Thermoelectric efficiency at maximum power in a quantum dot

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Abstract – We identify the operational conditions for maximum power of a nanothermoelectric
engine consisting of a single quantum level embedded between two leads at different temperatures
and chemical potentials. The corresponding thermodynamic efficiency agrees with the Curzon-
Ahlborn expression up to quadratic terms in the gradients, supporting the thesis of universality
beyond linear response.

The purpose of this letter is to present a detailed
thermodynamic analysis of electron transport through
a single quantum dot connecting two leads at different
temperatures and chemical potentials. Of particular inter-
est to us is the efficiency of the thermal motor function, in
which electrons are pumped upward in chemical potential
under the impetus of a downward temperature gradient.
The study of this model addresses several issues of timely
interest: nanotechnology, the study of thermodynamic
properties of small devices that are prone to fluctuations,
the question of universality for thermodynamic properties
away from equilibrium, the role of quantum features in this
respect, and the promise of thermoelectricity generated by
nanodevices. We briefly comment on each of these topics.

Spectacular technical and experimental progress in
nano- and bio-technology have greatly increased our abil-
ity to observe, manipulate, control, and even manufacture
systems on a very small scale [1,2]. In parallel, new theo-
retical tools and concepts have been developed that make
it possible to exhibit the deeper relationship between
fluctuations, entropy production and work, and the role
of stochasticity in small scale non-linear nonequilibrium
phenomena. In particular, stochastic thermodynamics
formulates the thermodynamics of small entities subject
to thermal fluctuations [3–7]. These developments are
closely related to the celebrated fluctuation [8] and work
theorems [9].

The concept of Carnot efficiency is a central cornerstone
of thermodynamics. According to this principle, the effi-
ciency, defined as the ratio of work output over heat input
for a machine operating between two thermal baths at
temperatures T_l and T_r ($T_r > T_l$) is at most equal to

$$\eta_c = 1 - \frac{T_l}{T_r}. \qquad (1)$$

The equality is only reached for reversible operation. This
is a universal result which remains valid for small-scale
fluctuating systems such as the well-documented case
of Brownian motors, see [10] and references therein.
However, reversible processes require infinitely slow
operation, implying that such engines produce zero power.
One of the important questions, when operating away
from equilibrium, is the efficiency at maximum power.
In a groundbreaking paper, Curzon and Ahlborn [11]
calculated this efficiency for the Carnot engine in the
so-called endo-reversible approximation (taking into
account the dissipation only in the heat transfer process).
They found a strikingly simple formula, namely

$$\eta_{CA} = 1 - \sqrt{1 - \eta_c} \approx \eta_c/2 + \eta_c^2/8 + 6\eta_c^3/96 + \dots . \qquad (2)$$

Recently, it has been shown that the Curzon-Ahlborn
efficiency is an exact consequence of *linear* irreversible
thermodynamics when operating under conditions of
strong coupling between the heat flux and the work [12].
The value of $1/2$ for the linear coefficient in eq. (2) is
therefore universal for such systems.
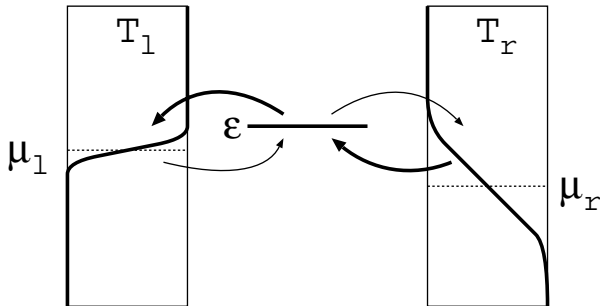
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Fig. 1: Sketch of the nanothermoelectric engine consisting of a single quantum level embedded between two leads at different temperatures and chemical potentials. We choose by convention $T_l < T_r$. Maximum power is observed in the regime $\varepsilon > \mu_l > \mu_r$.

The efficiency at maximum power was also addressed in the context of stochastic thermodynamics in [13], where it was shown that the efficiency at maximum power for a Brownian particle undergoing a Carnot cycle through the modulation of a harmonic potential is given by $\eta_S = 2\eta_c/(4 - \eta_c) \approx \eta_c/2 + \eta_c^2/8 + 3\eta_c^3/96 + \dots$. By an entirely different calculation, dealing with the Feynman ratchet and pawl model (which operates under steady rather than cyclic conditions), the efficiency at maximum power was found to be [14] $\eta_T = \eta_c^2/[\eta_c - (1 - \eta_c)\ln(1 - \eta_c)] \approx \eta_c/2 + \eta_c^2/8 + 7\eta_c^3/96 + \dots$. All three of the above results agree, as they should [12], to linear order in η_c. More surprisingly, the coefficient of the quadratic term is also identical. This raises the question as to whether universality also applies to the coefficient of the quadratic term.

The field of thermoelectricity went through a revival in the early 1990s due to the discovery of new thermoelectric materials with significantly higher thermodynamic yields [15]. Of particular interest are the developments in the context of nanostructured materials [16]. for example, thermoelectric experiments have been reported on silicon nanowires [17], individual carbon nanotubes [18] and molecular junctions [19]. Furthermore, it has been reported that Carnot efficiency can be reached for electron transport between two leads at different temperatures and chemical potentials, by connecting them through a channel sharply tuned at the energy for which the electron density is the same in both leads [20,21]. A double-barrier resonant tunneling structure has been proposed as a possible technological implementation [22].

The thermoelectric device whose properties we explore below is arguably the simplest prototype of such systems. It consists of a quantum dot with a single resonant energy level in contact with two thermal reservoirs at different temperatures, see fig. 1. The dot can contain one single electron with a sharply defined energy ε. The exchange of electrons between the leads through the dot will be described by a stochastic master equation [23–25], and the corresponding thermodynamic properties can be obtained from stochastic thermodynamics [3–7]. In anticipation

of the forthcoming analysis, we note that this model displays perfect coupling between energy and matter flow: because of the sharply defined dot energy, every single electron carries exactly the same amount of energy. Hence, Carnot efficiency will be reached when operating close to equilibrium [10,20,21], while Curzon-Ahlborn efficiency will be obtained at maximum power in the regime of linear response [12]. Going beyond these results, we will identify the operational conditions for working at maximum power. In particular, the efficiency at maximum power will be found to be $\eta \approx \eta_c/2 + \eta_c^2/8 + \dots$, with the coefficient of η_c^2 again equal to $1/8$. This provides further support for the thesis of universality for this value, especially since the regime of maximum power is found to lie entirely in the quantum regime.

We now turn to the mathematical analysis of the thermoelectric engine represented in fig. 1. A single-level quantum dot, with orbital energy ε, exchanges electrons with a cold left lead, temperature T_l and chemical potential μ_l, and with a hot right lead, temperature T_r and chemical potential μ_r. The quantum dot is either empty (state 1) or filled (state 2). The crucial variables of the problem are the scaled energy barriers (with $k_B = 1$)

$$x_\nu = \frac{\varepsilon - \mu_\nu}{T_\nu}, \qquad \nu = l, r. \tag{3}$$

The exchange of electrons with the leads is described by the following quantum master equation [23–25]:

$$\begin{pmatrix} \dot{p}_1(t) \\ \dot{p}_2(t) \end{pmatrix} = \begin{pmatrix} -W_{21} & W_{12} \\ W_{21} & -W_{12} \end{pmatrix} \begin{pmatrix} p_1(t) \\ p_2(t) \end{pmatrix}. \tag{4}$$

The rates are given by

$$W_{12} = \sum_{\nu=l,r} W_{12}^{(\nu)} = \sum_{\nu=l,r} a_\nu(1 - f_\nu) \tag{5}$$

$$W_{21} = \sum_{\nu=l,r} W_{21}^{(\nu)} = \sum_{\nu=l,r} a_\nu f_\nu, \tag{6}$$

where $f_\nu = [\exp(x_\nu) + 1]^{-1}$ is the Fermi distribution. The fact that a_ν is independent of the dot energies is known as the wide-band approximation.

We are interested in the properties of the device at the steady state. The steady-state distributions for the dot occupation follow from $W_{21}p_1^{ss} = W_{12}p_2^{ss}$ with $p_1^{ss} + p_2^{ss} = 1$. The resulting probability current from the lead ν to the dot is then

$$\mathcal{I}_\nu \equiv W_{21}^{(\nu)}p_1^{ss} - W_{12}^{(\nu)}p_2^{ss}. \tag{7}$$

Using $\mathcal{I}_r = -\mathcal{I}_l$ and $W_{12} + W_{21} = a_r + a_l$, we can rewrite the result for the flux from the right lead as

$$\mathcal{I}_r = \alpha(f_r - f_l), \tag{8}$$

where $\alpha = a_r a_l/(a_r + a_l)$. Equation (8) is essentially the Landauer formula for a single infinitely sharp resonance (*i.e.* without broadening).

The steady-state heat per unit time $\dot{\mathcal{Q}}_r$ extracted from the lead r, and the steady-state work per unit time (power) $\dot{\mathcal{W}}$ performed by the device upon bringing electrons from right to left lead, are respectively given by

$$\dot{\mathcal{Q}}_r = (\varepsilon - \mu_r)\mathcal{I}_r = \alpha T_r x_r (f_r - f_l), \qquad (9)$$

$$\dot{\mathcal{W}} = (\mu_l - \mu_r)\mathcal{I}_r = \alpha T_r \big(x_r - (1 - \eta_c)x_l \big)(f_r - f_l). \qquad (10)$$

The corresponding thermodynamic efficiency reads

$$\eta \equiv \frac{\mathcal{W}}{\mathcal{Q}_r} = \frac{\dot{\mathcal{W}}}{\dot{\mathcal{Q}}_r} = \frac{\mu_l - \mu_r}{\varepsilon - \mu_r} = 1 - (1 - \eta_c)\frac{x_l}{x_r}. \qquad (11)$$

The entropy production associated with the master equation (4) is given by [3,4,6,7]

$$\sigma = \sum_{i,j,\nu} W_{ij}^{(\nu)} p_j^{ss} \ln \frac{W_{ij}^{(\nu)} p_j^{ss}}{W_{ji}^{(\nu)} p_i^{ss}} \geqslant 0, \qquad (12)$$

where $i, j = 1, 2$. Noting that $\ln[W_{12}^{(\nu)}/W_{21}^{(\nu)}] = x_\nu$, one finds, in agreement with standard irreversible thermodynamics [26], the following expression for the entropy production:

$$\sigma = F_m J_m + F_e J_e = \alpha(x_l - x_r)(f_r - f_l) \geqslant 0, \qquad (13)$$

with thermodynamic forces for matter and energy flow, F_m and F_e, given by

$$F_m \equiv -\left(\frac{\mu_r}{T_r} - \frac{\mu_l}{T_l}\right), \quad F_e \equiv \frac{1}{T_r} - \frac{1}{T_l}. \qquad (14)$$

We stress that the corresponding matter and heat flow, given by

$$J_m \equiv -\mathcal{I}_r, \quad J_e \equiv -\varepsilon\mathcal{I}_r, \qquad (15)$$

are proportional to each other. In other words, matter and heat flow are perfectly coupled and the condition for attaining both Carnot and Curzon-Ahlborn efficiency, namely, that the determinant of the corresponding Onsager matrix be zero, is fulfilled [10,12].

We first discuss the case of equilibrium. Due to the perfect coupling, it is enough to stop one current, matter or energy, and the other one will automatically vanish. Under this condition, detailed balance is valid, $\mathcal{I}_\nu = 0$. It is clear from eq. (8) that the matter flux (and hence also the energy flux) vanishes if and only if $f_l = f_r$ or, equivalently, $x_l = x_r$. The efficiency then becomes equal to Carnot efficiency, cf. eq. (11), and the entropy production vanishes, $\sigma = 0$ (cf. eq. (13)). Note that $x_l = x_r$ does not require that the thermodynamic forces F_m and F_e vanish separately, i.e., at this singular balancing point equilibrium does not require temperature and chemical potential to be identical in both reservoirs [10,12,20,21].

We next turn to the operational condition for maximum power. For given temperatures T_l and T_r, we search for the values of the scaled electron energy barriers x_l and x_r

that maximize $\dot{\mathcal{W}}$. From $\partial_{x_l}\dot{\mathcal{W}} = \partial_{x_r}\dot{\mathcal{W}} = 0$, we find the following two equations determining these values:

$$(f_l - f_r) + [x_r - (1 - \eta_c)x_l] f_r^2 e^{x_r} = 0 \qquad (16)$$

$$(f_l - f_r) + \left(\frac{x_r}{1 - \eta_c} - x_l\right) f_l^2 e^{x_l} = 0. \qquad (17)$$

A first observation is that these equations depend only on the ratio of the two temperatures. Second, while the equations involve transcendental relations, one obtains the following explicit result by subtracting the first equation from the second,

$$x_l = 2\ln\left[\frac{\cosh\{x_r/2\}}{\sqrt{1 - \eta_c}} + \sqrt{\frac{\cosh^2\{x_r/2\}}{1 - \eta_c} - 1}\right]. \qquad (18)$$

Substitution of this result in (16) gives

$$x_r - \sqrt{2}\cosh(x_r/2)\sqrt{2\eta_c - 1 + \cosh(x_r)} + 2(\eta_c - 1)$$
$$\times \ln\left[\frac{\cosh(x_r/2) + \sqrt{2\eta_c - 1 + \cosh(x_r)}/\sqrt{2}}{\sqrt{1 - \eta_c}}\right]$$
$$+ \sinh(x_r) = 0. \qquad (19)$$

Since an analytic solution of this equation is not possible, we first turn to perturbative solutions for η_c close to the limiting values 0 (reservoirs of equal temperatures) and 1 (cold reservoir at zero temperature). For the case $\eta_c \to 0$, we substitute $x_r = a_0 + a_1\eta_c + a_2\eta_c^2 + \mathcal{O}(\eta_c^3)$ in eq. (19) and expand the resulting equation in η_c. The coefficients a_0, a_1, a_2, etc., are found recursively by solving order by order in η_c. At order zero, we find an identity. At first order, we find the transcendental equation $a_0 = 2\coth(a_0/2)$. The numerical solution is $a_0 = 2.39936$. At second order and third order in η_c, we find $a_1 = -a_0/4$ and $a_2 = \sinh(a_0)/\{6[1 - \cosh(a_0)]\}$. Substitution of these results and (18) in (11) leads to the following expansion of the efficiency at maximum power in the regime of small η_c:

$$\eta = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + \frac{[7 + \operatorname{csch}^2(a_0/2)]}{96}\eta_c^3 + \mathcal{O}(\eta_c^4). \qquad (20)$$

The expansion features the expected coefficient $1/2$ for the linear term, but also supports the thesis that the coefficient of η_c^2 has a universal value, namely, $1/8$.

We next turn to the analysis of the case $\eta_c \to 1$ ($T_l \to 0$). As we will see by self-consistency, the value of x_r converges to a finite limiting value. With this a posteriori insight, we can easily identify the leading behavior of x_l from eq. (18), namely, $x_l \sim -\ln(1 - \eta_c)$. Substitution of this result in (16) leads to the conclusion that $x_r \to b$, where b is a solution of the transcendental equation

$$e^{-b} + 1 = b, \qquad (21)$$

with numerical solution $b = 1.27846$. The corresponding efficiency converges to 1, albeit rather slowly, cf. eq. (11).
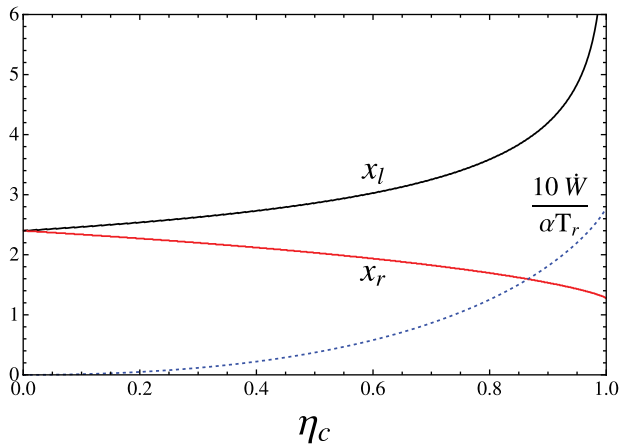
Fig. 2: (Color online) Scaled electron energy barriers x_l and x_r at maximum power, cf. eqs. (18) and (19), as a function of the Carnot efficiency $\eta_c = 1 - T_l/T_r$. The dotted line represents the corresponding (scaled) power $10 \times \dot{\mathcal{W}}/(\alpha T_r)$, cf. eq. (10).
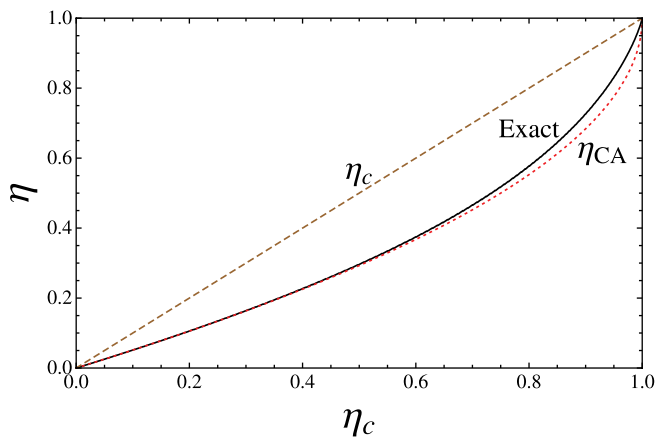

Fig. 3: (Color online) Efficiency at maximum power in a single-level quantum dot as a function of the Carnot efficiency $\eta_c = 1 - T_l/T_r$ (full line), as compared to Curzon-Ahlborn efficiency (dotted line) and Carnot efficiency (dashed line).

To complete the picture, we show in fig. 2 the numerical solutions for x_l and x_r as functions of η_c as well as the corresponding rescaled maximum power $\dot{\mathcal{W}}/(\alpha T_r)$. Note that x_r is always of order unity, so that the regime of maximum power cannot be well described by either a high- or a low-temperature expansion. It can also be seen that the maximum power is a monotonically increasing function of η_c. The corresponding efficiency is reproduced in fig. 3. It is very close to the Curzon-Ahlborn efficiency, with relative deviations largest for large η_c.

In conclusion, nanosystems with perfectly coupled fluxes, such as the quantum dot described here, are of great interest. They can operate as steady-state Carnot engines. They probably possess universal features up to quadratic terms in nonlinear response when working at maximum power. One can speculate that they offer, from a technological point of view, advantages over their macroscopic counterparts. Our model assumes a single infinitely sharp level or resonance (*i.e.* no broadening). This occurs when the quantum dot barriers are thick (*i.e.* weak system-lead coupling regime). In this case, α and therefore also current and power will be small. Models providing bigger powers could be considered by increasing the system-lead coupling. However, this would result in increasing the broadening and thus prevent a strong coupling between the heat and matter flow. As a result, the efficiency at maximum power would invariably be lower than $\eta_c/2$ even in the linear regime. The same would be true when considering models with multiple resonances. The above analysis can be repeated for the quantum dot operating as a refrigerator, corresponding to the regime $x_r \geqslant x_l$. Such an analysis reveals that maximum cooling power (maximum $\dot{\mathcal{Q}}_r$ extracted from the cold lead) is attained for $x_r \to \infty$ and $x_l \to b$, where b is again the solution to the transcendental equation (21). The corresponding cooling power is thus bT_l per transported particle, to be compared with the cooling power of T_l for a classical engine.

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