A one dimensional hard-point gas as a thermoelectric engine

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We demonstrate the possibility to build a thermoelectric engine using a one dimensional gas of molecules with unequal masses and hard-point interaction. Most importantly, we show that the efficiency of this engine is determined by a new parameter YT which is different from the well known figure of merit ZT. Even though the efficiency of this particular model is low, our results shed new light on the problem and open the possibility to build efficient thermoelectric engines.

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A combination of mathematical results, numerical studies and even laboratory experiments have greatly improved our understanding of phenomenological transport equations in recent years. The derivation of such equations from purely dynamical laws, classical or quantum, has been one of the main subject of interest. Even though a complete rigorous picture is still lacking, it is however clear that dynamical chaos is an essential ingredient.

A better understanding of the above problem is important not only from a fundamental point of view in order to provide a justification of phenomenological laws. It is also relevant for several applications. One particular important aspect is the connection with thermoelectric power generation and refrigeration. Indeed, due to the increasing environmental concern and energy demand, thermoelectric phenomena are expected to play an increasingly important role in meeting the energy challenge of the future. However, the main difficulty is the poor efficiency of existing devices. Indeed the suitability of a thermoelectric material for energy conversion or electronic refrigeration is characterized by the thermoelectric figure of merit \( Z = \alpha S^2 / \kappa \), where \( \alpha \) 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.

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

\[
\eta = \frac{P}{J_Q} = \eta_{\text{Carnot}} \cdot \frac{\sqrt{ZT + 1} - 1}{\sqrt{ZT + 1} + 1}.
\]

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 \( ZT \). However, in spite of the fact that the second principle of thermodynamics does not impose any restriction on the value of \( ZT \), all attempts to find high \( ZT \) values (let us say \( ZT > 3 \) at room temperature) have failed. The problem is that the different transport coefficients \( S, \alpha \) and \( \kappa \) are interdependent, making the optimization of \( ZT \) extremely difficult. We believe that a better understanding of the possible microscopic mechanisms which determine the value of \( ZT \) may lead to a substantial improvement.

In a recent paper, a dynamical system approach to a Lorenz gas type model has been used and an interesting mechanism to reach high \( ZT \) value has been discovered. More recently, a one-dimensional, di-atomic disordered chain of hard-point elastic particles has been considered and it has been found that \( ZT \) diverges to infinity with increasing the number of particles inside the chain. This result suggests the possibility to build a thermoelectric engine by connecting two heat baths with two chains of different sizes.

In this paper we analyze such an engine and we show that, indeed, a non zero circular current is established inside the system when the stationary state is reached. Quite interestingly the efficiency of such an engine appears to be unrelated to the figure of merit \( ZT \) and it remains quite low in spite of the fact that \( ZT \) becomes larger and larger with increasing the system size. Indeed we analytically show and numerically confirm that the efficiency of such engine is determined by a new figure of merit \( YT \). From one hand the low value of \( YT \) explains the poor efficiency of the engine; on the other hand, it sheds new light on future directions for increasing the efficiency of thermoelectric engines.

We consider a simple model of the engine (see Fig.
FIG. 1: Scheme of the thermoelectric engine studied in this paper. It consists of two heat baths at different temperature $T_L$ and $T_R$ and two channels of different lengths. See text for the details.

I which consists of two heat baths and two connecting channels $A$ and $B$ of length $L_A$ and $L_B$ respectively. We assume that the whole system does not exchange particles with the outside. Therefore the total number of particles $N$ in the two channels and in the two baths remains constant during the simulation. The two heat baths are kept at different temperatures $T_L$ and $T_R$, and have the same finite length $V$. Each channel is a one-dimensional, di-atomic disordered chain, of hard-point elastic particles with velocities $v_k$ and masses $m_k \in \{M_1, M_2\}$ randomly distributed (we use convenient non-dimensional units).

The particles interact among each other through elastic collisions only. A collision between two neighboring particles with mass $m_k$ and $m_l$ causes a change of their velocities $v_k$ and $v_l$ as $\Delta v_k = 2m_l(v_l - v_k)/(m_k + m_l)$ and $\Delta v_l = 2m_k(v_k - v_l)/(m_k + m_l)$. An efficient algorithm has been developed which performs correct chronological order of collisions and update particle’s positions and velocities in $\sim \log N$ computer operations per collision. We fix the length of the channel $B$ to be small and study how the properties of the engine vary as the length of the channel $A$ is increased. In particular, if channel $B$ is small enough then particles can pass through it without suffering any collisions.

The heat baths are modeled in the following way. Suppose $n_1$ particles of mass $M_1$ and $n_2$ particles of mass $M_2$ are confined in a box of length $V$. The particles collision rate with one end of the box is given by

$$\gamma = \frac{\rho_1}{P} \gamma_1 + \frac{\rho_2}{P} \gamma_2$$

where $\gamma_i = \rho \sqrt{\frac{2}{\pi M_i}}, \rho_i = n_i/V (i = 1, 2)$, $\rho = n/V$ and $n = n_1 + n_2$. Then the heat bath model is straightforward: if one end of the box is opened, the particles are emitted with the same rate $\gamma$, and the time interval $t$ between two consecutive emissions is a random variable which obeys the distribution

$$P(t) = \frac{1}{t_0} e^{-\frac{t}{t_0}}$$

with $t_0 = 1/\gamma$. The mass of the emitted particle is assigned to be $M_i (i = 1, 2)$ randomly according to the probability

$$\Pi_i = \frac{\rho_i \gamma_i}{\rho \gamma_1 + \rho_2 \gamma_2},$$

and its velocity is generated from the distribution

$$P_i(v) = \frac{M_i |v|}{T} e^{-\frac{|v|^2}{T}}.$$

As expected, when $M_1 = M_2$, the heat bath model of identical particles is recovered.

The emission rate from the left heat bath into channel $A$ is therefore $\gamma_L = \frac{\rho}{P} \gamma_1 L_A + \frac{\rho}{P} \gamma_2 L_B$ where $\rho_L$ is the total particle number density at the left heat bath, $\rho_i, L$ is that of particles with mass $M_i$, and $\gamma_i, L = \rho L \sqrt{\frac{T}{2 \pi M_i}} (i = 1, 2)$. Similarly one can write the expression for the emission rate $\gamma_R$ from the right heat bath.

As to the channel $B$ we assume that the emission rates are proportional to $\gamma_L$ and $\gamma_R$:

$$\gamma_B^L = r \gamma_L, \quad \gamma_B^R = r \gamma_R,$$

where $r$ is an adjustable parameter. For $r = 0$ channel $B$ is in fact closed hence there is no net particle current.

Conversely, whenever a particle from each channel arrives at the border with the bath it is absorbed by the bath, so that a stationary state is established after sufficiently long time. If the stationary state is such that there is a net particle current around the system, then one can use it to extract work. To this end we insert inside the channel $B$ an auxiliary potential $U_B$ which the particles have to climb thus performing useful work. Let us first consider the case where the channel $B$ is short enough (i.e. $L_B = 1$) so that the probability of particles collision inside it is negligible. Suppose $T_L > T_R$ then the current runs clockwise at $U_B = 0$ due to the pressure balance between the two heat baths. Thus a particle emitted from the right heat bath can pass through the channel $B$ only when its kinetic energy is larger than $U_B$, otherwise it will return back. Therefore the probability with which the emitted particle passes through the channel $B$ is

$$P_{RL} = e^{-\frac{U_B}{T} R}$$

for both particles of masses $M_1$ and $M_2$. Hence the work extracted per unit of time is

$$P = r (\gamma_R P_{RL} - \gamma_L U_B).$$

The efficiency of the engine thus reads

$$\eta = \frac{P}{J_{Q,A} + J_{Q,B}}.$$
where $J_{Q,A}^r$ and $J_{Q,B}^r$ are the net thermal energy flows from the left heat bath in a unit time into the channel A, and B, respectively, which can be measured by numerical simulations. Notice that, in particular, $J_{Q,B}^r$ can be expressed analytically through

$$J_{Q,B} = r(T_L \gamma_L - P_R T_\gamma R).$$  \hspace{1cm} (10)

As it is seen from Fig. 2 our engine works. Here we plot the numerically computed efficiency $\eta$ against the potential $U_B$ for various lengths of the channel A. The solid curves are polynomial (3-order) fittings of the numerical data.

In this calculation the length of channel B is set to unity and the length of both heat baths is very large, namely $V = 10^3$. The total number of particles in the system is set to be $N = 2V + L_A + L_B$ such that the overall averaged particle density is unity. The two types of molecules are set to be equal in number and have masses $M_1 = 1$ and $M_2 \approx 0.618$ respectively. In addition, for a given length $L_A$ of the channel A, there is an optimal value of $U_B$ such that the efficiency is maximized. Denoting the maximum efficiency by $\eta_{\text{max}}$, it is interesting to compute the dependence of $\eta_{\text{max}}$ on $L_A$ and compare it with theoretical expectations.

Extensive and accurate numerical computations, summarized in Fig. 3, show that even though $\eta_{\text{max}}$ increases with $L_A$, i.e. with the average number of molecules in the channel A, the increasing rate slows down very fast. Also it seems hard to find a simple fitting for the dependence of $\eta_{\text{max}}$ on $L_A$.

We should notice that $\eta_{\text{max}}$ depends also on $T_L$ and $T_R$. However if $\eta_{\text{max}}$ is rescaled to the Carnot efficiency, its behavior with $L_A$ is the same for all $(T_L, T_R)$ pairs, given that the temperature difference is small enough. This can be seen clearly in Fig. 3.

**Remarks:** We have also investigated carefully several variants of the engine model. First, we have studied the dependence of $\eta_{\text{max}}$ on $r$. We have found that indeed $\eta_{\text{max}}$ can be slightly improved by adjusting $r$ (e.g. $\sim 30\%$) as compared to Fig. 2, however the efficiency remains very low. Then we have checked whether adding a potential $U_A$ against the current in the channel A can improve efficiency. In this case a particle in the channel A would undergo a parabolic motion between two consecutive collisions with its neighbors. This variant does not increase the maximum efficiency $\eta_{\text{max}}$ either which has been found to depend only on the sum $U_A + U_B$ rather than on $U_A$ and $U_B$ separately. Also a longer length of channel B has been considered but it turns out that for a given $L_A + L_B$, the efficiency reaches its highest value when $L_B \leq 1$. To summarize, the various modifications to the engine model we have considered do not improve the efficiency significantly.

Let us now explain why our engine works at a rather low efficiency in spite of the fact that $ZT$ goes to infinity. In order to derive a theoretical expression for the efficiency we use thermodynamic linear response relations for the heat currents $J_{Q,A}$, $J_{Q,B}$, and for the particle currents $J_{P,A}$, $J_{P,B}$, in the channels A and B, respectively, namely

$$J_{Q,A} = -\kappa_A \Delta T / L_A - T \sigma_A S_A (\Delta \mu / L_A + U_A)$$

$$J_{P,A} = -\sigma_A S_A \Delta T / L_A - \sigma_A (\Delta \mu / L_A + U_A)$$

$$J_{Q,B} = -\kappa_B \Delta T / L_B - T \sigma_B S_B (\Delta \mu / L_B - U_B)$$

$$J_{P,B} = -\sigma_B S_B \Delta T / L_B - \sigma_B (\Delta \mu / L_B - U_B)$$

where $\kappa_A = \kappa + T \sigma_A S_A^2$, $\kappa_B = \kappa + T \sigma_B S_B^2$, $\mu$ is the chemical potential, and $\Delta T = T_R - T_L$, $\Delta \mu = \mu_R - \mu_L$. In addition, in the stationary state we must also have

$$J_{P,A} + J_{P,B} = 0.$$  \hspace{1cm} (12)

The relations given by Eq. (11) and (12) represent...
In order to understand why our engine model has a low efficiency, we investigate carefully the dependence of the parameters $\sigma$, $\kappa$ and $S$ on the channel length. These quantities can be obtained from the Onsager coefficients which in turn are calculated by measuring the transport or Onsager coefficients are considered to be known. From the solutions of the above equations we compute the efficiency $\eta$ as a function of the two bias potentials:

$$\eta(U_A, U_B) = \frac{P}{J_Q} = \frac{J_{p,A}U_A - J_{p,B}U_B}{J_{Q,A} + J_{Q,B}}$$  \quad (13)$$

Since $\eta(U_A, U_B)$ is a quadratic function, we can easily maximize it by computing the optimal values of $U_A, U_B$. The final result can be expressed in a simple form as

$$\eta_{\text{max}}/\eta_{\text{Carnot}} = 1 - 2\sqrt{(YT)^{-2} + (YT)^{-1} + 2(YT)^{-1}}$$  \quad (14)$$

with a new figure of merit

$$YT = \frac{(\sigma_A/L_A)(\sigma_B/L_B)}{\sigma_A/L_A + \sigma_B/L_B} \cdot \frac{(S_A - S_B)^2}{\kappa_A/L_A + \kappa_B/L_B} \cdot T$$  \quad (15)$$

From Eq. (14) it can be seen that efficiency is given by this new figure of merit exclusively and it has nothing to do with the merit $ZT$. Clearly, as $YT \to 0$ ($YT \to \infty$) we have $\eta_{\text{max}} \to 0$ ($\eta_{\text{max}} \to \eta_{\text{Carnot}}$).

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In Fig. 4 we present the numerical results for a 1D mixed gas chain with $M_1 = 1, M_2 \approx 0.618, T = 1$ and $2\rho_1 = 2\rho_2 = \rho = 1$. The constant in Eq. (17) is set to be $\ln 2 + 1$ such that $\mu = 1$. The results clearly show that, as the channel length is increased, while the ratio $\sigma/\kappa$ increases as a power law, the Seebeck coefficient $S$ undergoes a slower and slower increase. As a result, while $ZT$ increases indefinitely with the channel length $L$, the merit $YT$ remains small.

In summary, for the engine model (Fig. 1) based on a one dimensional mixed gas, the efficiency is governed by a new figure of merit. Based on its relation to the thermoelectric parameters (Eq. (15)), it can be expected that an efficient mixed gas type engine should be such that its Seebeck coefficient changes fast when the channel length is changed. Such a mixed gas might be that consisting of three, or more, types of molecules. We believe that our method of analysis of thermoelectric or thermochemical heat engines should be applicable to a wide range of models which consist of two transport channels between a pair of baths.

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