Increasing thermoelectric efficiency towards the Carnot limit

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We study the problem of thermoelectricity and propose a simple microscopic mechanism for the increase of thermoelectric efficiency. We consider the cross transport of particles and energy in open classical ergodic billiards. We show that, in the linear response regime, where we find exact expressions for all transport coefficients, the thermoelectric efficiency of ideal ergodic gases can approach Carnot efficiency for sufficiently complex charge carrier molecules. Our results are clearly demonstrated with a simple numerical simulation of a Lorentz gas of particles with internal rotational degrees of freedom.

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Although thermoelectricity was discovered almost 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 the Ioffe suggestion that home refrigerators could be built with semiconductors \cite{1, 2}. As a result of these efforts the thermoelectric material Bi\textsubscript{2}Te\textsubscript{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 decade there has been an increasing pressure to find better thermoelectric materials with higher efficiency. The reason is the strong environmental concern about chlorofluorocarbons used in most compressor-based refrigerators. Also the possibility to generate electric power from waste heat using thermoelectric effect is becoming more and more interesting \cite{1–3}.

The suitability of a thermoelectric material for energy conversion or electronic refrigeration is evaluated by the thermoelectric figure of merit $Z$,

$$Z = \frac{\sigma S^2}{\kappa},$$

where \(\sigma\) is the coefficient of electric conductivity, \(S\) is the Seebeck coefficient and \(\kappa\) is the thermal conductivity. The Seebeck coefficient \(S\), also called thermopower, is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across the material.

For a given material, and a pair of temperatures \(T_1\) and \(T_2\) of hot and cold thermal baths respectively, \(Z\) is related to the efficiency \(\eta\) of converting the heat current \(J_Q\) into the electric power \(P\) which is generated by attaching a thermoelectric element to an optimal Ohmic impedance.

Namely, in the linear regime:

$$\eta = \frac{P}{J_Q} = \eta_{\text{carnot}} \cdot \frac{\sqrt{ZT + 1} - 1}{\sqrt{ZT + 1} + 1}, \quad (2)$$

where \(\eta_{\text{carnot}} = 1 - T_C/T_H\) is the Carnot efficiency and \(T = (T_H + T_C)/2\). Thus a good thermoelectric device is characterized by a large value of the non-dimensional figure of merit \(ZT\).

Since the 1960’s many materials have been investigated but the maximum value found for \(ZT\) was achieved for the (Bi\textsubscript{1−\(x\)}Sb\textsubscript{\(x\)})\textsubscript{2}(Se\textsubscript{1−\(y\)}Te\textsubscript{\(y\)})\textsubscript{3} alloy family with \(ZT \approx 1\). However, values \(ZT > 3\) are considered to be essential for thermoelectrics to compete in efficiency with mechanical power generation and refrigeration at room temperatures. The efforts recently focused on a bulk of new advanced thermoelectric materials and on low-dimensional materials, and only a small increment of the efficiency, \(ZT \lesssim 2.6\), has been obtained \cite{3}.

One of the main reasons for this partial success is a limited understanding of the possible microscopic mechanisms leading to the increase of \(ZT\), with few exceptions \cite{4}. From a dynamical point of view, cross effects in transport have been barely studied \cite{5, 6}. So far, the challenge lies in engineering a material for which the values of \(S\), \(\sigma\) and \(\kappa\) can be controlled independently. However, the different transport coefficients are interdependent, making optimization extremely difficult.

In this paper we take a completely different approach. Inspired by kinetic theory of ergodic gases and chaotic billiards, we show that large values of \(ZT\), in principle approaching to Carnot’s efficiency, can be obtained when the energy of the carrier particles does not depend on the thermodynamic forces.

In the linear response regime (see e.g. \cite{7}), one writes the general expressions for the heat current \(J_Q\) and the electric current \(J_e\) through an homogeneous sample subjected to a temperature gradient \(\partial_x T\) and a electrochemical potential gradient \(\partial_x \mu\) as

$$J_Q = -\kappa' \partial_x T - T \sigma S \partial_x \mu,$$

$$J_e = -\sigma S \partial_x T - \partial_x \mu.$$

\(\Box\)
Here and in what follows, we assume that the transport occurs along the $x$-direction and the temperature is given in units where the Boltzmann constant $k_B = 1$.

The electrochemical potential is the sum of a chemical and an electric part $\mu = \mu + \mu_e$, where $\mu$ is the chemical potential of the particles and, if $e$ is the particle’s charge, $\mu_e = e\phi$ is the work done by the particles against an external electric field $E = -\partial_x \phi$. From (3) the usual phenomenological relations follow: if the thermal gradient vanishes, $\partial_x T = 0$, then $J_r = -\sigma \partial_x \phi = \sigma E$, since for an isothermal homogeneous system $\mu$ is uniform. If the electric current vanishes, $J_e = 0$, then $\partial_x \mu = S \partial_x T$, which is the definition of the Seebeck coefficient, and $J_Q = -\kappa \partial_x T$ where $\kappa = \kappa' - T \sigma S^2$ is the usual thermal conductivity (see e.g. [9]).

From the theory of irreversible thermodynamics, $\mu$ and $\mu_e$ cannot be determined separately; only their combination in $\mu$ appears in (3) [8]. Based on this equivalence, in what follows we take into account the chemical part only, i.e., $\mu = \mu$.

Our aim is to study thermolectricity from an “energy transport” point of view. To linear order, the energy and particle density currents $J_u$ and $J_\phi$ respectively, can be written in terms of the Onsager matrix $\mathbf{L}$ [9, 10] as

\[ J_u = L_{uu} \partial_x \left( \frac{\mu}{T} \right) + L_{u\phi} \partial_x \left( -\frac{\mu}{T} \right), \]

\[ J_\phi = L_{\phi u} \partial_x \left( \frac{1}{T} \right) + L_{\phi \phi} \partial_x \left( -\frac{\mu}{T} \right), \]

where $J_e = eJ_\phi$. In the absence of magnetic fields, the Onsager reciprocity relations states that $\mathbf{L}$ is symmetric, $L_{uu} = L_{\phi\phi}$. From the entropy balance equation for open systems

\[ J_u = J_Q + \mu J_\phi, \]

and substituting $J_Q$ in (3) in favor of $J_u$ and comparing the resulting equations with (4) it follows that the transport coefficients can be written in terms of the $L$-coefficients as

\[ \sigma = \frac{e^2}{T} L_{ee}, \quad \kappa = \frac{1}{T^2} \det \mathbf{L}, \quad S = \frac{1}{eT} \left( \frac{L_{uu}}{L_{ee}} - \mu \right). \]

Eqs. (4) and (6) are completely equivalent to the description (3). Furthermore, from Eq. (1), we obtain for the figure of merit

\[ ZT = \frac{(L_{uu} - \mu L_{ee})^2}{\det \mathbf{L}}. \]

Expressions (4) and (7) provide a very convenient way for numerical or analytical evaluation of $ZT$ for different kinds of dynamical models.

The second law of thermodynamics only requires that $\mathbf{L}$ is positive definite. Therefore, from (7) it is clear that the second law does not impose any upper bound on the value of $ZT$. Furthermore, the crucial observation is that the Carnot’s limit $ZT = \infty$ is reached when the energy density current and the electric current become proportional, since then $\det \mathbf{L} = 0$. Suppose for example that both energy and charge are carried only by non-interacting particles, like in a dilute gas. Then the microscopic instantaneous currents per particle at position $x$ and time $t$, are

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

\[ j_e(x^*, t) = e v_x \delta(x^* - x(t)), \]

where $E$ is the energy of the particle, $x$ its position and $v_x$ its velocity along the field. The thermodynamic averages of the two currents (appearing in Eq. (4)) become proportional precisely when the variables $E$ and $v_x$ are un-correlated

\[ J_u = \langle j_u \rangle = \langle E \rangle \langle v_x \rangle = \frac{\langle E \rangle}{e} \langle j_x \rangle = \langle E \rangle J_e. \]

Therefore, $ZT = \infty$ follows from the fact that the average particle’s energy $\langle E \rangle$ 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 (d.o.f.), provided the dynamics is ergodic.

We consider an ergodic gas of non-interacting, electrically neutral particles of mass $m$ with $d_{in}$ internal d.o.f. (rotational or vibrational), enclosed in a $d$ dimensional container. To study the non-equilibrium state of such dilute poly-atomic gas we consider a chaotic billiard channel (Fig. 1) connected through openings of size $\lambda$ to two reservoirs of particles which are idealized as infinite chambers with the same poly-atomic gas at equilibrium density $\varrho$ and temperature $T$. From the reservoirs, particles are injected into the channel at a rate $\gamma$ obtained by integration over energy of the appropriate canonical distribution to give

\[ \gamma = \frac{\lambda}{(2\pi m)^{1/2}} \varrho T^{1/2}. \]

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 $D = d + d_{in}$ d.o.f., reads

\[ \mu = T \ln \left( \frac{c_D \gamma}{T(D+1)^{1/2}} \right), \]

where $c_D$ is a $D$-depending constant. Furthermore, averaging the energy of the injected particles over the canonical distribution, denoted as $\langle E \rangle$, we obtain the rate at which energy is injected from the reservoirs as $\varepsilon = \gamma \langle E \rangle = \gamma T(D + 1)/2$.

Let $p_i(l)$ be the transmission probability of the channel of length $l$. For a billiard system of noninteracting particles [11], the density currents $J_u, J_\phi$ assume a simple form: they are $p_i(l)$ times the difference between the left and right corresponding injection rates, $\varepsilon, \gamma$, respectively, namely

\[ J_u = p_i(\gamma l - \varepsilon R), \quad J_\phi = p_i(\varepsilon L - \varepsilon R). \]

Using (11) to eliminate $\gamma$ in favor of $\mu$ we obtain,

\[ J_e = -\frac{\lambda p_i(l)}{(2\pi m)^{1/2}} \partial_x \left( T^{(D+1)/2} e^{\mu/T} \right), \]

\[ J_u = -\frac{\lambda p_i(l)}{(2\pi m)^{1/2}} \frac{D + 1}{2} \partial_x \left( T^{(D+3)/2} e^{\mu/T} \right), \]

where $E$ is the particle’s charge, $\mu$ is the particle’s chemical potential, $\gamma$ is the particle’s momentum, $S$ is the particle’s entropy, $\lambda$ is the particle’s length, $\mu$ is the particle’s magnetic moment, $D$ is the particle’s dimension, $c_D$ is a $D$-depending constant, $p_i(l)$ is the transmission probability of the channel of length $l$. For a billiard system of noninteracting particles [11], the density currents $J_u, J_\phi$ assume a simple form: they are $p_i(l)$ times the difference between the left and right corresponding injection rates, $\varepsilon, \gamma$, respectively, namely

\[ J_u = p_i(\gamma l - \varepsilon R), \quad J_\phi = p_i(\varepsilon L - \varepsilon R). \]
Interestingly enough, we have found that Eq. (15) is an upper limit of the interacting case when the interaction strength vanishes [14].

We shall now confirm Eq. (15) with a very simple numerical demonstration of a 2-dimensional chaotic Lorentz gas channel of particles elastically colliding with circular obstacles of radius \( R \). In what follows, we fix the unit length setting \( R = 1 \). The geometry of the model is shown in Fig. 1.

We consider composite particles with \( d_{\text{int}} \geq 1 \) internal rotational d.o.f. Each “particle” of mass \( m \) can be imagined as a stack of small identical disks of mass \( m/d_{\text{int}} \) and radius \( r \ll R \), rotating freely and independently at a constant angular velocity \( \omega_i \), \( i = 1, \ldots, d_{\text{int}} \). The center of mass of the particle moves with velocity \( \vec{v} = (v_x, v_y) \).

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 \( D \) d.o.f. occurs according to the following collision rules

\[
\begin{align*}
  v'_n &= -v_n, \\
  v'_t &= \frac{1 - \eta d_{\text{int}}}{1 + \eta d_{\text{int}}} v_t + \frac{2\eta}{1 + \eta d_{\text{int}}} \sum_{k=1}^{d_{\text{int}}} \omega_k, \\
  \omega'_t &= \frac{2}{1 + \eta d_{\text{int}}} \sum_{k=1}^{d_{\text{int}}} \left( \delta_{ik} - \frac{2}{d_{\text{int}}(1 + \eta d_{\text{int}})} \right) \omega_k,
\end{align*}
\]

where \((v_n, v_t)\) are the normal and tangent components of the particle velocity at the collision point and the parameter \( \eta = \Theta/m \), with \( \Theta \) being the moment of inertia of each small fictitious internal disk. The primed (unprimed) quantities refer to their values after (before) the collision. These collision rules are a generalization of the ones introduced in [6]. Thus, they are deterministic, time reversible and preserve the energy and local angular momentum. The derivation of the collision rules will appear elsewhere [14].

First we considered a closed system in a finite container and we checked energy equipartition among all d.o.f. Then we have opened the system from both ends and allowed it to exchange particles with the two baths at temperatures \( T_L, T_R \) and with chemical potentials \( \mu_L, \mu_R \). The coupling among the system and the baths is defined as follows: whenever a particle in the system crosses the opening which separates it from the bath, it is removed from the system. On the other hand, with frequency \( \gamma \), particles are injected into the system, with a velocity distributed according to the canonical distribution at the corresponding temperature.

\[
\begin{align*}
  P_n(v_n) &= \frac{m}{T} |v_n| \exp \left( -\frac{mv_n^2}{2T} \right), \\
  P_t(v_t) &= \sqrt{\frac{m}{2\pi T}} \exp \left( -\frac{mv_t^2}{2T} \right), \\
  P(\omega_i) &= \frac{m}{4D\pi T} \exp \left( -\frac{m\omega_i^2}{4DT} \right),
\end{align*}
\]

reflecting the assumption that the bath is an ideal gas at equilibrium temperature \( T \).
By two different simulations with two linearly independent sets of thermodynamic forces we have numerically determined the Onsager’s matrix $L$ and the value of $ZT$ (see Fig.2). Numerical results excellently confirm the theoretical prediction (15). We have also carefully checked that all Onsager coefficients, or conductivities, decay with the size $l$ of the system as $1/l$ which indicates a diffusive transport.

The simple mechanism for the growth of $ZT$ with $d_{int}$ is nicely illustrated in Fig.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 de-correlated from $v_x$ as $d_{int}$ grows.

In conclusion, we have discovered a simple general theoretical mechanism which may find a way to applications of thermoelectricity in real world materials. Even though the case of an ionized polyatomic gas may seem a little artificial in this context, there may be other important instances where each charge would be carried by many effectively classical d.o.f.

We have also performed the first numerical computation of $ZT$ from deterministic microscopic equations of motion. Our method can easily be implemented for more realistic models where also quantum effects can be taken into account.

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[1] G. Mahan, B. Sales, J. Sharp, Phys. Today 50, 42 (March 1997).
[2] A. Majumdar, Science 303, 778 (2004).
[3] M. S. Dresselhaus et al, Adv. Mater. 19, 1043-1053 (2007).
[4] T. E. Humphrey and H. Linke, Phys. Rev. Lett. 94, 096601 (2005).
[5] C. Maes and M. H. van Wieren, J. Phys. A: Math. Gen. 38 (2005) 1005; J. Vollmer, T. Tell, and L. Mátýás, J. Stat. Phys. 101 (2000) 79; C. Van den Broeck, in Advances in Chemical Physics Vol.135 Eds. S. A. Rice, (2007 John Wiley & Sons, Inc.).
[6] C. Mejia-Monasterio, H. Larralde, and F. Leyvraz, Phys. Rev. Lett. 86 (2001) 5417.
[7] D. J. Bergman and O. Levy, Appl. Phys. 70 (1991) 6821.
[8] P. L. Walstrom, Am. J. Phys. 56 (1988), 890. See also H. Larralde, F. Leyvraz, and C. Mejia-Monasterio, J. Stat. Phys. 113 (2003), 197, where the equivalence between $\mu$ and $\mu_e$ has been studied for a similar model to the one we study here.
[9] C. A. Domenicali, Rev. Mod. Phys. 26 (1954), 237.
[10] H. B. Callen, Phys. Rev. 73 (1948) 1349; S. R. de Groot and P. Mazur, Non-equilibrium Thermodynamics (Dover, New York, 1984).
[11] Assuming that particles do not interact means that we fully neglect the phonon transport.
[12] C. B. Vining, Mat. Res. Soc. Symp. Proc. 478 (1997) 3.
[13] J.-P. Eckmann, C. Mejia-Monasterio, and E. Zabey, J. Stat. Phys. 123 (2006) 1339.
[14] G. Casati, C. Mejia-Monasterio, and T. Prosen, to be published.