Increasing thermoelectric efficiency: dynamical models unveil microscopic mechanisms

BY GIULIANO BENENTI1,2,* AND GIULIO CASATI1,2,3

1 CNISM, CNR-INFM, and Centre for Nonlinear and Complex Systems, Università degli Studi dell’Insubria, Via Valleggio 11, 22100 Como, Italy
2 Istituto Nazionale di Fisica Nucleare, Sezione di Milano, Via Celoria 16, 20133 Milano, Italy
3 Centre for Quantum Technologies, National University of Singapore, Singapore 117543, Republic of Singapore

Dynamical nonlinear systems provide a new approach to the old problem of increasing the efficiency of thermoelectric machines. In this review, we discuss stylized models of classical dynamics, including non-interacting complex molecules in an ergodic billiard, a disordered hard-point gas and an abstract thermoelectric machine. The main focus will be on the physical mechanisms, unveiled by these dynamical models, which lead to high thermoelectric efficiency approaching the Carnot limit.

Keywords: thermoelectricity; nonlinear dynamics; coupled particle–energy transport; Onsager coefficients

1. Introduction

Although thermoelectricity was discovered almost 200 years ago, strong interest in the scientific community arose only in the 1950s when Abram Ioffe discovered that doped semiconductors exhibit a relatively large thermoelectric effect. This discovery initiated intense research activity in semiconductor physics, which was motivated not by microelectronics but by Ioffe’s suggestion that home refrigerators could be built with semiconductors (see [1–3]). Such solid-state devices would have the advantage of long life, no moving parts, low maintenance, no emission of toxic gases and high reliability. However, the above activity lasted only a few years until the mid-1960s, as, in spite of all the efforts and the consideration of all types of semiconductors, it turned out that thermoelectric refrigerators still have poor efficiency when compared with compressor-based refrigerators. Nowadays, Peltier refrigerators are mainly used in situations in which reliability and quiet operation, and not cost and conversion efficiency, are the main concern, such as equipment in medical applications, space probes, etc.

*Author for correspondence (giuliano.benenti@uninsubria.it).

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In the last decade there has been increasing pressure to find better thermoelectric materials with higher efficiency. The reason is the strong environmental concern about the chlorofluorocarbons used in most compressor-based refrigerators. Also, the possibility to generate electrical power from waste heat using the thermoelectric effect is becoming more and more interesting (see [1–4]).

The thermodynamic efficiency can be conveniently written in terms of a dimensionless quantity, the so-called figure of merit, \( ZT = (\sigma S^2/\kappa) T \), where \( \sigma \) is the electrical conductivity, \( S \) the thermoelectric power (Seebeck coefficient), \( \kappa \) the thermal conductivity and \( T \) the absolute temperature. Ideal Carnot efficiency is reached in the limit \( ZT \to \infty \). In spite of worldwide research efforts to identify thermoelectric materials with high \( ZT \) values, so far the best thermoelectric materials are characterized by values of \( ZT \sim 1 \), at room temperature. Values of \( ZT > 3 \) are considered to be essential for thermoelectric devices to compete in efficiency with mechanical power generation and refrigeration.

The challenge lies in engineering a material for which the values of \( \sigma, S \) and \( \kappa \) can be controlled in order to optimize thermoelectric efficiency. The problem is that the different transport coefficients are interdependent, thus making optimization extremely difficult. On the other hand, thermodynamics does not impose any upper bound on \( ZT \), so that efficient thermoelectric devices could in principle be engineered. The present understanding of the possible microscopic mechanisms leading to an increase of \( ZT \) is quite limited, with a few exceptions. Notably, Mahan & Sofo [5], Humphrey et al. [6] and Humphrey & Linke [7] have shown that the optimal density of states in a thermoelectric material is a delta function. Such sharp energy filtering allows one to reach, in principle, the Carnot efficiency.

Here, we consider the problem of increasing thermoelectric efficiency from a new perspective, that is, we pursue a dynamical systems approach. Transport coefficients and thermoelectric efficiency are computed from first principles, namely from the underlying microscopic dynamical processes, which are known to be predominantly nonlinear in nature. In this paper, we review previous works [8–12], where the thermoelectric problem has been investigated by numerical solution of the microscopic equations of motion. In spite of the abstract nature of the models so far considered, they have unveiled physical mechanisms that can lead to large \( ZT \) factors. In Casati et al. [8], the cross transport of particles and energy has been considered for an open classical ergodic billiard, showing that the Carnot efficiency can be approached for sufficiently complex charge carrier molecules. For a large number of internal degrees of freedom of the molecules, the particle energy per degree of freedom is sharply peaked, thus leading to decorrelation of energies and velocities. As a result, the \( ZT \) factor diverges.

High \( ZT \) factors, diverging in the thermodynamic limit, have also been observed [9] for an open one-dimensional disordered hard-point gas. This result has been explained [12] in terms of the emergence, in the linear response regime, of an out-of-equilibrium ‘modified Maxwell–Boltzmann velocity distribution’, of width much larger than the mean velocity of the particle flow. Such a broad distribution limit is opposite to the limit of a peaked distribution, corresponding to the delta-like energy filtering put forward by Mahan & Sofo [5], Humphrey et al. [6] and Humphrey & Linke [7].
Finally, microscopic thermoelectric machines, consisting of two heat baths or reservoirs connected by two channels, have been investigated by Wang et al. [10] and Horvat et al. [11]. Efficiencies close to the Carnot efficiency can be obtained when scatterers placed in the two channels act as appropriate energy filters, transmitting particles only above or below a given energy. The models of Wang et al. [10] and Horvat et al. [11] also show that the $ZT$ factor is not a suitable figure of merit for microscopic thermoelectric engines leading to a steady current circulating in a two-channel set-up.

Our paper is organized as follows. Section 2 reviews introductory material on coupled particle and energy transport. Sections 3 and 4 describe the above-mentioned nonlinear dynamical systems exhibiting high thermoelectric efficiency, focusing on the physical mechanisms rather than on the details of the models. Concluding remarks are drawn in §5.

2. The thermoelectric figure of merit, $ZT$

Let us focus our attention on a conductor in which both electric and heat currents flow in one dimension (say, parallel to the $x$-direction). Assuming local equilibrium, a local entropy (per unit volume) $s$ can be defined, and the rate of entropy production reads [13]

$$\dot{s} = J_u \partial_x \left( \frac{1}{T} \right) + J_\rho \partial_x \left( -\frac{\mu}{T} \right),$$

(2.1)

in which $J_u$ and $J_\rho$ are the energy and particle current densities (fluxes), and $\partial_x (1/T)$ and $-\partial_x (\mu/T)$ the associated generalized forces (affinities), where $T$ is the temperature and $\mu$ the electrochemical potential.

Assuming that the generalized forces are small, the relationship between fluxes and forces is linear and described by the phenomenological non-equilibrium thermodynamic kinetic equations [13,14]

$$J_u = L_{uu} \partial_x \left( \frac{1}{T} \right) + L_{up} \partial_x \left( -\frac{\mu}{T} \right)$$

(2.2)

and

$$J_\rho = L_{\rho u} \partial_x \left( \frac{1}{T} \right) + L_{\rho \rho} \partial_x \left( -\frac{\mu}{T} \right),$$

(2.3)

with $L_{\alpha\beta} \ (\alpha, \beta \in \{u, \rho\})$ the Onsager coefficients. In the absence of magnetic fields, owing to microscopic reversibility of the dynamics, the Onsager reciprocity relation $L_{up} = L_{pu}$ holds.

In analogy with the relation $dQ = T \, dS$, the heat current density $J_q$ can be defined by the relation

$$J_q = TJ_s,$$

(2.4)

with

$$J_s = \frac{1}{T} J_u - \frac{\mu}{T} J_\rho$$

(2.5)

the current density of entropy, and therefore

$$J_q = J_u - \mu J_\rho.$$
The entropy production rate equation can then be written in terms of the fluxes $J_q$ and $J_\rho$ and of the corresponding generalized forces $\partial_x (1/T)$ and $-(1/T) \partial_x \mu$:

$$\dot{s} = J_q \partial_x \left( \frac{1}{T} \right) + J_\rho \left( -\frac{\partial_x \mu}{T} \right).$$

(2.7)

The linear relationship between fluxes and forces reads as follows:

$$J_q = \tilde{L}_{qq} \partial_x \left( \frac{1}{T} \right) + \tilde{L}_{q\rho} \left( -\frac{\partial_x \mu}{T} \right),$$

(2.8)

and

$$J_\rho = \tilde{L}_{\rho q} \partial_x \left( \frac{1}{T} \right) + \tilde{L}_{\rho\rho} \left( -\frac{\partial_x \mu}{T} \right),$$

(2.9)

with $\tilde{L}_{pp} = L_{pp}$, $\tilde{L}_{qp} = \tilde{L}_{pq}$ (Onsager relation), $\tilde{L}_{qp} = L_{qp} - \mu L_{\rho\rho}$ and $\tilde{L}_{qq} = L_{uu} - 2\mu L_{up} + \mu^2 L_{pp}$. Note that, if we call $L$ and $\tilde{L}$ the $2 \times 2$ Onsager matrices with matrix elements $L_{\alpha\beta}$ ($\alpha, \beta \in \{u, \rho\}$) and $\tilde{L}_{\gamma\delta}$ ($\gamma, \delta \in \{q, \rho\}$), it turns out that $\det \tilde{L} = \det L$.

The Onsager coefficients can be expressed in terms of more familiar quantities, the electrical conductivity $\sigma$, the thermal conductivity $\kappa$ and the Seebeck coefficient (thermopower) $S$. Let us first consider the case in which the thermal gradient vanishes, $\partial_x T = 0$, and the system is homogeneous, so that the chemical potential $\mu_c$ is uniform. Since the electrochemical potential $\mu$ is composed of a chemical part $\mu_c$ and an electrical part $\mu_e$, $\mu = \mu_c + \mu_e$, it turns out that for a homogeneous isothermal system $\partial_x \mu = \partial_x \mu_c$. The electric current $J_e = e J_\rho$, with $e$ the charge of the conducting particles, is then given by $J_e = \sigma_\mathcal{E} = -(\sigma/e) \partial_x \mu_e$, with $\mathcal{E}$ the external electric field applied to the system. The quantities $\mu_c$ and $\mu_e$ cannot be determined separately by the theory of irreversible thermodynamics (see [15]): only their combination $\mu = \mu_c + \mu_e$ appears in the kinetic equations (2.2) and (2.3). Based on this equivalence, we can write $J_\rho = J_e/e = -(\sigma/e^2) \partial_x \mu$ even when $\mu_c \neq 0$, provided $\partial_x T = 0$; hence equation (2.9) gives

$$\sigma = \frac{e^2}{T} \tilde{L}_{pp} = \frac{e^2}{T} L_{pp}. \quad (2.10)$$

The heat conductivity $\kappa$ is defined as the heat current density per unit temperature gradient for zero electric current: $J_q = -\kappa \partial_x T$, at $J_e = 0$. Solving the two kinetic equations (2.8) and (2.9) simultaneously, we obtain

$$\kappa = \frac{1}{T^2} \frac{\det \tilde{L}}{\tilde{L}_{pp}} = \frac{1}{T^2} \frac{\det L}{L_{pp}}. \quad (2.11)$$

Finally, the Seebeck coefficient $S$ is defined as the change in electrochemical potential per unit charge, $-\partial_x \mu/e$, per unit change in temperature difference: $S = -(1/e) \partial_x \mu/\partial_x T$, at $J_e = 0$. We then obtain from equation (2.9)

$$S = \frac{\tilde{L}_{qp}}{e T \tilde{L}_{pp}} = \frac{1}{e T} \left( \frac{L_{up}}{L_{pp}} - \mu \right). \quad (2.12)$$

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It is of course possible to eliminate the three Onsager coefficients $\tilde{L}_{qq}$, $\tilde{L}_{qp}$ and $\tilde{L}_{pp}$ from the kinetic equations (2.8) and (2.9), and rewrite such equations in terms of the conductivities $\sigma$ and $\kappa$, and of the thermopower $S$:

\[ J_q = - (\kappa + T \sigma S^2) \partial_x T - \frac{T \sigma S}{e} \partial_x \mu \]  

(2.13)

and

\[ J_p = - \frac{\sigma}{e^2} \partial_x \mu - \frac{\sigma S}{e} \partial_x T. \]  

(2.14)

The thermoelectric efficiency $\eta$, of converting the input heat into output work, is determined by the non-dimensional figure of merit,

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

(2.15)

To derive the relation between $\eta$ and $ZT$, we consider a one-dimensional system whose left/right ends are connected with left/right thermochemical reservoirs, with small temperature difference $\Delta T \equiv T_R - T_L$ and electrochemical potential difference $\Delta \mu \equiv \mu_R - \mu_L$. The efficiency $\eta$ is given, under steady-state conditions, by the ratio of the time derivatives of the extracted work over the heat leaving the hot reservoir:

\[ \eta = \frac{\dot{W}}{\dot{Q}} = \frac{\Delta \mu J_p}{J_q}. \]  

(2.16)

Using equations (2.13) and (2.14) to eliminate $\partial_x \mu$ and $J_q$, we obtain

\[ \eta = \eta_C \frac{T J_e^2 + \sigma S \partial_x TJ_e}{\sigma \partial_x T TSJ_e - k \partial_x T} \]  

(2.17)

where $\eta_C = 1 - T_R / T_L$ is the Carnot efficiency (here we assume $T_L > T_R$). The maximum efficiency for a given $\Delta T$ is derived after optimizing equation (2.17) with respect to $J_e$:

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

(2.18)

The Carnot efficiency is therefore achieved in the limit $ZT \to \infty$.

Using equations (2.10)–(2.12), we can express $ZT$ in terms of the Onsager coefficients:

\[ ZT = \frac{\tilde{L}_{qq}^2}{\det \tilde{L}} = \frac{(L_{qp} - \mu L_{pp})^2}{\det L}. \]  

(2.19)

The only thermodynamic restrictions on the Onsager coefficients come from the positivity of the entropy production, $\dot{s} \geq 0$, which is a quadratic form in the generalized forces $\partial_x (1/T)$ and $-\partial_x (\mu / T)$ (see equations (2.1)–(2.3)) or $\partial_x (1/T)$ and $-(1/T) \partial_x \mu$ (see equations (2.7)–(2.9)). Condition $\dot{s} \geq 0$ implies $L_{uu}, L_{pp} \geq 0$, $\det L \geq 0$ in the first case, and $\tilde{L}_{qq}, \tilde{L}_{pp} \geq 0$, $\det \tilde{L} \geq 0$ in the latter. Thus, the only restriction on the thermoelectric figure of merit is $ZT \geq 0$, so that in principle the Carnot efficiency can be achieved.
It is clear from equation (2.19) that $ZT$ diverges if and only if the Onsager matrix $L$ (or, equivalently, $\hat{L}$) is ill-conditioned, that is, when the condition number $\lambda_1(L)/\lambda_2(L)$ diverges, where $\lambda_1(L)$ and $\lambda_2(L)$ are the largest and the smallest eigenvalue of $L$, respectively. The condition number diverges if and only if the quantity

$$\text{cond}(L) \equiv \frac{(\text{Tr}(L))^2}{\det(L)}$$

(2.20)

diverges. In this case, systems (2.2) and (2.3) (or, equivalently, systems (2.8) and (2.9)) become singular, and therefore $J_u \propto J_r$. In short, the Carnot efficiency is obtained if and only if the energy and particle currents are proportional.

3. Increasing $ZT$: dynamical models

The purpose of the stylized nonlinear dynamical models discussed in this section is to unveil two microscopic mechanisms that can lead to high thermoelectric efficiencies: energy filtering in complex non-interacting molecules undergoing ergodic dynamics, and the emergence of a broad out-of-equilibrium modified Maxwell–Boltzmann distribution in a one-dimensional gas of interacting particles.

(a) Non-interacting ergodic gas

Let us assume that both energy and charge are carried only by non-interacting particles, as in a dilute gas. Then the microscopic instantaneous currents per particle at position $x^*$ and time $t$ are

$$j_u(x^*, t) = E(t)v_x(x(t), t)\delta(x^* - x(t))$$

and

$$j_e(x^*, t) = ev_x\delta(x^* - x(t)),$$

(3.1)

where $E$ is the energy of the particle, $x$ its position and $v_x$ its velocity along the field. The condition of proportionality between energy and charge currents, $J_u \propto J_r$ (or, equivalently, the divergence of the condition number cond($L$) in equation (2.20)), is satisfied when the variables $E$ and $v_x$ are uncorrelated:

$$J_u = \langle j_u \rangle = \langle E \rangle \langle v_x \rangle = \frac{\langle E \rangle}{\epsilon} \langle j_e \rangle = \langle E \rangle J_r.$$

(3.2)

Therefore, $ZT = \infty$ follows from the fact that the average particle’s energy $\langle E \rangle$ equals $J_u/J_r$ and therefore does not depend on the generalized forces to which both $J_u$ and $J_r$ are proportional (see equations (2.2) and (2.3)). In the context of classical physics, this independence of $\langle E \rangle$ on generalized forces happens, for instance, in the limit of a large number of internal degrees of freedom, provided the dynamics is ergodic.

In order to illustrate this point, let us consider an ergodic gas of non-interacting, electrically neutral particles of mass $m$ with $d_{\text{int}}$ internal degrees of freedom (rotational or vibrational), enclosed in a $d$-dimensional container. To study the non-equilibrium state of such a dilute polyatomic gas, we consider a chaotic billiard channel (sketched in figure 1) connected through openings of size $\lambda$ to two reservoirs of particles that are idealized as infinite chambers with the same polyatomic ideal gas at equilibrium density $\rho$ and temperature $T$. From
the reservoirs, particles are effused into the channel at a rate $\gamma$ obtained by
assuming that particle velocities in the reservoirs are distributed according to the
Maxwell–Boltzmann distribution. We obtain (see [16,17])

$$\gamma = \frac{\lambda}{(2\pi m)^{1/2}} \rho T^{1/2}. \quad (3.3)$$

(Note that we set the Boltzmann constant $k_B = 1$.)

The particle injection rate $\gamma$ is related to the value of the chemical potential $\mu$
at the reservoirs, which, for polyatomic molecules with a total of $D = d + d_{int}$
degrees of freedom, reads

$$\mu = T \ln \left( \frac{c_D \gamma}{T^{(D+1)/2}} \right) = T \ln \left( \frac{c'_D \rho}{T^{D/2}} \right), \quad (3.4)$$

where $c_D$ and $c'_D = [\lambda/(2\pi m)^{1/2}]c_D$ are $D$-dependent constants.\(^1\) Furthermore, the
rate at which energy is injected from the reservoirs is given by $\varepsilon = \gamma \langle E \rangle$, where $\langle E \rangle = \gamma T(D + 1)/2$ denotes the mean energy of the injected particles.

Let $p_t(l)$ be the transmission probability of the channel of length $l$. For a billiard
system of non-interacting particles (thus neglecting the phonon transport), the
density currents $J_p$ and $J_u$ assume a simple form: they are $p_t(l)$ multiplied by
the difference between the left and right corresponding injection rates, $\gamma$ and $\varepsilon$,
respectively; namely,

$$J_p = p_t(\gamma_L - \gamma_R) \quad \text{and} \quad J_u = p_t(\varepsilon_L - \varepsilon_R). \quad (3.5)$$

\(^1\)Such constants can be determined in terms of the de Broglie thermal wavelength (see [12]);
however, their expression is irrelevant here.

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Using equation (3.4) to eliminate $\gamma$ in favour of $\mu$, we obtain

$$J_\rho = -\frac{\lambda p_l(l)}{c_D'(2\pi m)^{1/2}} \partial_x (T^{(D+1)/2} e^{\mu/T}) \left\{ \begin{array}{c}
\end{array} \right.$$  

and

$$J_u = -\frac{\lambda p_l(l)}{c_D'(2\pi m)^{1/2}} \frac{D + 1}{2} \partial_x (T^{(D+3)/2} e^{\mu/T}). \right\} (3.6)$$

Taking total differentials of equations (3.6) in the variables $1/T$ and $\mu/T$, and comparing the resulting expression with equations (2.2) and (2.3), we obtain exact microscopic expressions for the Onsager coefficients, namely

$$L_{\rho\rho} = \frac{\lambda p_l(l)}{(2\pi m)^{1/2}} \rho T^{1/2},$$

$$L_{\rho u} = L_{u\rho} = \frac{\lambda p_l(l)}{(2\pi m)^{1/2}} \frac{(D + 1)}{2} \rho T^{3/2},$$

$$L_{uu} = \frac{\lambda p_l(l)}{(2\pi m)^{1/2}} \frac{(D + 1)(D + 3)}{4} \rho T^{5/2}. \right\} (3.7)$$

Note that, for a chaotic billiard channel with diffusive dynamics, the transmission probability decays as $p_l(l) \propto l^{-1}$ (see [18,19]), which means that all the elements of the Onsager matrix $\mathbf{L}$ become size-independent.

For large $D$, the condition number $\text{cond}(\mathbf{L}) \propto D^3$, thus implying a diverging $ZT$. With regard to the transport coefficients, $\sigma$ is $D$-independent, $\kappa \propto D$ and $S \propto D$, so that $ZT \propto D$. Indeed, we obtain

$$ZT = \frac{1}{\hat{c}_V} \left( \hat{c}_V - \frac{\mu}{T} \right)^2, \right(3.8)$$

where $\hat{c}_V = c_V^* + 1/2$, with $c_V^* = D/2$ the dimensionless heat capacity at constant volume of the gas.

A numerical demonstration of equation (3.8) for a dynamical system has been presented by Casati et al. [8]. The model (figure 1) consists of composite particles with $d_{\text{int}} \geq 1$ internal degrees of freedom. Each ‘particle’ of mass $m$ can be imagined as a stack of $d_{\text{int}}$ small identical discs of mass $m/d_{\text{int}}$, rotating freely and independently at a constant angular velocity $\omega_i$, $i = 1, \ldots, d_{\text{int}}$. The centre of mass of the particle moves with velocity $\mathbf{v} = (v_x, v_y)$. Such ‘molecules’ collide elastically with circular obstacles in a two-dimensional chaotic Lorentz-gas channel. At each collision of the particle with the boundary of the billiard (either one of the circular obstacles or the outer wall), an energy exchange among all the $D$ degrees of freedom occurs; see Casati et al. [8] for a description of the collision rules and further details on the model. Numerical results (figure 2) confirm the theoretical prediction (equation (3.8)).

The simple mechanism for the growth of $ZT$ with $d_{\text{int}}$ is nicely illustrated in figure 3, which shows that the particle velocity $v_x$ has a Maxwellian (Gaussian) distribution (inset), while the equilibrium distribution of the particle energy per degree of freedom, $E_D$, becomes more and more sharply peaked, and thus decorrelated from $v_x$, as $D$ grows. Finally, we note that the model discussed
Figure 2. Figure of merit $ZT$ as a function of the number of degrees of freedom $D$ (main figure) and channel length $l$ (inset). In both cases, the dashed line corresponds to the theoretical prediction (3.8). Figure taken from Casati et al. [8]. (Online version in colour.)

Figure 3. Probability distribution function of the energy per degree of freedom, $E_D = E/D$, for different numbers of degrees of freedom: $D = 3, 13$ and $43$. Sharper distributions correspond to larger $D$. The inset (in which $\xi_i$ stands for either $v_x$ or $\omega_i$) shows the probability distribution function $P(v_x)$ for the particle velocity $v_x$ (sharper histogram) and the probability distribution function $P(\omega_i)$ for the momentum $\omega_i$ of one of the particle’s discs (broader histogram). The dashed curves correspond to Maxwellian distributions. Figure taken from Casati et al. [8]. (Online version in colour.)
in this section can be considered as a dynamical realization of the delta-like energy-filtering mechanism for increasing thermoelectric efficiency, pointed out by Mahan & Sofo [5], Humphrey et al. [6] and Humphrey & Linke [7].

(b) One-dimensional interacting gas

Let us now turn to a gas with particle–particle interactions. We consider a one-dimensional, diatomic disordered chain of hard-point elastic particles with coordinates $x_i \in [0, L]$, $L$ being the system size, velocities $v_i$ and masses $m_i \in \{m, M\}$ randomly distributed. The particles interact among themselves through elastic collisions only. The system-contact reservoirs are described in the same way as in §3a (see Saito et al. [12] for details). A schematic of the model is drawn in figure 4. For this model, numerical results obtained in Casati et al. [9] suggest that, for mass ratio $M/m \neq 1$, the figure of merit $ZT$ diverges in the thermodynamic limit.

The average currents $J_\rho$ and $J_u$ are computed at the contacts between the system and the baths. If, in a period of time $t$, the left bath injects $N_i$ particles with masses $m_j^{(i)}$ and velocities $v_j^{(i)}, j = 1, \ldots, N_i$, and absorbs $N_a$ particles with masses $m_j^{(a)}$ and velocities $v_j^{(a)}, j = 1, \ldots, N_a$, then in the large $t$ limit, the currents $J_\rho$ and $J_u$ are given by

$$J_\rho = \frac{1}{t}(N_i - N_a) \quad (3.9)$$

and

$$J_u = \frac{1}{t} \left( \sum_{j=1}^{N_i} \frac{1}{2} m_j^{(i)} [v_j^{(i)}]^2 - \sum_{j=1}^{N_a} \frac{1}{2} m_j^{(a)} [v_j^{(a)}]^2 \right). \quad (3.10)$$

Note that, in the steady state, owing to particle and energy conservation, these currents are equal to the corresponding currents computed for the right bath.

Then the Onsager matrix elements, from which $\sigma$, $S$, $\kappa$ and $ZT$ can be readily derived, are obtained from equations (2.2) and (2.3). We set the mass ratio $M/m = \pi$ and calculate currents up to an average number of particles inside the system $\langle N \rangle \approx 515$.

Numerical results for the transport coefficients are shown in figure 5. A power-law dependence for $\sigma/L$, $\kappa/L$ and $ZT$ is observed. In particular, the figure of merit $ZT$ increases with increasing system size, $ZT \propto L^{0.79}$. Correspondingly, the condition number cond(L) diverges, as expected from the general theoretical considerations of §2.

These numerical results naturally raise a question: Is the mechanism leading to high $ZT$ quality factor for interacting gases related to the energy-filtering
mechanism as in §3a for non-interacting ergodic gases? To address this question, we measure the particle current at the position \( x \in [0, L] \) as

\[
J_p = \int_0^\infty dE \, D(E), \quad D(E) \equiv D_L(E) - D_R(E),
\]

where the ‘transmission function’ \( D_L(E) \) is the density of particles with energy \( E \) crossing \( x \) and coming from the left side, while \( D_R(E) \) is the density of particles with energy \( E \) from the right side. We enquire how \( D(E) \) changes as a function of the system size \( L \); in particular, if \( D(E) \) becomes more and more delta-like (peaked in energy) with increasing \( L \). The transmission function \( D(E) \) is shown in figure 6, at \( x = L/2 \) and for different system sizes. There is no sign of narrowing of \( D(E) \) when increasing the system size. We can therefore conclude that the
mechanism leading to the large $ZT$ values observed in Figure 5 must be different from the energy filtering discussed in the studies of Mahan & Sofo [5], Humphrey et al. [6] and Humphrey & Linke [7].

To understand the mechanism, we first write the particle and energy currents as

$$J_p = \overline{v(x,t)\rho(x,t)} \quad \text{and} \quad J_u = \frac{1}{2}mv(x,t)^3\overline{\rho(x,t)},$$  

(3.12)

where $x \in [0, L]$, the overbar denotes time averaging, and $v(x,t)$ and $\rho(x,t)$ are, respectively, the particle velocity and density at position $x$ and time $t$. If the relaxation time scales for density and velocity are well separated, as is the case in our model (where the relaxation time scale for density is much faster than that for velocity), then expressions (3.12) can be approximated as

$$J_p \sim \overline{v(x,t)\times\rho(x,t)} \quad \text{and} \quad J_u \sim \frac{1}{2}mv(x,t)^3 \times \overline{\rho(x,t)}.$$  

(3.13)

From the discussion of §2, it is clear that $ZT$ diverges when $J_u \propto J_p$. According to expressions (3.13), this is the case when $\overline{v^3} \propto \overline{v}$. As we are interested in the steady-state transport properties and we are considering systems with the mixing property, it is natural to assume that the time averages $\overline{v}$ equal the ensemble averages $\langle v \rangle = \int_{-\infty}^{+\infty} dv v^n F(v)$, with $F(v)$ the velocity distribution function for the steady state. At equilibrium ($T_L = T_R$, $\mu_L = \mu_R$), the system thermalizes and $F(v)$ is the Maxwell–Boltzmann distribution at any $x$. In the linear response regime, we assume that $F(v)$ is given by a modified Maxwell–Boltzmann distribution,

$$F_M(v) = \sqrt{\frac{m^*}{2\pi T}} \exp \left( -\frac{m^*(v - \langle v \rangle)^2}{2T} \right),$$  

(3.14)

where the mean velocity $\langle v \rangle$ and the effective mass $m^*$ are fitting parameters, and $T \approx T_L \approx T_R$. That is to say, we assume that the out-of-equilibrium stationary distribution (3.14) differs from the equilibrium Maxwell–Boltzmann distribution only in the position $\langle v \rangle$ of the peak, while the Gaussian shape is unchanged. As shown in Figure 7, such an assumption is in good agreement with the numerically computed $F(v)$, apart from deviations in the tails, which however do not affect
the values of $\langle v \rangle$ and $\langle v^3 \rangle$ too much. Equation (3.14) is very convenient for analytical considerations and to unveil the mechanism at the origin of the large thermoelectric efficiencies observed in the hard-point gas model.

From equation (3.14), we obtain
\begin{equation}
\langle v^3 \rangle = \langle v \rangle^3 + 3v^2 \langle v \rangle,
\end{equation}
where $v = \sqrt{T/m^*}$ is the width of distribution (3.14). We obtain $\langle v^3 \rangle \propto \langle v \rangle$ when $v \gg \langle v \rangle$, that is, in the broad distribution limit. It is clear from figure 7 that, for the one-dimensional interacting hard-point gas, indeed $v \gg \langle v \rangle$.

4. Microscopic model of an efficient thermoelectric machine

In this section, we briefly review an abstract model of a thermoelectric engine, which captures essential physical features of thermoelectricity and which, in the linear response regime, can be solved analytically [11]. It is based purely on deterministic classical dynamics and stochastic baths. The model is composed of two thermochemical reservoirs of ideal gas of equal point particles connected by two one-dimensional wires indexed by $i \in \{1, 2\}$. In the middle of each wire, we place a deterministic and energy-conserving scatterer, which either reflects or transmits the particle depending on its kinetic energy $\epsilon$. This behaviour is completely described by the transmission function $\tau_i(\epsilon) \in \{0, 1\}$ of the $i$th scatterer.

The scheme of the heat engine is shown in figure 8. In the wires we introduce bias forces $E_i$ (say electric fields), which can be described by bias voltages $U_i$ or any other form of external potential energy that can be used to extract useful
work. In the stationary state, at some temperature difference, there is a non-zero (circular) particle current in the wires that, by climbing against the electric potential, can perform useful work. In the left (right) reservoir, the particles are at chemical potential $\mu_L$ ($\mu_R$) and temperature $T_L$ ($T_R$) (here we assume $T_L > T_R$) and are effused into the wires with the injection rates $p_i \gamma_L$ ($p_i \gamma_R$) into the first ($i = 1$) and the second ($i = 2$) channel, respectively, where $p_i \in [0,1]$, $p_1 + p_2 = 1$, represent the relative openings into the two channels. We note that, both in the reservoirs and in the channels, the motion of particles is assumed to be (quasi-) one-dimensional, so we consider a single component of the velocity. The injection rates are connected to the chemical potentials $\mu_v$ and inverse temperatures $\beta_v = 1/T_v$ (note that hereafter we set units in which particle mass $m = 1$, particle charge $e = 1$ and Boltzmann constant $k_B = 1$) via the formula $\mu_v \beta_v = \log(C \beta_v \gamma_v)$, $(v \in \{L,R\})$, where $C$ is a constant depending only on the properties of the particles and on the geometry of the reservoir opening (see §3a). The velocity $v$ of effused particles is distributed in each side according to a canonical distribution:

$$P_v(v) = \beta_v v e^{-(1/2)\beta_v v^2} \theta_v(v).$$

(4.1)

Here $\theta_v(v)$ are step functions: $\theta_L(v) = 1$ if $v \geq 0$, and 0 otherwise; $\theta_R(v) = 1$ if $v \leq 0$, and 0 otherwise.

In the steady state, the particle current $J_{\rho,i}$ within the $i$th wire reads

$$J_{\rho,i} = p_i (\gamma_L t_{L,i} - \gamma_R t_{R,i}),$$

(4.2)

where $t_{\nu,i}$ is the transmission probability for a particle to transit from the side $\nu$ to the other side over the $i$th wire. Assuming linear potentials $U_i$ and scatterers
being in the middle of each wire, we obtain

\[ t_{L,i} = \beta_L \int_{\max(0,U_i)}^{\infty} \mathrm{d}\epsilon \, e^{-\beta_L \epsilon} \tau_i(\epsilon - \frac{U_i}{2}) \]

and

\[ t_{R,i} = \beta_R \int_{\max(0,-U_i)}^{\infty} \mathrm{d}\epsilon \, e^{-\beta_R \epsilon} \tau_i(\epsilon + \frac{U_i}{2}) \]  \hspace{1cm} (4.3)

By imposing the stationarity condition \( J_{r,1} + J_{r,2} = 0 \), we obtain the particle current in the wires, \( J_{r,1} \propto \det(t_{\tau,i}) = t_{L,1}t_{R,2} - t_{L,2}t_{R,q} \). Therefore, at \( \det(t_{\tau,i}) = 0 \), the particle current vanishes. This result outlines the importance of energy filtering. In the steady state, a non-vanishing circular particle current exists only if the transmission functions are energy-dependent.

A simple energy filtering is given by the step-like transmission function

\[ \tau_i(\epsilon) = \theta(s_i(\epsilon - \epsilon_i)) \]  \hspace{1cm} (4.4)

where \( s_i \in \{1, -1\} \). Efficiencies approaching the Carnot limit can be obtained when \( s_1 \) and \( s_2 \) have opposite signs, that is, when one scatterer transmits the fast particles and the other scatterer transmits slower ones. The model can be solved exactly in the linear response regime (see Horvat et al. [11] for details). Here we simply remark that the efficiency is determined by a figure of merit that, for the two-channel geometry under consideration, is different from \( ZT \). Notably, the efficiency vanishes when the Seebeck coefficients in the two channels are equal, independently of the possible divergence of \( ZT \) for each channel [10,11].

5. Conclusions

We have studied the thermoelectric efficiency of classical dynamical models: non-interacting particles in a chaotic billiard, interacting particles in a regime of anomalous diffusion, and finally an abstract thermoelectric engine. It is possible to argue that our models are quite abstract in nature and therefore far from possible realistic implementations. We think, on the contrary, that this is the main advantage of our approach. After more than 50 years during which thermoelectric efficiency did not substantially increase, we propose here to take a completely opposite point of view. Starting from fundamental microscopic equations and considering the most general schematized framework, we hope to understand the basic dynamical mechanisms that can lead to an increase of thermoelectric efficiency. In this spirit, the models discussed here are the first preliminary steps in this direction. Of course, more realistic models should eventually be considered, to understand, for instance, dimensionality effects and the impact of quantum phenomena on thermoelectricity.

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