

Stochastic Thermodynamics and Sustainable Efficiency in Work Production

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We propose a novel definition of efficiency, valid for motors in a nonequilibrium stationary state exchanging heat and possibly other resources with an arbitrary number of reservoirs. This definition, based on a rational estimation of all irreversible effects associated with power production, is adapted to the concerns of sustainable development. Under conditions of maximum power production the new efficiency has for upper bound $\frac{1}{2}$ in situations relevant for mesoscopic systems. These results imply that at maximum power bithermal, stationary motors could reach a higher Carnot efficiency than the usual cyclic motors.

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From the very beginnings of thermodynamics, efficiency in work production from heat exchanges played a basic theoretical and practical role. In the case of a cyclic motor functioning between two reservoirs at respective temperatures T_1 and T_2 ($T_1 > T_2$), the historical Carnot efficiency [1] is defined as the ratio of the work produced to the heat provided by the high temperature reservoir during a cycle, which gives a very different status to the heat sources. The same definition can be used for stationary motors, which are systems exchanging heat with reservoirs while remaining in a nonequilibrium stationary state. If the heats exchanged per unit time with reservoirs at temperatures T_1 and T_2 are \dot{Q}_1 and \dot{Q}_2 , respectively, and if the (positive) power production of the motor is $-\mathcal{P}$, its Carnot efficiency is $\gamma_C = -\mathcal{P}/\dot{Q}_1 \leq 1 - T_2/T_1$: again, the cost of rejecting the heat \dot{Q}_2 to the cold source is not taken into account directly. Our main purpose is to introduce a logical definition of efficiency which avoids this disadvantage, and can be extended to systems exchanging other resources with the reservoirs, since biological processes, for instance, usually do not involve significantly different temperatures. On the other hand, the power vanishes at the maximum value of Carnot efficiency [2–9], and it is more realistic to consider the efficiency at maximum power production: thus, we will compute the new efficiency in this situation. In order to do it, we use the formalism of stochastic thermodynamics [10–17] and the notations introduced in previous articles [15,16].

In this framework we consider a mesoscopic, discrete system s undergoing a discrete time process, for the sake of simplicity. The elementary time step τ is taken as time unit. The dynamics is defined by the stochastic matrix $\mathbf{R} \equiv (R_{xy})$, where $R_{xy} \equiv p(x, t + \tau | y, t)$ is the probability of transition $y \rightarrow x$ from y to x in time τ , y and x being two states of s . For each elementary transition $y \rightarrow x$ such that R_{yx} and R_{xy} differ from 0, we suppose that the following asymmetry relation holds:

$$R_{xy}/R_{yx} = \exp(\delta S^{\text{tot}})_{xy}, \quad (1)$$

where $(\delta S^{\text{tot}})_{xy}$ is the total entropy variation of all systems implied in the transition. Relation (1) was introduced and discussed in previous articles [15–17]. For discrete Markov dynamics, it is equivalent to the time reversal asymmetry relation found by Gallavotti and Cohen [18] and developed later by several authors [19,20]. We assume that the system s can exchange energy with several reservoirs S_ν , labeled by index $\nu = 1, 2, \dots$. Reservoir S_ν is characterized by its inverse temperature $\beta_\nu = 1/T_\nu$, the Boltzmann factor k_B being taken to be unity, and its entropy variation is $-\beta_\nu \delta q_\nu$ when it supplies heat δq_ν to the system. The system s can also receive work from a mechanical system S_0 , whose entropy does not change with time and whose inverse temperature can be defined as $\beta_0 = 0$. During an elementary transition $y \rightarrow x$, we suppose that s exchanges heat with at most one of the reservoirs, and we denote δq_{xy} the heat it receives from this reservoir. Similarly, δw_{xy} is the work received from the mechanical system and $\delta_{xy,s}$ is the entropy variation of s during transition $y \rightarrow x$. Here the symbol $\delta_{xy}f$, for a state function f of system s , represents the variation of f during the transition, whereas δw_{xy} (or any quantity denoted δX_{xy} associated to the transition) is not, in general, the variation of any function of the state of s alone [11]. So, relation (1) can be written

$$R_{xy}/R_{yx} = \exp(\delta S^{\text{tot}})_{xy} = \exp(\delta_{xy}s - \beta_{xy} \delta q_{xy}). \quad (2)$$

The classical equilibrium relation between entropy and extensive variables is satisfied for the reservoirs. On the other hand, we assume that the system s is out of equilibrium, but close to local equilibrium at the molecular scale, which, nevertheless, allows for strong disequilibrium at macroscopic and mesoscopic scales [21]. If it only exchanges energy with the reservoirs, its energy variation during transition $y \rightarrow x$ is simply $\delta_{xy}e = \delta q_{xy} + \delta w_{xy}$. When s exchanges not only energy, but also m other extensive quantities A^1, \dots, A^m with one of the reservoirs during transition $y \rightarrow x$, the entropy variation of this reservoir is

$$\delta S_{xy} = \beta_{xy} \delta E_{xy} + \sum_{i \geq 1} \chi_{xy}^i \delta A_{xy}^i, \quad (3)$$

where $\chi_{xy}^i = \partial S_{xy} / \partial A_{xy}^i$ is the intensive variable of the reservoir associated to the extensive variable A^i , and δA_{xy}^i is the variation of resource A^i in this reservoir. In the same transition, system s receives energy $-\delta E_{xy}$ and quantity $\delta_{xy} a^i = -\delta A_{xy}^i$ of resource A^i ($i = 1, \dots, m$) from the reservoir. Correspondingly, s receives the heat $\delta q_{xy} = -\beta_{xy} \delta S_{xy}$ from the reservoir and work δw_{xy} from the mechanical system. So, the energy variation of s during the transition $y \rightarrow x$ is

$$\begin{aligned} \delta_{xy} e &= -\delta E_{xy} + \delta w_{xy} \\ &= \delta_{xy} q - (\beta_{xy})^{-1} \left[\sum_{i \geq 1} \chi_{xy}^i \delta_{xy} a^i \right] + \delta w_{xy}. \end{aligned} \quad (4)$$

We now assume that system s obeys the nonequilibrium stationary probability distribution $p^0(x)$. The probability current corresponding to the elementary transition $y \rightarrow x$ is [16,17]

$$J_{xy} = R_{xy} p^0(y) - R_{yx} p^0(x), \quad (5)$$

which differs from 0 for at least one transition $y \rightarrow x$, since s is not in equilibrium. The stationary total entropy production per unit time [21,22] is

$$\mathcal{D} = \frac{1}{2} \sum_{x,y,\beta_{xy}>0} J_{xy} \delta \bar{S}_{xy} \equiv \frac{1}{2} \sum_{x,y,\beta_{xy}>0} \mathcal{D}_{xy} \geq 0 \quad (6)$$

with

$$\delta \bar{S}_{xy} = \ln \frac{R_{xy} p^0(y)}{R_{yx} p^0(x)} = \delta S_{xy} + \delta_{xy} (s + \phi). \quad (7)$$

The last expression can be interpreted as the variation $\delta \bar{S}_{xy}$ of the overall entropy in transition $y \rightarrow x$, including the variation of the information potential [16], or stochastic potential [23–25], $\phi(x) = -\ln p^0(x)$, of system s . The power produced by s can be written [16]

$$-\mathcal{P} = -\mathcal{D}_{\mathcal{W}} + \mathcal{A} \leq \mathcal{A} \quad (8)$$

where the power dissipation $\mathcal{D}_{\mathcal{W}}$ and \mathcal{A} are defined by

$$\mathcal{D}_{\mathcal{W}} = \frac{1}{2} \sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} \mathcal{D}_{xy} = \frac{1}{2} \sum_{x,y,\beta_{xy}>0} J_{xy} \frac{1}{\beta_{xy}} \delta \bar{S}_{xy} \geq 0, \quad (9)$$

$$\begin{aligned} \mathcal{A} &= \frac{1}{2} \sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} J_{xy} \left[-\sum_{i>0} \chi_{xy}^i \delta_{xy} a^i + \delta_{xy} (s + \phi) \right] \\ &\equiv \frac{1}{2} \sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} J_{xy} B_{xy}. \end{aligned} \quad (10)$$

The irreversible power dissipation $-\mathcal{D}_{\mathcal{W}}$ is the energetic equivalent of the entropy produced per unit time by the irreversible phenomena. On the other hand, \mathcal{A} may be called the reversible resources consumption per unit time:

in fact, the sign of \mathcal{A} is reversed if the currents can be reversed by changing the stochastic dynamics, contrarily to the power dissipation $-\mathcal{D}_{\mathcal{W}}$ which cannot be negative. The upper bound \mathcal{A} of $-\mathcal{P}$ is obtained if and only if $\mathcal{D}_{xy} = 0$ for any transition with $\beta_{xy} > 0$, which implies that $J_{xy} = 0$ for any transition: detailed balance is then satisfied and \mathcal{P} vanishes. Thus, in order that a system can act as a motor ($-\mathcal{P} > 0$), a necessary condition is that it is not in equilibrium: the power dissipation should be positive [16].

The previous discussion allows one to define a new efficiency γ taking the entropic dissipation into account rationally, by comparing the mechanical power actually produced $-\mathcal{P}$ to the maximum power \mathcal{A} obtained from the same resources consumption if all irreversible effects can be avoided

$$\gamma = \frac{-\mathcal{P}}{\mathcal{A}} = 1 - \frac{\mathcal{D}_{\mathcal{W}}}{\mathcal{A}} \leq 1. \quad (11)$$

Because this definition considers all the irreversible effects due to the power production from the heat sources, it seems adapted to the concerns of sustainable development and we may call γ “sustainable efficiency.” It is clear that γ cannot be expressed in terms of Carnot efficiency γ_C alone, but we will see later that the upper bounds of both efficiencies can be related.

Like γ_C , γ is maximum when detailed balance is satisfied: then power production vanishes. Thus, as mentioned in the introduction, we will consider it in the conditions of maximum power production [2–9]. From (9) and (10) it is seen that if the stochastic potential is supposed to be fixed, \mathcal{A} is a linear function of the currents J_{xy} , whereas the power dissipation $\mathcal{D}_{\mathcal{W}}$ can be approximated by a quadratic function of the currents near detailed balance conditions. These remarks suggest [16] that if maximum power production can be attained close to equilibrium, then the power dissipation is equal to the power production (a comparable result was obtained by Van den Broeck [8] when studying the maximum power of a Carnot machine in the framework of linear irreversible thermodynamics): then, the corresponding value of γ should be $\frac{1}{2}$. In fact, the constraints existing on the transition probabilities must be taken into account, but they can be expressed linearly in terms of the currents: so, they just reduce the number of independent variables in \mathcal{A} and $\mathcal{D}_{\mathcal{W}}$, which remains linear and quadratic, respectively, and the conclusion still holds: $\gamma \sim \frac{1}{2}$ at maximum power close to reversibility. We will show, however, that this conclusion can be generalized even far from reversibility under wide conditions. Clearly, it is essential to specify which parameters are varied for the maximization. Again, we assume that the stationary distribution $p^0(x)$ is fixed. Fixing $p^0(x)$ amounts to fixing the stationary average of any observable, so that the variations we are considering concern the purely kinetics characteristics of the system: this condition is meaningful for mesoscopic or macroscopic systems. Under this constraint,

relevant variable parameters are described in the section “Methods.” Then it is proved that the sustainable efficiency has the upper bound $\bar{\gamma} = 1/2$

$$\gamma \leq \bar{\gamma} = \frac{1}{2}. \quad (12)$$

As mentioned above, the upper bound $\frac{1}{2}$ can be attained close to reversibility, i.e., when the currents are small enough, a condition that can be realized even for a large temperature difference and strong disequilibrium. These results are obtained by maximizing the power $-\mathcal{P}$ under the relevant constraints. For clarity, the calculations are summarized and discussed in the section Methods. They are presented more completely in online supplementary material [26], as well as other derivations of the article. We remark that the upper bound $\bar{\gamma}$ of the sustainable efficiency can be different in a different situation, in particular, if the stationary distribution is varied. On the other hand, as discussed in the supplementary information [26], the previous conditions may be irrelevant for a very small system, such as the “three-level motor” introduced in 1959 by Scovil *et al.* [27] and recently considered by other authors [17,28,29].

In spite of its theoretical interest, the sustainable efficiency γ can be difficult to evaluate from experiments: thus, for historical and practical reasons, the Carnot efficiency γ_C remains a basic concept for stationary thermal motors. For such a motor functioning between temperatures T_1 and T_2 ($T_1 > T_2$), it is easily written

$$\gamma_C = \frac{-\mathcal{P}}{\dot{Q}_1} = 1 - \frac{T_2}{T_1} - T_2 \frac{\mathcal{D}}{\dot{Q}_1}, \quad (13)$$

where \mathcal{D} is the entropy production per unit time, given by (6). The heat \dot{Q}_1 received per unit time at temperature T_1 can also be expressed in term of the mesoscopic quantities used in the stochastic formalism, and we obtain after some algebra

$$\gamma_C = \left(1 - \frac{T_2}{T_1}\right)(1 - \Gamma) \quad (14)$$

with $\Gamma = T_2 \frac{\mathcal{D}_0 + \mathcal{D}_1 + \mathcal{D}_2}{\frac{T_1 \mathcal{D}_1 + T_2 \mathcal{D}_2}{1-\gamma} + T_2 \mathcal{D}_0 - (T_1 - T_2) \mathcal{D}_1}$.

Here, γ is the sustainable efficiency (11) and \mathcal{D}_i ($i = 0, 1, 2$) is the entropy produced during the exchanges with the reservoir of inverse temperature β_i . Focusing on the case when the system only exchanges energy with the reservoirs, it can be shown that if we know an upper bound $\bar{\gamma}$ of the sustainable efficiency, the Carnot efficiency at maximum power satisfies the inequality

$$\gamma_C \leq \frac{\bar{\gamma}(T_1 - T_2)}{\bar{\gamma}T_1 + (1 - \bar{\gamma})T_2}. \quad (15)$$

If, in particular, $\bar{\gamma} = \frac{1}{2}$ as discussed previously, inequality (15) yields a new upper bound $\bar{\gamma}_C$ of Carnot efficiency at maximum power

$$\gamma_C \leq \bar{\gamma}_C = \frac{T_1 - T_2}{T_1 + T_2}. \quad (16)$$

The upper bound $\bar{\gamma}_C$ can be reached close to reversibility conditions, with the conditions that the entropy production \mathcal{D}_0 during the exchanges with the mechanical system vanishes (which can be obtained by a convenient lubrication of the mechanisms), and that $\mathcal{D}_2/\mathcal{D}_1 \rightarrow 0$. Thus $\bar{\gamma}_C$ is an asymptotic bound: it cannot be attained exactly in realistic conditions, but it can be approached thanks to technical advances. This is also true for the classical Carnot bound and most other bounds. It should be pointed out that the upper bound (16) of Carnot efficiency is larger than so-called Curzon-Ahlborn upper bound $\bar{\gamma}_D$ for cyclic motors, suggested by Yvon [2], then studied in more detail by Curzon and Ahlborn and various authors [3–9]. In fact

$$\bar{\gamma}_D \equiv 1 - \left(\frac{T_2}{T_1}\right)^{1/2} \leq \frac{T_1 - T_2}{T_1 + T_2} \equiv \bar{\gamma}_C < 1 - \frac{T_2}{T_1}$$

$\bar{\gamma}_C$ and $\bar{\gamma}_D$ being equivalent when $T_2/T_1 \sim 1$: then $\bar{\gamma}_C \sim \bar{\gamma}_D \sim (T_1 - T_2)/(2T_1)$, as found [8,9,29] for cyclic $\bar{\gamma}_C$ motors. Inequality (16) should be compared with other results recently presented by several authors in different contexts [9,29–34]. Although the three-level motor [17,27,29] has not enough degrees of freedom to satisfy the conditions leading to the upper bound $\frac{1}{2}$ of γ , it can be analyzed completely [28]: the results show that its Carnot efficiency can indeed be significantly higher than the Curzon-Ahlborn bound γ_D .

Thus, the sustainable efficiency γ defined in this Letter proves to be useful both for ideological reasons and for theoretical purposes. First, it is appropriate to take into account the actual “price” that should be paid for power production from heat sources, because it compares this power to the irreversible power dissipation due to the information loss implied by the processes. This loss cannot be avoided, but should be minimized in order to preserve our living conditions in the best possible way. The sustainable efficiency γ is an indicator of how much this objective is fulfilled in power production: for this reason, it may be useful for new technologies aiming at sustainable development and green energy production. A remarkable property of the sustainable efficiency is that, in situations which are relevant for mesoscopic systems, its upper bound is $\frac{1}{2}$. It should be emphasized that, using the general formula (4), the concept of sustainable efficiency can also be applied for power production from other forms of energy, such as chemical energy: so, it is well adapted for biological processes which, in general, do not involve heat exchanges with reservoirs at significantly different temperatures.

Another, perhaps more fundamental, interest of sustainable efficiency is that it can be related to Carnot efficiency, universally used for thermal motors. We have shown that the properties of sustainable efficiency imply a new upper bound for Carnot efficiency at maximum power which in many cases can be written $(T_1 - T_2)/(T_1 + T_2)$. This upper bound is higher than the Curzon-Ahlborn bound derived for cyclic motors. This result suggests that stationary motors can reach higher efficiency than the macroscopic engines usually designed in engineering.

Methods.—We assume that the user can control the ratio $[R_{xy}p_0(y)]/[R_{yx}p_0(x)]$, related to the exchanges with the reservoirs by (1), and we set

$$\begin{aligned} R_{xy}p^0(y) &= C_{xy} \exp(\lambda_{xy}), \\ R_{yx}p^0(x) &= C_{xy} \exp(-\lambda_{xy}), \end{aligned} \quad (17)$$

with $C_{xy} = C_{yx}$. The condition $\lambda_{xy} = 0$ for all x, y corresponds to detailed balance. We suppose that for each non-ordered pair (x, y) with $x \neq y$ the λ_{xy} can be varied independently of the others without changing C_{xy} nor the stationary distribution $p^0(x)$. As remarked above, fixing $p^0(x)$ means that the observable properties of the system are kept constant. It should be pointed out that the previous constraints on λ_{xy} may be irrelevant for very small systems, which do not have enough degrees of freedom: they are further discussed in the supplementary information [26]. With these assumptions the quantities B_{xy} defined by (10) remain constant when the λ_{xy} are varied and by (8) we have

$$-\mathcal{P} = \sum_{(x,y), \beta_{xy} \neq 0} \frac{2C_{xy}}{\beta_{xy}} \sinh(\lambda_{xy})(-2\lambda_{xy} + B_{xy}) \quad (18)$$

where the sum runs on distinct pairs (x, y) . We now maximize $-\mathcal{P}$ with respect to the λ_{xy} ($x \neq y$) when the C_{xy} ($x \neq y$) are kept constant, but the C_{xx} are varied in order that the stationary distribution p^0 remains unchanged. In the present situation, the only constraints on the λ_{xy} are

$$\sum_{y, y \neq x, \beta_{xy} \neq 0} C_{xy} \sinh(\lambda_{xy}) = 0 \quad \text{for all } x. \quad (19)$$

which can be realized if the number of degrees of freedom is sufficient. Maximizing $-\mathcal{P}$ under these constraints allows one to conclude (see supplementary information [26]) that

$$\gamma \leq \bar{\gamma} = \frac{1}{2}, \quad (20)$$

the maximum $\frac{1}{2}$ being attained close to reversibility conditions. Thus this upper bound, suggested by a coarse reasoning close to reversibility, remains valid in all conditions in the situation considered here.

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