_{12}/L_{21} \) were obtained in \cite{Saito et al. 2011} by means of a three-dot Aharonov-Bohm interferometer model. The asymmetry was found also for chaotic cavities, ballistic microjunctions \cite{Sanchez and Serra 2011}, and random Hamiltonians drawn from the Gaussian unitary ensemble \cite{Balachandran, Benenti, and Casati 2013}. In \cite{Sanchez and Serra 2011} it was shown that the asymmetry is a higher-order effect in the Sommerfeld expansion and therefore disappears in the low temperature limit. The asymmetry was demonstrated also in the framework of classical physics, for a three-terminal deterministic railway switch transport model \cite{Horvat et al. 2012}. In such model, only the values zero and one are allowed for the transmission functions \( \tau_{j \to i}(E) \), i.e., \( \tau_{j \to i}(E) = 1 \) if particles injected from terminal \( i \) with energy \( E \) go to terminal \( j \) and \( \tau_{j \to i}(E) = 0 \) is such particles go to a terminal other than \( j \). The transmissions \( \tau_{j \to i}(E) \) are piecewise constant in the intervals \( [E_i, E_{i+1}], \) \( (i = 1, 2, \ldots) \), with switching \( \tau_{j \to i} = 1 \to 0 \) or viceversa possible at the threshold energies \( E_i \), with the constraints \( \tau_{l \to k} \) always fulfilled.

In all the above instances, it was not possible to find at the same time large values of asymmetry parameter \( B \neq 0 \) and high thermoelectric efficiency. Such failure was explained by \cite{Brandner, Saito, and Seifert 2013} and is generic for non-interacting three-terminal systems. In that case, when the magnetic field \( B \neq 0 \), current conservation, which is mathematically expressed by unitarity of the scattering matrix \( S \), imposes bounds on the Onsager matrix stronger than those derived from positivity of entropy production. We have

\[ L_{11} L_{22} - \frac{1}{4} (L_{12} + L_{21})^2 \geq \frac{3}{4} (L_{12} - L_{21})^2. \tag{68} \]

Such constraint reduces to the third inequality of Eq. \( \eta_{CA} = \eta_C/2 \) for the efficiency at maximum power can be overcome for moderate asymmetries, \( 0 < x < 2 \), with a maximum of \( 4\eta_C/7 \) at \( x = 4/3 \). The bounds obtained by \cite{Brandner, Saito, and Seifert 2013} are in practice saturated in a quantum transmission model reminiscent of the above described railway switch model \cite{Balachandran, Benenti, and Casati 2013}. Multi-terminal cases with more than three terminals were also discussed for noninteracting electronic transport \cite{Brandner and Seifert 2013}. By increasing the number \( n_p \) of probe terminals, the constraint from current conservation on the maximum efficiency and the efficiency at maximum power becomes weaker than that imposed by \cite{Brandner, Saito, and Seifert 2013}. However, the bounds \( \eta_C \) and \( \eta_{CA} \) from the second law of thermodynamics are saturated only in the limit \( n_p \to \infty \). It is an interesting open question whether similar bounds on efficiency, tighter that those imposed by the positivity of entropy production, exist in more general transport models for interacting systems.

Probe-reservoir models unveil several other nontrivial aspects of inelastic processes. For instance, the third reservoir may be a phonon bath connected to a nanostucture (e.g., a molecule), and it has been shown that such setup can be very favorable for thermoelectric energy conversion \cite{Jiang, Entin-Wohlman, and Imry 2012}, notably the setup can act as a refrigerator for the local phonon system. The cooling by heating phenomenon can also be interpreted in terms of a third, photonic terminal powering refrigeration \cite{Pekola and Hekking 2007} (see also \cite{Muhonen, Meschke, and Pekola 2012; Peltonen et al. 2011; Van den Broeck and Kawal 2006}) considered the case in which the photons emitted by a hot resistor can extract heat from a cold metal, providing the energy needed to electrons to tunnel to a superconductor (separated from the metal by a thin insulating junction; no voltage is applied over the junction). If the temperature of the resistor is suitably set, only the high energy electrons are removed from the metal, thus cooling it. Such Brownian refrigerator is still to be experimentally demonstrated. Similar mechanisms have been discussed for cooling a metallic lead, connected to another, higher
temperature lead by means of two adjoining quantum dots (Cleuren, Rutten, and Van den Broeck 2012) or for cooling an optomechanical system (Mari and Eisert, 2012). In both cases, refrigeration is powered by absorption of photons.

V. INTERACTING SYSTEMS

A. Green-Kubo formula

The Green-Kubo formula expresses linear response transport coefficients in terms of dynamic correlation functions of the corresponding current operators, calculated at thermodynamic equilibrium (see for instance Kubo, Toda, and Hashitsume 1985; Mahan 1990):

\[
L_{a,b} = \lim_{\omega \to 0} \text{Re} L_{a,b}(\omega),
\]

\[
L_{a,b}(\omega) = \lim_{\epsilon \to 0} \int_{-\infty}^{\infty} dt e^{-i(\omega-\epsilon)t} \lim_{\Omega \to \infty} \frac{1}{\Omega} \int_0^\beta \! d\tau \langle \hat{J}_a \hat{J}_b(t + i\tau) \rangle,
\]

where \( \beta = 1/k_BT \) (\( k_B \) it the Boltzmann constant), \( \langle \cdot \rangle = \{ \text{tr}(\cdot) \exp(-\beta H) \} / \text{tr} \exp(-\beta H) \) denotes the thermodynamic expectation value, \( \Omega \) is the system's volume, and the currents are \( \hat{J}_a = \langle \hat{J}_a \rangle \), with \( \hat{J}_a \) the current operator. Note that in extended systems, the operator \( \hat{J}_a = \int_\Omega \! d\vec{r} \hat{j}_a(\vec{r}) \) is an extensive quantity, \( \hat{j}_a(\vec{r}) \) is the current density operator, satisfying the continuity equation

\[
\frac{d\hat{\rho}_a(\vec{r},t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{\rho}_a] = -\nabla \cdot \hat{j}(\vec{r},t),
\]

where \( \hat{\rho}_a \) is the density of the corresponding conserved quantity, say, energy, electric charge, magnetization etc. Eq. (70) can be equally well written in classical mechanics, provided the commutator is substituted by the Poisson bracket multiplied by the factor \( i\hbar \). The real part of \( L_{a,b}(\omega) \) can be decomposed into a \( \delta \)-function at zero frequency defining a generalized Drude weight \( D_{a,b} \) (for \( a = b \) this is the conventional Drude weight) and a regular part \( L_{a,b}^{\text{reg}}(\omega) \):

\[
\text{Re} L_{a,b}(\omega) = 2\pi D_{a,b}\delta(\omega) + L_{a,b}^{\text{reg}}(\omega).
\]

The matrix of Drude weights can be within linear response also expressed in terms of time-averaged current-current correlations directly:

\[
D_{a,b} = \lim_{t \to \infty} \frac{1}{t} \int_0^t \! dt \lim_{\Omega \to \infty} \frac{1}{\Omega} \int_0^\beta \! d\tau \langle \hat{J}_a \hat{J}_b(t + i\tau) \rangle.
\]

Note that for finite systems, i.e. disregarding the thermodynamic limit \( \Omega \to \infty \), it is possible to give a spectral representation of both \( D_{a,b} \) and \( L_{a,b}^{\text{reg}} \) in terms of the eigenenergies and eigenstates of the system and of the corresponding Boltzmann weights (Kohn, 1964; Zotos, Naef, and Prelovšek, 1997; Zotos and Prelovšek, 2004).

The linear response Kubo formalism has been recently used to investigate the thermoelectric properties of one-dimensional integrable and non-integrable strongly correlated lattice models (Arsenault et al., 2013; Chaikin and Beni, 1976; Deng et al., 2012; Furukawa, Ikeda, and Sakai, 2005; Peterson et al., 2007; Peterson and Shastry, 2010; Shastry, 2009; Zemilić and Prelovšek, 2007). Thermoelectrics of strongly correlated materials are of fundamental interest. Moreover, experimental results have revealed that some materials, such as sodium cobalt oxide, possess unusually large thermopower (Terasaki, Sasago, and Uchinokura, 1997; Wang et al., 2003), due to strong electron interactions (Peterson, Shastry, and Haertel, 2007).

B. Conservation laws and thermoelectric transport

In interacting (quantum) many-body systems one has to often resort to more abstract mathematical frameworks to describe linear response theory, Green-Kubo formulae and Onsager reciprocity relations (Jaksić, Ogata, and Pilled, 2006). For describing correlated transport in extended interacting quantum systems with local interaction, one can use the formalism of C*-algebraic dynamical systems (Bratelli and Robinson, 1997). There we can take advantage of an emerging causality (Bravyi, Hastings, and Verstraete, 2006) as the consequence of the Lieb-Robinson bounds stating that correlations, even in nonrelativistic systems with local interactions, propagate with a finite maximum velocity which is essentially given by the strength of the interaction. In addition, one can use the Mermin-Wagner theorem to conclude that in one- and two-dimensional systems the static correlations always decay exponentially in non-zero temperature (Gibbsian) equilibrium. Consequently, one can prove finite-temperature ballistic transport for systems with relevant local conservation laws (Ilievski and Prosen, 2013; Prosen, 2011). Similarly, one can prove (Prosen, 2013) nonvanishing lower bounds on Green-Kubo diagonal diffusive transport coefficients \( L_{a,a} \) in terms of quadratically-extensive conserved quantities (in non-ballistic cases when linearly-extensive – local conserved quantities do not exist, or are irrelevant, such as in the case of one-dimensional half-filled fermi Hubbard chain or non-magnetized Heisenberg spin 1/2 chain). A constant of motion \( \hat{K}_m \) is by definition relevant if \( \langle \hat{J}\hat{K}_m \rangle \neq 0 \), where \( J \) is the current under consideration. Ballistic finite-temperature transport as a consequence of the existence of relevant conservation laws is a typical feature of completely integrable strongly interacting systems, as suggested some time ago by Zotos, Naef, and Prelovšek (1997) (see also Garst and Rosch, 2001; Heidrich-Meisner, Honecker, and Brenig, 2003)). In a similar way, the theory of quantum integrable systems implies ballistic coupled transport, i.e. thermoelectric and thermomagnetic, properties of such systems, e.g.
in the anisotropic Heisenberg XXZ spin 1/2 chain [Furukawa, Ikeda, and Sakai 2003; Sakai 2005]. More specifically, let us consider a strongly interacting system with a set of \( M \) constants of motion \( \hat{K}_m, m = 1, \ldots, M \), i.e., Hermitian operators \( \hat{K}_m \) which commute with the Hamiltonian and among themselves, \( \{ \hat{K}_m, \hat{K}_l \} = 0 \). Therefore, it can always be chosen to be orthogonal, i.e., \( \langle \hat{K}_m, \hat{K}_l \rangle = \delta_{m,l} (\hat{K}_m^2) \) via a Gram-Schmidt procedure. Furthermore, let us assume that \( \hat{K}_m \) are linearly extensive, i.e., \( \langle \hat{K}_m^2 \rangle \propto \Omega \). Then, provided that the set \( \{ \hat{K}_m \} \) exhausts all extensive conserved quantities (in the thermodynamic limit \( \Omega \rightarrow \infty \)), the matrix of generalized Drude weights \((72)\) can be expressed explicitly by means of Suzuki's formula [Benenti, Casati, and Wang 2013; Suzuki 1971]:

\[
D_{a,b} = \lim_{\Omega \rightarrow \infty} \frac{1}{2\Omega} \sum_{m=1}^{M} \frac{\langle \hat{J}_a \hat{K}_m \rangle \langle \hat{J}_b \hat{K}_m \rangle}{\langle \hat{K}_m^2 \rangle}. \tag{73}
\]

At zero frequency \( \omega = 0 \), the elements of Onsager matrix \( L_{a,b} \) can be replaced by \( D_{a,b} \) in the expression for the figure of merit of thermoelectric, thermomagnetic or thermochemical efficiency \( ZT \).

Conservation laws have an interesting consequence for thermoelectric efficiency, when there is a single relevant conserved quantity, \( M = 1 \) in \( Eq. \ (73) \). In that case all Onsager matrix elements \( L_{a,b} \) are size independent and therefore also the electric conductance \( G \propto L_{11} \) and the thermopower \( S \propto L_{12}/L_{11} \) are size independent. On the other hand, the thermal conductance \( \Xi \propto \text{det}(L)/L_{11} \) drops with the system size. Indeed the Drude weight contribution to \( \text{det}(L) \) vanishes, since it is given by \( D_{11}D_{22} - D_{12}^2 \), which vanishes as a consequence of \( Eq. \ (73) \) for \( M = 1 \) states that the matrix \( D_{a,b} \) has rank 1. Since the electric conductance is ballistic, the thermopower size-independent and the thermal conductance subballistic (i.e., it drops with the system size), we can conclude that the figure of merit \( ZT = (GS^2/\Xi)T \) diverges with the system size [Benenti, Casati, and Wang 2013]. Note that these conclusions for the transport and the figure of merit do not hold when \( M > 1 \), as is typical for completely integrable systems. In that case we have, in general, \( D_{11}D_{22} - D_{12}^2 \neq 0 \), so that thermal conductance is ballistic and therefore \( ZT \) is size-independent. This result is not limited to quantum systems and has no dimensional restrictions; it has been illustrated by means of a diatomic chain of hardpoint colliding particles [Benenti, Casati, and Wang 2013], where the divergence of the figure of merit with the system size [Casati, Wang, and Prosen 2009] cannot be explained in terms of the energy filtering mechanism [Saito, Benenti, and Casati 2010], and in a two-dimensional system connected to reservoirs [Benenti, Casati, and Mejía-Monasterio 2013] with the dynamics simulated by the multiparticle collision dynamics method [Malevans and Kapral 1999]. In both (classical) models collisions are elastic and the component of momentum along the direction of the charge and heat flows is the only relevant constant of motion. Divergence of \( ZT \) has been also predicted, by different theoretical arguments, for a quantum wire with weak electron-electron interactions, in the limit of infinite wire length [Micklitz, Rech, and Matveev 2010].

When the underlying many-body system is strongly non-integrable, or when all the extensive local conservation laws are irrelevant for the transporting quantities, i.e., when \( \langle \hat{J}_a \hat{K}_m \rangle = 0 \) for all \( m \), then the transport is typically diffusive. In the latter case one often finds diffusive transport even if the system is completely integrable [Prosen and Znidaric 2009; Steinigeweg 2011]. Then, within the linear response approach, one has to apply the regularized Onsager matrix \( L_{a,b}^{\text{reg}}(\omega) \) of \( Eq. \ (71) \) for estimation of \( ZT \).

### C. Thermalization

One of the essential prerequisites for using the methods of canonical statistical mechanics is establishing precise conditions under which the system discussed can be claimed to be in thermal equilibrium. The understanding of thermalization in closed (isolated) but complex quantum systems is one of the most intriguing problems in quantum physics, with deep connections with the field of quantum chaos [Breuer and Petruccione 2002].

Recent progress has been made in understanding the conditions under which closed but complex systems undergo relaxation to equilibrium. The conditions for thermalization are essentially related to the systems’ integrability and localization properties (e.g., due to disorder). Non-ergodic systems, such as those possessing some number of exact local conservation laws \( K_m \) (for example, completely integrable systems) undergo relaxation to a generalized Gibbs state [Barthel and Schollwöck 2011], which can again facilitate application of standard statistical mechanics methods.

Thermalization of simple or complex quantum systems immersed into large (many-body), complex, or chaotic environment can be described very conveniently by the methods of open quantum systems [Breuer and Petruccione 2002]. One can treat also extended many-body systems, say particle (or spin) chains, in this way by using a convenient setup in which only boundary (local, on-site) degrees of freedom are directly coupled with the environment. Within the Markovian approximation, the system’s many-body density matrix undergoes a time-evolution dictated by the Lindblad-Gorini-Kossakowski-Sudarshan equation [Gorini, Kossakowski, and Sudarshan 1976; Lindblad...
\[
\frac{d}{dt} \rho(t) = \hat{L}\rho(t),
\]
(74)

where the Liouvillian superoperator is defined as
\[
\hat{L}\rho := -\frac{i}{\hbar} [H, \rho] + \sum_{\mu} \left( L_{\mu} \rho L_{\mu}^\dagger - \frac{1}{2} \{ L_{\mu}^\dagger L_{\mu}, \rho \} \right).
\]
(75)

The Hamiltonian \( H \) is here considered to be a sum of locally interacting terms, \( H = \sum_{n=1}^{N-1} H_{[n,n+1]} \) and \( L_{\mu} \) are the Lindblad (or so-called quantum jump) operators, which are in the simplest case supported only at the boundary sites, \( n = 1 \) or \( n = N \), of the system. This setup can be justified [Benenti et al., 2009] in the regime of weak tunneling interaction between different constituents (particles, spins) of the system, but provides also a more general paradigm of open many-body quantum systems with fully coherent bulk dynamics and incoherent boundary conditions, which is particularly suited for studying non-equilibrium steady state phenomena, such as quantum transport [Wichterich et al., 2007]. It has been demonstrated by numerical simulations that coupling a many-body locally interacting quantum system to a pair of equal Markovian baths through the system’s ends in this way, results in thermalization if, and only if, the system’s bulk Hamiltonian is not integrable (via Bethe ansatz) [Znidaric et al., 2010]. Further theoretical work is needed to deeper understand these results.

D. Local equilibrium and non-equilibrium steady states

Using the just described boundary driven open system’s setup, but putting small biases on the rates with which Lindblad jump operators \( L_{\mu} \) target certain locally canonical states near the boundaries, one can address also the problem of bulk transport properties of the system. For example, measuring expectation values of the current observables in the steady states of the Lindblad equation reveals, in the thermodynamic limit \( N \to \infty \), bulk conductivities [Prosen and Znidaric, 2009], and in principle also the off-diagonal elements of the Onsager matrix. Nevertheless, the problem of establishing local equilibrium in such situations seems to be quite nontrivial [Prosen and Znidaric, 2010]. Namely, fixed points of Liouvillian dynamics can describe a variety of qualitatively distinct non-equilibrium quantum phases, ranging from equilibrium-like states where spatial correlations decay exponentially and where local equilibrium can be well defined, to states where spatial correlations only depend on the bias (voltage, temperature drop, etc.) between the reservoirs, but not on the system size. In the latter case one lacks any sensible definition of local equilibrium. Nevertheless, the approach to non-equilibrium steady states in terms of the methods of open quantum systems appears to be very promising, in particular since strong interactions in the system can easily be treated. It is, however, difficult to control the dependence of the results on the type of reservoirs used, as the reservoirs’ degrees of freedom are traced out in the very setup.

Markovian master equation models can also be used to treat heat and particle/spin transport in models with conservative noise in the bulk (e.g. dephasing noise which conserves the number of quasi-particle excitations) [Manzano et al., 2012; Znidaric, 2010]. Such models of noise, close in spirit to the probe terminals discussed in Sec. IV.B, can be interesting for applications to coupled transport. They offer elegant ways of treating unwanted degrees of freedom in the bulk, such as lattice vibrations, and they often lead to surprising results, such as noise-induced enhancement of transport [Mendoza-Arenas et al., 2013].

Complementarily, instead of using quantum master equations, one may use another, perhaps more standard approach to non-equilibrium steady states via a Keldysh formalism of non-equilibrium Green’s functions [Haug and Jauho, 2008], where one essentially discusses the scattering of elementary quasi-particle excitations between two or more infinite non-interacting Hamiltonian reservoirs. This approach was used, among other things, to study heat transport in driven nanoscale engines [Arrachea et al., 2012; Arrachea, Moskalets, and Martin-Moreno, 2007] and spin heterostructures [Arrachea, Lozano, and Aligia, 2009]. Clearly, for this method to be feasible the full self-energy of the central system has to be somehow tractable. Thus the Keldysh technique is usually used when the bulk dynamics is simple and details of coupling to the reservoirs (i.e. physical leads) are important. Open quantum system’s approach, on the other hand, has the advantage of allowing numerical and non-perturbative treatments for the many-body central (bulk) Hamiltonians. Another setup in which the Keldysh treatment of infinite Hamiltonian reservoirs can be explicitly implemented is when the bulk dynamics can be treated with integrable effective quantum field theory. For example, if the bulk Hamiltonian is critical, having massless (gapless) low energy excitations and if the temperatures of the reservoirs are small, one may use conformal field theory to describe effective non-equilibrium steady states [Bernard and Doyon, 2013].

VI. NUMERICAL APPROACHES

Numerical computations in various classical and quantum dynamical transport problems in low dimensions, in particular in one-dimensional particle chains, have a rich and long history (see e.g. the reviews of Lenzi, Livi, and Politi [2003] and Dhar [2008], and references therein). In this section we only mention classical and quantum molecular dynamics approaches which are suitable for efficient computer simulations. In the context of simulating coupled heat and matter
transport from deterministic classical dynamical system's perspective one has to mention the references Mejía-Monasterio, Larralde and Levraz (2001) and Mejía-Monasterio, Larralde and Levraz (2003) which provided the first numerical measurements of the Onsager matrix for interacting chaotic classical gasses.

A. Classical

The aforementioned and related studies simulate transport in an extended classical particle chain, or a particle container, by using a hybrid deterministic/stochastic method. The bulk dynamics is simulated deterministically using the standard techniques of molecular dynamics, i.e. solving Hamilton’s equations for all particles’ coordinates and momenta, while at the extreme (left and right) ends of the system, particles are exchanged with the left/right reservoirs (baths), or their energy is exchanged, in a stochastic fashion, so that after the event of stochastic interaction the particle’s density and energy is distributed according to the grand-canonical distribution, determined by the temperatures and the chemical potentials of the baths. This can be viewed as a classical analog of the boundary driven open quantum many-body setup described in the previous section, and can be implemented efficiently to estimate numerically the figure of merit $ZT$ (Casati, Mejía-Monasterio, and Prosen 2008).

There is also an alternative deterministic approach of the Nosé-Hoover thermostats (Evans and Holian 1985), in which also the dynamics of end (left or right) particles is purely deterministic, but it is dissipative and typically chaotic, so that these end particles are correctly thermalized (only for the average values, not for correlations). Nosé-Hoover baths are nevertheless somewhat less used than the stochastic ones, as one can never be sure when deterministic dynamics of the baths may bring in some unwanted (spurious) correlation effects into the system’s dynamics.

B. Quantum

For quantum systems, boundary driven locally interacting Lindblad equation (74) is particularly suitable since it allows for efficient numerical simulation of the steady state in terms of the time-dependent-density-matrix-renormalization-group method (tDMRG) (Daley et al. 2004; Schollwöck 2011; White and Feiguin 2004) in the Liouville space of linear operators acting on wave functions (Prosen and Znidaric 2009). The reason for efficiency of this method in the long time limit as compared to the usual tDMRG algorithm lies in typically effective suppression of entanglement (correlations) in the operator space due to the coupling to Markovian baths. In the Liouvillian tDMRG approach, the state of the system, say of $N$ quantum spins 1/2 or qubits (abstract two-level systems) described by Pauli matrices $\sigma^0 \equiv \mathbb{1}, \sigma^{1,2,3} \equiv \sigma^{x,y,z}$, encoded in a many-body density operator is at all times $t$ represented in the form of a matrix product ansatz,

$$
\rho(t) = \sum_{s_j \in \{0,1,2,3\}} \langle L|A_1^{(s_1)}(t) \cdots A_N^{(s_N)}(t)|R\rangle \sigma^{s_1} \otimes \cdots \otimes \sigma^{s_N},
$$

by means of a set of $4n$ time-dependent matrices $A_j^{(s)}(t)$, and an appropriate pair of boundary vectors $(L|, |R)$, of some finite dimension $D$. The simplest strategy for calculating the density matrix of non-equilibrium steady state $\rho_\infty = \lim_{t \to \infty} \rho(t)$ is then simply to simulate time evolution of the master equation (74), $\rho(t) = \exp(\hat{L}t)\rho(0)$. Namely, $\exp(\hat{L}t)$ can be decomposed into a product of local operators for systems with local interactions and local Lindblad dissipators $L_\mu$ which can be handled fully within the ansatz (76). The crucial approximation of the method lies in the fact that application of local two-site interaction operators $h_{i,j,i+1}$ on (76) results in amplification of dimension $D$ to $4D$, which in turn need to be truncated to $D$ by means of the singular value decomposition. The overall error of such truncations is related to the growth of entanglement entropy (in the Hilbert-Schmidt space of density operators), which can be intuitively understood to be smaller for systems with dissipation as compared to fully coherent (Hamiltonian) evolution. Having matrix product representation $\rho_\infty$ of the steady state one can then compute easily the local observables such as energy density, particle density or magnetization profiles and currents from which the full Onsager matrix can be calculated.

One can also apply linear response approach and calculate Onsager coefficients from Green-Kubo expressions (69) based on tDMRG calculations of current-current time-correlation functions of pure Hamiltonian (coherent) dynamics. Here accessible time scales $t^*$, due to entanglement entropy growth, are much smaller than in Liouville space approach with dissipative boundaries, but $t^*$ does not need to be longer than the time up to which all current-current correlations essentially vanish. State-of-the-art algorithm for such calculations is described in Karrasch, Bardarson, and Moore (2013).

In cases where the coupling among the particles is non-local, say we have residual long-range (e.g. Coulomb) interaction, or some other complications arise which prohibit efficient use of tDMRG, one can simulate quantum master equation using the method of quantum trajectories (see, for example, Mejía-Monasterio and Wichterich 2007). The idea there is to represent the density operator as an expectation of $|\Psi(t)\rangle\langle\Psi|$ where the many-body wavefunction $\Psi$ is a solution of a stochastic Schrödinger equation $i\hbar \dot{\Psi}(t) = -i\hbar H\Psi dt + d\xi$, with $d\xi$ being an appropriate stochastic process simulating the action of the baths. The advantage of this technique is that non-Markovian effects can be treated easily and intuitively.

For even more general problems, one can always solve the many-body quantum master equation numerically. 

thermodynamic heat engines. Devices. In this section, we discuss several paradigms of efficiency at maximum power and new ideas for making such finite-time thermodynamics are universal nature of efficiency at maximum power is achievable. This consideration opens the way to the concept of finite-time thermodynamics, discussed in Sec. III.A Paradigms of finite-time thermodynamic engine are the Carnot or Otto cycles with a finite time period. Recent technological developments enable us to consider and realize finite-time thermodynamic devices with high controllability. Main issues of finite-time thermodynamics are universal nature of efficiency at maximum power and new ideas for making such devices. In this section, we discuss several paradigms of thermodynamic heat engines.

VII. MODELS OF THERMODYNAMIC ENGINES

Since the pioneering work by Carnot (1824), a huge number of physical phenomena have been recognized as heat engines, including thermoelectric phenomena. In original Carnot’s idea, the maximum efficiency was studied for an ideal gas confined by a piston and is bounded by the Carnot efficiency. The Carnot efficiency is achievable for the celebrated Carnot cycle, that consists of isothermal and adiabatic processes. Otto invented a more practical heat engine (Otto engine) (Callen 1985) which consists of adiabatic compression, heat addition at constant volume, adiabatic expansion, and rejection of heat at constant volume. In all heat engines the maximum efficiency is obtained for a quasi-static process where asymptotically vanishing power output is generated. From the practical viewpoint, finite power with high efficiency is desirable. This consideration opens the way to the concept of finite-time thermodynamics, discussed in Sec. III.A Paradigms of finite-time thermodynamic engine are the Carnot or Otto cycles with a finite time period. Recent technological developments enable us to consider and realize finite-time thermodynamic devices with high controllability. Main issues of finite-time thermodynamics are universal nature of efficiency at maximum power and new ideas for making such devices. In this section, we discuss several paradigms of thermodynamic heat engines.

A. Stochastic thermodynamics

Stochastic thermodynamics is a framework to study non-equilibrium thermodynamics in small systems like colloids or biomolecules driven out of equilibrium (Seifert 2012; Sekimoto 2010). In most cases, this field treats classical systems. The system is always attached to a thermal environment like water. The time scales of environment and system are sufficiently separated and the system’s dynamics is well described by the Langevin equation. Suppose that one colloidal particle is trapped by an external potential and the dynamics is overdamped; the Langevin equation of motion is given by

$$\dot{x} = \mu F(x, \lambda(t)) + \eta(t),$$

where \(x(t)\) is the particle’s coordinate, \(\eta(t)\) a Langevin thermal noise satisfying \(\langle \eta(t)\eta(t') \rangle = 2D \delta(t - t')\) with \(D\) being the diffusion constant. The function \(F(x, \lambda(t))\) is a time-dependent force field, which is given by

$$F(x, \lambda(t)) = -\partial_x V(x, \lambda(t)) + f,$$

where \(V(x, \lambda(t))\) is a potential and \(f\) is a nonconservative force which can not be expressed as the gradient of a potential. The parameter \(\lambda(t)\) is a time-dependent external control parameter. In equilibrium, the diffusion constant \(D\) and the mobility \(\mu\) are related by the Einstein relation \(D = T\mu\).

The Langevin dynamics is endowed with a thermodynamic interpretation by applying the energy balance to any individual stochastic trajectory:

$$\delta U = \delta Q - \delta W,$$

where \(\delta U\) is the heat absorbed from the environment, \(\delta Q\) the variation of internal energy, and \(\delta W\) the work performed by the particle. Note that \(-\delta W\) is the work applied to the particle due to a time-dependent potential (i.e., \(\lambda\) changes in time) or to a nonconservative force \(f\). Since the dynamics is overdamped, the kinetic energy does not change in time. Hence, the variation \(\delta U\) of the internal energy is equivalent to the change \(\delta V\) of the potential. The work applied to the particle reads

$$-\delta W = (\partial V / \partial \lambda) \lambda dt + f dx,$$

and therefore the absorbed heat is

$$\delta Q = \delta V + \delta W = -F dx.$$

The work and heat defined above are the basis to consider thermodynamic efficiency in stochastic thermodynamics.

An intriguing and solvable heat engine in the framework of stochastic thermodynamics was introduced by Schmiedl and Seifert (2008). Suppose that one particle is trapped by a time-dependent harmonic potential \(V(x, \lambda(t)) = \lambda(t) x^2 / 2\) without nonconservative force, i.e. \(f = 0\). We consider a cycle, depicted in Fig. 7 composed of the following four steps.
van Kampen, 1988). In BL model a particle is trapped in a periodic potential \( V(x) \) and subject to a nonuniform, spatially periodic temperature profile. Although there is no time-dependent driving this system satisfies Curie’s principle (Curie, 1894), namely, rectification effect occurs as it is not ruled out by symmetries. This situation is analyzed using the Langevin dynamics where the particle is alternately attached along the spatial coordinate, to thermal baths at different temperatures. The equation of motion is given by

\[
 m \ddot{x} = -\gamma(x) \dot{x} - V'(x) - f + \sqrt{2\gamma(x)T(x)} \xi(t), \tag{82}
\]

where \( \gamma(x) \) is the coefficient of a viscous friction, \( f \) is the external force, and \( \xi(t) \) is a white Gaussian noise satisfying \( \langle \xi(t) \xi(t') \rangle = \delta(t - t') \). We assume that the potential and temperature depend on the position and are periodic with period \( L \), and take \( (T(x), \gamma(x)) = (T_1(\lambda), \gamma_1(\lambda)) \) for \( x \leq (\lambda) L/2 \), with \( T_1 > T_2 \). A schematic picture for the potential and temperature is presented in Fig. [\textcolor{red}{5}].

The energetics and transport properties of the BL motor have been studied by many authors. Landauer (1988) proposed the idea of the BL motor and showed the physical significance of nonuniform temperature in changing the relative stability of otherwise locally stable states, a phenomenon he termed as the blowtorch effect. Periodic temperature with a periodic potential induces a net transport of Brownian particles (Büttiker, 1987; Landauer, 1988; Parrondo and de Cisneros, 2002). In the hot region the Brownian particle can move more easily than in the cold region. Hence, a finite net current is generated. Efficiency \( \eta \) is calculated by \( \eta = W/Q_1 \), where \( W \) is the work done by the particle per unit time: \( W = \mathcal{F} \langle \dot{x} \rangle \). The denominator \( Q_1 \) is the heat supply (per unit time) from the hot region, evaluated as (see Sekimoto (2010))

\[
 Q_1 = \langle (-\gamma \dot{x} + \sqrt{2 \gamma T_1} \xi(t)) \dot{x} \rangle, \tag{87}
\]

where the statistical average is taken only over the hot region, \( 0 < x \leq L/2 \).

In the overdamped limit (\( \dot{x} \to 0 \)) the net current can be derived using the Fokker-Planck equation. Then one can show that, under suitable conditions, the efficiency can reach the Carnot efficiency (Asfaw and Bekedo, 2004, 2007; Matsuo and Sasa, 2000). However, it was pointed out that reaching the Carnot efficiency is problematic due to the abrupt change of temperature at the boundaries (Ai et al., 2005; Ai, Wang, and Liu, 2006; Derényi and Astumian, 1999; Hondou and Sekimoto, 2000). Carnot efficiency is unattainable due to the irreversible heat flow via kinetic energy. Recent first principle calculations using molecular dynamics simulation support the unattainability of Carnot efficiency (Benjamin and Kawal, 2008).

Brownian motors driven by temporal rather than spatial temperature oscillations are discussed in Reimann et al. (1996), where the potential has broken spatial symmetry (“ratchet” potential). The constructive role of Brownian motion for various physical and technological setups is reviewed in Hänggi and Marchesoni (2009).

**B. Heat engine with blowtorch effect**

Büttiker and Landauer’s (BL) model is one example of heat engine (Büttiker, 1987; Landauer, 1988; Schmiedl and Seifert, 2008). Later, this result was proved in a more general context (Esposito, Lindenberg, and Van den Broeck, 2009b). The above described engine is quite realistic, since it models the trapping of a colloidal particle in a time-dependent harmonic potential. The stochastic heat engine was experimentally demonstrated (Blickle and Bechinger, 2012).

The CA efficiency was also studied in gas systems where the Carnot cycle is performed within a finite time cycle. The validity of CA efficiency was numerically discussed by means of molecular dynamics simulations (Izumida and Okuda, 2008, 2009b).

**FIG. 7 (color online).** Schematic picture of a stochastic thermodynamic engine. In each plot the curve shows the potential \( V \) versus \( x \), the filled region is limited by the curve \( p(x) \), representing the (time-dependent) probability density to find the trapped particle at \( x \).

1. Isothermal transition at the hot temperature \( T_1 \) during \( 0 < t < t_1 \). The potential \( V(x, \lambda(t)) \) changes in time and work is extracted (\( W > 0 \)).

2. Adiabatic transition (instantaneously) from the hot temperature \( T_1 \) to the cold temperature \( T_2 \).

3. Isothermal transition at the cold temperature \( T_2 \) during the time interval \( t_1 < t < t_2; \) \( V(x, \lambda(t)) \) changes in time and work is applied to the particle (\( W < 0 \)).

4. Adiabatic instantaneous transition from the cold temperature \( T_2 \) to the hot temperature \( T_1 \).

This heat engine captures important aspects of finite-time thermodynamics. Exact analysis of this model shows that the next leading order \( \eta^2 / 8 \) in the CA formula is correct (Schmiedl and Seifert, 2008). Later, this result was proved in a more general context (Esposito, Lindenberg, and Van den Broeck, 2009b). The above described engine is quite realistic, since it models the trapping of a colloidal particle in a time-dependent harmonic potential. The stochastic heat engine was experimentally demonstrated (Blickle and Bechinger, 2012).

The CA efficiency was also studied in gas systems where the Carnot cycle is performed within a finite time cycle. The validity of CA efficiency was numerically discussed by means of molecular dynamics simulations (Izumida and Okuda, 2008, 2009b).
C. Driven quantum dot

Among electric devices, the quantum dot (QD) has the potential to provide many kinds of thermodynamic engines (Esposito, Lindenberg, and Van den Broeck 2009a; Esposito et al. 2010b; Humphrey et al. 2002; Nakpathomkun, Xu, and Linke 2010). Finite-time heat engines can be illustrated by means of quantum-dot systems, where one controls the gate voltage in time to change the on-site energy of the dot. We assume that a single-level quantum dot with time-dependent energy $\epsilon(t)$ is attached to one lead which has temperature $T_1$ and chemical potential $\mu_1$. Although the engine should work at the nanoscale, the dynamics is assumed to be classical, in that the off-diagonal elements of the density matrix are neglected in the time-evolution.

Let $p(t)$ be the occupation probability for the state of the quantum dot. Then the time-evolution is governed by the following master equation:

$$\dot{p}(t) = -W_1(t)p(t) + W_2(t)[1-p(t)], \quad (83)$$

where the transition rates read

$$W_1(t) = C\left[\exp(-\beta(\epsilon(t)-\mu(t))) + 1\right]^{-1},$$
$$W_2(t) = C\left[\exp(\beta(\epsilon(t)-\mu(t))) + 1\right]^{-1}, \quad (84)$$

with a constant $C$. The internal energy $U(t)$ of the quantum-dot system at time $t$ is defined as $U(t) = \epsilon(t)p(t)$; the output work $\delta W(t)$ and the absorbed heat $\delta Q(t)$ are given by

$$\delta W(t) = -[d\epsilon(t) - d\mu(t)]p(t), \quad (85)$$
$$\delta Q(t) = [\epsilon(t) - \mu(t)]dp(t). \quad (86)$$

Esposito et al. (2010b) proposed a solvable engine using the following cycle (see Fig. 9):

1. Isothermal process: The quantum dot is in contact with a cold lead at temperature $T_2$ and chemical potential $\mu_2$. The energy is raised during a finite time $\tau_a$ as $\epsilon(t) : \epsilon_0 \rightarrow \epsilon_1$ ($\epsilon_1 > \epsilon_0$).

2. Adiabatic process: The quantum dot is disconnected from the lead, and the energy is abruptly lowered as $\epsilon(t) : \epsilon_1 \rightarrow \epsilon_2$ ($\epsilon_1 > \epsilon_2$).

3. Isothermal process: The quantum dot is connected to a hot lead with temperature $T_1$ and chemical potential $\mu_1$. The energy is lowered during a finite time $\tau_b$, $\epsilon(t) : \epsilon_2 \rightarrow \epsilon_3$ ($\epsilon_2 > \epsilon_3$).

4. Adiabatic process: The dot is disconnected, and the energy abruptly returns to the original value: $\epsilon(t) : \epsilon_3 \rightarrow \epsilon_0$.

The period of one cycle is $\tau = \tau_a + \tau_b$, the output power is given by $P = W/\tau = Q/\tau = \int_0^\tau dt \dot{p}(t)[\epsilon(t) - \mu(t)]$. Finding the set of parameters that maximize the power may be done with a variational equation. In particular, the CA efficiency is recovered in the limit of weak dissipation (Esposito et al. 2010b).

D. Quantum heat engines

Quantum mechanics and thermodynamics have a deep connection, whose investigation started from thermodynamic studies by Planck (1901) and Einstein (1917). Due to recent progress of micro-fabrication technology, quantum effects in small heat engines have become an important subject.

The expectation value of the measured energy of a whole quantum system is $U = \sum_i p_i E_i$, where $E_i$ are the energy levels and $p_i$ are the corresponding occupation probabilities. This implies that

$$dU = \sum_i (E_i dp_i + p_i dE_i), \quad (87)$$
from which the absorbed heat is recognized to be \( \delta Q = \sum E_i dp_i \) and the output work \( \delta W = -\sum p_i dE_i \). Then, the first law \( dU = \delta Q - \delta W \) is satisfied.

The quantum-mechanical analogue of Carnot cyclic engine is introduced by identifying isothermal processes with quantum processes at constant expectation values of the energy (Bender, Brody, and Meister, 2000). For a single quantum mechanical particle confined to a potential well, the Carnot efficiency in this framework takes the form

\[
\eta_{\text{C}} = 1 - E_2/E_1,
\]

where \( E_1 \) and \( E_2 \) are the energy expectation values during the isothermal transformations at temperatures \( T_1 \) and \( T_2 \), respectively. Extensions of this approach include ideal Fermi gas with an arbitrary number of particles (Wang et al., 2012), Otto cycle (Quan et al., 2010), and the investigation of the efficiency at maximum power for the engine introduced by (Abdulrahman et al., 2011).

Quantum version of the Carnot heat engine and Otto heat engine for finite temperature was discussed without ambiguities in (Quan et al., 2007). Effect of multi-level systems was investigated (Quan, Zhang, and Sun, 2007). A class of quantum heat engines consisting of two subsystems interacting with a work source was studied to maximize the extracted work under various constraints (Alhverdyan, Jalal, and Mahler, 2008). Concepts from quantum information theory also provide new insights into the working of quantum heat engines (Kieu, 2004, 2006; Maruyama, Nori, and Vedral, 2008; Quan et al., 2006; Zhou and Segal, 2010).

Open systems attached to a thermal environment can be analyzed by means of the quantum master equation in the form (Kubo, Toda, and Hashitsume, 1985; Lindblad, 1976; Redfield, 1957)

\[
\dot{\rho} = \frac{i}{\hbar} \left[ \rho, H(\lambda(t)) \right] - \sum_{\alpha} \hat{\Gamma}_\alpha(t) \rho(t),
\]

where \( \rho \) is the density matrix of the system and \( \hat{\Gamma}_\alpha(t) \) denotes a superoperator representing dissipative effects arising from a reservoir labeled by index \( \alpha \). The parameter \( \lambda \) is a control parameter for the system. Then the output work \( \delta W \) and the heat \( \delta Q_\alpha \) absorbed from the \( \alpha \) reservoir are given by

\[
\delta W = -\text{Tr} \left[ \rho(t) \partial_\lambda H(\lambda) \right] \lambda dt , \tag{88}
\]

\[
\delta Q_\alpha = -\text{Tr} \left[ H(\lambda) \hat{\Gamma}_\alpha(t) \rho(t) \right] dt . \tag{89}
\]

The master equation approach reproduces the Carnot efficiency for the Carnot cycle (Alicki, 1979). The performance of a quantum heat engine or heat pump with the working fluid composed of noninteracting two-level systems was investigated by using a master equation (Feldmann and Kosloff, 2000). Kosloff (1984) showed that two coupled oscillators interacting with hot and cold quantum reservoir exhibit Curzon-Ahlborn efficiency in the limit of weak coupling. The quantum master equation was applied to analyze the performance of heat engines working with spins (Chen, Lin, and Hua, 2002; Geva and Kosloff, 1992; He, Lin, and Hua, 2002), harmonic oscillators (Arnaud, Chusseau, and Philippe, 2002; Lin and Chen, 2003a,b; Lin, Chen, and Hua, 2003), and multi-level systems (Geva and Kosloff, 1994). Characteristics of the steady state achieved by the iteration of cyclic process and monotonic approach to the limit cycle was discussed making use of the quantum conditional entropy (Feldmann and Kosloff, 2004). The unavoidable irreversible loss of power in a heat engine was considered for harmonic systems in the framework of quantum master equation approach (Rezek and Kosloff, 2006).

Fifty years after the pioneering works on quantum mechanics and thermodynamics by Planck (1901) and Einstein (1917), models of lasers and masers were realized as quantum heat engines (Scully and Schultz-DuBois, 1959) and the relation between the quantum efficiency of the maser and the Carnot cycle was investigated. Detailed balance imposed by thermodynamics limits the efficiency of quantum heat engines, including solar cells (Shockley and Queisser, 1961). Scully et al. analyzed the performance of a quantum heat engine operating by means of the radiation pressure from a single mode radiation field which drives a piston engine or a photon-Carnot engine. They pointed out that the phase associated with the atomic coherence provides a new control parameter, which can be varied to increase the temperature of the radiation field and to extract work from a single heat bath, while the real physics behind the second law of thermodynamics is not violated (Scully et al., 2002; Scully et al., 2003). This photon-Carnot engine was discussed in a quantum information context (Dillenschneider and Lutz, 2004) and decoherence mechanisms were studied (Quan, Zhang, and Sun, 2006).

Breakdown of detailed balance due to quantum coherence has been discussed for a quantum-dot photocell (Scully et al., 2010) and a photon-Carnot quantum heat engine (Scully et al., 2002). Noise-induced coherence was proposed as a potential ingredient to enhance quantum power (Scully et al., 2011). Quantum Otto engine in two-atom cavity quantum electrodynamics (Wang, Liu, and Hua, 2009) was studied to understand the role of thermal entanglement, and realization of Otto engine in single-modes fields was discussed (Wang, Wu, and Hua, 2012).

Photosynthetic reaction center is a quantum engine where energy is supplied from the light and hence it has similarities to heat engine (Dorfman et al., 2013). This also provides an important intersection between physics and biology. The rich history and ongoing studies suggest that the deep underlying connection between thermodynamics and quantum mechanics may be useful for improving the design and boosting the efficiencies of light-harvesting devices.

The concept of ideal quantum heat engine was introduced in cold bosonic atoms confined to a double well potential where thermalization occurs, and operation of a
heat engine with a finite quantum heat bath was theoretically demonstrated (Fialko and Hallwood 2012). A thermoelectric heat engine with ultracold fermionic atoms was demonstrated, both theoretically and experimentally (Brantut et al. 2013).

The fundamental limits to the dimensions of (steady-state) self-contained quantum machines, i.e. machines working without the supply of external work but only due to interactions with thermal baths at various temperatures, were investigated by Brunner et al. (2012); Linden, Popescu, and Skrzypczyk (2010); Skrzypczyk et al. (2011). In particular, it was shown that also a small self-contained refrigerator consisting of three qubits, each one in contact with a thermal reservoir, can achieve the Carnot efficiency (Skrzypczyk et al., 2011). In Venturelli, Fazio, and Giovannetti (2013) an electronic quantum refrigerator based on four quantum dots in contact with as many thermal reservoirs was theoretically investigated.

VIII. PHENOMENOLOGICAL LAWS AND THERMOELECTRIC TRANSPORT

A. Wiedemann-Franz law

In a wide range of macroscopic electronic conduction, the electron conductivity and the electronic contribution to the thermal conductivity are not independent. They are connected to each other by an empirical relation called the Wiedemann-Franz (WF) law (Wiedemann and Franz 1853). The WF law states that the ratio of the thermal conductivity $\kappa$ to the electric conductivity $\sigma$ of a metal is proportional to the temperature:

$$\frac{\kappa}{\sigma} = L T,$$

where the constant $L$ is known as the Lorenz number. In non-interacting electronic systems at low temperatures, the Lorenz number is given by

$$L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2.$$

This law is derived by using either kinetic theory or Landauer formula. In the kinetic theory approach (Kittel 2004), one uses the expression of electronic conductivity $\sigma \sim ne^2\tau/m$, where $n$ is the electronic density and $\tau$ is the mean-free time. Thermal conductivity $\kappa$ is given by $\kappa \sim C\tau^2/3$, with $C$ the specific heat and $v_F$ the Fermi velocity. The specific heat for a free electronic system at low temperatures is given by $C \sim \pi^2k_B^2T/mv_F^2$, which immediately yields the constant value $L/2$ for the Lorenz number. Another approach is based on the Landauer’s expressions of electric and thermal conductance, Eq. (55). In these expressions, we assume that the transmission is weakly energy-dependent, hence

$$\tau(E) \approx \tau(\mu).$$

Under this assumption, one can derive the WF law for the ratio of thermal and electric conductances: $\Xi/G = L T$. Both derivations of the WF law are substantiated by the Sommerfeld expansion (Ashcroft and Mermin 1976) of integrals (54) or (58) to the lowest order in $k_B T/E_F$, with $E_F$ being the Fermi energy. Such expansion is valid for a smooth function $\tau(E)$ or $\Sigma(E)$. Note that to derive the WF law the off-diagonal Onsager coefficient $L_{12}$ has to be neglected, i.e., one needs $L_{11}L_{22} \gg L_{12}^2$ in order to approximate the thermal conductance $\Xi$ with $L_{22}/T^2$ (van Houten et al. 1992).

B. Mott’s formula

The Mott’s formula states that the Seebeck coefficient $S$ in a metal is approximately given by the formula (Cutler and Mott 1969; Macdonald 2006; Mott and Davis 1971)

$$S \sim \frac{\pi^2 k_B^2 T}{3e} \partial_E \ln G(E) \bigg|_{E=\mu},$$

where $G(E)$ is the electric conductance at chemical potential $E$ in the leads. This relation is obtained under the assumption that the system is non-interacting and that conduction mainly occurs around the Fermi energy. Thus, the transmission probability is approximated as follows:

$$\tau(E) \approx \tau(\mu) + \partial_E \tau(\mu)(E - \mu).$$

The Mott’s relation (94) is derived after inserting this expansion into (53). An analogous derivation is obtained by considering the conductivity $\sigma(E)$ rather than conductance $G(E)$ and (77) rather than (53).

C. Thermolectricity

The Mott’s formula tells us that a sharp energy-dependence of electric conductivity is crucial for increasing the Seebeck effect. This is consistent with the importance of energy filtering structure of transmission discussed in Sec. IV.A. Both the WF law and the Mott’s relation follow from the single particle Fermi-liquid (FL) theory, so that the Sommerfeld expansion can be applied. If the FL theory holds in non-interacting systems, the WF law is valid in the presence of arbitrary disorder (Chester and Thellung 1961; Jonson and Mahan 1980). When the WF law is valid, it is not possible to obtain large thermolectric efficiency. Indeed, the WF law is obtained under the condition $L_{11}L_{22} \gg L_{12}^2$, hence the figure of merit $ZT = L_{22}/\det L \approx L_{12}^2/L_{11}L_{22} \ll 1$. This implies that to get large $ZT$ one should search for physical situations where the WF law is violated. The WF law is largely violated in low-dimensional interacting systems that exhibit non-FL behavior (Dora 2006; Garg et al.)
for making narrow energy window in transmission and
2010; Pauly, Viljias, and Cuevas, 2008; Reddy
2011; Finch, García-Suárez, and Lambert, 2009;
thermoelectric conversion (Balachandran
molecules weakly coupled to electrodes and for this
Sharp electronic resonances can be found also in
shows that in nanowires small diameter is desired
quantum dot can be used to obtain thermal rectification,
et al.
2007; Widawsky
wide-gap oxide semiconductor (Okazaki
i.e. the contribution of photo-induced carriers to the
thermoelectric properties of a
Thermopower measurements have been used to study
parametric conductance derivatives was analyzed using random matrix theory
Brouwer et al. 1997; and fluctuations of thermopower were discussed in van Langen, Silvestrov, and Beenakker
1998). Thermopower fluctuations exhibit a non-
Gaussian distribution, experimentally demonstrated in
Godijn et al. 1999). Effects of the spectrum edges of a
chaotic scatterer on thermopower distributions and its
universal aspects were studied in Abbont et al. 2013.
Fluctuations and nonlinear response of thermoelectricity were studied in terms of time-reversal symmetry
Ivoda, Utsumi, and Kata 2010) in analogy to the expansion using the fluctuation theorem for electric transport
Andrieux et al. 2009; Saito and Utsumi 2008). Nernst effect was theoretically studied to get strict bounds on efficiency (Stark et al. 2013).

IX. CONCLUSIONS

In this Colloquium we have presented a simple and self-contained account of few main theoretical approaches to discuss the problem of thermoelectric efficiency and the efficiency of steady-state heat to work conversion in general. Even though the problem has a long history, we believe that many recent theoretical advances described here, being in turn stimulated by new generations of experiments with nano-scale systems, should be somewhat taken from a new, more abstract perspective. Namely, we believe that the powerful machinery of non-equilibrium statistical mechanics and dynamical systems’ theory has not yet been fully explored in connection to coupled heat and electric, magnetic or particle transport and in particular in analyzing the figure of merit of thermoelectric, thermomagnetic or thermochemical efficiency. This being particularly so in view of some very recent new fundamental results on the behavior of thermoelectric efficiency in the presence of time-reversal symmetry breaking of the underlying equations of motion, such as by means of the magnetic field (Benenti, Saito, and Casati 2011; Brandner, Saito, and Seifert 2013; Brandner and Seifert 2014).

The central question which identifies this paper is: What limits, if any, the microscopic dynamical laws – for a particular model, or for a particular non-equilibrium steady-state setup – impose on the thermodynamic heat-to-work efficiency? While the theory for non-interacting systems discussed here seems to be well understood, the understanding of general mechanisms connected to strong interactions are only beginning to emerge. This justifies the importance of efficient numerical simulations of interacting systems at this point. While this Colloquium is focused on linear transport, thermoelectric devices often operate in the nonlinear regime of

Small systems such as quantum dots have an advantage for making narrow energy window in transmission and breaking the WF law. On the other hand, small systems exhibit large fluctuations in physical quantities. In open chaotic quantum dots, thermopower shows significant fluctuations. The distribution of parametric conductance derivatives was analyzed using random matrix theory (Brouwer et al. 1997; and fluctuations of thermopower were discussed in van Langen, Silvestrov, and Beenakker 1998). Thermopower fluctuations exhibit a non-Gaussian distribution, experimentally demonstrated in Godijn et al. 1999). Effects of the spectrum edges of a chaotic scatterer on thermopower distributions and its universal aspects were studied in Abbont et al. 2013. Fluctuations and nonlinear response of thermoelectricity were studied in terms of time-reversal symmetry (Ivoda, Utsumi, and Kata 2010) in analogy to the expansion using the fluctuation theorem for electric transport (Andrieux et al. 2009; Saito and Utsumi 2008). Nernst effect was theoretically studied to get strict bounds on efficiency (Stark et al. 2013).
transport. In that regime, reciprocity relations break down, as experimentally observed in a four-terminal mesoscopic device (Matthews et al. 2013), and the figure of merit $ZT$ fails to describe thermoelectric performance (Meair and Jacquod 2013; Whitney 2013; Zebarjadi, Esfariani, and Shakouri 2007). The observed breakdown of the Onsager-Casimir relations increasing thermal bias could in principle allow for improved thermoelectric efficiencies. In the nonlinear regime, rectification effects occur and their impact on thermoelectricity is still not well understood. In this regard, the recently developed (Meair and Jacquod 2013; Sánchez and López 2013; Whitney 2013) scattering theory of nonlinear thermoelectricity could pave the way to deeper investigations of quantum coherent conductors working beyond the linear response regime.

We expect to see in near future a burst of applications of fundamental ideas on abstract dynamical mechanisms for analyzing, or engineering particular practically relevant models, or for designing experiments and technological applications.

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