Thermoelectric mesoscopic phenomena / Phénomènes thermoélectriques mésoscopiques

The thermoelectric working fluid: Thermodynamics and transport

Le fluide de travail thermoélectrique : thermodynamique et transport

Giuliano Benenti [a,b,*], Henni Ouerdane [c,d,e], Christophe Goupil [c]

[a] Center for Nonlinear and Complex Systems, Dipartimento di Scienza e Alta Tecnologia, Università degli Studi dell'Insubria, via Valleggio 11, 22100 Como, Italy
[b] Istituto Nazionale di Fisica Nucleare, Sezione di Milano, via Celoria 16, 20133 Milano, Italy
[c] Laboratoire interdisciplinaire des énergies de demain (LIED), UMR 8236, Universitié Paris-Diderot, CNRS, 5, rue Thomas-Mann, 75013 Paris, France
[d] Russian Quantum Center, 100 Novaya Street, Skolkovo, Moscow region 143025, Russian Federation
[e] UFR LVE, Université de Caen Normandie, Esplanade de la Paix, 14032 Caen, France

A R T I C L E   I N F O

A B S T R A C T

Thermoelectric devices are heat engines, which operate as generators or refrigerators using the conduction electrons as a working fluid. The thermoelectric heat-to-work conversion efficiency has always been typically quite low, but much effort continues to be devoted to the design of new materials boasting improved transport properties that would make them of the electron crystal–phonon glass type of systems. On the other hand, there are comparatively few studies where a proper thermodynamic treatment of the electronic working fluid is proposed. The present article aims at contributing to bridge this gap by addressing both the thermodynamic and transport properties of the thermoelectric working fluid covering a variety of models, including interacting systems.

© 2016 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

R É S U M É

Les dispositifs thermoélectriques sont des machines thermiques pouvant opérer en mode générateur ou réfrigérateur en utilisant les électrons de conduction comme fluide de travail. Le rendement de conversion chaleur–travail a toujours été typiquement bas, mais la conception de nouveaux matériaux thermoélectriques fait l'objet d'efforts conséquents en vue d'obtenir des systèmes de type cristal électronique–verre de phonons. Par comparaison, il y a cependant un déficit de traitement approfondi des propriétés thermodynamiques du fluide de travail thermoélectrique. Le présent article vise à contribuer à combler cet écart en examinant les propriétés thermodynamiques et de transport du fluide de

* Corresponding author.
  E-mail addresses: giuliano.benenti@uninsubria.it (G. Benenti), henni.ouerdane@rqc.ru (H. Ouerdane), christophe.goupil@univ-paris-diderot.fr (C. Goupil).

travail thermoélectrique dans le cadre de différents modèles, incluant les systèmes en interaction.

1. Introduction

In a general manner, transport phenomena are irreversible processes: the generation of fluxes within the system upon which external constraints are applied are accompanied by energy dissipation and entropy production [1]. Now, assume a thermodynamic system in which electric transport and heat transport may take place. Thermoelectric effects may be thus viewed as the result of the mutual interaction of two irreversible processes, electrical transport and heat transport, as they take place [2,3]. This mutual interaction may be quantified by the so-called degree of coupling [4] upon which the thermoelectric conversion efficiency depends. Owing to the coupling of electrical charges with heat transport (the strength of which is given by the Seebeck coefficient), thermoelectric systems thus form a most interesting class of heat engines, not only for practical purposes, but also from a fundamental viewpoint: some of the theoretical developments of the mathematical relationships between forces and fluxes in coupled transport rest on the analysis of thermoelectric systems [2,5], and thermoelectricity is a touchstone for theories of irreversible thermodynamics [6]. On the practical side, thermoelectric devices may be used to collect and transform waste heat into electrical power, to pump heat for cooling or heating, and for temperature measurement. These devices are particularly reliable, even in hostile places, as demonstrated in the context of deep-space probe missions. Indeed, since thermoelectric phenomena are electronic in nature, their energy conversion efficiency is not system-size-dependent, their operation does not rely on moving parts, and there is no need for refrigerant fluids for coolers.

The thermoelectric performance is governed by the thermoelectric figure of merit [7,8]

$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_{ph}} \tag{1}$$

where σ is the electrical conductivity, S the thermopower (or Seebeck coefficient), κ_e and κ_{ph} the electronic and the phononic heat conductivities, respectively, and T the system's temperature. To envisage applications for thermoelectric systems other than those for which sustainability and reliability are more important than low-level efficiency and high cost, values of ZT greater than 4 are mandatory [9]. The great challenge to increase thermoelectric efficiency relies on understanding the microscopic mechanisms that may allow one to control individually σ, S, and $\kappa = \kappa_e + \kappa_{ph}$. However, the different transport coefficients are interdependent, making optimization extremely difficult and so far, no clear paths exist which may lead to reach that target. A significant example of this interdependence is the Wiedemann–Franz law [10], which states that for metallic materials, σ and κ_e are proportional, thus making metals poor thermoelectric materials in general.

The energy transferred by phonons represents a useless heat leak and recent efforts in materials science and engineering focused on strategies to lower lattice heat conduction [11,12], in particular in low-dimensional nanostructures where rough surfaces can efficiently scatter phonons [13,14]. On the other hand, even ideally reducing $\kappa_{ph} \rightarrow 0$, as in the electron crystal–phonon glass paradigm [15], would not by itself guarantee $ZT \gg 1$, due to the remaining electronic contribution κ_e to the thermal conductivity. However, it must be clearly mentioned that κ_e accounts for two physical phenomena: heat transfer by conduction (Fourier's law) and heat transfer by electron *convection* [16], which is the so-called Peltier term of the heat flux [17]. Note that the latter represents the actual and global electronic movement within the conduction band of the system submitted to a thermal gradient, hence convection only can be seen as the "useful" contribution to heat transfer across the system. Here, we will thus rather focus on an aspect of thermoelectricity, which is nearly always neglected: investigate suitable strategies to improve the properties of the thermoelectric working fluid itself.

The article is organized as follows: in Section 2, we cover the thermodynamics and transport properties of the noninteracting working fluid. We then focus on phase transitions in Section 3 and finally consider interacting working fluids in Section 4, covering momentum-conserving systems. In Section 5, we discuss the question of optimization of device operation, as the system's working fluid is dissipatively coupled with a hot and to a cold temperature bath, and we end the article with concluding remarks.

2. The noninteracting thermoelectric working fluid

2.1. The Onsager approach to coupled transport

In the linear response regime, the relationship between currents and generalized forces is linear [18,19] and in the case of thermoelectric transport we have

$$\begin{cases} j_e = L_{ee} \mathcal{F}_e + L_{eh} \mathcal{F}_h \\ j_h = L_{he} \mathcal{F}_e + L_{hh} \mathcal{F}_h \end{cases} \tag{2}$$

where j_e is the electric current density, j_h is the heat current density, and the conjugated local generalized forces are given by $\mathcal{F}_e = -\nabla\mu/eT$ and $\mathcal{F}_h = \nabla(1/T)$, μ is the electrochemical potential and $e < 0$ is the electron charge. The coefficients L_{ab} ($a, b = e, h$) are known as kinetic coefficients or Onsager coefficients; we will denote $\boldsymbol{L}$ the Onsager matrix with matrix elements L_{ab}.

The Onsager coefficients are subject to two fundamental constraints. First, the second law of thermodynamics requires the positivity of the entropy production rate,

$$\dot{s} = \mathcal{F}_e J_e + \mathcal{F}_h J_h = L_{ee}\mathcal{F}_e^2 + L_{hh}\mathcal{F}_h^2 + (L_{eh} + L_{he})\mathcal{F}_e\mathcal{F}_h \geq 0 \tag{3}$$

where s is the local entropy density. Eq. (3) is equivalent to the conditions

$$L_{ee} \geq 0, \quad L_{hh} \geq 0, \quad L_{ee}L_{hh} - \frac{1}{4}(L_{eh} + L_{he})^2 \geq 0 \tag{4}$$

Second, assuming the property of time-reversal invariance of the equations of motion, Onsager derived [2] fundamental relations, known as Onsager reciprocal relations for the cross coefficients of the Onsager matrix: $L_{ab} = L_{ba}$.

The kinetic coefficients L_{ab} are related to the thermoelectric transport coefficients: the electrical conductivity σ, the thermal conductivity κ, the Seebeck coefficient S, and the Peltier coefficient Π, as

$$\sigma = -e\left(\frac{j_e}{\nabla\mu}\right)_{\nabla T=0} = \frac{L_{ee}}{T} \tag{5}$$

$$\kappa = -\left(\frac{j_h}{\nabla T}\right)_{j_e=0} = \frac{1}{T^2}\frac{\det \boldsymbol{L}}{L_{ee}} \tag{6}$$

$$S = -\frac{1}{e}\left(\frac{\nabla\mu}{\nabla T}\right)_{j_e=0} = \frac{1}{T}\frac{L_{eh}}{L_{ee}} \tag{7}$$

$$\Pi = \left(\frac{j_h}{j_e}\right)_{\nabla T=0} = \frac{L_{he}}{L_{ee}} \tag{8}$$

For systems with time reversal symmetries, $\Pi = TS$ due to the Onsager reciprocal relations [17].

Using Eqs. (1) and (5)–(7), the thermoelectric figure of merit reads

$$ZT = \frac{L_{eh}^2}{\det \boldsymbol{L}} \tag{9}$$

Thermodynamics only imposes a lower bound on the figure of merit: $ZT \geq 0$, and the thermoelectric conversion efficiency is a monotonous increasing function of ZT, the ideal Carnot efficiency being achieved in the limit $ZT \to \infty$. To understand why thermoelectric systems boast rather poor performance levels in terms of conversion efficiency, and how one may obtain high values of ZT, which ideally should be "only" greater than 4 for practical purposes, we must compute and analyze the transport coefficients.

2.2. Transport parameters

For non-interacting systems, Mahan and Sofo showed long ago [20] that the best thermoelectric efficiency can be obtained in systems with *energy filtering*, namely where the energy width of the main conducting channel is very narrow. This result can be understood as follows. We can write the Onsager coefficients as [20,21]:

$$L_{ee} = 2e^2 T K_0, \;\; L_{eh} = L_{he} = 2eT K_1, \;\; L_{hh} = 2T K_2 \tag{10}$$

where the factor 2 is due to spin degeneracy, and the integrals

$$K_n \equiv \int_{-\infty}^{\infty} dE(E-\mu)^n \Sigma(E)\left(-\frac{\partial f}{\partial E}\right) \tag{11}$$

are written in terms of the Fermi distribution function $f(E) = \{\exp[(E-\mu)/k_B T] + 1\}^{-1}$ and of the transport distribution function $\Sigma(E)$, which can be derived both in the semiclassical Boltzmann approach [20] or using Green's function techniques[1] [22]. We can therefore write the transport coefficients as follows:

$$\sigma = 2e^2 K_0, \;\; \kappa = \frac{2}{T}\left(K_2 - \frac{K_1^2}{K_0}\right), \;\; S = \frac{1}{eT}\frac{K_1}{K_0} \tag{12}$$

---

[1] In the Landauer approach, where conductances rather than conductivities are used, similar expressions are derived with the transport distribution function substituted by the transmission function [21,24,25].

The Seebeck coefficient may be seen as the average value of the entropy involved in the thermoelectric transport, $(E - \mu)/T$, over a probability density function given by the product of the transport distribution function and the energy derivative of f. In metals and degenerate semiconductors, where electrons above the Fermi level carry a heat current that is practically the opposite of that carried by the electrons below the Fermi level, the Seebeck coefficient is typically small: since $E - \mu$ changes sign as E varies, it is essential that Σ presents an asymmetric profile [23] to avoid cancellation of K_1.

The Carnot efficiency is achieved in the case of energy filtering, i.e. when the transmission is possible only within a tiny energy window around a value $E = E_\star$. Indeed, in this case from Eq. (11), we obtain $K_n \approx (E_\star - \mu)^n K_0$, and therefore

$$ZT = \frac{\sigma S^2}{\kappa} T = \frac{K_1^2}{K_0 K_2 - K_1^2} \to \infty \tag{13}$$

On the other hand, the Wiedemann–Franz law is recovered in the limit of a broad and smooth transmission function. More precisely, we consider the Sommerfeld expansion [10] of integrals (11) to the leading order in $k_B T / E_F$, with k_B being the Boltzmann constant and $E_F = \mu(T = 0)$ being the Fermi energy. Such an expansion is valid for a smooth function $\Sigma(E)$. The transport distribution function is approximated as follows:

$$\Sigma(E) \approx \Sigma(\mu) + \frac{d\Sigma(E)}{dE}\bigg|_{E=\mu} (E - \mu) \tag{14}$$

After inserting this expansion into (11), we obtain the leading order terms of the Sommerfeld expansion of integrals K_n:

$$K_0 \approx \Sigma(\mu), \quad K_1 \approx \frac{\pi^2}{3}(k_B T)^2 \frac{d\Sigma(E)}{dE}\bigg|_{E=\mu}, \quad K_2 \approx \frac{\pi^2}{3}(k_B T)^2 \Sigma(\mu) \tag{15}$$

In this derivation, we have used the fact that $\partial f / \partial E$ is an even function of $\epsilon \equiv (E - \mu)/k_B T$. Hence, K_0 and K_2 are determined to the leading order by $\Sigma(\mu)$. In contrast, $(E - \mu)\partial f / \partial E$ is an odd function of ϵ, so that K_1 is determined by the derivative $\frac{d\Sigma(E)}{dE}\big|_{E=\mu}$. We then derive from Eq. (12)

$$\sigma \approx 2e^2 \Sigma(\mu), \quad \kappa \approx \frac{2\pi^2 k_B^2 T}{3}\Sigma(\mu) \tag{16}$$

and from these relations we find the Wiedemann–Franz law

$$\frac{\kappa}{\sigma T} \approx \mathfrak{L} \tag{17}$$

where the constant value

$$\mathfrak{L} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \tag{18}$$

is known as the Lorenz number.

To derive the Wiedemann–Franz law, we have considered only the leading order term in the Sommerfeld expansion, i.e. we have neglected in the heat conductivity K_1^2/K_0 with respect to K_2. This in turn implies that $L_{ee}L_{hh} \gg L_{eh}^2$ and the thermal conductivity $\kappa \approx L_{hh}/T^2$. When the Wiedemann–Franz law is valid, it is not possible to obtain large thermoelectric efficiency, as in this case the figure of merit $ZT = L_{eh}^2/\det \boldsymbol{L} \approx L_{eh}^2/L_{ee}L_{hh} \ll 1$. Consequently, to get large values of ZT, one should search for physical situations where the Wiedemann–Franz law is violated. For non-interacting particles, violations can occur in small systems where transmission shows a significant energy dependence [26–31] or in bulk systems in the vicinity of a phase transition, where the transport distribution function is not an analytic function.

2.3. Anderson transition

We consider first the metal-insulator transition in the three-dimensional Anderson model, and we define $\sigma_0(E) = 2e^2 \Sigma(E)$, so that

$$\sigma = \int_{-\infty}^{\infty} dE \, \sigma_0(E) \left(-\frac{\partial f}{\partial E}\right) \tag{19}$$

In this case, $\sigma_0(E)$ corresponds to the $T = 0$ electrical conductivity of the system when the Fermi energy $E_F = E$. In the Anderson transition, a mobility edge E_m separates localized states (for $E < E_m$) from extended states (for $E > E_m$), and the zero temperature conductivity changes non-analytically at $E = E_m$:

$$\sigma_0(E) = \begin{cases} A(E - E_m)^x, & \text{if } E \geq E_m \\ 0, & \text{if } E \leq E_m \end{cases} \tag{20}$$

where A is a constant and x the conductivity critical exponent whose value is unknown, in spite of several analytical and numerical methods used to attempt its evaluation [32].

We can here express the thermopower S, the ratio $\kappa/\sigma T$ and the figure of merit ZT in terms of a single scaling parameter,

$$z \equiv \frac{\mu - E_{\mathrm{m}}}{k_{\mathrm{B}} T} \tag{21}$$

We then calculate:

$$S = \frac{k_{\mathrm{B}}}{e} \frac{\displaystyle\int_{-z}^{\infty} \mathrm{d}y \, y(y+z)^x f'(y)}{\displaystyle\int_{-z}^{\infty} \mathrm{d}y \, (y+z)^x f'(y)} \tag{22}$$

with $f'(y) = -1/[4\cosh^2(y/2)]$ is the derivative of the Fermi function, and

$$\frac{\kappa}{\sigma T} = \left(\frac{k_{\mathrm{B}}}{e}\right)^2 \frac{\displaystyle\int_{-z}^{\infty} \mathrm{d}y \, y^2(y+z)^x f'(y)}{\displaystyle\int_{-z}^{\infty} \mathrm{d}y(y+z)^x f'(y)} - S^2 \tag{23}$$

so that also the figure of merit ZT only depends on the scaling parameter z.

The ratio $\kappa/\sigma T$, the figure of merit ZT and the thermopower[2] S, are depicted in Fig. 1, for various values of the critical exponent x. For low enough temperatures, that is, for $k_{\mathrm{B}} T \ll \mu - E_{\mathrm{m}}$, the nonanalytic behavior of $\sigma_0(E)$ at the mobility edge is not relevant. We can therefore apply the Sommerfeld expansion and obtain

$$S \approx \frac{\pi^2}{3} \frac{k_{\mathrm{B}}}{e} \left(\frac{x}{z}\right), \quad \frac{\kappa}{\sigma T} \approx \mathfrak{L}, \quad ZT \approx \frac{\pi^2}{3} \left(\frac{x}{z}\right)^2 \tag{24}$$

On the other hand, increasing the temperature, the non-analyticity at E_{m} plays an important role, and the Sommerfeld expansion can no longer be applied; the Wiedemann–Franz law is then violated, and relatively large values of ZT may be obtained. More interesting enhancements of ZT can be obtained close to electronic phase transitions in interacting systems.

3. Phase transitions

A reasoning by Vining [33] suggests that large values of ZT can be expected near electronic phase transitions. First of all, we consider the thermal conductivity κ' at zero voltage ($\mathcal{F}_e = 0$), which is related to the thermal conductivity κ measured at zero electric current as $\kappa = \kappa' + \sigma S \Pi$. The thermoelectric figure of merit can then be written as

$$ZT = \gamma_{\mathrm{K}} - 1, \quad \gamma_k \equiv \frac{\kappa'}{\kappa} \tag{25}$$

and we see that ZT diverges if and only if the ratio γ_k diverges. Of course, there is no such a thing as a liquid–gas phase transition in electronic systems, but other types of transitions, involving electron pairing mechanism as is the case for superconductivity, exist, and it is worthwhile to focus now on the thermodynamic properties of the working fluid itself rather than on transport.

Vining's initial idea [33] was refined and developed by Ouerdane et al. [34]: the rationale of their analysis rests on the facts that thermoelectric transport is essentially a convective process [16], and that convection may be enhanced in the vicinity of a phase transition. The key point was then to see how to characterize the thermoelastic properties of the electronic working fluid and its capacity for enhanced convective transport. This they did by introducing the *thermodynamic figure of merit*, the meaning of which is physically transparent: it is related to the compressibility of the considered fluid and the Prandtl number, given by the ratio of the kinematic viscosity over the thermal diffusivity [35]. As a matter of fact, this characteristic number in fluid dynamics provides a direct link between the thermodynamic properties of the fluid and its capacity for convective transport.

Now, consider an open system characterized by the number N of particles, the electrochemical potential μ and the temperature T. We have [33]:

---

[2] See Ref. [32] also for a detailed discussion of thermopower close to the Anderson transition.
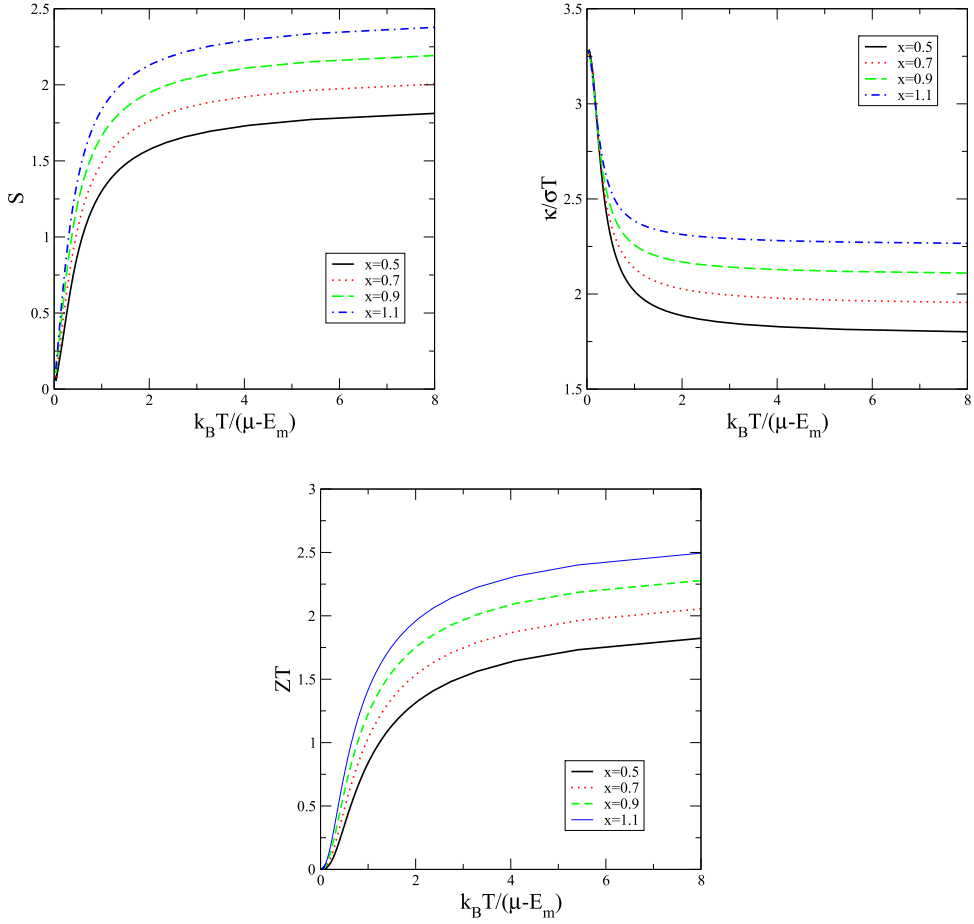
Fig. 1. Thermopower (in units of k_B/e) (top left), ratio $\kappa/\sigma T$ (in units of $(k_B/e)^2$) (top right), and thermoelectric figure of merit ZT (bottom) as a function of the inverse of the scaling parameter $z = (\mu - E_m)/k_B T$, for different values of the critical exponent x.

$$
\begin{cases}
dN = \left(\frac{\partial N}{\partial \mu}\right)_T d\mu + \left(\frac{\partial N}{\partial T}\right)_\mu dT \equiv C_{NN}d\mu + C_{N\mathscr{S}}dT \\
d\mathscr{S} = \left(\frac{\partial \mathscr{S}}{\partial \mu}\right)_T d\mu + \left(\frac{\partial \mathscr{S}}{\partial T}\right)_\mu dT \equiv C_{\mathscr{S}N}d\mu + C_{\mathscr{S}\mathscr{S}}dT
\end{cases}
\tag{26}
$$

where $\mathscr{S}$ denotes the system's entropy. These equations are formally similar to the coupled transport equations (2), with the *capacity matrix* **C** (with matrix elements C_{ab}, $a, b = N, \mathscr{S}$) rather than the Onsager matrix **L**. Note that $C_{N\mathscr{S}} = C_{\mathscr{S}N}$ due to the extended Maxwell relation

$$
\left(\frac{\partial N}{\partial T}\right)_\mu = \left(\frac{\partial \mathscr{S}}{\partial \mu}\right)_T
\tag{27}
$$

Moreover, $C_{\mathscr{S}\mathscr{S}} \equiv C_\mu$ is the entropy capacity at constant μ. Finally, the entropy capacity at constant N is

$$
C_N \equiv \left(\frac{\partial \mathscr{S}}{\partial T}\right)_N = \frac{\det \mathbf{C}}{C_{NN}}
\tag{28}
$$

where the last equality is derived after setting $dN = 0$ in (26).

We now consider a thermodynamic cycle consisting of two constant electrochemical potential strokes $d\mu$ apart and two constant particle number strokes dN apart. The infinitesimal work performed by this cyclic process is $-d\mu\, dN$ and we can compare it with the work $d\mathscr{S}dT$ performed by a Carnot cycle consisting of two isothermal strokes dT apart and two adiabatic strokes $d\mathscr{S}$ apart. The ratio between the heat-to-work conversion efficiencies of the above two processes is therefore given by

$$
\frac{\eta}{\eta_C} = \frac{-d\mu\, dN}{d\mathscr{S}\, dT}
\tag{29}
$$

As the Carnot efficiency for a cycle operating between temperatures T and $T + dT$ is $\eta_C = dT/T$, we obtain

$$\eta = \frac{-\mathrm{d}\mu \, \mathrm{d}N}{T \, \mathrm{d}\mathscr{S}} = \frac{-\mathrm{d}\mu \, (C_{NN}\mathrm{d}\mu + C_{N\mathscr{S}}\mathrm{d}T)}{T(C_{\mathscr{S}N}\mathrm{d}\mu + C_{\mathscr{S}\mathscr{S}}\mathrm{d}T)} \tag{30}$$

and, similarly to thermoelectric transport, one can show [34] that the maximum efficiency of this thermodynamic cycle is a monotonous growing function of the thermodynamic figure of merit:

$$Z_{\mathrm{th}}T = \frac{C_{N\mathscr{S}}^2}{\det \boldsymbol{C}} = \gamma_{\mu N} - 1, \quad \gamma_{\mu N} \equiv \frac{C_\mu}{C_N} \tag{31}$$

We point out that $Z_{\mathrm{th}}T$ is purely determined by the properties of the working fluid, without referring to thermoelectric transport. Consequently, it does not include any contribution from phonons, which instead affect the thermoelectric figure of merit ZT.

As a final step, we use the mapping $\mu \to -p$ and $N \to V$, with p and V pressure and volume of a gas. We then consider the infinitesimal work $\mathrm{d}p \, \mathrm{d}V$ performed by a cycle consisting of two isobaric strokes $\mathrm{d}P$ apart and two isochoric strokes $\mathrm{d}V$ apart and compare it again with the work $\mathrm{d}\mathscr{S}\mathrm{d}T$ performed by a Carnot cycle. By using the same steps as above for the $\mu - N$ system, we find that the heat to work conversion efficiency is a monotonous function of the thermodynamic figure of merit for the $p - V$ systems:

$$Z_{\mathrm{th}}T = \gamma_{pV} - 1, \quad \gamma_{pV} \equiv \frac{C_p}{C_V} \tag{32}$$

where

$$C_p \equiv T \left(\frac{\partial \mathscr{S}}{\partial T} \right)_p, \quad C_V \equiv T \left(\frac{\partial \mathscr{S}}{\partial T} \right)_V \tag{33}$$

are the heat capacity at constant pressure and volume, respectively. For a classical ideal (noninteracting) gas, $1 < \gamma_{pV} \leq \frac{5}{3}$, with the upper bound achieved for monoatomic gases. Hence, $Z_{\mathrm{th}}T \leq \frac{2}{3}$. On the other hand, the ratio γ_{pV} (and Z_{th}) can diverge for condensable gases, at the critical temperature T_{c} between the gas phase and the two-phase region (gas–liquid coexistence). The analogy with a classical gas suggests the possibility of large values of Z_{th} close to electronic phase transitions, strongly improving the thermoelectric properties of the working fluid with respect to noninteracting systems in their normal state. Indeed, it has been recently demonstrated [34] that $Z_{\mathrm{th}}T$ diverges when approaching from the normal phase the critical point for the transition to the superconducting phase, in the fluctuation regime [36].

More specifically, to analyze the thermodynamic properties of the electronic working fluid near the superconducting phase transition, one needs a set of four thermoelastic coefficients: $\beta N = (\partial N/\partial T)_\mu$: analogue to thermal dilatation coefficient; $\chi_T N = (\partial N/\partial \mu)_T$: analogue to isothermal compressibility; $c_\mu N = T (\partial \mathscr{S}/\partial T)_\mu$: analogue to specific heat at constant pressure; $c_N N = T (\partial \mathscr{S}/\partial T)_N$: analogue to specific heat at constant volume. Application of the extended Maxwell's relations yields $\beta/\chi_T = \mathscr{S}_N$ with $\mathscr{S}_N = (\partial \mathscr{S}/\partial N)_T$, which reflects the notion of entropy per particle introduced by Callen [3] and the ensuing thermodynamic definition of the thermoelectric coupling: $s_{\mathrm{th}} = \beta \chi_T^{-1}/e$.

The heat capacity at constant particle number can be derived from the knowledge of the free energy of the fluctuation Cooper pairs: $c_N = (-T/N_{\mathrm{cp}})\partial^2 \mathcal{F}_{\mathrm{cp}}/\partial T^2$, where N_{cp} is the number of fluctuation Cooper pairs; the other three thermoelastic coefficients β, χ_T, and c_μ are given below. For clarity, we give the derivation steps for χ_T; the other two follow similar steps. For a many-particle system with energy distribution function f and density of state g, the number of particles N is given by:

$$N = \int_0^\infty g(E) f(E) \mathrm{d}E \tag{34}$$

By definition, $\chi_T N = (\partial N/\partial \mu)_T$, and the first partial derivative of N with respect to μ at constant temperature takes the form:

$$\frac{\partial N}{\partial \mu} = \int_0^\infty g(E) \frac{\partial f}{\partial \mu} \mathrm{d}E = \int_0^\infty g(E) \left(-\frac{\partial f}{\partial E} \right) \mathrm{d}E \tag{35}$$

since the density of state does not depend on μ and $\partial f/\partial \mu = -\partial f/\partial E$. We thus obtain χ_T as well as the other two coefficients in the same fashion:

$$\chi_T N = \int_0^\infty g(E) \left(-\frac{\partial f}{\partial E} \right) \mathrm{d}E$$

$$\beta N = \frac{1}{T_{\mathrm{a}}} \int_0^\infty g(E) (E - \mu_{\mathrm{a}}) \left(-\frac{\partial f}{\partial E} \right) \mathrm{d}E$$

$$c_\mu N = \frac{1}{T_a} \int\limits_0^\infty g(E)\,(E-\mu_a)^2 \left(-\frac{\partial f}{\partial E}\right) dE$$

where μ_a and T_a are the average values of the electrochemical potential and temperature across the considered system. The shape of the derivative of the Fermi function is given in Section 2.3.

As shown in Ref. [34], $Z_{\rm th}$ may diverge at *finite* temperature in the fluctuation regime case, while it does not for the standard Bose and Fermi gases. This explains why thermoelectric devices, which use the noninteracting electron gas a working fluid, are not very efficient energy conversion devices, despite the intense efforts to improve their performance over decades. The fluctuation regime studied in Ref. [34], where phonons are put to work to bind electrons, shows that it is possible to prepare highly compressible electrically charged working fluids, but other electronic systems could also present enhanced thermoelectric properties as long as they boast a high-compressibility factor.

4. Interacting working fluids

4.1. General considerations

The thermoelectric properties of strongly interacting systems are of great interest, since their efficiency is not bounded by limitations due to the Wiedemann–Franz law, which applies for bulk non-interacting metallic-like systems. Moreover, experimental results on some strongly correlated materials such as sodium cobalt oxides revealed unusually large thermopower values [37,38], in part attributed to strong electron–electron interactions [39] due to the d or f character of the band structure in the vicinity of the Fermi level, and also to the fact that oxides have both spin and orbital degrees of freedom, hence high entropy. Further, strong correlations may be acted upon to increase the power factor $S\sigma^2$ through the tuning of crystal–field and spin–orbit coupling up to an optimum, as shown for correlated Kondo insulators in Ref. [40].

As a matter of fact, fairly little is known about the thermoelectric properties of strongly correlated systems. Theoretical formalisms include the dynamical mean field theory [41] for non-perturbative computation of the self-energy of the many-body systems and of the thermoelectric and thermodynamic properties of, e.g., a hole-doped Mott insulator [42], the slave boson formalism [43,44] to treat the large on-site repulsion term in lattice models as in Ref. [40], and the Green–Kubo approach employed below. Analytical results are thus rare and numerical simulations (Monte Carlo and numerical renormalization group), even if based on simple effective Hamiltonian models, such as the single-band Hubbard model or the single impurity Anderson model, are challenging. However, on the basis of the Green–Kubo formula, we can discuss a thermodynamic argument suggesting that the Carnot efficiency is achieved in the thermodynamic limit for non-integrable momentum-conserving systems, which we cover hereafter.

4.2. Momentum-conserving systems

A general thermodynamic argument [45] corroborated by numerical simulations [45–47] predicts that nonintegrable systems with momentum conservation achieve the Carnot efficiency at the thermodynamic limit. Such an argument is rooted in the Green–Kubo formula, which expresses the Onsager kinetic coefficients in terms of dynamic correlation functions of the corresponding current operators, calculated at thermodynamic equilibrium [48,49]:

$$L_{ab} = \lim_{\omega \to 0} {\rm Re}[L_{ab}(\omega)], \quad L_{ab}(\omega) = \lim_{\epsilon \to 0} \int\limits_0^\infty dt\, e^{-i(\omega - i\epsilon)t} \lim_{\Omega \to \infty} \frac{1}{\Omega} \int\limits_0^\beta d\tau\, \langle \hat{J}_a \hat{J}_b(t+i\tau)\rangle \tag{36}$$

where $\beta = 1/k_B T$, $\langle \cdot \rangle = \{{\rm tr}[(\cdot)\exp(-\beta H)]\}/{\rm tr}[\exp(-\beta H)]$ denotes the thermodynamic expectation value at temperature T, Ω is the system's volume, and the currents are $J_a = \langle \hat{J}_a \rangle$, with $\hat{J}_a$ being the total 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, where $\hat{j}_a(\vec{r})$ is the current density operator, satisfying the continuity equation

$$\frac{d\hat{\rho}_a(\vec{r},t)}{dt} = \frac{i}{\hbar}[H,\hat{\rho}_a] = -\nabla \cdot \hat{j}_a(\vec{r},t) \tag{37}$$

where $\hat{\rho}_a$ is the density of the corresponding conserved quantity, that is, electric charge for the electric current and energy for the energy current [3] and $\hbar$ is the reduced Planck constant. Equation (37) can be equally well written in classical mechanics, provided the commutator is substituted by the Poisson bracket multiplied by the factor $i\hbar$. It can be shown that the real part of $L_{ab}(\omega)$ can be decomposed into a δ-function at zero frequency defining a generalized *Drude weight* D_{ab} (for $a=b$, this is the conventional Drude weight) and a regular part $L_{ab}^{\rm reg}(\omega)$:

---

[3] The heat current is the difference between the total *energy current* J_u and the electrochemical potential energy current μJ_ρ: $J_h = J_u - \mu J_\rho = J_u - (\mu/e)J_e$ [18].

$$\mathrm{Re}L_{ab}(\omega) = 2\pi \, D_{ab}\delta(\omega) + L_{ab}^{\mathrm{reg}}(\omega) \tag{38}$$

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

$$D_{ab} = \lim_{\bar{t}\to\infty} \frac{1}{\bar{t}} \int\limits_0^{\bar{t}} \mathrm{d}t \lim_{\Omega\to\infty} \frac{1}{\Omega} \int\limits_0^{\beta} \mathrm{d}\tau \, \langle \hat{J}_a(0)\hat{J}_b(t+\mathrm{i}\tau)\rangle \tag{39}$$

Note that it has been shown that non-zero Drude weights, $D_{ab} \neq 0$, are a signature of ballistic transport [50–53], namely in the thermodynamic limit the kinetic coefficients L_{ab} diverge linearly with the system size.

The way in which the dynamic correlation functions in Eq. (36) decay determines the ballistic, anomalous, or diffusive character of the heat and charge transport, and it has been understood that this decay is directly related to the existence of conserved dynamical quantities [50,51]. For quantum spin chains and under suitable conditions, it has been proved that systems possessing conservation laws exhibit ballistic transport at finite temperature [54].

The following argument [45] highlights the role that conserved quantities play in the thermoelectric efficiency. The decay of time correlations for the currents can be related to the existence of conserved quantities by using *Suzuki's formula* [55], which generalizes an inequality proposed by Mazur [56]. Consider a system of size Λ along the direction of the currents (we denote its volume as $\Omega(\Lambda)$, and in the thermodynamic limit $\Omega \to \infty$) and Hamiltonian H, with a set of M *relevant conserved quantities* Q_m, $m = 1, \ldots, M$, namely the commutators $[H, Q_m] = 0$. A constant of motion Q_m is by definition relevant if it is not orthogonal to the currents under consideration, in our case $\langle \hat{J}_e Q_m \rangle \neq 0$ and $\langle \hat{J}_h Q_m \rangle \neq 0$. It is assumed that the M constants of motion are orthogonal, i.e., $\langle Q_m Q_n \rangle = \langle Q_n^2 \rangle \delta_{mn}$ (this is always possible via a Gram–Schmid procedure). Furthermore, we assume that the set $\{Q_m\}$ exhausts all relevant extensive conserved quantities. Then using Suzuki's formula, we can express the *finite-size Drude weights*[4]

$$d_{ab}(\Lambda) \equiv \frac{1}{2\Omega(\Lambda)} \lim_{\bar{t}\to\infty} \frac{1}{\bar{t}} \int\limits_0^{\bar{t}} \mathrm{d}t \langle \hat{J}_a(0)\hat{J}_b(t)\rangle \tag{40}$$

in terms of the relevant conserved quantities:

$$d_{ab}(\Lambda) = \frac{1}{2\Omega(\Lambda)} \sum_{m=1}^{M} \frac{\langle \hat{J}_a Q_m \rangle \langle \hat{J}_b Q_m \rangle}{\langle Q_m^2 \rangle} \tag{41}$$

On the other hand, the thermodynamic Drude weights can also be expressed in terms of time-averaged current–current correlations as

$$D_{ab} = \lim_{\bar{t}\to\infty} \lim_{\Lambda\to\infty} \frac{1}{2\Omega(\Lambda)\bar{t}} \int\limits_0^{\bar{t}} \mathrm{d}t \langle \hat{J}_a(0)\hat{J}_b(t)\rangle \tag{42}$$

If the thermodynamic limit $\Lambda \to \infty$ commutes with the long-time limit $\bar{t} \to \infty$, then the thermodynamic Drude weights D_{ab} can be obtained as

$$D_{ab} = \lim_{\Lambda\to\infty} d_{ab}(\Lambda) \tag{43}$$

Moreover, if the limit does not vanish, we can conclude that the presence of relevant conservation laws yields non-zero generalized Drude weights, which in turn imply that transport is ballistic, $L_{ab} \sim \Lambda$. As a consequence, the electrical conductivity is ballistic, $\sigma \sim L_{ee} \sim \Lambda$, while the thermopower is asymptotically size-independent, $S \sim L_{eh}/L_{ee} \sim \Lambda^0$.

We can see from Suzuki's formula that for systems with a single relevant constant of motion ($M = 1$), the ballistic contribution to $\det \boldsymbol{L}$ vanishes, since it is proportional to $D_{ee}D_{hh} - D_{eh}^2$, which is zero from Eqs. (41) and (43). Hence, $\det \boldsymbol{L}$ grows slower than Λ^2, and therefore the thermal conductivity $\kappa \sim \det \boldsymbol{L}/L_{ee}$ grows sub-ballistically, $\kappa \sim \Lambda^{\alpha}$, with $\alpha < 1$. Since $\sigma \sim \Lambda$ and $S \sim \Lambda^0$, we can conclude that $ZT \sim \Lambda^{1-\alpha}$ [45]. Hence ZT diverges in the thermodynamic limit $\Lambda \to \infty$. This general theoretical argument applies for instance to systems where momentum is the only relevant conserved quantity. Note that these conclusions for the thermal conductance and the figure of merit do not hold when $M > 1$, as it is typical for completely integrable systems. In that case, we have, in general, $D_{ee}D_{hh} - D_{eh}^2 \neq 0$, so that thermal conductance is ballistic and therefore ZT is size-independent.

The above reasoning is not limited to quantum systems and has no dimensional restrictions; it has been illustrated by means of a diatomic chain of hard-point colliding particles [45], where the divergence of the figure of merit with the system size cannot be explained in terms of the energy filtering mechanism [57], in a two-dimensional system connected to

---

[4] Note that hereafter we shall use the simple thermal average correlator $\langle \hat{J}_a(0)\hat{J}_b(t)\rangle$ rather than the Kubo–Mori inner product $\int_0^{\beta} \mathrm{d}\tau \langle \hat{J}_a(0)\hat{J}_b(t+\mathrm{i}\tau)\rangle$; see Ref. [54] for a discussion of the assumptions needed to justify the use of the simple thermal-averaged expression.
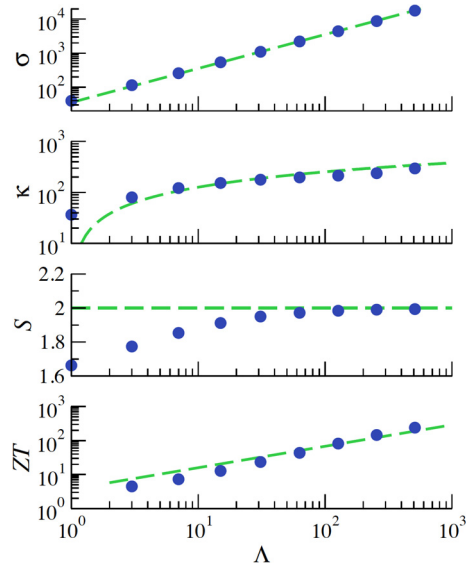
Fig. 2. Thermoelectric transport coefficients for the two-dimensional multiparticle collision dynamics gas of interacting particles as a function of the system size Λ (for details see [46]). The dashed curves correspond from top to bottom to $\sigma \propto \Lambda$, $\kappa \sim \log \Lambda$, $S = 2$, and $ZT \sim \Lambda / \log \Lambda$.

reservoirs [46], with the dynamics simulated by the multiparticle collision dynamics method [58] and in a one-dimensional gas of particles with nearest-neighbor Coulomb interaction, modeling a screened Coulomb interaction between electrons [47]. In all these (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. Results for the two-dimensional multiparticle collision dynamics model are reported in Fig. 2. While the electrical conductivity grows ballistically, $\sigma \propto \Lambda$, the thermopower saturates to a value $S = 2$ that can be also predicted analytically for this model [46]. Finally, the thermal conductivity grows according to the prediction of hydrodynamic theories [59,60], namely $\kappa \propto \log \Lambda$ in two dimensions. These results for the transport coefficients imply that the figure of merit diverges with the system size, $ZT \propto \Lambda / \log \Lambda$, and therefore the Carnot efficiency is achieved in the thermodynamic limit.

We point out that it is a priori not excluded that there exist models where the long-time limit and the thermodynamical limit do not commute when computing the Drude weights. However, numerical evidence shows that for the models so far considered, these two limits commute [45–47]. Finally, we note that divergence of ZT has been also predicted, on different theoretical considerations, for an ideal homogeneous quantum wire with weak electron-electron interactions, in the limit of infinite wire length [61].

5. Discussion and concluding remarks

Research in thermoelectricity remains widely regarded as a strategic activity in view of the critical problems related to energy production and storage, and considering that thermoelectric devices may be designed for specific purposes involving powers over a range spanning ten orders of magnitude: typically from microwatts to several kilowatts. However, despite all the money and efforts invested in the field of thermoelectricity over several decades, no one has managed yet to make decisive progress to break the glass ceiling over performance, thus enabling the much sought-after wide-scale applications. Non-interacting model systems provide a wealth of results and a solid socle to understand many aspects of the basic mechanisms that govern thermoelectric transport and energy conversion, and we saw that they also shed light on the reasons why in terms of performance of current devices, we are still in the range of what became standard 30 years ago.

It must also be said that the performance of a thermoelectric system does not rely solely on the intrinsic properties of the thermoelectric working fluid, but also entails its interaction with its environment: poor thermal contacts with heat source and sink deteriorates significantly the overall energy conversion process. It is thus worthwhile to consider the optimization of the working conditions of thermoelectric devices, which necessitates a sound understanding of the coupling of these heat engines with their environment [16,62,63] to ensure the highest possible efficiency at maximum output power. Finite-time thermodynamics is very well suited for such a purpose. Interestingly, thermoelectricity provides model systems that, in turn, are extremely useful in the development of theories in irreversible thermodynamics [6], and more generally in finite-time thermodynamics, which to date continues to attract much attention [64,65]. Indeed a number of outstanding questions in these fields related to finite-time optimization may be advantageously tackled using thermoelectric systems as case studies since their basic operation allows for a physically transparent description of the phenomena at stake [66–69].

However, optimization procedures for device operation, as necessary as they are, do not improve the fundamental energy conversion performed by the working fluid. The understanding of general mechanisms to improve thermoelectric efficiency

by means of strongly interacting systems is only beginning to emerge. In particular, regimes near electronic phase transitions might be favorable for higher-efficiency thermoelectric conversion. Nonlinear momentum-conserving systems are also interesting, due to the ballistic nature of electrical conductivity combined with the anomalous behavior of thermal conductivity. Such dependence of thermal conductivity, growing slower than ballistically with the system size, is characteristic of the hydrodynamic regime. In this respect, it might be useful to remark that the hydrodynamic regime has been observed in graphene up to almost room temperature [70].

To conclude, it is our hope that our theoretical results and analysis will help identify areas where genuine and significant progress is yet to be made to stimulate experimental research in the proposed directions.

References

[1] N. Pottier, Non-equilibrium Statistical Physics, Oxford University Press, 2010.
[2] L. Onsager, Reciprocal relations in irreversible processes. I, Phys. Rev. 37 (1931) 405.
[3] H.B. Callen, The application of Onsager's reciprocal relations to thermoelectric, thermomagnetic, and galvanomagnetic effects, Phys. Rev. 73 (1948) 1349.
[4] O. Kedem, S.R. Caplan, Degree of coupling and its relation to efficiency of energy conversion, Trans. Faraday Soc. 61 (1965) 1897.
[5] W. Thomson, On the restoration of mechanical energy from an unequally heated space, Philos. Mag. 5 (1853) 102.
[6] S.R. de Groot, Thermodynamics of Irreversible Processes, Interscience, New York, 1958.
[7] A.F. Ioffe, Semiconductor Thermoelements, and Thermoelectric Cooling, Infosearch Limited, London, 1957.
[8] H.J. Goldsmid, Introduction to Thermoelectricity, Springer-Verlag, Berlin, 2010.
[9] C.B. Vining, An inconvenient truth about thermoelectrics, Nat. Mater. 8 (2009) 83.
[10] N.W. Aschcroft, N.D. Mermin, Solid State Physics, Saunders College Publishing, Philadelphia, 1976.
[11] G.J. Snyder, E.S. Toberer, Complex thermoelectric materials, Nat. Mater. 7 (2008) 105.
[12] A. Shakouri, Recent developments in semiconductor thermoelectric physics and materials, Annu. Rev. Mater. Res. 41 (2011) 399.
[13] A.I. Hochbaum, R. Chen, R. Diaz Delgado, W. Liang, E.C. Garnett, M. Najarian, A. Majumdar, P. Yang, Enhanced thermoelectric performance of rough silicon nanowires, Nature 451 (2008) 163.
[14] C. Blanc, A. Rajabpour, S. Volz, T. Fournier, O. Bourgeois, Phonon heat conduction in corrugated silicon nanowires below the Casimir limit, Appl. Phys. Lett. 103 (2013) 043109.
[15] G.A. Slack, in: D.M. Rowe (Ed.), CRC Handbook of Thermoelectrics, CRC Press, Boca Raton, 1995.
[16] Y. Apertet, H. Ouerdane, C. Goupil, Ph. Lecoeur, Internal convection in thermoelectric generator models, J. Phys. Conf. Ser. 95 (2012) 012103.
[17] C. Goupil, W. Seifert, K. Zabrocki, E. Müller, G.J. Snyder, Thermodynamics of thermoelectric phenomena and applications, Entropy 13 (2011) 1481.
[18] H.B. Callen, Thermodynamics and an Introduction to Thermostatics, John Wiley & Sons, New York, 1985.
[19] S.R. de Groot, P. Mazur, Non-equilibrium Thermodynamics, Dover, New York, 1984.
[20] G.D. Mahan, J.O. Sofo, The best thermoelectric, Proc. Natl. Acad. Sci. USA 93 (1996) 7436.
[21] G. Benenti, G. Casati, K. Saito, R. Whitney, Fundamental aspects of steady-state conversion of heat to work at the nanoscale, preprint.
[22] G.D. Mahan, Mott's formula for the thermopower and the Wiedemann–Franz law, Phys. Rev. B 21 (1980) 4223.
[23] A. Abbout, H. Ouerdane, C. Goupil, Mesoscopic thermoelectric transport near zero transmission energies, Phys. Rev. B 87 (2013) 155410.
[24] S. Datta, Electronic Transport in Mesoscopic Systems, Cambridge University Press, Cambridge, UK, 1995.
[25] Y. Imry, Introduction to Mesoscopic Physics, Oxford University Press, 1997.
[26] M.G. Vavilov, A.D. Stone, Failure of the Wiedemann–Franz law in mesoscopic conductors, Phys. Rev. B 72 (2005) 205107.
[27] Z. Bian, M. Zebarjadi, R. Singh, Y. Ezzahri, A. Shakouri, G. Zeng, J.-H. Bahk, J.E. Bowers, J.M.O. Zide, A.C. Gossard, Cross-plane Seebeck coefficient and Lorenz number in superlattices, Phys. Rev. B 76 (2007) 205311.
[28] J.P. Bergfield, M.A. Solis, C.A. Stafford, Giant thermoelectric effect from transmission supernodes, ACS Nano 4 (2010) 5314.
[29] J.P. Bergfield, Ph. Jacquod, C.A. Stafford, Coherent destruction of Coulomb blockade peaks in molecular junctions, Phys. Rev. B 82 (2010) 205405.
[30] V. Balachandran, R. Bosisio, G. Benenti, Validity of the Wiedemann–Franz law in small molecular wires, Phys. Rev. B 86 (2012) 035433.
[31] R. López, D. Sánchez, Nonlinear heat transport in mesoscopic conductors: rectification, Peltier effect, and Wiedemann–Franz law, Phys. Rev. B 88 (2013) 045129.
[32] Y. Imry, A. Amir, The localization transition at finite temperatures: electric and thermal transport, in: E. Abrahams (Ed.), 50 Years of Anderson Localization, World Scientific, Singapore, 2010.
[33] C.B. Vining, The thermoelectric process, Mater. Res. Soc. Symp. 478 (1997) 3.
[34] H. Ouerdane, A.A. Varlamov, A.V. Kavokin, C. Goupil, C.B. Vining, Enhanced thermoelectric coupling near electronic phase transition: the role of fluctuation Cooper pairs, Phys. Rev. B 91 (2015) 100501(R).
[35] S.J. Blundell, K.M. Blundell, Thermal Physics, 2nd ed., Oxford University Press, Oxford, UK, 2009.
[36] A. Larkin, A. Varlamov, Theory of Fluctuations in Superconductors, rev. ed., Oxford University Press, Oxford, UK, 2009.
[37] I. Terasaki, Y. Sasago, K. Uchinokura, Large thermoelectric power in NaCo$_2$O$_4$ single crystals, Phys. Rev. B 56 (1997) R12685.
[38] Y. Wang, N.S. Rogado, R.J. Cava, N.P. Ong, Spin entropy as the likely source of enhanced thermopower in Na$_x$Co$_2$O$_4$, Nature 423 (2003) 425.
[39] M.R. Peterson, S. Mukerjee, B.S. Shastry, J.O. Haerter, Dynamical thermal response functions for strongly correlated one-dimensional systems: Hubbard and spinless fermion $t - V$ model, Phys. Rev. B 76 (2007) 125110.
[40] S. Hong, P. Ghaemi, J.E. Moore, P.W. Phillips, Tuning thermoelectric power factor by crystal-field and spin-orbit couplings in Kondo-lattice materials, Phys. Rev. B 88 (2013) 075118.
[41] A. Georges, G. Kotliar, W. Krauth, M.J. Rozenberg, Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions, Rev. Mod. Phys. 68 (1996) 13.
[42] X. Deng, J. Mravlje, R. Žitko, M. Ferrero, G. Kotliar, A. Georges, How bad metals turn good: spectroscopic signatures of resilient quasiparticles, Phys. Rev. Lett. 110 (2013) 086401.
[43] A.J. Millis, P.A. Lee, Large-orbital-degeneracy expansion for the lattice Anderson model, Phys. Rev. B 35 (1987) 3394.
[44] R. Frésard, H. Ouerdane, T. Kopp, Slave bosons in radial gauge: a bridge between path integral and Hamiltonian language, Nucl. Phys. B 785 (2007) 286.
[45] G. Benenti, G. Casati, J. Wang, Conservation laws and thermodynamic efficiencies, Phys. Rev. Lett. 110 (2013) 070604.
[46] G. Benenti, G. Casati, C. Mejía-Monasterio, Thermoelectric efficiency in momentum-conserving systems, New J. Phys. 16 (2014) 015014.
[47] S. Chen, J. Wang, G. Casati, G. Benenti, Thermoelectricity of interacting particles: a numerical approach, Phys. Rev. E 92 (2015) 032139.
[48] R. Kubo, M. Toda, N. Hashitsume, Statistical Physics II: Nonequilibrium Statistical Mechanics, Springer-Verlag, 1985.
[49] G.D. Mahan, Many-Particle Physics, Plenum Press, New York, 1990.
[50] X. Zotos, F. Naef, P. Prelovšek, Transport and conservation laws, Phys. Rev. B 55 (1997) 11029.

[51] X. Zotos, P. Prelovšek, Transport in one dimensional quantum systems, in: D. Baeriswyl, L. Degiorgi (Eds.), Strong Interactions in Low Dimensions, Kluwer Academic Publishers, Dordrecht, 2004.
[52] M. Garst, A. Rosch, Transport in a classical model of a one-dimensional Mott insulator: influence of conservation laws, Europhys. Lett. 55 (2001) 66.
[53] F. Heidrich-Meisner, A. Honecker, W. Brenig, Thermal transport of the XXZ chain in a magnetic field, Phys. Rev. B 71 (2005) 184415.
[54] E. Ilievski, T. Prosen, Thermodyamic bounds on Drude weights in terms of almost-conserved quantities, Commun. Math. Phys. 318 (2013) 809.
[55] M. Suzuki, Ergodicity, constants of motion, and bounds for susceptibilities, Physica 51 (1971) 277.
[56] P. Mazur, Non-ergodicity of phase functions in certain systems, Physica 43 (1969) 533.
[57] K. Saito, G. Benenti, G. Casati, A microscopic mechanism for increasing thermoelectric efficiency, Chem. Phys. 375 (2010) 508.
[58] A. Malevanets, R. Kapral, Mesoscopic model for solvent dynamics, J. Chem. Phys. 110 (1999) 8605.
[59] S. Lepri, R. Livi, A. Politi, Thermal conduction in classical low-dimensional lattices, Phys. Rep. 377 (2003) 1.
[60] A. Dhar, Heat transport in low-dimensional systems, Adv. Phys. 57 (2008) 457.
[61] T. Micklitz, J. Rech, K.A. Matveev, Transport properties of partially equilibrated quantum wires, Phys. Rev. B 81 (2010) 115313.
[62] Y. Apertet, H. Ouerdane, O. Glavatskaya, C. Goupil, Ph. Lecoeur, Optimal working conditions for thermoelectric generators with realistic thermal coupling, Europhys. Lett. 97 (2012) 28001.
[63] Y. Apertet, H. Ouerdane, C. Goupil, Ph. Lecoeur, Influence of thermal environment on optimal working conditions of thermoelectric generators, J. Appl. Phys. 116 (2014) 144901.
[64] B. Andresen, Current trends in finite-time thermodynamics, Angew. Chem., Int. Ed. 50 (2011) 2690.
[65] H. Ouerdane, Y. Apertet, C. Goupil, Ph. Lecoeur, Continuity and boundary conditions in thermodynamics: from Carnot's efficiency to efficiencies at maximum power, Eur. Phys. J. Spec. Top. 224 (2015) 839.
[66] J.M. Gordon, Generalized power versus efficiency characteristics of heat engines: the thermoelectric generator as an instructive illustration, Am. J. Phys. 59 (1991) 551.
[67] Y. Apertet, H. Ouerdane, C. Goupil, Ph. Lecoeur, Efficiency at maximum power of thermally coupled heat engines, Phys. Rev. E 85 (2012) 041144.
[68] Y. Apertet, H. Ouerdane, C. Goupil, Ph. Lecoeur, From local force-flux relationships to internal dissipations and their impact on heat engine performance: the illustrative case of a thermoelectric generator, Phys. Rev. E 88 (2013) 022137.
[69] Y. Apertet, H. Ouerdane, C. Goupil Ph, Lecoeur revisiting Feynman's ratchet with thermoelectric transport theory, Phys. Rev. E 90 (2014) 012113.
[70] D.A. Bandurin, I. Torre, R. Krishna Kumar, M. Ben Shalom, A. Tomadin, A. Principi, G.H. Auton, E. Khestanova, K.S. Novoselov, I.V. Grigorieva, L.A. Ponomarenko, A.K. Geim, M. Polini, Negative local resistance caused by viscous electron backflow in graphene, Science 315 (2016) 10.