Stochastic efficiency for effusion as a thermal engine

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Abstract – The stochastic efficiency of effusion as a thermal engine is investigated within the framework of stochastic thermodynamics. Explicit results are obtained for the probability distribution of the efficiency both at finite times and in the asymptotic regime of large deviations. The universal features, derived in Verley et al. (Nat. Commun., 5 (2014) 4721), are reproduced. The effusion engine is a good candidate for both the numerical and experimental verification of these predictions.

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Effusion is the escape of particles through a narrow aperture. The phenomenon has been used for many applications such as to enrich uranium, to coat light bulbs and as a cooling device. Effusion between two compartments, cf. fig. 1(a), can also operate as a thermal engine, namely when there is a net flow of particles \( n \geq 0 \) from the hot compartment, temperature \( T_h \), with low chemical potential \( \mu_h \), to the cold compartment, temperature \( T_c \), with high chemical potential \( \mu_c \). The work produced is \( w = n \Delta \mu \) \((\Delta \mu = \mu_c - \mu_h)\). If we denote by \( q \) the net heat leaving the hot reservoir, the resulting thermodynamic efficiency reads

\[
\eta = \frac{w}{q}.
\]  

(1)

When operating for long times \( t \), the quantities \( n/t \) and \( q/t \) converge to the average particle and heat flux. Concomitantly, the efficiency \( \eta \) converges to its most probable value \( \eta_0 \), which corresponds to the standard “macroscopic” efficiency. It is reproduced in fig. 1(b) for the case of an ideal gas. As required by the second law of thermodynamics, this long-time efficiency is always below the Carnot efficiency \( \eta_c = 1 - T_c/T_h \).

When operating for a finite time, the quantities \( w \) and \( q \), and hence also the stochastic efficiency \( \eta \), are different from one run to another [1]. One may wonder about thermodynamic implications for the probability distribution \( P(\eta) \) of \( \eta \). In a recent paper [2] (see also [3,4]), the following remarkable result was derived: in a non-macroscopic machine operating in a time-symmetric manner, the reversible efficiency is least likely in the long-time limit. This property is based on the generalisation of the second law of thermodynamics for small systems, the so-called fluctuation theorem [5,6], and parallels the derivation of

\[
\eta = \frac{w}{q}.
\]  

Fig. 1: (Colour on-line) (a) Effusion as a thermal engine. (b) Efficiency \( \eta \) for an ideal (mono-atomic) gas, plotted in colour code as a function of \( \mu_h/k_B T_h \) and \( \mu_c/k_B T_c \) for \( \eta_c = 0.8 \). The chemical potential is found from the Sackur–Tetrode formula, \( \mu = k_B T \ln(\rho \Lambda^3) \), where \( \Lambda = \hbar/\sqrt{2\pi mk_B T} \) is the thermal de Broglie wavelength, \( k_B \) is Boltzmann’s constant, \( T \) the temperature, \( \rho \) the density and \( m \) the mass per particle. The engine regime \((T_h > T_c)\) is determined by \( \mu_h < \mu_c < (1 - \eta_c) \mu_h - 2k_B T_c \ln(1 - \eta_c) \).
Carnot or reversible efficiency of macroscopic machines. The simplest illustration is the work to work transformation by a Brownian particle subjected to competing external forces [2]. The reversible efficiency is here 100%. Both work components are Gaussian and the explicit analytic result is available for the probability distribution of the stochastic efficiency [7] and its large deviation function [2,8]. In this letter, we calculate the stochastic efficiency [7] and its large deviation function [9,10]. The crucial condition is that one operates under equilibrium conditions, i.e., the Maxwell-Boltzmann density of particles of energy $E$ has to be the same in both compartments: $\rho_h \exp(-\beta_h E)/T_h^{3/2} = \rho_c \exp(-\beta_c E)/T_c^{3/2}$. This indeed yields for an ideal gas ($\mu \sim T \ln(\rho/T^{3/2})$ apart from an additive constant): $\eta = \mu/q = (\mu_h - \mu_c)/(E - \mu_h) = \eta_c$. Note that equilibrium is reached even though density, chemical potential and temperature need not be the same in both compartments.

To obtain a non-trivial result for the probability distribution $P_1(\eta)$ of the efficiency, we consider next effusion through two separate windows, selective for energies $E_1$ and $E_2$, respectively. The discrete amounts of work and heat, produced upon a net transfer (from hot to cold) of $i$ particles through window 1 and $n-i$ particles through window 2, are obviously given by

$$w = n\Delta\mu, \quad q = \delta q_1 + \delta q_2(n-i),$$

with $\delta q_1$ and $\delta q_2$ the transported heat per particle leaving the hot reservoir via filter 1 and 2, respectively:

$$\delta q_1 = E_1 - \mu_c, \quad \delta q_2 = E_2 - \mu_h.$$  

Since the transport through both filters is statistically independent, the joint probability $P_t(w,q)$ for work and heat is given by the following convolution:

$$P_t(w,q) = \sum_{i_1,i_2} P_1(i_1,t)P_2(i_2,t)\delta(q_1+t\delta q_1(i_1+i_2)+\delta q_2(i_1+i_2)) = P_1\left(\frac{q - \delta q_2 n}{\delta q_1 - \delta q_2}, t\right)P_2\left(\frac{\delta q_1 n - q}{\delta q_1 - \delta q_2}, t\right).$$

This is nothing but the probability distribution for a biased continuous-time random walk with stepping rates $k$ and $l$. The so-called large deviation function $\varphi(\bar{n})$ describes the asymptotic probability for observing an empirical particle flux $n = n/t$:

$$P(n = \bar{n} t, t) \sim e^{-t\varphi(\bar{n})} \text{ or } \varphi(\bar{n}) = -\lim_{t \to \infty} \frac{\ln P(n = \bar{n} t, t)}{t}.$$  

It is found from eq. (5) by Stirling’s formula

$$\varphi(\bar{n}) = k + l - \frac{\sqrt{4kl + n^2 - \bar{n}^2}}{2l} \ln \left[\frac{\sqrt{4kl + n^2 - \bar{n}^2}}{2l}\right].$$

Note that in the presence of a single energy filter, the net energy transfer $w$ and net particle transfer $n$ become “strongly coupled”: $w = E\bar{n}$. Also work $w = n\Delta\mu$ and heat $q = u - n\mu_h = n(E - \mu_h)$ are proportional to each other. Hence, even while both $w$ and $q$ fluctuate through their dependence on $n$, the efficiency, $\eta = w/q$, remains constant. Since in this case $\eta = \eta_c$, the second law requires $\eta \leq \eta_c$. It is revealing to show how Carnot efficiency can be reached in this case [9,10].

The simplicity of the effusion engine stems from the fact that there is no auxiliary engine part that transfers the energy. Furthermore, for an ideal gas, the crossing of the particles with energies in a small window $[E - \Delta E/2, E + \Delta E/2]$ are allowed to cross. The number $n_h$ of particles leaving the hot reservoir during a time $t$ is described by a Poisson distribution:

$$P(n_h, t) = \frac{\bar{n}_h^n}{n_h!} e^{-\bar{n}_h}, \quad \bar{n}_h = kt,$$

with the crossing rate $k$ prescribed by kinetic theory [1]:

$$k = \frac{E\Delta E}{t_0 (k_B T_h)^2} e^{-E/k_B T_h}.$$  

Here we introduced the average escape time $t_0$ for a particle in the absence of an energy filter:

$$t_0 = \frac{\sqrt{2\pi m}}{\sigma \rho_h \sqrt{k_B T_h}}.$$  

and $\sigma$ is the surface area of the effusion hole. A similar result holds for the crossing of particles coming from the cold reservoir by formally replacing the subscript $h$ by $c$ and $k$ by $l$. Since the crossings are independent of each other, we find by convolution that the probability to have a net transfer of $n = n_h - n_c$ particles, is given by

$$P(n, t) = e^{-t(k+l)\left(\frac{k}{k} + \frac{l}{l}\right)} I_n\left(2t\sqrt{kl}\right).$$

This is nothing but the probability distribution for a biased continuous-time random walk with stepping rates $k$ and $l$. The so-called large deviation function $\varphi(\bar{n})$ describes the asymptotic probability for observing an empirical particle flux $n = n/t$:  

$$P(n = \bar{n}, t) \sim e^{-t\varphi(\bar{n})} \text{ or } \varphi(\bar{n}) = -\lim_{t \to \infty} \frac{\ln P(n = \bar{n}, t)}{t}.$$
can be obtained for any finite time by combination with eq. (10), cf. fig. 2(a). For the corresponding large deviation function \( J(\eta) \), one finds

\[
J(\eta) = -\lim_{t \to \infty} \frac{\ln(P_t(\eta))}{t} = \min_{\tilde{\eta}} I(\eta \tilde{\eta}, \tilde{q})
\]

\[
= \min_{\tilde{\eta}} \left\{ \varphi_1 \left( \frac{\gamma_1(\eta)}{\Delta \mu} \tilde{q} \right) + \varphi_2 \left( \frac{\gamma_2(\eta)}{\Delta \mu} \tilde{q} \right) \right\},
\]

with

\[
\gamma_1(\eta) = \frac{\Delta \mu - \delta q_2 \eta}{\delta q_2 - \delta q_1}, \quad \gamma_2(\eta) = \frac{\Delta \mu - \delta q_1 \eta}{\delta q_2 - \delta q_1}.
\]

We have used the contraction principle [8], expressing the fact that a given value of \( \eta \) is realised by the most likely values of \( \tilde{w} \) and \( \tilde{q} \) for which \( \tilde{w}/\tilde{q} = \eta \). The above minimization involves a transcendental equation, requiring a numerical solution. The resulting large deviation function \( J(\eta) \) has the familiar shape [2], with a zero in \( \eta \), a maximum at Carnot efficiency, and equal asymptotes for \( \eta \to \pm \infty \), cf. fig. 2(b).

One can repeat the above calculation for effusion without energy filters. Results are shown in fig. 3. Note in fig. 3(a) the “fine structure” appearing for small times around \( \eta = 0 \), due to the fact that very few particles will cross. The observed local minimum of \( P_t(\eta) \) around zero is for example due to the very unlikely single particle crossing with high energy, the latter being required to obtain a small value of \( \eta \).

We turn to a discussion of the salient features and implications of our analysis. The first conclusion is that all the predictions of the general theory [2] are verified, and in particular the generic properties of the large deviation function \( J(\eta) \). Second, both the Gaussian regime and the strongly non-Gaussian regime can be easily observed, as well as other special limits such as the “strong coupling” limit or the limit to “reversibility”. Third, the local minimum of the probability or the maximum of the large deviation function at Carnot efficiency can be made very pronounced, rendering the most striking feature, the local minimum at Carnot efficiency, easy to observe. Fourth, an accurate estimation of the large deviation function \( J(\eta) \) is possible by extrapolating the results from finite time, as is shown in the insets of figs. 2(a) and 3(a). Fifth, the probability distribution for the efficiency of effusion displays long tails, similar to the one observed in the Gaussian scenario [7]. This appears to be a generic result [3]. Indeed it follows from (12) that

\[
P_t(\eta) \approx \frac{P_t(w, 0) w}{\eta^2},
\]

provided \( P_t(w, q) \) has a smooth behavior around \( q = 0 \) and the integral converges. Sixth, even for relatively short times (less than \( 10^{-4} \)) and with rather small statistics (200 samples), the local minimum of the probability \( P_t(\eta) \) can clearly be identified, as can be seen in fig. 4. This
observation shows that, for a given Carnot efficiency, a direct experimental verification of the local minimum in the probability distribution is possible. We note that fluctuations of heat, work and even efficiency have been measured in a range of systems [11–14]. We discuss the experimental setting for an effusion engine displaying the salient features of stochastic efficiency. To obtain a sharp local minimum of $\eta$ at Carnot efficiency, a large value of $J(\eta_c)/J(\infty)$ is required. One way to do so in the twofilter effusion engine is by considering $\mu_c \approx \mu_b T_b/\eta_c + E_1/\eta_c$ and $E_2 \gg E_1$. This region is described by the pressure ratio $P_b/P_c = (T_b/T_c)^{3/2} e^{\eta_c/(1-\eta_c)}$ (see appendix B). With this condition in mind, we have performed simulations for the stochastic efficiency of an effusion engine operating with helium gas. In fig. 4, we represent $P_t(\eta) d\eta$ (window $d\eta = 0.01$) obtained after 200, 500 and 1000 samplings. The local minimum in the vicinity of Carnot efficiency $\eta_C = 0.75$ is clearly visible, even at these very short times. Experimental measurements of $w$ and $q$ can be done as follows. Consider a single compartment. A high-resolution calorimeter is used to measure the (kinetic) energy of every escaping particle. Since these particles, and their energies, are all independent (cf. ideal gases) the effect of the two filters is incorporated by retaining only data of those particles with energy in the ranges $E_1 \pm \Delta E/2$ or $E_2 \pm \Delta E/2$. Together with similar data from the other compartment, this information suffices to calculate the corresponding probability distribution of the efficiency. We note that the calculation of $w$ and $q$ from $n$ and the energies requires knowledge of the temperatures and the chemical potentials.

In conclusion, effusion as a thermal engine displays all the key features of stochastic efficiency. The model combines conceptual simplicity with analytic tractability and experimental relevance. It is generic for the case in which transitions are ruled by Poisson statistics, such as in Kramers’ escape over a potential barrier, or for transitions ruled by a chemical reaction.

**Appendix A: the large deviation function by extrapolation.** – To estimate the LDF $J(\eta)$ from finite time measurements of $P_t(\eta)$, we use the following ansatz:

$$P_t(\eta) = A(\eta) t^{B(\eta)} \exp(-t J(\eta)).$$ (A.1)

To fit the values of $A(\eta)$, $B(\eta)$ and $J(\eta)$, it is sufficient to have a measurement of $P_t(\eta)$ at 3 different times. More precisely, from the values

$$\tau_i(\eta) = \frac{1}{t_i} \ln(P_{t_i}(\eta)), \quad i = 1, 2, 3,$$ (A.2)

we get

$$\begin{bmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{bmatrix} = \begin{bmatrix} 1 & 1/t_1 & \ln(t_1)/t_1 \\ 1 & 1/t_2 & \ln(t_2)/t_2 \\ 1 & 1/t_3 & \ln(t_3)/t_3 \end{bmatrix} \begin{bmatrix} J(\eta) \\ A(\eta) \\ B(\eta) \end{bmatrix}.$$ (A.3)

By inversion of the matrix, we find the required estimate of $J(\eta)$. 

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![Fig. 3](image-url)  
Fig. 3: (Colour on-line) Results for plain effusion (no filters): (a) $P_t(\eta)$ for $t/t_0 = 5, 10, 20$, after $2 \cdot 10^7$ runs. Parameter values: $\eta_c = 0.7$, $\mu_b = -5k_BT_b$, $\mu_c = -\mu_b (1-\eta_c) - 2k_BT_c \ln(1-\eta_c)$. Upper inset: approach to the large deviation limit, $-\ln(P_t(\eta))/t$ for $t/t_0 = 5, 10, 20$. Lower inset: $J(\eta)/J(\infty)$ as a function of $t$ (dashed line) compared to extrapolation from finite time (crosses). (b) $J(\eta)/J(\infty)$ for $\eta_c = 0.8, \mu_b = -k_BT_b$ and $\mu_c = 0$ (dot in fig. 4(b)). Inset: $J(\eta)/J(\infty)$ as a function of $\mu_c$ in the engine regime.

![Fig. 4](image-url)  
Fig. 4: (Colour on-line) Number of events as a function of $\eta$ (sample width $d\eta = 0.01$) for 200, 500 and 1000 runs. Parameter values: $E_1 = k_BT_b$, $E_2 = 10k_BT_b$, $P_c = 6.3 \cdot 10^4 \text{ Pa}$, $T_b = 100 \text{ K}$, $P_b = 1.0 \cdot 10^5 \text{ Pa}$, $T_c = 400 \text{ K}$, $\sigma = 100 \text{ nm}^2$ and $\Delta E = k_BT_b/1000$. The running time is $t = 7.6 \cdot 10^{-5} \text{ s}$ (value for helium).
Appendix B: effusion engine operating with helium. – From the mass of a helium atom,

\[ m_{\text{helium}} = 6.65 \times 10^{-27} \text{ kg,} \quad (B.1) \]

we find the corresponding thermal de Broglie wavelength:

\[ \lambda_{\text{helium}} = \frac{8.87 \times 10^{-10}}{\sqrt{T}} \text{ m.} \quad (B.2) \]

The relation between chemical potential, temperature and density thus becomes

\[ \rho = \frac{N}{V} = 1.50 \times 10^{27} T^{3/2} e^{\mu/k_{B}T} \text{ K}^{-3/2} \text{ m}^{-3}, \quad (B.3) \]

or in terms of the pressure:

\[ P = \rho k_{B}T = T^{5/2} e^{\mu/k_{B}T+9.94} \text{ K}^{-5/2} \text{ Pa} \quad (B.4) \]

If we set

\[ \mu_{c} = (1 - \eta_{c})\mu_{h} + E_{1} \eta_{c}, \quad (B.5) \]

and \( E_{1} = kT_{h} \), we get

\[ P_{h} = T_{h}^{5/2} e^{\frac{\mu_{h}}{k_{B}T_{h}}+9.94} \text{ K}^{-5/2} \text{ Pa}, \quad (B.6) \]

\[ P_{c} = T_{c}^{5/2} e^{\frac{\mu}{k_{B}T_{c}}+\frac{\mu_{h}}{k_{B}T_{h}}+9.94} \text{ K}^{-5/2} \text{ Pa}. \quad (B.7) \]

The validity of the Sackur-Tetrode and the ideal gas law requires

\[ e^{\frac{\mu}{k_{B}T}} \ll 1. \quad (B.8) \]

This condition is satisfied for

\[ P = 10^{5} \text{ Pa,} \quad T = 400 \text{ K}, \quad (B.9) \]

corresponding to

\[ \mu = -13.40 k_{B}T. \quad (B.10) \]

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