From thermal rectifiers to thermoelectric devices

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Abstract We discuss thermal rectification and thermoelectric energy conversion from the perspective of nonequilibrium statistical mechanics and dynamical systems theory. After preliminary considerations on the dynamical foundations of the phenomenological Fourier law in classical and quantum mechanics, we illustrate ways to control the phononic heat flow and design thermal diodes. Finally, we consider the coupled transport of heat and charge and discuss several general mechanisms for optimizing the figure of merit of thermoelectric efficiency.

1 Dynamical Foundations of Fourier law

The possibility to manipulate the heat current represents a fascinating challenge for the future, especially in view of the need of future society of providing a sustainable
supply of energy and due to the strong concerns about the environmental impact of the combustion of fossil fuels. However along these lines there are severe difficulties both of theoretical and experimental nature. In particular it turns out that manipulation of the heat current is much more difficult than the manipulation of the electric current.

It is therefore necessary to start from first principles in order to get a deep and systematic understanding of the properties of heat transport. Namely we would like to understand these properties starting from the microscopic dynamical equations of motion.

Along these lines a necessary step is the derivation of the Fourier heat law from dynamical equations of motion. In particular we would like to understand under what conditions Fourier law is valid. What are the dynamical properties needed to have normal transport in a given system? This is a nontrivial question and for many years it has been addressed according to different perspectives. It concerns, on one hand, the foundations of nonequilibrium statistical mechanics and, on the other hand, the practical issue of constructing microscopic models which agree with the macroscopic equations which describe transport. For example, for a class of hyperbolic systems (transitive Anosov) a guiding principle was proposed (the so-called chaotic hypothesis [60]) as a prescription for extending equilibrium methods to nonequilibrium situations. We remark that in these works the randomness needed to obtain a consistent description of the irreversible macroscopic phenomena comes from the exponential instability of the microscopic chaotic dynamics.

First numerical evidence of the validity of Fourier heat conduction law in an exponentially unstable system was reported in [34] where the so-called ding-a-ling model was considered (Fig. 1). The model consists of harmonic oscillators which exchange their energy via elastic, hard-core collisions, with intermediate hard spheres. The even-numbered particles in Fig. 1 form a set of equally spaced lattice oscillators with each oscillator being harmonically bound to its individual lattice site and with all oscillators vibrating at the same frequency \( \omega \). The odd-numbered particles are free particles constrained only by the two adjacent even-numbered oscillators. It can be shown that the dynamics of this model is uniquely determined by the parameter \( \omega^2 / E \) (where \( E \) is the energy per particle) and that the dynamics becomes exponentially unstable when this parameter is \( \gg 1 \). The validity of Fourier law was established in the standard way by putting the two end particles in contact with thermal reservoirs, taken as Maxwellian gases, at different temperatures. The system was then numerically integrated until the stationary state was reached.

![The ding-a-ling model. Here the springs merely symbolize the harmonic restoring force.](image-url)
and the energy exchange at the left and right reservoir became equal. This gives the average heat flux \( j \). After defining the particle temperature to be twice its average kinetic energy, the value of the steady-state internal temperature gradient \( \nabla T \) was computed. Then the thermal conductivity \( \kappa \) was computed via the heat Fourier law \( j = -\kappa \nabla T \). A normal conductivity independent on the system length was found.

It is important to stress however that hard chaos with exponential instability is not a necessary condition to induce normal transport properties. Moreover rigorous results are still lacking and in spite of several efforts, the connection between Lyapunov exponents, correlations decay and diffusive properties is still not completely clear. As a matter of facts it turns out that mixing property is sufficient to ensure normal heat transport \[84\]. This might be an important step in the general attempt to derive macroscopic statistical laws from the underlying deterministic dynamics. Indeed, systems with zero Lyapunov exponent have zero algorithmic complexity and, at least in principle, are analytically solvable.

A particular case is given by total momentum conserving systems which typically exhibit anomalous conductivity. This type of systems is largely discussed in other contributions of this volume and therefore will not be considered here any longer. Here we would like to add only a word of caution, and to suggest that anomalous behavior in such systems is perhaps more general than so far believed. The point is that our present understanding of the heat conduction problem is mainly based on numerical empirical evidence while rigorous analytical results are difficult to obtain. Numerical analysis consists of steady state, nonequilibrium simulations or of equilibrium simulations based on linear response theory and Green-Kubo formula. Typically, if both methods give reasonable evidence for Fourier law and if, moreover, they lead to the same numerical value of the coefficient of thermal conductivity \( \kappa \), then this is generally considered as an almost conclusive evidence that Fourier law is indeed valid.

This conclusion, however, might be not correct as shown in \[42\], where the heat conductivity of the one-dimensional diatomic hard-point gas model was studied. As shown in Fig. 2, the Fourier-like behavior, seen in both equilibrium and nonequilibrium simulations, turns out to be a finite-size effect and Fourier law appear to hold up to some size \( N \) after which anomalous behavior sets in. This behavior requires a better understanding. Indeed, while it is natural to expect an initial ballistic behavior for larger and larger \( N \) as one approaches the integrable limit, it is absolutely not clear why the value of \( \kappa \) appears to saturate to a constant value before entering the anomalous regime \( \kappa \sim N^\alpha \) (with \( \alpha \approx 1/3 \)) at an even larger system size \( N \).

To summarize, while establishing a complete connection between ergodic properties and macroscopic transport features is still beyond the reach of present understanding, we may conclude that apart some particular notable exceptions, dynamical mixing property induces deterministic diffusion and hence Fourier law.
Fig. 2 The heat conductivity $\kappa$ versus the system size $N$ for the one-dimensional diatomic gas model, with alternative mass $M$ and $m$. From top to bottom, the mass ratio $M/m$ is respectively $1.07, 1.10, 1.14, 1.22, 1.30, 1.40$, the golden mean ($\approx 1.618$), and $3$. 

2 Fourier law in quantum mechanics

The next step is to discuss whether or not Fourier heat law can be derived from quantum dynamics without a priori statistical assumptions. This calls directly in question the issue of "Quantum chaos". The first attempts to provide a microscopic description of heat transport in quantum systems dates back to the beginning of the 20th century with the work of Debye in 1912 [50] and subsequently of Peierls in 1929 [111]. Based on modifications of the kinetic Boltzmann equation these theories are classical in essence by considering classical-like quasi-particles, and fail to describe systems out of equilibrium with dimensions comparable to the electron and phonon mean free paths.

The recent achievements in the miniaturisation of devices have boosted the interest in understanding the conditions under which heat is transported diffusively in quantum systems. In spite of the many efforts a rigorous derivation of a quantum Fourier law for general Hamiltonians remains an unsolved problem. A main difficulty to the study of heat conduction in quantum mechanics is the lack of appropriate definitions of local quantities such as the temperature and the heat current [54], and calls in question the problem of thermalization, namely the relaxation to a state in local equilibrium, in isolated [11] and open quantum systems [30]. It has been found that the conditions for thermalization are essentially related to the systems’ integrability and localization properties (e.g. due to disorder). Non-ergodic systems, undergo relaxation to a generalized Gibbs state [14], so that the application of standard statistical mechanics methods is possible.

Quantum systems in contact with external heat baths can be treated by using the Lindblad-Gorini-Kossakowski-Sudarshan equation [85] [63] in a convenient setup in
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which only boundary degrees of freedom are coupled with the environment. Within the Markovian approximation, the system’s many-body density matrix evolves according to

$$\frac{d}{dt} \rho(t) = \mathcal{L} \rho(t),$$  \hspace{1cm} (1)

where the Liouvillian superoperator is defined as

$$\mathcal{L} \rho := -\frac{i}{\hbar} [\mathcal{H}, \rho] + \sum_{\mu} \left( L_{\mu} \rho L_{\mu}^\dagger - \frac{1}{2} \{ L_{\mu}^\dagger L_{\mu}, \rho \} \right).$$  \hspace{1cm} (2)

We assume here that the Hamiltonian $\mathcal{H}$ can be written as a sum of locally interacting terms, $\mathcal{H} = \sum_n H_n$ and $L_{\mu}$ are the Lindblad (or so-called quantum jump) operators, which are assumed to act only at the boundary sites of the system. This setup provides a fully coherent bulk dynamics and incoherent boundary conditions, which is particularly suited for studying nonequilibrium heat transport in a setup similar to the classical case [151].

The Quantum Master Equation (QME) approach can be used to study not only heat transport, but also nonequilibrium processes in general (particle transport, spin transport, etc.). Depending on the process in question the Lindblad operators $L_{\mu}$ target specific canonical states, creating a local equilibrium state near the boundaries of the system. The conductivities are then obtained by measuring expectation values of the current observables in the steady states of the Lindblad equation, in the thermodynamic limit $N \to \infty$ (see e.g., [115]). This approach has been extensively used in recent years to study heat transport in one-dimensional models of quantum spin chains coupled at their ends with Lindblad heat baths [54, 153, 106, 103, 91, 138, 2], as well as in chains of quantum oscillators [160, 62] (for a recent review see e.g., [104, 18]).

The Lindblad equation (1) allows efficient numerical simulation of the steady state of locally interacting systems, in terms of the time-dependent-density-matrix-renormalization-group method (tDMRG) [46, 149, 130] in the Liouville space of linear operators acting on wave functions [113]. In cases where the tDMRG method cannot be applied, like when the interaction is long-range (e.g., Coulomb), the QME can be solved using the method of quantum trajectories, (see, for example, [103]). In the latter case the idea is to represent the density operator as an expectation of $|\Psi\rangle \langle \Psi|$ where the many-body wave function $\Psi$ is a solution of a stochastic Schrödinger equation $d \Psi(t) = -\frac{(i/\hbar)}{H} \Psi dt + d \xi$, with $d \xi$ being an appropriate stochastic process simulating the action of the baths. In addition, this method has the advantage that non-Markovian effects can be treated easily and intuitively. In more general settings, the QME can always be solved exactly through numerical integration where the quantum canonical heat baths are often modeled in terms of the Redfield equation [117]. Such approach has found a broad applicability in many-body systems and has been used to investigate heat transport [123, 119, 131, 153].

One alternative of using the QME approach is the Keldysh formalism of nonequilibrium Green’s functions, where one essentially discusses the scattering of elementary quasi-particle excitations between two or more infinite non-interacting Hamil-
tonian reservoirs. The Keldysh formalism considers an initial product state density matrix describing the finite system and two infinite baths in thermal equilibrium at \textit{e.g.}, different temperatures. The system and the reservoirs are then coupled and the density matrix is evolved according to the full Hamiltonian. In the steady state, currents and local densities can be obtained in terms of the so-called Keldysh Greens functions. This approach has been used, among other things, to study heat transport in driven nanoscale engines \cite{6, 8} and spin heterostructures \cite{7}. Another commonly used approach to study heat transport in quantum systems is based on the Green-Kubo formula, originally developed to study electric transport \cite{80}.

Within linear response theory, the current is taken as the system’s response to an external perturbative potential which can be included within the Hamiltonian of the system. First order perturbation theory yields the Green-Kubo formula relating the nonequilibrium conductivity with the equilibrium current-current correlation. This formula is naturally extended to study heat transport, where the heat current appears as the response to an external temperature gradient. This \textit{ad-hoc} generalization remains conceptually troublesome since there is no potential term in the system’s Hamiltonian representing a temperature gradient situation \cite{80, 86}. In spite of this, the Green-Kubo approach has become a widely employed \cite{158, 159, 61, 65}.

In spite of all efforts, a microscopic derivation of Fourier law in quantum mechanics is still lacking, and only partial understanding concerning the conditions under which this is expected to hold has been gained. Particularly, in analogy with the studies at the classical level the relation between the validity of Fourier law and the onset of quantum chaos has been investigated in recent years \cite{123, 105, 102, 137, 115, 116}.

As it has been shown in the previous section for classical systems, diffusive heat transport is directly related to the chaoticity of the dynamics. While such relation is not strict, classical deterministic chaos is yet expected to yield diffusive behavior. It is nowadays well established that quantum systems for which their classical analogues are chaotic, exhibit characteristic signatures in the spectra and the eigenfunctions that are different from those observed in systems that are classically integrable \cite{21, 37}. The global manifestation of the onset of chaos in quantum systems consists of a very complex structure of the quantum states as well as in spectral fluctuations that are statistically described by Random Matrix Theory \cite{64}. In the following we discuss the relation among the validity of quantum Fourier law and the onset of quantum chaos.

### 2.1 Fourier law and the onset of quantum chaos

The relation between the validity of the quantum Fourier law and the onset of quantum chaos in a genuinely nonequilibrium situation was studied in \cite{102}. There a quantum Ising chain of \(N\) spins 1/2 subjected to a uniform magnetic field \(\mathbf{h} = (h_x, 0, h_z)\) and coupled at its extremes with quantum heat baths, was considered. The Hamiltonian of this system is
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The finite quantum spin chain model coupled to external heat baths at different temperatures. The dotted lines represent the nearest neighbour interaction. The double dashed lines represent the coupling Ξ with the baths. The angle \( \theta \) of the magnetic field is measured with respect to the direction \( x \) of the chain.

\[
\mathcal{H} = \sum_{n=0}^{N-2} H_n + \frac{\hbar}{2} (\sigma_L + \sigma_R),
\]

(3)

where \( H_n \) are local energy density operators appropriately defined as

\[
H_n = -Q\sigma_n^z\sigma_{n+1}^z + \frac{\hbar}{2} (\sigma_n + \sigma_{n+1}),
\]

(4)

and \( \sigma_L = \hbar \cdot \sigma_0 / h, \sigma_R = \hbar \cdot \sigma_{N-1} / h \) are the spin operators along the direction of the magnetic field of \( s_0 \) and \( s_{N-1} \) respectively. The operators \( \sigma_n = (\sigma_n^x, \sigma_n^y, \sigma_n^z) \) are the Pauli matrices for the \( n \)-th spin, \( n = 0, 1, \ldots N - 1 \). A schematic representation of this model is shown in Fig. 3.

In this model, the angle \( \theta = \arctan(h_z / h_x) \) of the magnetic field makes with the chain affects the dynamics of the system. If \( \theta = 0 \), the Hamiltonian (3) corresponds to the Ising chain in a transversal magnetic field, which is integrable as (3) can be mapped into a model of free fermions through standard Wigner-Jordan transformations. For \( \theta > 0 \), the system is no longer integrable and for \( \theta \approx \pi / 4 \), quantum chaos sets in. The system becomes again (nearly) integrable when \( \theta \approx \pi / 2 \). Therefore, by tuning \( \theta \) one can explore different regimes of quantum dynamics and study the relation between the integrability of the system and the validity of Fourier’s law.

The integrability of a quantum system can be characterised by the Nearest Neighbour Level Spacing (NNLS) distribution \( P(s) \), which is the probability density to find two adjacent levels at a distance \( s \). For an integrable system the distribution \( P(s) \) has typically a Poisson distribution:

\[
P_p(s) = \exp(-s).
\]

(5)

In contrast, in the quantum chaos regime, Hamiltonians obeying time-reversal invariance exhibit a NNLS distribution that corresponds to the Gaussian Orthogonal Ensemble of random matrices (GOE). This distribution is well-approximated by the Wigner surmise, which reads

\[
P_{WD}(s) = \frac{\pi s}{2} \exp\left(-\frac{\pi s^2}{4}\right),
\]

(6)

exhibiting “level repulsion”.
Figure 4 shows the NNLS distribution $P(s)$ for three different directions of the magnetic field: (i) **integrable case** $\mathbf{h} = (3.375, 0, 0)$, at which $P(s)$ is well described by $P_P(s)$, (ii) **intermediate case** $\mathbf{h} = (7.875, 0, 2)$ at which the distribution $P(s)$ shows a combination of (weak) level repulsion and exponential decay, and (iii) **chaotic case** $\mathbf{h} = (3.375, 0, 2)$ at which the distribution $P(s)$ agrees with $P_{WD}(s)$ and thus corresponds to the regime of quantum chaos.

![Fig. 4 NNLS distribution $P(s)$ for the integrable (left panel), intermediate (middle panel) and chaotic (right panel) spin chains. The histogram was numerically obtained for a chain of $N = 12$ spins by diagonalizing Hamiltonian (3) and averaging over the spectra of even and odd parity. The dotted curve corresponds to $P_P$ and the dashed curve to $P_{WD}$.]

In Ref. [102] a numerical method to solve the dynamics of open quantum spin chains was introduced. This method consists in periodically and stochastically collapsing the state of the spins at the boundaries of the chain to a state that is consistent with local equilibrium states at different temperatures. These stochastic quantum heat baths are analogous to the stochastic baths used in classical simulations and even when this method does not yield a stochastic unravelling of QME, it is numerically simple to implement and analyse (for more details see Refs. [102, 103]).

![Fig. 5 Local temperature in the center of the chain $\beta^{-1}$ as a function of the temperature of the baths $T$, obtained from equilibrium simulations in a chain of 7 spins, as the best fit to exponential of the local density matrix $\rho_0(E_n)$ in the central symmetry band. The dashed line stands for the identity.]

Using this method, local thermal equilibrium was first checked by computing time averages of the density matrix of the system:

\[
\bar{\rho} = \lim_{t \to \infty} \int_0^t |\psi(s)\rangle \langle \psi(s)| ds,
\]

where \(\psi(s)\) is the state of the system at time \(s\). Setting both heat baths to the same temperature \(T_L = T_R = T\), it was found that \(\rho\) is diagonal within numerical accuracy and consistent with

\[
\langle \phi_n | \rho | \phi_m \rangle = e^{-\beta E_n} Z^{\delta_{m,n}},
\]

inside each symmetry band. Here \(|\phi_n\rangle\) are the eigenfunctions in the energy basis, \(H |\phi_n\rangle = E_n |\phi_n\rangle\), and \(Z = \sum_n e^{-\beta E_n}\) is the canonical partition function. From a best fit to exponential of Eq. (8) a value of the local temperature in the bulk of the system can be extracted. The results are shown in Fig. 5 as a function of the temperature of the heat baths. It can be seen that for large enough temperatures of the heat baths \((T \gtrsim 5)\) the system thermalizes to exactly the same temperature \([103]\).

Out of equilibrium expectation values in the nonequilibrium steady state were obtained as follows: for each realization, the initial wavefunction \(|\psi(0)\rangle\) of the system is chosen at random. The system is then evolved for some relaxation time \(\tau_{\text{rel}}\) after which it is assumed to fluctuate around a unique steady state. Measurements are then performed as time averages of the expectation value of the observables, that are further averaged over different random realizations.

Figure 6 shows the energy profile obtained from the time average of the local energy density operator \(E_x = \langle H_x \rangle\) (with \(x = n/N\)), for the above three different spin chains. Interestingly, for the chaotic chain, a linear energy profile in the bulk of the chain was found. This indicates that the chaotic chain is able to sustain a heat current which depends on the nonequilibrium imposed by the external heat baths. In contrast, the integrable chain shows a flat constant energy profile. The intermediate chain which is neither chaotic nor integrable is not able to sustain a diffusive heat current and shows and energy profile which is flat except near the boundaries.

To directly check the validity of Fourier’s law it is possible to define local heat current operators using the continuity equation for the local energy density operators \(\partial_t H_n = i \{ H_n, H \} = -(j_{n+1} - j_n)\), requiring that \(j_n = [H_n, H_{n-1}]\). From Eqs. (3) and (4) the local current operators are explicitly given by

\[
j_n = h_x Q (\sigma_{n-1}^z - \sigma_{n+1}^z) \sigma_n^y, \quad 1 \leq n \leq N - 2.
\]

Figure 7 shows the heat conductivity as a function of the system size \(N\), calculated as \(\kappa = -j/\nabla T\). The mean current \(j\) was calculated as an average of \(\langle J_n \rangle\) over time and over the \(N - 8\) central spins. For the particular choice of the energy density operator \(\hat{\mathcal{H}}\), its averaged expectation value is related to the local temperature as \(\langle H_n \rangle \propto -1/T\) \([102]\). The temperature difference was thus obtained as \(\Delta T = -1/\langle H_{N-5} \rangle + 1/\langle H_3 \rangle\). For large \(N\) the heat conductivity of the chaotic chain was found to converge to a constant value, thus confirming the validity of
the Fourier’s law. On the contrary, for the integrable and an intermediate chains, $\kappa$ diverges linearly with $N$, which is a signature of ballistic transport.

These results represent a solid suggestion that, in analogy to what is observed in classical systems, in the quantum realm Fourier law holds once quantum chaos has set in. Arguably, quantum chaos yields diffusive heat transport as it leads to exponential decay of the “dynamic” correlations, in particular the energy current-current correlation that defines the heat conductivity through a Green-Kubo formula.

The crucial relation between diffusive transport and quantum chaos was later investigated in [137] for models of isolated quantum chains made of interacting subunits, each containing a finite number of energy levels. These models representing single-particle multi-channel quantum wires, exhibit a transition to quantum chaos as the strength of the interaction between the subunits increases. By solving the corresponding Schrödinger equation, it was found that the evolution of the local energy density operators is in agreement with the corresponding diffusion equation only when the system level statistics is chaotic. There, a Heisenberg spin chain in an external magnetic field was also studied, yielding the same result.

Later, in Ref. [115] heat and spin transport in several open quantum spin chains was considered and numerically solved by means of the DMRG method. The same model considered in [102] was studied for much larger system sizes and the relation between quantum Fourier law and quantum chaos put forward there, was confirmed with high accuracy.

3 Controlling the heat flow: thermal rectifiers

Contrary to the case of electronic transport, where the concept of diode is well known, when one thinks of heat flow and Fourier law, the idea of directed transport does not come to mind at all. It is even counter intuitive. However, as shown
3.1 The Fourier law and the design of a thermal rectifier

Thermal rectification is everyday’s experience: due to thermal convection a fluid heated from below efficiently transfers heat upwards, while the same fluid, heated from the top surface shows a much weaker transfer rate downwards. In this case this is because the heat flow is due to a transfer of matter. The idea that one could build a solid-state device that lets heat flow more easily in one way than in the other is less intuitive, and may even appear in contradiction with thermodynamics at first examination. However this is not so, and the design of a thermal rectifier is perfectly compatible with the Fourier law [114].

Let us consider the heat flow along the x-direction, in a material in contact with two different heat baths at temperature $T_1$ for $x = 0$ and $T_2$ for $x = L$. A rectification can only be expected if the device has some spatial dependence which allows us to distinguish its two ends, i.e. if the local thermal conductivity depends on $x$. This can either come from an inhomogeneity of the material or from its geometry. Moreover the thermal conductivity $\kappa(x, T)$ may also depend on temperature so that the Fourier law relates the heat flux $j_f$ to the local temperature $T(x)$ by

$$j_f = -\kappa(x, T) \nabla T(x).$$
\[ T(x) = T_1 + \int_0^x \frac{j_f}{\kappa[\xi, T(\xi)]} \, d\xi. \]  

(10)

Solving this equation with the boundary condition \( T(x = L) = T_2 \) determines the value of \( j_f \). If the boundary conditions are reversed, imposing temperature \( T_2 \) for \( x = 0 \) and temperature \( T_1 \) for \( x = L \), solving the same equation leads to another temperature distribution and another distribution of the local thermal conductivity \( \kappa(x, T) \). Therefore the reverse flux \( j_r \) is not equal to the forward flux \( j_f \). The rectifying coefficient can be defined as

\[ R = \left| \frac{j_r}{j_f} \right|. \]  

(11)

In general, for arbitrary \( \kappa(x, T) \), there is no condition that imposes that \( R \) should be unity.

Figure 8 shows a simple example where the spatial dependence is obtained by juxtaposing two different homogenous materials, each one having a thermal conductivity that strongly depends on temperature. In this case \( \kappa(x, T) \) is a sigmoidal function in both cases, but on one side \( \kappa \) is large at low temperature while, on the other side it is large at high temperature. An even simpler device can be obtained by combining one material with a temperature dependent thermal conductivity with another one which has a constant thermal conductivity [114]. Such a device has a lower rectifying coefficient but nevertheless behaves as a thermal diode.

### 3.2 A one-dimensional model for a thermal rectifier

As shown in Sec. 3.1, in order to obtain a thermal rectifier, we need two basic ingredients, a temperature dependent thermal conductivity and the breaking of the inversion symmetry of the device in the direction of the flow. In this section we show how this can be obtained in a simple model system.

In a solid the heat transfer by conduction is a transfer of energy without a transport of matter. Heat can be carried either by the propagation of atomic vibrations, i.e. phonons, or by the diffusion of the random fluctuations of mobile particles, which are generally charged so that electrical and heat conductivity are closely related as stated by the Wiedemann-Franz law for metals [10]. Here we consider the case of electrical insulators in which heat is only carried by lattice vibrations. The simplest model of a thermal diode can be designed with a one dimensional lattice of interacting particles having a single degree of freedom. However, in the search of simplicity, one should make sure that the model does not lead to unphysical properties. In particular we want to select a model system that obeys the macroscopic Fourier law, with a well defined thermal conductivity \( \kappa \), which may not be the case for a one-dimensional lattice [83]. However if the translational invariance is broken by a substrate potential, so that momentum is not a constant of the motion, a simple one-dimensional lattice of harmonically coupled particles subjected to an external
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Fig. 8 Thermal rectifier made by the juxtaposition of two different homogeneous materials which have a thermal conductivity that highly depends on temperature. The boundary temperatures are $T_1 = 1.0$ and $T_2 = 0.2$ in arbitrary scale. (a) Schematic view of the device. (b) Variation of $\kappa(x, T)$. (c) The temperature distributions (solution of Eq. (10)) (full lines) and the variation versus space of the local conductivity $\kappa[x, T(x)]$ (dashed lines) are shown for the forward boundary condition ($T(x = 0) = T_1, T(x = L) = T_2$) (thick lines) and reverse boundary condition (thin lines). For this choice of $\kappa(x, T)$, the rectifying coefficient is $R = |j_r/j_f| = 4.75$.

Fig. 9 Schematic picture of the one-dimensional model used as the basis for a simple thermal rectifier. Upper part: the harmonically coupled particles are subjected to an on-site potential, here a Morse potential. Lower part: the model used in numerical simulations to measure the heat flow. The two end-segments (boxes) are in contact with a numerical Langevin thermostat, while the central part of the lattice is evolving according to the equations of motions that derive from the Hamiltonian $H$.

potential, known as a Klein-Gordon model, can show a well defined thermal con-
ductivity while allowing an easy analysis of the properties of the system. Such a lattice can form the basis for a thermal rectifier [141].

As an example, let us consider the model schematized in Fig. 9, i.e. a chain of $N$ particles with harmonic coupling constant $K$ and a Morse on-site potential $V_n = D_n \left[ \exp(-\alpha_n y_n) - 1 \right]^2$. The variable $y_n$ designates the displacement of the particles with respect to their equilibrium positions, $p_n$ their momentum, and $H_n$ is the local energy density. This model was introduced as a simple one-dimensional model of DNA [48]. In this case the on-site potential describes the interaction between the two strands of DNA.

In the present context this model can simply be viewed as a simple example to study heat transfer in a one-dimensional lattice, with Hamiltonian

$$\mathcal{H} = \sum_{n=1}^{N} H_n = \sum_{n=1}^{N} \left[ \frac{p_n^2}{2m} + \frac{1}{2} K (y_n - y_{n-1})^2 + D_n (\exp(-\alpha_n y_n) - 1)^2 \right].$$

(12)

In such a system we can define a local temperature by $T_n = \langle p_n^2 / m \rangle$ where the brackets designate a statistical average. Expressing $dH_n/dt$ with the Hamilton equations and using the continuity equation from the energy flux,

$$\frac{dH(x,t)}{dt} + \frac{\partial j(x,t)}{\partial x} = 0,$$

(13)

in a finite difference form leads to a discrete expression for the local heat flux:

$$j_n = K \langle \dot{y}_n (y_{n+1} - y_n) \rangle.$$

(14)

The thermal properties of the model subjected to a temperature difference, in a steady state, can be studied by molecular dynamics simulations by imposing fixed temperatures $T_1$ and $T_2$ at the two ends with Langevin thermostats. The simulations have to be carried long enough to reach a steady state in which the heat flux $j$ is constant along the lattice.

If the system is homogeneous ($D_n = D$ and $\alpha_n = \alpha$ for all $n$) such calculations show that, as expected, a well defined uniform thermal gradient is observed along the lattice, except in the immediate vicinity of the thermostats where a sharp temperature change is observed due to a Kapiza resistance between the thermostats and the bulk lattice (Fig. 10, circles). For large $N$ the effect of the contact resistance becomes negligible. The calculation shows that, with a fixed temperature difference the flux decreases as $1/N$, where $N$ is the number of lattice sites, which indicates that the model has a well defined thermal conductivity per unit length [114].

If the system is inhomogeneous, by including a central region in which the parameters are different from those in the two side domains, as shown in Fig. 10 (top), the heat flow is determined by the overlap of the phonon bands in the different regions. For the example shown in Fig. 10 with $T_1 = 0.16$ and $T_2 = 0.15$, the flux is equal to $j = 0.35 \times 10^{-3}$ for $D_1 = 0.5$ (corresponding to an homogeneous lattice) and decreases to $j = 0.18 \times 10^{-3}$ for $D_1 = 0.8$ for which the phonon bands partly overlap and $j = 0.48 \times 10^{-5}$ when there is no overlap between the phonon bands.
This provides a clue on a possible way to get the temperature dependent thermal conductivity needed to build a thermal rectifier as shown in Sec. 3.1: a nonlinearity of the on-site potential amounts to having temperature dependent phonon bands. In the case of the model with Hamiltonian (12), this can easily be checked by a self-consistent phonon approximation [48]. The idea is to expand the free energy by separating the mean value of $y_n$, $\eta = \langle y_n \rangle$, and the deviations $u_n$ around this value $y_n = \eta + u_n$. Then the Hamiltonian is approximated by $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, where

$$\mathcal{H}_0 = \sum_n \left[ \frac{1}{2} m u_n^2 + \frac{1}{2} \phi (u_n - u_{n-1})^2 + \frac{1}{2} \Omega_2 u_n^2 \right]$$

(15)

describes an effective harmonic lattice. The free energy can be expanded as $\mathcal{F} = \mathcal{F}_0 + \mathcal{F}_1$, where $\mathcal{F}_1 = \langle \mathcal{H}_1 \rangle_0$. Then, by minimizing $\mathcal{F}_1$ with the variational parameters $\eta$, $\phi = K$, $\Omega_2$, one gets the lower bound of the effective phonon band of the lattice as $\Omega_2^2 = 2 \alpha^2 D \exp[-2 \alpha \eta / 3]$. As $T$ grows so does $\eta$, so that the band shifts downwards. Therefore, if the central region has a value $D_1 > D$ so that the phonon bands do not overlap at low temperature, as $T$ increases the decay of the effective lower bound of the phonon band leads to an increased overlap, and therefore an increased thermal conductivity.

Expanding on these ideas one can build a thermal rectifier by introducing the necessary asymmetry pointed out in Sec. 3.1. Using left and right side regions with a weak nonlinearity ($\alpha = 0.5$) and different values of the parameter $D$ ($D_{\text{left}} = 4.5$ and $D_{\text{right}} = 2.8$) and a harmonic coupling constant $K = 0.18$, one gets two domains with phonon bands that do not overlap. Nevertheless a good thermal conductiv-
Fig. 11 Properties of a model for a thermal rectifier with two different boundary conditions: left figures: energy flow from left to right $T_{\text{left}} = 0.7$, $T_{\text{right}} = 0.1$, right figures: energy flow from right to left $T_{\text{right}} = 0.7$, $T_{\text{left}} = 0.1$. The upper figures show the theoretical phonon bands along the device obtained from the self-consistent phonon approximation with the assumed temperature distribution shown by the dash line. The middle figures show the actual distribution of the phonon frequencies deduced from numerical simulations, and the lower figures show the variation of the local temperature along the system, determined from the numerical results. The ratio of the flux in the two directions is $|j_{\text{right} \rightarrow \text{left}}| / |j_{\text{left} \rightarrow \text{right}}| = 2.4$.

...ity can be restored with a central region with a high nonlinearity ($\alpha = 1.1$) and $D_{\text{center}} = 1.1338$ which is such that, when the highest temperature is on the right side of the device the variation versus space of the effective phonon band in the central region provides a match between the left and right phonon bands, while, if the...
From thermal rectifiers to thermoelectric devices

highest temperature is on the left side of the device, the variation versus space of the effective phonon band in the central region leads to a large phonon-band mismatch, as shown in Fig. 11. Figure 11 shows that such a system does indeed lead to thermal rectification because, when the hot side is on the left, the mismatch of the phonon bands leads to temperature jumps at the junctions between the different parts. This is due to a large contact thermal resistance. When the hot side is on the right the temperature evolves continuously along the device. The contact resistances are then low, and the energy flux is 2.4 times larger in this configuration. The calculation of the theoretical phonon bands, based on the self-consistent phonon approximation, is only approximately correct, first because the method itself is only approximate but also because the calculation is made by assuming a linear temperature variation inside the device, which is a crude approximation. However this method provides a first step to design a rectifier, which has to be improved with the results of the numerical simulations.

The results shown in Fig. 11 only provide a simple illustration of what can be done with the idea of phonon-band matching, combined to nonlinearity to allow the local phonon frequency spectra to vary with temperature. One can imagine many possible improvements, for instance by stacking devices, or increasing the number of interfaces, to increase the rectifying coefficient. Another approach is to design a system with a continuous variation of the vibrational properties versus space, which amounts to stacking an infinity of interfaces which have temperature dependent properties and therefore have different transmissivities when the direction of the temperature gradient is reversed. This allows a better control of the rectifying effect. Figure 12 shows such an example, which has a rectifying coefficient $R = 4.95$ and exhibits an effective phonon band which is almost flat when the thermal gradient is in the favorable direction.

In spite of these achievements there are still several problems which are difficult to overcome. In particular in the model thermal rectifiers described above, the
rectification power is small and rapidly decays to zero as the system size increases. A possible way to overcome this difficulty has been discussed in [41] where, by considering one dimensional anharmonic chains of oscillators, empirical evidence is provided that graded mass distribution and long range interparticle interactions, lead to a substantial improvement of the thermal rectification phenomenon which moreover does not decay to zero with increasing system size.

The system is a one-dimensional chain of $N$ oscillators described by the Hamiltonian

$$\mathcal{H} = \sum_{j=1}^{N} \left( \frac{p_j^2}{2m_j} + \frac{q_j^4}{4} \right) + \sum_{i,j} \frac{(q_j - q_i)^2}{2 + 2|i-j|^{\lambda}},$$

(16)

where $q_j$ is the displacement of the $j$th particle with mass $m_j$ and momentum $p_j$ from its equilibrium position. A graded mass distribution is used. The exponent $\lambda$ controls the decay of the interparticle interactions with distance.

In view of previous results [154, 146], it is expected that in a system with graded mass distribution, e.g. $m_1 < m_2 < \ldots < m_N$, thermal rectification will be present, even for the simple case of nearest neighbor interaction (NN). Long range interactions (LRI) introduce new channels for the heat transport through the new links (interactions) between the different sites. Moreover in a graded system, the new channels connect distant particles with very different masses. Therefore new, asymmetric channels, are created which in turn favors the asymmetric flow, i.e., rectification. Hence, by introducing long range interactions in a graded system, an increase of the thermal rectification is expected. Moreover, as we increase the system size, new particles are introduced that, in the case of long range interactions, create new channels for the heat current. This may avoid the usual decay of rectification with increasing system length.

In Fig. 13 we plot the rectification factor as a function of the system size. Here the mass gradient is fixed. It is seen that the presence of LRI leads to a very large rectification and prevents the decay of the rectification factor with the system size. Strictly speaking we cannot make any claim for larger system sizes. However it is clear from Fig. 13 that the $N$-dependence for the LRI case is qualitatively different from the NN case where the decay of the rectification factor with $N$ is observed.

### 3.3 Model in higher dimension

Extending the same concept to higher dimension is of course important for actual applications. For instance two dimensional models could describe smart conducting layers to carry heat out of some nano-devices. The same idea of playing with the phonon bands is indeed also valid in two dimensions.

Figure 14 shows a two-dimensional lattice of local oscillators which is described by the Hamiltonian

$$\mathcal{H} = \sum_{j=1}^{N} \left( \frac{p_j^2}{2m_j} + \frac{q_j^4}{4} \right) + \sum_{i,j} \frac{(q_j - q_i)^2}{2 + 2|i-j|^{\lambda}},$$

where $q_j$ is the displacement of the $j$th particle with mass $m_j$ and momentum $p_j$ from its equilibrium position. A graded mass distribution is used. The exponent $\lambda$ controls the decay of the interparticle interactions with distance.
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Fig. 13 Dependence of rectification factor on the system size $N$. Here $T_1 = 9.5$, $T_2 = 0.5$, $m_1 = 1$. Triangles are for LRI with $\lambda = 1.2$, circles are for LRI with $\lambda = 1.4$, squares are for the NN case. The mass gradient is fixed ($m_N = 2$ for $N=64$; $m_N = 3$ for $N=128$; $m_N = 4$ for $N=192$; $m_N = 5$ for $N=256$).

$$\mathcal{H} = \sum_{i=1,N_x,j=1,N_y} \left[ \frac{p_{ij}^2}{2m} + \frac{1}{2} C_x(i,j)(u_{i+1,j} - u_{i,j})^2 + \frac{1}{2} C_y(i-1,j)(u_{i,j} - u_{i-1,j})^2 \\
\quad + \frac{1}{2} C_y(i,j)(u_{i,j+1} - u_{i,j})^2 + \frac{1}{2} C_y(i,j-1)(u_{i,j} - u_{i,j-1})^2 \\
\quad + D(i,j)(\exp[-\alpha(i,j)u_{i,j}] - 1)^2 \right]$$

(17)

Fig. 14 Two dimensional lattice described by Hamiltonian (17).

With appropriate parameters, as indicated in Fig. 15 (top), this system can operate as a rectifier with a rectifying ratio $R = 1.69$ because, while the interfaces show a large thermal resistance causing a sharp temperature drop if the left edge of the lattice is connected to the hot bath, when the gradient is reversed, the temperature
varies smoothly along the device because there are no interfacial thermal resistances (see Fig. 15 (bottom left and right)).

3.4 Building an actual thermal rectifier

Actually the experimental observation of heat flow rectification has a long history [93]. The early observations made in 1975 with a GaAs crystal found a small rectification effect ($R \approx 1$), which was strongly dependent on the location of the contacts on the sample, but an asymmetry of the heat flow was nevertheless clear. A first analysis made by assuming that the thermal conductivity was the sum of a space-dependent term and a temperature dependent term showed that the observation was compatible with the Fourier law [94], and provided the first view of the ideas presented in Sec. 3.1. These results were followed by some debates over the actual origin of the observed rectification [12], and a rectification coefficient $R \approx 1.35$ could then be obtained with a two-component sample made of tin in contact with α-brass. Heat flow rectification could also be observed with a carbon nanotube [40], loaded with $C_9H_{16}Pt$ molecules on one part of its length, but the origin of the rectification was still not clearly established.

More recently the ideas presented in Sec. 3.1 were systematically exploited to build rectifiers [77], using two cobalt oxides with different thermal conductivities. The vicinity of a structural phase transition could be used to enhance the tempera-
ture dependence of the thermal conductivity \[\kappa(x, T)\] [128]. The measurements show a good quantitative agreement with the results of Sec. 3.1 and [114], if one takes into account the experimental data for the thermal conductivity of the materials used in the device. A quantitative microscopic calculation of \(\kappa(T)\) is however a harder challenge. The control of the temperature dependence of \(\kappa\), trough a control of the phonon bands, discussed in Sec. 3.2 is only one possibility but other mechanisms can be considered whether they use a structural change through a phase transition, or variations of the density of mobile carriers in materials which are also electrical conductors. And of course, in such materials the use of an electric field to manipulate the spatial distribution of the carriers in a solid state device can also open other possibilities to control the heat flow. It is also worth mentioning recent experimental implementations of thermal rectifiers, exploiting phononic [142], electronic [92], or photonic [44] thermal currents. Possibilities to manipulate phonons and devise heat diodes, transistors, thermal logic gates and thermal memories are reviewed in Ref. [100].

4 Thermoelectric Efficiency

Thermoelectricity concerns the conversion of temperature differences into electric potential or vice-versa. It can be used to perform useful electrical work or to pump heat from a cold to a hot place, thus performing refrigeration. Although thermoelectricity was discovered about 200 years ago, a strong interest of the scientific community arose only in the 1950’s when Abram Ioffe discovered that doped semiconductors exhibit relatively large thermoelectric effect. This initiated an intense research activity in semiconductors physics which was not motivated by microelectronics but by Ioffe’s suggestion that home refrigerators could be built with semiconductors [87, 89]. As a result of these efforts the thermoelectric material Bi$_2$Te$_3$ was developed for commercial purposes. However this activity lasted only few years until the mid 1960’s since, in spite of all efforts and consideration of all type of semiconductors, it turned out that thermoelectric refrigerators have still poor efficiency as compared to compressor based refrigerators. Nowadays Peltier refrigerators are mainly used in situations in which reliability and quiet operation, and not the cost and conversion efficiency, is the main concern, like equipments in medical applications, space probes, etc.

In the last two decades thermoelectricity has experienced a renewed interest [32, 53, 134, 132, 55, 79] due to the perspectives of using tailored thermoelectric nanomaterials, where a dramatic enhancement of the energy harvesting performances can be envisaged [66]. Indeed layering in low-dimensional systems may reduce the phonon thermal conductivity as phonons can be scattered by the interfaces between layers. Moreover, sharp features in the electronic density of states, favorable for thermoelectric conversion (see the discussion below) are in principle possible due to quantum confinement. Recent efforts have focused on one hand, on
the study of nanostructured materials and on the other hand, in understanding the fundamental dynamical mechanisms which control the coupled transport of heat and particles \[18\].

### 4.1 The thermoelectric figure of merit $ZT$

For a material subject to a temperature gradient $\nabla T$ and an external uniform electric field $\mathcal{E}$, within linear response the equations describing thermoelectric transport are

\[
\begin{align*}
    j_q &= -\kappa' \nabla T + \sigma \Pi \mathcal{E}, \\
    j_e &= -\sigma S \nabla T + \sigma \mathcal{E},
\end{align*}
\]

where $j_q$ and $j_e$ denote the heat and electric local currents appearing in the material due to the external forcing, $\sigma$ is the coefficient of electrical conductivity, $S$ is the thermopower (or Seebeck coefficient), $\Pi$ is the Peltier coefficient, and $\kappa'$ is the heat conductivity measured at zero electric field and is related to the usual heat conductivity $\kappa$ measured at zero electric current as $\kappa' = \kappa + T \sigma S \Pi$. From (18) the usual phenomenological relations follow: if the temperature gradient vanishes, $\nabla T = 0$, then $j_e = \sigma \mathcal{E}$ is Ohm’s law and the Peltier coefficient $\Pi = j_q/j_e$. If the electric current vanishes, $j_e = 0$, then $j_q = -\kappa \nabla T$ is Fourier’s law, and $\mathcal{E} = S \nabla T$, which is the definition of the thermopower. We start by considering systems with time-reversal symmetry, for which the Onsager reciprocity relations imply $\Pi = TS$ (see Sect. 4.2).

The suitability of a thermoelectric material for energy conversion or electronic refrigeration is evaluated by the dimensionless thermoelectric figure of merit $ZT$ \[72\]

\[ ZT = \frac{\sigma S^2}{\kappa} T, \]

as follows. Consider a material maintained on one end at temperature $T_H$ and on the other at temperature $T_C$, and subject to an external electric field $\mathcal{E}$. Then $ZT$ is related to the efficiency $\eta = P/j_q$ of converting the heat current $j_q$ (flowing between the thermal baths) into electric power $P \equiv \mathcal{E} j_e$, generated by attaching the thermoelectric element to an Ohmic impedance. If we optimize the efficiency over $\mathcal{E}$ we obtain the maximum efficiency

\[ \eta_{\text{max}} = \eta_C \sqrt{\frac{ZT + 1}{ZT + 1} - 1}, \]

where $\eta_C = 1 - T_C/T_H$ is the Carnot efficiency and $T = (T_H + T_C)/2$ is the average temperature. Thermodynamics only imposes (see Sect. 4.2) $ZT \geq 0$ and $\eta_{\text{max}}$ is a monotonous growing function of $ZT$ (see Fig. 16), with $\eta_{\text{max}} = 0$ when $ZT = 0$ and $\eta_{\text{max}} \rightarrow \eta_C$ when $ZT \rightarrow \infty$. 
Fig. 16 Linear response efficiency for heat to work conversion, in units of the Carnot efficiency $\eta_C$, as a function of the figure of merit $ZT$. The top and the bottom curve correspond to the maximum efficiency $\eta_{\text{max}}$ and to the efficiency at the maximum power $\eta(P_{\text{max}})$, respectively.

The Carnot efficiency is obtained for reversible quasi-static transformations, which require infinite time and consequently the extracted power is zero. An important question is how much the efficiency deteriorates when transformations are operated in a finite time. This is a central question in the field of finite-time thermodynamics [4]. Hence, the notion of efficiency at maximum power $\eta(P_{\text{max}})$ was introduced: it is obtained by optimizing over $\delta$ the power $P$ rather than the efficiency $\eta$. Within linear response we obtain [143]

$$\eta(P_{\text{max}}) = \frac{\eta_C ZT}{ZT + 2}.$$  \quad (21)

Note that also $\eta(P_{\text{max}})$ is a growing function of $ZT$ (see Fig. 16). In the limit $ZT \to \infty$, $\eta(P_{\text{max}})$ takes its maximum value of $\eta_C/2$. Such value also corresponds to the linear response expansion of the so-called Curzon-Ahlborn upper bound [155, 39, 108, 45, 143, 129, 59, 5]. Therefore, high values of $ZT$ are favorable for thermoelectric conversion.

Nowadays, most efficient thermoelectric devices operate at around $ZT \approx 1$, whilst it is generally accepted that $ZT > 3$ is the target value for efficient, commercially competing, thermoelectric technology [89]. The great challenge to increase thermoelectric efficiency relies on understanding the microscopic mechanisms that may allow to control individually $S$, $\sigma$ and $\kappa$. However, the different transport coefficients are generally interdependent making optimisation extremely difficult and so far, no clear paths exist which may lead to reach that target. A particular example of this interdependence is the Wiedemann-Franz law [10] which states that for metallic materials, $\sigma$ and $\kappa$ are, as a matter of fact, proportional, thus making metals poor thermoelectric materials in general.

Note that $ZT$ is related to the heat conductivities defined above as $\frac{\kappa}{\kappa'} = 1 + ZT$, which has been used in Ref. [145] to make an analogy between a classical heat engine and a thermoelectric material. The used correspondence is $N \to V$ and $\mu_e \to -p$, with $N$ number of charge carriers, $\mu_e$ the electrochemical potential, and $V, p$...
volume and pressure of the gas in the engine. As a consequence, \( \frac{c_p}{c_v} \rightarrow c_p \), with \( c_p \) and \( c_v \) specific heat at constant pressure and volume, respectively. The ratio \( \frac{c_p}{c_v} \) is bounded for ideal (non interacting) gases, but diverges at the gas-liquid critical conditions. These considerations suggest that large values of \( ZT \) could be expected near electronic phase transitions, for systems with strong interactions between the charge carriers \([110]\).

### 4.2 The Onsager matrix

Let us consider a system of particles enclosed in a chamber, coupled to two particle reservoirs. Calling the energy balance for the thermoelectric process, the energy current can be written in terms of the heat and electric currents as \( j_u = j_q + \mu_e e j_e \), where \( \mu_e \) is the electrochemical potential. For particles having electric charge \( e \) the electrochemical potential is simply \( \mu_e = e \phi \), where \( \phi \) is the ordinary electrostatic potential \( \mathcal{E} = -\nabla \phi \). Assuming that the particles are the only carriers of heat, one may interchange the electrochemical potential with the chemical potential \( \mu \) corresponding to the work generated by the exchange of particles between the system and the reservoirs. Within the linear response regime, the energy current and the particle current \( j \rho = \frac{1}{e} j_e \) are related to the conjugated thermodynamic forces (gradient of chemical potential \( \mu \) and gradient of temperature \( T \)) as \([51, 33]\)

\[
\mathbf{j} = L \mathbf{F}, \tag{22}
\]

where \( \mathbf{j} \equiv (j_\rho, j_u) \), \( \mathbf{F} \equiv (\nabla(-\mu/T), \nabla(1/T)) \), and

\[
L \equiv \begin{pmatrix} L_{\rho\rho} & L_{\rho u} \\ L_{u\rho} & L_{uu} \end{pmatrix} \tag{23}
\]

is the Onsager matrix of kinetic transport coefficients. In the absence of magnetic fields (or other effects breaking time reversibility), the Onsager reciprocity relations state that the crossed kinetic coefficients are equal: \( L_{\rho u} = L_{u\rho} \). Moreover, the second law of thermodynamics imposes that the entropy production rate \( \dot{s} = \mathbf{j} \cdot \mathbf{F} = j_\rho \nabla(-\mu/T) + j_u \nabla(1/T) \geq 0 \). Therefore \( L \) has to be nonnegative, i.e. \( L_{\rho\rho}, L_{uu} \geq 0 \) and \( \det L \geq 0 \).

The kinetic coefficients \( L_{ij} \) are related to the thermoelectric transport coefficients as

\[
\sigma = \frac{e^2}{T} L_{\rho\rho}, \quad \kappa = \frac{1}{T^2} \frac{1}{L_{\rho\rho}}, \quad S = \frac{1}{eT} \left( \frac{L_{pu}}{L_{\rho\rho}} - \mu \right) = \frac{\Pi}{T}, \quad \tag{24}
\]

where the temperature \( T \) and chemical potential \( \mu \) are taken as mean values in the bulk. Moreover, using Eqs. \([19]\) and \([24]\), the thermoelectric figure of merit reads

\[
ZT = \frac{(L_{uu} - \mu L_{\rho\rho})^2}{\det L}. \tag{25}
\]
Note that the limit $ZT \to \infty$ can be reached if and only if the Onsager matrix $L$ is ill-conditioned, namely when the ratio

$$\frac{[\text{tr}(L)]^2}{\det L} \to \infty$$

and therefore the linear system (22) becomes singular. That is, the Carnot efficiency is obtained when the energy current and the particle current become proportional: $j_u = c j_\rho$, with the proportionality factor $c$ independent of the values of the applied thermodynamic forces. Such condition is refereed to as tight coupling condition.

### 4.3 Non-interacting systems

We consider a system whose ends are in contact with left/right baths (reservoirs), which are able to exchange energy and particles with the system, at fixed temperature $T_\alpha$ and chemical potential $\mu_\alpha$, where $\alpha = L,R$ denotes the left/right bath. The reservoirs are modeled as infinite ideal gases, and therefore particle velocities are described by the Maxwell-Boltzmann distribution. We use a stochastic model of the thermochemical baths [101, 82]: Whenever a particle of the system crosses the boundary which separates the system from the left or right reservoir, it is removed. On the other hand, particles are injected into the system from the boundaries, with rates $\gamma_\alpha$ computed by counting how many particles from reservoir $\alpha$ cross the reservoir-system boundary per unit time. For one-dimensional reservoirs we obtain $\gamma_\alpha = \frac{1}{\hbar} \int_0^\infty d\epsilon (\epsilon - \mu_\alpha)(e^{-\beta_\alpha(\epsilon - \mu_\alpha)} - e^{-\beta_\alpha(\epsilon - \mu_\beta)}) \tau(\epsilon)$, where $\beta_\alpha = \frac{1}{k_B T_\alpha}$ ($k_B$ is the Boltzmann constant and $\hbar$ is the Planck’s constant). Assuming that both energy and charge are carried only by non-interacting particles, like in a dilute gas, we arrive at simple expressions for the particle and heat currents [121]:

$$j_\rho = \frac{1}{\hbar} \int_0^\infty d\epsilon \left( e^{-\beta_L(\epsilon - \mu_L)} - e^{-\beta_R(\epsilon - \mu_R)} \right) \tau(\epsilon),$$

$$j_{q,L} = j_{q,R} = \frac{1}{\hbar} \int_0^\infty d\epsilon (\epsilon - \mu_\alpha)(e^{-\beta_L(\epsilon - \mu_\alpha)} - e^{-\beta_R(\epsilon - \mu_\alpha)}) \tau(\epsilon),$$

where $j_{q,\alpha}$ is the heat current from reservoir $\alpha$ and $\tau(\epsilon)$ denotes the transmission probability for a particle with energy $\epsilon$ to transit from one end to the other end of the system ($0 \leq \tau(\epsilon) \leq 1$). The thermoelectric efficiency is then given by (we assume $T_L > T_R$, $\mu_R > \mu_L$, and $j_\rho, j_{q,L} \geq 0$)

$$\eta = \frac{j_{q,L} - j_{q,R}}{j_{q,L}} = \frac{\int_0^\infty d\epsilon (\epsilon - \mu_L)(e^{-\beta_L(\epsilon - \mu_L)} - e^{-\beta_R(\epsilon - \mu_R)}) \tau(\epsilon)}{\int_0^\infty d\epsilon (\epsilon - \mu_L)(e^{-\beta_L(\epsilon - \mu_L)} - e^{-\beta_R(\epsilon - \mu_R)}) \tau(\epsilon)}.$$
In the limit $j_\rho \to 0$, corresponding to reversible transport \cite{69, 68}, we get $\varepsilon_\star$ from Eq. (27):

$$\varepsilon_\star = \frac{\beta_L \mu_L - \beta_R \mu_R}{\beta_L - \beta_R}. \quad (31)$$

Substituting such $\varepsilon_\star$ in Eq. (30), we obtain the Carnot efficiency

$$\eta = \frac{\mu_R - \mu_L}{\varepsilon_\star - \mu_L}. \quad (30)$$

In the linear response regime, using a delta-like energy filtering, i.e. $\tau(\varepsilon) = 1$ in a tiny interval of width $\delta \varepsilon$ around some energy $\bar{\varepsilon}$ and 0 otherwise, we obtain

$$L_{\rho \rho} = \frac{\Lambda(\delta \varepsilon)}{h \kappa_B} e^{-\beta(\bar{\varepsilon} - \mu)}; \quad L_{\mu \rho} = \frac{\Lambda \beta(\delta \varepsilon)}{h \kappa_B} e^{-\beta(\bar{\varepsilon} - \mu)}; \quad L_{\mu \mu} = \frac{\Lambda \beta^2(\delta \varepsilon)}{h \kappa_B} e^{-\beta(\bar{\varepsilon} - \mu)}; \quad (32)$$

where $\Lambda$ is the length of system. From these relations we immediately derive that the Onsager matrix is ill-conditioned and therefore $ZT = \infty$ and $\eta = \eta_C$. We point out that the parameters $\bar{\varepsilon}$ and $\delta \varepsilon$ characterizing the transmission window, appear in the Onsager matrix elements \cite{88, 69, 68} and therefore are assumed to be independent of the applied temperature and chemical potential gradients. On the other hand, the energy $\varepsilon_\star$ in Eqs. (30) and (31) depends on the applied gradients. There is of course no contradiction since (30) and (31) have general validity beyond the linear response regime.

A dynamical realization of the energy-filtering mechanism was discussed in Ref. \cite{36}. We start by writing for a gas of non-interacting particles the microscopic instantaneous charge and energy currents per particle at position $\mathbf{r}^*$ and time $t$:

$$i_\rho(\mathbf{r}^*, t) = \nu_x \delta(\mathbf{r}^* - \mathbf{r}(t)), \quad (33)$$

$$i_u(\mathbf{r}^*, t) = \varepsilon(t)\nu_x(\mathbf{r}(t), t) \delta(\mathbf{r}^* - \mathbf{r}(t)), \quad (34)$$

where $\varepsilon$ is the energy of the particle, $\mathbf{r}$ its position and $\nu_x$ its velocity along the direction of the currents. The thermodynamic averages of the two currents become proportional precisely when the variables $\varepsilon$ and $\nu_x$ are uncorrelated:

$$j_u = \langle i_u \rangle = \langle \varepsilon \nu_x \rangle = \langle \varepsilon \rangle \langle \nu_x \rangle = \langle \varepsilon \rangle \langle i_\rho \rangle = \langle \varepsilon \rangle j_\rho. \quad (35)$$

Therefore, $ZT = \infty$ follows from the fact that the average particle’s energy $\langle \varepsilon \rangle$ does not depend on the thermodynamic forces. In the context of classical physics this happens for instance in the limit of large number of internal degrees of freedom, provided the dynamics is ergodic.
This observation was used in Ref. [36] where an ergodic gas of non-interacting particles with \( d_{\text{int}} \) internal degrees of freedom in a \( d \) - dimensional chamber connected to reservoirs was studied. It was shown that for such systems the thermoelectric figure of merit becomes

\[
ZT = \frac{1}{c_V} \left( c_V - \frac{\mu}{T} \right)^2,
\]

(36)

where \( c_V = c_V^* + 1/2 \) and \( c_V^* = D/2 \) \( (D = d + d_{\text{int}}) \) is the dimensionless heat capacity at constant volume of the gas. Fig. 17 shows the figure of merit \( ZT \) numerically computed for a gas of noninteracting point-like particles as a function of the specific heat (internal degrees of freedom are modeled as free rotating modes). The particles evolve inside a Lorentz gas channel with finite horizon, so that the particles motion is diffusive (see the inset of Fig. 17). The channel is connected at its boundaries to stochastic reservoirs at different temperatures and chemical potentials. The numerical results confirm the analytical expression of Eq. (36). The simple mechanism for the growth of \( ZT \) also implies that the equilibrium distribution of the particle energy per degree of freedom becomes more sharply peaked as \( D \) increases.

![Fig. 17](image)

**Fig. 17** Figure of merit \( ZT \) as a function of the heat capacity \( c_V \), at \( \mu = 0 \). Numerical results are obtained from nonequilibrium simulations (for the details of the simulations see Ref. [36]). The dashed line corresponds to the analytical expression of Eq. (36). Inset: schematic drawing of the model used in the numerical simulations.

We point out that, while the discussion in this section was focused on classical systems, noninteracting systems can be easily treated in quantum mechanics too by means of the Landauer-Büttiker formalism. [49, 71]. In this approach, the particle and heat currents are given, similarly to Eqs. (27) and (28), in terms of integrals over the energy distribution of the particles injected from the reservoirs and the scattering transmission probability of the system (for the use of this formalism in thermoelectricity see Ref. [18]). Implementations of the energy filtering mechanism may be possible in, e.g., nanowires or nanostructured materials for which the shape
of the transmission function can be controlled more easily than in bulk materials. Finally, we note that the results of this section are obtained in the absence of phonon heat leaks.

4.4 Interacting systems

The thermoelectric properties of strongly interacting systems are of fundamental interest since their efficiency is not bounded by inherent limitations of non-interacting systems, such as the Wiedemann-Franz law. Experiments on some strongly correlated materials such as sodium cobalt oxides revealed unusually large thermopower values \[140, 148\], due in part to the strong electron-electron interactions \[113\]. Very little is known about the thermoelectric properties of interacting systems: analytical results are rare and numerical simulations are challenging. The linear response Kubo formalism has been used to investigate the thermoelectric properties of one-dimensional integrable and nonintegrable strongly correlated quantum lattice models \[9, 113, 133, 156\]. With regard to the simulation of classical dynamical models, an extension of the model discussed in Sect. (4.3), with inter-particle interactions added by substituting the Lorentz lattice with the rotating Lorentz gas model \[101, 82\] was studied in Ref. \[35\]. It was shown that while \(ZT\) is bounded from above by its value obtained at zero interaction, it still increases with \(c V\). On the other hand, for a one-dimensional di-atomic disordered hard-point gas coupled to particle reservoirs (see the upper panel in Fig. 18 for a schematic representation of the model), it was numerically found \[38\] that \(ZT\) diverges in the thermodynamic limit as a power-law, \(ZT \sim \langle N \rangle^\alpha\), where \(\langle N \rangle\) is the average number of particles in the system and \(\alpha \approx 0.79\). Note that if the masses of all particles are the same, the dynamics is integrable and one can find analytically that \(ZT\) is independent of \(\langle N \rangle\) (in particular, \(ZT = 1\) when the chemical potential \(\mu = 0\)). Later Ref. \[121\] showed that the numerically observed large values of \(ZT\) could not be explained in terms of the energy filtering mechanism. Indeed, the particle current at the position \(x \in [0, \Lambda]\) (\(\Lambda\) is the system size) can be expressed as \(j_\rho = \int_0^{\infty} d\epsilon D(\epsilon)\), where \(D(\epsilon) \equiv D_L(\epsilon) - D_R(\epsilon)\) plays the role of “transmission function”: \(D_L(\epsilon)\) is the density of particles with energy \(\epsilon\) crossing \(x\) and coming from the left side, while \(D_R(\epsilon)\) is the density of particles with energy \(\epsilon\) from the right side. If the divergence of \(ZT\) with \(\Lambda\) was due to energy filtering, then \(D(\epsilon)\) would sharpen with increasing the system size. Conversely, no sign of narrowing of \(D(\epsilon)\) was found in Ref. \[121\]. As discussed below in Sect. (4.4.2), the divergence of \(ZT\) can be explained on the basis of a theoretical argument \[19\] applicable to non-integrable systems with momentum conservation.
Fig. 18 Thermoelectric transport coefficients for the one-dimensional di-atomic disordered hard-point gas model, as a function of the system size $\Lambda$. The dashed curves correspond from top to bottom to $\sigma \sim \Lambda$, $\kappa \sim \Lambda^{-0.33}$, $S = 1.5$, and $ZT \sim \Lambda^{-0.67}$. In the upper panel a schematic representation of the model is shown.

4.4.1 Green-Kubo formula

While the Landauer-Büttiker approach cannot be applied to interacting systems, the linear response regime can be numerically investigated in equilibrium simulations by using the Green-Kubo formula. This formula expresses the Onsager kinetic coefficients in terms of equilibrium dynamic correlation functions of the corresponding current at finite temperature $\beta^{-1}$ \[80, 86\] as

$$L_{ij} = \lim_{\omega \to 0} \text{Re} L_{ij}(\omega),$$

where

$$L_{ij}(\omega) \equiv \lim_{\epsilon \to 0} \int_0^\infty dt e^{-i(\omega - i\epsilon)t} \lim_{\Omega \to \infty} \frac{1}{\Omega} \int_0^\beta d\tau \langle J_i(0)J_j(t + i\tau) \rangle,$$
where $\langle \cdot \rangle = \{ \text{tr} \left[ (\cdot) \exp^{-\beta \mathcal{H}} \right] \} / \text{tr}[\exp(-\beta \mathcal{H})]$ denotes the equilibrium expectation value at temperature $T$. $\mathcal{H}$ is the system’s Hamiltonian, $\Omega$ is the system’s volume, and $J_i(t) = \int_{\Omega} d\mathbf{r} j_i(\mathbf{r}, t)$ is the total current ($i = \rho, u$).

Within the framework of Kubo linear response approach, the real part of $L_{ij}(\omega)$ can be decomposed into a singular contribution at zero frequency and a regular part $L_{ij}^{\text{reg}}(\omega)$ as

$$\text{Re}L_{ij}(\omega) = 2\pi D_{ij} \delta(\omega) + L_{ij}^{\text{reg}}(\omega). \quad (39)$$

The coefficient of the singular part defines the generalized Drude weights $D_{ij}$ (for $i = j = \rho$, we have the conventional Drude weight $D_{\rho\rho}$). Importantly, it has been shown that non-zero Drude weights, $D_{ij} \neq 0$, are a signature of ballistic transport [158, 159, 61, 65], namely in the thermodynamic limit the kinetic coefficients $L_{ij}$ diverge linearly with the system size. Moreover, it has been conjectured that at finite temperature, an integrable system is an ideal conductor characterised by a finite Drude weight if at zero temperature the Drude weight is positive, while the system remains an insulator if the zero temperature Drude weight is zero. On the other hand nonintegrable systems are believed to have a vanishing Drude weight and thus, to exhibit normal transport.

### 4.4.2 Conservation laws and thermoelectric efficiency

The way in which the dynamic correlation functions in Eq. (38) decay, determines the ballistic, anomalous or diffusive character of the energy and particle transport, and it has been understood that this decay is directly related to the existence of conserved dynamical quantities [158, 159]. For quantum spin chains and under suitable conditions, it has been proved that systems possessing local conservation laws exhibit ballistic transport at finite temperature [70].

However, the role that the existence of conserved quantities plays on the thermoelectric efficiency has been considered only recently [38, 121, 19, 17, 43].

The decay of time correlations for the currents can be related to the existence of conserved quantities by using Suzuki’s formula [139], which generalizes and inequality proposed by Mazur [98]. Consider a system of size $\Lambda$ and Hamiltonian $\mathcal{H}$, with a set of $M$ relevant conserved quantities $Q_m$, $m = 1, \ldots, M$, namely the commutators $[\mathcal{H}, Q_m] = 0$. A constant of motion $Q_m$ is by definition relevant if it is not orthogonal to the currents under consideration, in our case $\langle J_{\rho} Q_m \rangle \neq 0$ and $\langle J_u Q_m \rangle \neq 0$. It is assumed that the $M$ constants of motion are orthogonal, i.e., $\langle Q_m Q_n \rangle = \langle Q^2_m \rangle \delta_{m,n}$ (this is always possible via a Gram-Schmid procedure). Furthermore, we assume that the set $\{Q_m\}$ exhausts all relevant conserved quantities. Then using Suzuki’s formula [139], we can express the finite-size Drude weights

$$d_{ij}(\Lambda) \equiv \frac{1}{2\Lambda} \lim_{\Lambda \to \infty} \frac{1}{t} \int_0^t dt' \langle J_i(t') J_j(0) \rangle \quad (40)$$

in terms of the relevant conserved quantities:
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\[ d_{ij}(\Lambda) = \frac{1}{2\Lambda} \sum_{m=1}^{M} \frac{\langle J_i Q_m \rangle \langle J_j Q_m \rangle}{\langle Q_m^2 \rangle} \]  

(41)

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

\[ D_{ij} = \lim_{t \to \infty} \lim_{\Lambda \to \infty} \frac{1}{2\Lambda t} \int_0^t dt' \langle J_i(t')J_j(0) \rangle . \]  

(42)

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

\[ D_{ij} = \lim_{\Lambda \to \infty} d_{ij}(\Lambda) . \]  

(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, \( L_{ij} \sim \Lambda \). As a consequence, the electrical conductivity is ballistic, \( \sigma \sim L_{pp} \sim \Lambda \), while the thermopower is asymptotically size-independent, \( S \sim L_{up}/L_{pp} \sim \Lambda^0 \).

We can see from Suzuki’s formula that for systems with a single relevant constant of motion \( (M = 1) \), the ballistic contribution to \( \det L \) vanishes, since it is proportional to \( D_{pp}D_{uu} - D_{pu}^2 \), which is zero from Eqs. (41) and (43). Hence, \( \det L \) grows slower than \( \Lambda^2 \), and therefore the thermal conductivity \( \kappa \sim \det L/L_{pp} \) grows sub-ballistically, \( \kappa \sim L^\alpha \), with \( \alpha < 1 \). Since \( \sigma \sim \Lambda \) and \( S \sim \Lambda^0 \), we can conclude that \( ZT \sim \Lambda^{1-\alpha} \) [19]. 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.

It has been recently shown that these expectations fully describe the results obtained for the one-dimensional disordered hard-point gas, see Fig. [18] and Ref. [19]. This enhancement of \( ZT \) has also been verified for more realistic models in Ref. [17], where the nonequilibrium steady state properties of a two-dimensional gas of particles interacting through elastic collisions and enclosed in a box connected to reservoirs at both ends were studied numerically. The inter-particle collisions were modeled by the method of Multiparticle Collision Dynamics (MPC) [90]. Similarly to Ref. [19], it was found that the generalized Drude weights are finite, leading to non decaying current-current time correlations. As a consequence, the transport coefficients exhibit an anomalous scaling yielding a figure of merit that for this model diverges as \( ZT \sim \Lambda/\log \Lambda \). The logarithmic term appears as a consequence of the existence of long time tails in the decay of the energy current-current time correlation, typically observed in two-dimensional hydrodynamic systems [3]. The dependence of the thermoelectric transport coefficients as a function of the system size is shown in Fig. [19]. Finally, results consistent with the above model have been obtained not only for instantaneous collision models but also for a system with finite range of the interaction, more precisely for a one-dimensional gas of particles with nearest-neighbor Coulomb interaction, modeling a screened Coulomb interaction.
between electrons [43]. This latter model takes advantage of the recently reported Fourier-like behavior of thermal conductivity [157, 147, 127, 42], namely, of the appearance of a very broad range of system size where the thermal conductivity behaves normally according to the Fourier law, i.e., $\kappa$ is size-independent, see Fig. 2. As a consequence, $ZT$ exhibits a rapid, linear growth with the system size. While the Fourier-like regime might be an intermediate (in the system size) regime, followed by an asymptotic regime of anomalous thermal conductivity $\kappa \sim \Lambda^{1/3}$ [83, 52], the range of validity of such regime may expand rapidly as an integrable limit is approached [42]. We point out that it is a priori not excluded that there exist models where the long-time limit $t \to \infty$ and the thermodynamical limit $\Lambda \to \infty$ do not commute when computing the Drude weights. However, numerical evidence shows that for the models so far considered these two limits commute [19, 17, 43].

![Graph](image)

**Fig. 19** Thermoelectric transport coefficients for the two-dimensional MPC gas of interacting particles as a function of the system size $\Lambda$ (for details see [17]). The dashed curves correspond from top to bottom to $\sigma = (\pi \langle N \rangle / 2m) \Lambda$ with $\langle N \rangle$ the mean number of particles, $\kappa \sim \log \Lambda$, $S = 2$, and $ZT \sim \Lambda / \log \Lambda$.

It is interesting to note the contrasting behavior obtained when more than one conserved quantities exist. For $M > 1$, in general $D_{\rho \rho} D_{uu} - D_{\rho \rho}^2 \neq 0$. As a consequence, $\det L \sim \Lambda^2$, and therefore the heat conductivity becomes ballistic and $ZT$ asymptotically independent of the system size. This situation is commonly found in integrable systems, for which infinite constants of motion exist at the thermodynamic limit. For instance, in noninteracting systems, momentum conservation implies that all transport coefficients are ballistic, thus leading to a constant $ZT$. The
enhancement in the efficiency due to the existence of conserved quantities is limited to systems of interacting particles.

### 4.5 Breaking time-reversibility

When time-reversal symmetry is broken, typically by a magnetic field $B$, Onsager-Casimir reciprocity relations no longer imply $L_{ji} = L_{ij}$, but rather $L_{ji}(B) = L_{ij}(-B)$. While these relations imply $\sigma(B) = \sigma(-B)$ and $\kappa(B) = \kappa(-B)$, the thermopower is not bounded to be a symmetric function under the exchange $B \rightarrow -B$. This simple remark has deep consequences on thermoelectric efficiency.

The maximum efficiency and the efficiency at maximum power are now determined by two parameters [20]: the asymmetry parameter

$$x = \frac{S(B)}{S(-B)} = \frac{S(B)}{\Pi(B)} T \quad (44)$$

and the “figure of merit”

$$y = \frac{\sigma(B) S(B) S(-B)}{\kappa(B)} T = \frac{\sigma(B) S(B) \Pi(B)}{\kappa(B)} \quad (45)$$

In terms of these variables, the maximum efficiency reads

$$\eta_{\text{max}} = \eta_C x \sqrt{y + 1} - 1 \quad (46)$$

while the efficiency at maximum power is

$$\eta(P_{\text{max}}) = \frac{\eta_C x y}{2 + y} \quad (47)$$

In the particular case $x = 1$, $y$ reduces to the $ZT$ figure of merit of the time-symmetric case, Eq. (46) reduces to Eq. (20), and Eq. (47) to Eq. (21). 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 $y$) $\bar{\eta}(P_{\text{max}})$ of $\eta(P_{\text{max}})$ and the maximum $\bar{\eta}_{\text{max}}$ of $\eta_{\text{max}}$ are obtained for $y = h(x)$:

$$\bar{\eta}(P_{\text{max}}) = \frac{\eta_C x^2}{x^2 + 1}, \quad (48)$$
\[ \eta_{\text{max}} = \begin{cases} \eta_C x^2 & \text{if } |x| \leq 1, \\ \eta_C & \text{if } |x| \geq 1. \end{cases} \] (49)

The functions \( \eta(P_{\text{max}})(x) \) and \( \eta_{\text{max}}(x) \) are drawn in Fig. 20. In the case \( |x| > 1 \), it is in principle possible to overcome the Curzon-Ahlborn limit within linear response (that is, to have \( \eta(P_{\text{max}}) > \eta_C/2 \)) 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 \( \text{det} L = \left( L_{\rho u} - L_{u\rho} \right)^2 / 4 > 0 \) when \( |x| > 1 \), that is, the tight coupling condition is not fulfilled.

The output power at maximum efficiency reads

\[ P(\eta_{\text{max}}) = \frac{\eta_{\text{max}} |L_{2\rho u}^2 - L_{u2\rho}^2|}{L_{\rho\rho}} \frac{T_H - T_C}{T^2}. \] (50)

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 \([27, 28]\). We first split the particle and energy currents into a reversible part (which changes sign by reversing \( \BBB \rightarrow -\BBB \)) and an irreversible part (invariant with respect to the inversion \( \BBB \rightarrow -\BBB \)), defined by

\[ j_{\text{rev}}(\BBB) = \frac{L(\BBB) - L(\BBB)^T}{2} F, \quad j_{\text{irr}}(\BBB) = \frac{L(\BBB) + L(\BBB)^T}{2} F. \] (51)

Only the irreversible part of the currents contributes to the entropy production: \( \dot{s} = j_{\text{irr}} \cdot F = j_{\text{irr}}^\nu \nabla (-\mu / T) + j_{\text{irr}}^\nu \nabla (1 / T) \). The reversible currents vanish for \( \BBB = 0 \). 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.
It is interesting to compare the performances of a system as a thermal machine or as a refrigerator. For a refrigerator, the most important benchmark is the coefficient of performance \( \eta(r) = j_q/P \) \((j_q < 0, P < 0)\), given by the ratio of the heat current extracted from the cold system over the absorbed power. The efficiency of an ideal, dissipationless refrigerator is given by \( \eta_C^{(r)} = T_C/(T_H - T_C) \). While in the time-reversal case the linear response normalized maximum efficiency \( \eta_{C}^{\text{max}}/\eta_C \) and coefficient of performance \( \eta_{C}^{(r)\text{max}}/\eta_C^{(r)} \) 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

\[
\eta_{C}^{(r)\text{max}} = \frac{1}{x} \frac{\sqrt{y+1} - 1}{\sqrt{y+1} + 1}. \tag{52}
\]

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

\[
\frac{1}{2} \left[ \frac{\eta_{C}^{\text{max}}(B)}{\eta_C} + \frac{\eta_{C}^{(r)\text{max}}(B)}{\eta_C^{(r)}} \right] = \frac{\eta_{C}^{\text{max}}(0)}{\eta_C} = \frac{\eta_{C}^{(r)\text{max}}(0)}{\eta_C^{(r)}}, \tag{53}
\]

up to second order corrections. Due to the Onsager-Casimir relations, \(x(-B) = 1/x(B)\) and therefore by inverting the direction of the magnetic field one can improve either power generation or refrigeration.

With regard to the practical relevance of the results presented in this section, we should note that, as a consequence of the symmetry properties of the scattering matrix [49] (see Sect. 4.6), in the non-interacting case the thermopower is a symmetric function of the magnetic field, thus implying \(x = 1\). On the other hand, as we shall discuss in Sect. 4.6, this symmetry may be violated when electron-phonon or electron-electron interactions are taken into account. Non-symmetric thermopowers have been reported in measurements for certain orientations of a bismuth crystal [152] and in Andreev interferometer experiments [58] (for a theoretical analysis of these latter experiments see [74]).

\subsection*{4.6 Inelastic scattering and probe terminals}

Inelastic scattering events like electron-phonon interactions, can be conveniently modeled 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. 21, left panel). 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 [31]. The advantage of such ap-
The 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 [49], heat transport and rectification [22, 23, 118, 52, 24, 112, 13, 22, 5], and thermoelectric transport [73, 57, 56, 75, 76, 124, 126, 135, 136, 122, 67, 15, 11, 27, 25].

The approach can be generalized to any number \( n_p \) of probe reservoirs. We call \( \mathbf{j}_k \equiv (j_{k,\rho}, j_{k,u})' \) the particle and energy currents from the \( k \)th terminal (at temperature \( T_k \) and chemical 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, \( \sum_k j_{k,\rho} = \sum_k j_{k,u} = 0 \), 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 \( \mathbf{X}_k \equiv (\Delta (\mu_k/T), \Delta T_k/T^2)' \), with \( \Delta \mu_k = \mu_k - \mu \), \( \Delta T_k = T_k - T \), \( \mu = \mu_2 \), and \( T = T_2 \). The linear response relations between currents and thermodynamic forces read as follows:

\[
\mathbf{j}_i = \sum_{j=1}^{n} \mathbb{L}_{ij} \mathbf{X}_j, \tag{54}
\]

where \( \mathbb{L}_{ij} \) are \( 2 \times 2 \) matrices, so that the overall Onsager matrix \( \mathbb{L} \) has size \( 2(n - 1) \). We then impose the condition of zero average currents through the probes, \( j_{k,\rho} = j_{k,u} = 0 \) for \( k = 3, \ldots, n \) to reduce the Onsager matrix to a \( 2 \times 2 \) matrix \( \mathbb{L}' \) connecting the fluxes \( \mathbf{j}_1 \) through the first reservoir and the conjugated forces \( \mathbf{X}_1 \) as \( \mathbf{j}_1 = \mathbb{L}' \mathbf{X}_1 \). The reduced matrix \( \mathbb{L}' \) fulfills the Onsager-Casimir relations and represents the Onsager matrix for two-terminal inelastic transport modeled by means of probe reservoirs. The transport coefficients and the thermodynamic efficiencies can then be computed in the usual way from the reduced matrix \( \mathbb{L}' \).
The particle and energy currents can be conveniently computed, for any number of probes, by means of the multi-terminal Landauer-Büttiker formula \( [49] \):

\[
j_{k\rho} = \frac{1}{\hbar} \int_{-\infty}^{\infty} d\varepsilon \sum_{l} \left[ \tau_{l\rightarrow k}(\varepsilon) f_{k}(\varepsilon) - \tau_{k\rightarrow l}(\varepsilon) f_{l}(\varepsilon) \right],
\]

\[
j_{k\nu} = \frac{1}{\hbar} \int_{-\infty}^{\infty} d\varepsilon \sum_{l} \left[ \tau_{l\rightarrow k}(\varepsilon) f_{k}(\varepsilon) - \tau_{k\rightarrow l}(\varepsilon) f_{l}(\varepsilon) \right],
\]

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

\[
\sum_{k} \tau_{k\rightarrow l} = \sum_{k} \tau_{l\rightarrow k} = M_{l},
\]

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

\[
\tau_{k\rightarrow l}(B) = \tau_{l\rightarrow k}(-B).
\]

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 \( [58] \). In the two-terminal case, Eq. \( [57] \) means \( \tau_{1\rightarrow 2} = \tau_{2\rightarrow 1} \). Hence, we can conclude from this relation and Eq. \( [58] \) that \( \tau_{2\rightarrow 1}(B) = \tau_{2\rightarrow 1}(-B) \), thus implying that the Seebeck coefficient is a symmetric function of the magnetic field.

Probe terminals 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 \( x = S(B)/S(-B) \) were obtained in \( [122] \) (see Fig. \( 21 \) right panel) by means of a three-dot Aharonov-Bohm interferometer model. The asymmetry was found also for chaotic cavities, ballistic microjunctions \( [126] \), and random Hamiltonians drawn from the Gaussian unitary ensemble \( [11] \), and also in the framework of classical physics, for a three-terminal deterministic railway switch transport model \( [67] \). In the latter model, only the values zero and one are allowed for the transmission functions \( \tau_{l\rightarrow i}(\varepsilon) \), i.e., \( \tau_{l\rightarrow i}(\varepsilon) = 1 \) if particles injected from terminal \( i \) with energy \( \varepsilon \) go to terminal \( j \) and \( \tau_{l\rightarrow i}(\varepsilon) = 0 \) if such particles go to a terminal other than \( j \). The transmissions \( \tau_{l\rightarrow i}(\varepsilon) \) are piecewise constant in the intervals \( [\varepsilon_{i}, \varepsilon_{i+1}] \), \( (i = 1, 2, \ldots) \), with switching \( \tau_{l\rightarrow i} = 1 \rightarrow 0 \) or vice versa possible at the threshold energies \( \varepsilon_{i} \), with the constraints \( [57] \) always fulfilled.

In all the above instances, it was not possible to find at the same time large values of asymmetry parameter \( [44] \) and high thermoelectric efficiency. Such failure was explained by \( [27] \) 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 the positivity of entropy production. As a consequence, Carnot efficiency can be achieved in the three-terminal setup only in the symmetric case \( x = 1 \). On the other hand, the Curzon-Ahlborn linear response
bound, $\eta_C/2$, for the efficiency at maximum power can be overcome for moderate asymmetries, $1 < x < 2$, with a maximum of $4\eta_C/7$ at $x = 4/3$. The bounds obtained by [27] are in practice saturated in a quantum transmission model reminiscent of the above described railway switch model [11] (see Fig. 22). The generic multi-terminal case was also discussed for noninteracting electronic transport [28]. 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. However, the bounds (48) and (49) from the second law of thermodynamics are saturated only in the limit $n_p \to \infty$. Moreover, numerical evidence suggests that the power vanishes when the maximum efficiency is approached [29]. It is an interesting open question whether similar bounds on efficiency, tighter than those imposed by the positivity of entropy production, exist in more general transport models for interacting systems.

Finally, we point out that in a genuine multi-terminal device all terminals should be treated on equal footing, without necessarily declaring some of them as probes. First investigations for a generic three-terminal system have shown that in some instances the coupling to a third terminal can improve both the extracted power and the efficiency of a thermoelectric device [96]. Moreover, with three terminals one can separate the currents, with charge and heat flowing to different reservoirs. As a result, it is possible to violate in a controlled fashion the Wiedemann-Franz law, greatly enhancing thermoelectric performances [97].

Fig. 22 Maximum efficiency $\bar{\eta}_{\text{max}}$ (left panel) and efficiency at maximum power $\bar{\eta}(P_{\text{max}})$ (right panel), both in units of $\eta_C$. Upper curves correspond to the thermodynamics bounds [20], lower curves to the more restrictive bounds [27] from the unitarity of the scattering matrix for three terminals, squares are obtained from a transmission model whose details are described in [11]. Dotted-dashed line corresponds to the Curzon-Ahlborn linear-response limit $\eta_C/2$. Note that such limit is exceeded in the interval [1,2] with the transmission model.
5 Concluding remarks

In this chapter we have discussed several microscopic mechanisms for the design of a thermal rectifier and the increase of the efficiency of thermoelectric energy conversion. Although not intuitive, solid-state thermal rectifiers do exist and there have already been the first experimental implementations. With regard to thermoelectricity, basic concepts to improve the efficiency have been identified: energy filtering for non-interacting systems and momentum conservation in non-integrable interacting systems.

Several questions remain open. An important point for thermal rectification is the need to have a strongly temperature dependent thermal conductivity. Some ideas have already been explored, but the microscopic theory is still incomplete. It appears promising in this connection to work in the vicinity of a structural phase transition. Moreover, the above discussed rectifiers are based on insulating materials. It would be interesting, in order to combine thermal rectification with thermoelectric power generation or cooling, to include and understand the role of mobile charge carriers. Recent experimental investigations are moving forward in this direction [92].

In spite of the long history of thermoelectricity, from the viewpoint of statistical physics the theory of the coupled transport of heat and charge is still in its infancy. With regard to the challenging problem of improving the efficiency of heat to work conversion, for non-interacting systems we have a quite complete theoretical picture and understand the limitations imposed by nature (notably, the Wiedemann-Franz law). On the other hand, the understanding of general mechanisms connected to strongly interacting systems, for which the Wiedemann-Franz law does not apply, are only beginning to emerge. In particular, regimes near electronic phase transitions might be favorable for thermoelectric conversion [145][110]. A deeper understanding of the nonlinear regime is also needed [99][125][150], since, as observed experimentally in mesoscopic devices [95], the Onsager-Casimir reciprocity relations break down and this fact could in principle allow for improved thermoelectric efficiencies. Furthermore, in the nonlinear regime rectification effects occur and their impact on thermoelectricity is still not well understood.

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