Constrained maximal power in small engines

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Efficiency at maximum power is studied for two simple engines (three- and five-state systems). This quantity is found to be sensitive to the variable with respect to which the maximization is implemented. It can be wildly different from the well-known Curzon-Ahlborn bound (one minus the square root of the temperature ratio), or can be even closer than previously realized. It is shown that when the power is optimized with respect to a maximum number of variables the Curzon-Ahlborn bound is a lower bound, accurate at high temperatures, but a rather poor estimate when the cold reservoir temperature approaches zero (at which point the Carnot limit is achieved).

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I. INTRODUCTION

The Carnot bound on efficiency lies at the foundations of equilibrium thermodynamics. But once time enters the picture there is no longer a unique criterion for the effectiveness of a process for turning heat into work. We are told [1] that early in the history of this subject various maximization issues were taken up, some leading to the efficiency now known as the Curzon-Ahlborn efficiency at maximum power is not generally the ultimate criterion for the system ac-

Although in engineering, biology, and other applications, efficiency at maximum power is not generally the ultimate criterion (e.g., a plant must also deal with predators, not only with glucose production), it has emerged as a significant test-

We have several objectives in this paper. First we point out that the notion of maximal is ambiguous and that under some circumstances the physically most natural definition gives bounds quite different from \( \eta_{CA} \). That many kinds of maximizing should exist is not be surprising in view of the richness of applications. Second we find that under other circumstances \( \eta_{CA} \) is even closer to the exact value than one had supposed. And finally, in a related issue, we find that the ladder, a system previously studied [13], can enhance the power output of an engine, although it is less effective with regard to efficiency.

Our method will be to look at small engines. By this we mean three- and five-state systems, that in a way are the simplest idealizations of work-producing processes. The context is stochastic dynamics [14–16] and we employ both numerical and analytic techniques, with a number of rigorous bounds emerging in the latter [17]. Although much of the recent work in this area concerns the temperature regime where \( T_c/T_h \leq 1 \), we will treat the entire range of temperatures, 0 \( \leq T_c \leq T_h \).

II. THREE-STATE MODEL

The simplest possible model involves three states (see Fig. 1). The names we have given the states call to mind a chemical reaction in which the hot reservoir drives a reaction starting in the ground state over a barrier state. From there it can descend, in contact with a lower temperature reservoir, into a product state. From the product state the system drops

\[ \eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}} \]
back to the ground state. The energy released at this point is the work extracted from the engine. In this identification we take a conventional view of work, as described in [16]; for example, to chemical species carried away from the site of our engine (by unspecified agency) would be attributed work $\mu dN$ [18,19]. Our application does not require analysis of some of the subtle heat and work issues taken up for example in [20].

One can think of the three-state system as a toy model for a variety of natural systems. For example, the product state could be ATP (adenosine triphosphate), which when it gives up its energy (typically to create mechanical work) becomes ADP (adenosine diphosphate) and is raw material for another cycle of our engine. It is photons from the sun that provide the high-temperature bath for the step level 1 $\rightarrow$ level 2. Stabilization of this excited state (by a “cold” reservoir) corresponds to level 2 $\rightarrow$ level 3. Other interpretations of the three-state system are possible (see for example [6,21]). (These are not quite the same, but share the simplicity of three-state systems.) The matrix of transition probabilities is

$$R = \begin{pmatrix}
1 - ae^{-\beta E_2} & a & c \\
be^{-\beta E_2} & 1 - a - b & be^{-\beta (E_2 - E_1)} \\
1 - be^{-\beta (E_2 - E_3)} & b & c
\end{pmatrix},$$

where the following conventions are adopted: 1, 2, and 3 are, respectively, the ground, barrier and product states; $\beta_0 = 1/T_0$, $\beta = 1/T$, $E_1 = 0$ is the ground-state energy, and $E_2$ and $E_3$ are the barrier and product state energies. $a$, $b$ and $c$ are strictly positive numbers such that $R$’s diagonal is nonnegative. Define $\alpha = T_\beta / T_0 = \beta_0 / \beta$. $R_{xy}$ is the probability that a system in state $y$ transitions to $x$ in unit time. The current through this loop is $J_{13} = R_{13}\beta_3 - R_{32}\beta_2 = abc(e^{-\beta E_2} - e^{-\beta(E_2 - E_1)})/Z$ with $\bar{p}$ the stationary state and $Z = (ab + abc + e^{-\beta E_2} + b)e^{-\beta(E_2 - E_1)} + 2(c(a+b) + a(c+b))e^{-\beta E_2}$. From $J_{13}$ it is evident that positive work will be obtained only for $E_2 \geq E_1 / (1 - \alpha)$.

The power is then $P = E_1 J_{13}$ and the efficiency $\eta = E_3/E_1$. It follows that Carnot efficiency $(1 - \alpha$ in our notation) is obtained only for $P = 0$, consistent with the requirements of reversibility. In some of our calculations we take $a = b = c$. (See Appendix A for details.)

To consider maximizing the power output of this simple engine one must first put the engine into some context so that one has an idea of what is controllable, what is not. For the interpretation we have given it is natural to consider $E_2$ the adjustable quantity: in a typical situation the barrier is a free energy and one uses a catalyst to lower it. Alternatively one could use an electric field to lower an electrostatic barrier. In any case, one can determine the maximum power output by solving $\partial P / \partial E_2 = 0$, with the efficiency at maximum power given by $\eta = \eta_{max} = E_3 / E_2$ at the corresponding $E_2$. One can show that there is a unique maximum of $P$ for $E_2 > E_1 / (1 - \alpha)$. The equation for this maximum is algebraically complicated and in making this calculation it is convenient to define a variable $\sigma$ such that $E_2 = E_1 (1 + \sigma) / (1 - \alpha)$, making the earlier constraint equivalent to $\sigma > 0$. By evaluating

$$\frac{\partial P}{\partial E_2} = 0$$

we find

$$\eta \leq \frac{1 - \alpha}{1 - \log \alpha}.$$
five, contains the new matrix elements $b_{is}$. The matrix of transition probabilities, now five by five, contains the new matrix elements $a_{is}$. The diagonal of $R$ is adjusted to have column sums unity. For the ladder, the requirement that the current be positive is $E_2 + E_{ab} > E_3/(1 - \alpha)$. Again it is possible to vary either $E_2$ or $E_3$ (and other variables as well).

As for the three-state engine, $E_2$ optimization bears little relation to $\eta_{CA}$. A bound on efficiency (using only the ladder mechanism) at maximal power (varying $E_2$) is

$$\eta \leq \frac{(1 - \alpha) E_3}{E_3 - \log \alpha + \frac{E_{ab}}{E_b}(1 - \alpha)}$$

(4)

In Fig. 6, which provides the results of $E_3$ variation with fixed $T_h$, the ladder is shown to produce more power than the three-state system. (Besides $E_3$, there is optimization with respect to $E_{ab}/E_2$ with $E_{ab} = E_a - E_b$.) In Fig. 7 however, it is seen that it is generally less efficient. This is because of the “wasteful” step down from $a$ to $b$, so that $\eta = E_3/[E_2 + E_{ab}]$. This step, however, is necessary [22] for the power output. Otherwise, systems reaching level-$a$ would drop immediately back to the ground state. With respect to $\eta_{CA}$, the $\eta$ of the ladder can be either larger or smaller, depending on temperature.

III. LADDER

In Ref. [13] we discussed a five-state engine that we called a ladder. The idea is that there exist a pair of intermediate levels between no. 1 (ground state) and no. 2 (barrier state). This enhances—exponentially—the $1 \rightarrow 2$ transition when the “hot” reservoir is not hot enough to excite level no. 2 in a single step. (This is the case for photosynthesis.) The level diagram is shown in Fig. 5, along with our convention that level $a$ is no. 4 and level $b$ is no. 5. The matrix of transition probabilities, now five by five, contains the new matrix elements $R_{41} = a_{lad} \exp(-\beta_a E_a)$, $R_{42} = a_{lad} \exp(-\beta_b E_b)$, $R_{43} = a_{lad}$, and $R_{45} = a_{lad} \exp(-\beta_c (E_2 - E_b))$. In Fig. 6, which provides the results of $E_3$ variation with fixed $T_h$, the ladder is shown to produce more power than the three-state system. (Besides $E_3$, there is optimization with respect to $E_{ab}/E_2$ with $E_{ab} = E_a - E_b$.) In Fig. 7 however, it is seen that it is generally less efficient. This is because of the “wasteful” step down from $a$ to $b$, so that $\eta = E_3/[E_2 + E_{ab}]$. This step, however, is necessary [22] for the power output. Otherwise, systems reaching level-$a$ would drop immediately back to the ground state. With respect to $\eta_{CA}$, the $\eta$ of the ladder can be either larger or smaller, depending on temperature.
IV. DISCUSSION

We have studied various measures of the effectiveness of an engine for producing work from heat. Among the many criteria for “effectiveness” is efficiency when the engine is operating at maximum power, but even that criterion is not unique. With a chemical-reaction interpretation of the three-state engine it is most natural to consider variation of the “barrier” height (cf. Fig. 1), yielding efficiencies much at odds with the well-known Curzon-Ahlborn bound [2–4]. For other criteria, however, that bound was quite good when reservoir temperatures were nearly equal (but not so good otherwise). Rigorous upper and lower bounds were also given here for various maximization criteria. Most of our work was done for the three-state engine, although additional support was found by studying the five-state ladder [13], where much the same qualitative picture emerged.

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APPENDIX A: DETAILS OF THE CURRENT CALCULATIONS AND THE MAXIMIZING OF POWER

1. Stationary state and the function $Z$

We review definitions and notation, mostly from our previous works [13,15,16,23–28]. Let $X$ be a discrete finite space and $R_{xy}$ a stochastic irreducible matrix. Then there exists a unique stationary state $\bar{\rho}$ such that

$$ \bar{\rho}(x) = \sum_y R_{xy} \bar{\rho}(y). $$

Let $T$ be the set of spanning trees with root $x \in X$, oriented toward $x$. For any $T \in T(x)$, $R(T)$ denotes the product of the $R_{yz}$ for all edges $(yz)$ of $T$ such that the direction $z \rightarrow y$ corresponds to the orientation of $T$. Then one has

$$ \bar{\rho}(x) = \frac{1}{Z} \sum_{T \in T(x)} R(T), $$

where $Z$ is a normalization factor,

$$ Z = \sum_x \sum_{T \in T(x)} R(T). $$

$Z$ is a kind of partition function.

2. Current matrix

The current matrix in the stationary state is

$$ J_{xy} = R_{xy} \bar{\rho}(y) - R_{yx} \bar{\rho}(x); $$

it is skew symmetric and satisfies identities analogous to the Kirchhoff laws. If the system has reached its stationary state, $J_{xy}$ measures the net flow of probability in one time step from $y$ to $x$. The system is said to be in detailed balance if $J_{xy}=0$ for all $x,y \in X$.

3. Power for the three-state system

For the three-state system only one distinct magnitude of current is possible, and one must have $J_{31} = J_{32} = J_{13} = J$. $J$ is thus the net flow in 1 time step from 3 to 1. By direct calculation

$$ ZJ = abc \{ e^{-\beta E_2} - e^{-\beta E_{23}} \}, $$

where $E_{23} = E_2 - E_3$ and $Z$ is the partition function. The power is therefore

$$ P = E_JJ. $$

It is positive (and thus the system acts as an engine) if and only if $J>0$. By Eq. (A1), this requires

$$ E_2 > E_{2,C} = \frac{E_1}{1 - \alpha}, \quad \text{where } \alpha = T_h/T_c $$

(3)

(which defines $E_{2,C}$, the Carnot energy for level no. 2). When $E_2=E_{2,C}$, $J=0$, and the system is in detailed balance. No power is produced and it is equally likely to go one way or the other. If it is tilted very slightly in one direction, say $J>0$ but small, it will (eventually) perform a cycle $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$, generating work $E_J$, while consuming $E_{2,C}$. In this case, the efficiency is $\eta = \frac{E_J}{E_2} = 1 - \alpha$.

In general when $E_2 > E_{2,C}$ (so that $J>0$) the efficiency is

$$ \eta = \frac{E_J}{E_2} > \frac{E_3}{E_2} < 1 - \alpha = \eta_C. $$

4. Variation with respect to $E_2$

For $E_2=E_{2,C}$, $J$ is zero, while for $E_2 \rightarrow +\infty$, $J \rightarrow 0$. Thus $J$ has at least one maximum. First we show that this maximum is unique. Suppose otherwise and let $E'_2 < E''_2$ be two con-
secutive zeros of $\partial f/\partial E_2$, with $E_2'$ corresponding to the first maximum of $J$ and $E_2''$ the minimum immediately after it. Thus
\[ \frac{\partial J(E_2'')}{\partial E_2} = 0, \quad \frac{\partial^2 J(E_2'')}{\partial E_2^2} \geq 0. \] (A5)

One has
\[ \frac{\partial J}{\partial E_2} = -\frac{1}{Z}(\beta R_1 R_2 R_3 R_4 - \beta R_1 R_2 R_3 R_4) - \frac{1}{Z} \frac{\partial Z}{\partial E_2} J. \] (A6)
\[ \frac{\partial^2 J}{\partial E_2^2} = \frac{1}{Z}(\beta R_1 R_2 R_3 R_4 - \beta R_1 R_2 R_3 R_4) \frac{1}{Z^2} \frac{\partial Z}{\partial E_2} + \left( \frac{1}{Z^2} \left( \frac{\partial Z}{\partial E_2} \right)^2 - 1 \right) \frac{\partial^2 Z}{\partial E_2^2} + J \left( \frac{1}{Z^2} \frac{\partial Z}{\partial E_2} - 1 \right) \frac{\partial Z}{\partial E_2} \frac{\partial J}{\partial E_2}. \] (A7)

At $E_2=E_2''$, the second term in Eq. (A5) is zero, and the second term in Eq. (A7) is equal to or greater than zero. Then using Eq. (A6) (which is zero) in Eq. (A7) at $E_2''$ one deduces from Eq. (A7)
\[ 0 \leq \frac{1}{Z} \beta (\beta - \beta R_1 R_2 R_3 R_4) - \frac{1}{Z} \frac{\partial Z}{\partial E_2} J + \left( \frac{1}{Z^2} \left( \frac{\partial Z}{\partial E_2} \right)^2 - 1 \right) \frac{\partial^2 Z}{\partial E_2^2} + J \left( \frac{1}{Z^2} \frac{\partial Z}{\partial E_2} - 1 \right) \frac{\partial Z}{\partial E_2} \frac{\partial J}{\partial E_2}. \]

The first term is (strictly) less than zero because $\beta < \beta$ and by a direct calculation $\frac{\partial Z}{\partial E_2} > 0$, so that we reach a contradiction; it follows that $J$ has a unique maximum with respect to $E_2$.

5. Maximum of power with respect to $E_2$, $E_3$ fixed

Recall that $\alpha = \frac{\beta}{\beta} \leq 1$. We can fix the energy scale so that $E_3 = 1$. Then $\frac{\partial E_3}{\partial E_2} = 0$ is equivalent to
\[ F(E_2) = K_1(1 - \alpha)e^{-\beta E_2^2(1 + \alpha)} + K_2e^{-\beta E_2^2(1 + \alpha)}[e^{\beta((1 - \alpha)E_2 - 1) - \alpha}] + K_3e^{-\beta E_2^2(1 + \alpha)}[1 - \alpha e^{\beta((1 - \alpha)E_2 - 1)}] = 0. \] (A8)

where the $K_i$ are positive constants depending only on $a$, $b$, and $c$ [of Eq. (1)]. Because $E_2 > E_3$, we define a new variable $\sigma$ by
\[ E_2 = \frac{\sigma + 1}{1 - \alpha}, \] (A9)
so that $\sigma \geq 1$ and Eq. (A8) can be rewritten as
\[ K_1(1 - \alpha)e^{-\beta((\alpha + 1)(1 - \alpha)E_3 - 1) + \alpha} + K_2e^{-\beta((\alpha + 1)(1 - \alpha)E_3 - 1) + \alpha}[e^{\beta\sigma - \alpha}] = K_3[1 - \alpha e^{\beta\sigma - \alpha}]. \] (A10)

We know from Appendix A 4 that this equation has a unique root $\sigma > 0$. The first term in Eq. (A10) is obviously strictly positive; the second term is strictly positive if and only if $\sigma > -\frac{\log \alpha}{\beta}$, thus the root of Eq. (A10) satisfies
\[ \sigma > -\frac{\log \alpha}{\beta}. \]

The efficiency at maximum power is thus
\[ \eta = \frac{1}{E_2} - \frac{1 - \alpha}{1 + \sigma(\alpha)} < \frac{1 - \alpha}{1 - \frac{\log \alpha}{\beta}}. \] (A11)

For $\alpha \to 0$, $\eta \to 0$, although the Carnot efficiency, $\eta_C$, approaches 1. For $\alpha \to 1$, Eq. (A10) shows that $\sigma(\alpha) \to 0$ and $\eta \to 1 - \alpha$.

6. Maximum power with respect to both $E_2$ and $E_3$

We now consider the system
\[ \frac{\partial P}{\partial E_2} = 0 \quad \text{and} \quad \frac{\partial P}{\partial E_3} = 0. \] (A12)

It is convenient to redefine variables
\[ e_j = \beta E_j, \quad e_2 = \frac{\tau + 1}{1 - \alpha} = \frac{e_3}{1 - \alpha}, \quad \text{so} \quad \tau \geq 0, \] (A13)

and we use $\tau$ and $e_3$ as new variables. A direct calculation shows that Eq. (A12) is equivalent to
\[ 4(\tau e_3 - 1) = 4(1 - \alpha)e^{-\alpha(\tau e_3 - 1)/1 - \alpha} + (e_3 - \alpha)e^{-\tau e_3}(1 + \alpha) - \alpha/(1 + \alpha) - \alpha, \] (A14)
\[ (e_3 - 1)(4 + 2e^{-\alpha(\tau e_3 - 1)/1 - \alpha} + 2e^{-\alpha(\tau e_3 - 1)/1 - \alpha} + e^{-\tau e_3}(1 + \alpha - \alpha) - \alpha) = e^{-\alpha(\tau e_3 - 1)/1 - \alpha}(2 + 1). \] (A15)

In the above, we have set $a = b = c$. This is a system of two equations for $e$ and $\tau$. We examine its solution in various regimes.

a. Asymptotics for $\alpha \to 1$

If $e$ does not tend to zero, Eq. (A14) shows that $\tau \to 0$ and Eq. (A15) cannot be satisfied. Thus $e \to 0$ if $\alpha \to 1$. We write
\[ e = (1 - \alpha)e_0 + \cdots. \]

Then Eq. (A15) shows that $\tau \to 1$, so that
\[ \eta \sim \frac{1 - \alpha}{2e_0}, \] (A16)
and Eq. (A14) shows that $e_0$ is the (unique) root of
\[ 4(e_0 - 1) = 4e^{-2e_0} + e^{-4e_0}(1 + e_0). \] (A17)

b. Asymptotics for $\alpha \to 0$

Equation (A14) shows that for $\alpha \to 0$, $\tau e \to +\infty$, so that $\alpha \exp(\tau e)$ has a finite limit, which we call $\lambda$. From Eq. (A15)
it follows that $\alpha e$ is also finite, and we designate its limit as $\ell$. Equation (A14) shows that
\[
\lambda = \frac{1}{4}(2 + e^{-\ell})^2
\]
and Eq. (A15) shows that $\ell$ satisfies
\[
\ell(2 + e^{-\ell})^2 = 4 + 2e^{-\ell},
\]
which has a unique root. Thus
\[
\varepsilon \sim \frac{\ell}{\alpha}, \quad \tau \sim -\frac{\alpha \log \alpha}{\ell} + \frac{\alpha \log \lambda}{\ell} \quad (A16)
\]
and
\[
\eta = \frac{1 - \alpha}{1 + \tau} \sim \frac{1 - \alpha}{\frac{\alpha \log \alpha}{\ell}} = \frac{1}{1 - \frac{\alpha \log \alpha}{\ell}}
\]
so that
\[
\frac{d\eta}{d\alpha} \sim \frac{\log \alpha}{\alpha} \quad \text{for} \quad \alpha \to 0.
\]

c. Global behavior

We want to show that at maximal power
\[
\eta > \eta_{CA} = 1 - \sqrt{\alpha} \quad \text{for all} \quad \alpha,
\]
with equality only at $\alpha=0$ or 1.

We again consider the root $[\varepsilon(\alpha), \tau(\alpha)]$ of Eqs. (A14) and (A15). Because $\eta_{CA} = \frac{1-\alpha}{1+\tau}$, at maximal power, the inequality Eq. (A16) is equivalent to $\tau(\alpha) \leq \sqrt{\alpha}$, with equality only at $\alpha=0$ and 1.

For $\alpha \to 0$, $\tau(\alpha) \sim -\frac{\alpha \log \alpha}{\ell} < \alpha$, and for $\alpha \to 1$, $\tau(\alpha) \to 1$. Thus if Eq. (A17) is not fulfilled at some $\alpha'$ one has $\tau(\alpha') > \sqrt{\alpha'}$, and there exists some $\bar{\alpha}$ with
\[
\tau(\bar{\alpha}) = \sqrt{\alpha} \quad \text{for} \quad 0 < \bar{\alpha} < 1. \quad (A18)
\]

A consequence of Eqs. (A14) and (A15) is the equation
\[
e^{\eta x} = 1 + \varepsilon(\bar{\alpha}) e^{\eta x/2}.
\]

But for $\tau=\tau(\bar{\alpha})$ at $\alpha=\bar{\alpha}$, one would obtain
\[
e^{\varepsilon(\bar{\alpha}) x} = 1 + \varepsilon(\bar{\alpha}) e^{\eta x/2}, \quad \varepsilon = \varepsilon(\bar{\alpha}). \quad (A20)
\]
Recall that $e^{\eta x} \leq e^{\frac{\varepsilon(\bar{\alpha}) x}{2}}$ with equality only at $x=0$. Equation (A20) therefore implies
\[
\sqrt{\alpha} \varepsilon(\bar{\alpha}) = 0.
\]

Because $\bar{\alpha} > 0$ [see Eq. (A18)], one has $\varepsilon(\bar{\alpha})=0$, and then Eq. (A14) implies $\bar{\alpha}=1$, which is a contradiction.

[1] Private communication, Kirone Mallick, SPhT, Saclay, May 2010. Jean-Louis Sikorav (also of the CEA, Saclay) has looked into the history of this matter and found various optimization problems treated (including the appearance of the efficiency defect $\sqrt{\mathcal{T}/\mathcal{T}_0}$) in *Elements de Thermodynamique*, by Jules Moutier [29]. Moutier in turn quoted work of Him [30] (which appears to be the original derivation) and of Zeuner [31].


[17] Some readers seem to have been confused by the stochastic dynamics formulation. The use of this method does not mean that the system is continuously in all states. Rather individual systems go from one state to another and at any given moment are definitely in a particular state. With the parameters we use they will mostly sequence from level 1 to level 2 to level 3, etc., but they need not. What is continuous in this approach is the probability distribution that describes the overall progress of a collection (or the likely progress of an individual exemplar, including probabilities for departing from average behavior).


[19] We use standard notation, $\mu$ for chemical potential and $N$ for particle number.


[22] Such a step does occur in photosynthesis.


