Efficiency of autonomous soft nano-machines at maximum power

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We consider nano-sized artificial or biological machines working in steady state enforced by imposing non-equilibrium concentrations of solutes or by applying external forces, torques or electric fields. For unicyclic and strongly coupled multicyclic machines, efficiency at maximum power is not bounded by the linear response value 1/2. For strong driving, it can even approach the thermodynamic limit 1. Quite generally, such machines fall in three different classes characterized, respectively, as "strong and efficient", "strong and inefficient", and "balanced". For weakly coupled multicyclic machines, efficiency at maximum power has lost any universality even in the linear response regime.

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Introduction.– Molecular motors [1] as well as the recently developed artificial nano-machines inspired by them [2, 3] operate in an aqueous solution of constant temperature. In contrast to heat engines limited by Carnot's law, thermodynamics constrains their efficiency by 1. Like for heat engines, however, operating at the upper bound comes at the price of zero power since it requires infinitely slow driving. A practically more relevant question then is about efficiency at maximum power (EMP). For heat engines this problem has a few decades of history [4] where the full picture exhibiting some universality close to the linear response regime has just emerged [5–8].

For machines working under isothermal conditions, which provide arguably a much more realistic route for a successful implementation on the nano to micro scale than dealing with heat baths of different temperature, efficiency has been discussed mostly in the context of molecular motors [9–16]. The issue of EMP, however, has received much less attention so far. For molecular motors, a case study has shown values well above the linear response result 1/2 [17]. On the other hand, this value has recently been derived as a universal bound even beyond the linear response regime under conditions claimed to be relevant for mesoscopic machines with a sufficiently large number of internal states [18].

In this paper, we address the issue of EMP for autonomous soft nano-machines using a quite general approach requiring minimal assumptions. "Autonomous" stands for steady state conditions as typical for molecular motors and envisaged for artificial machines. At present, the latter mostly still need a modulation of external parameters for driving them through a cycle as investigated theoretically in Refs. [19–21]. "Soft" is short for working in an aqueous environment which will require some flexibility in the molecule(s) allowing for conformational changes to operate as a machine. By implementing thermodynamic consistency from the very beginning and by separating universal from system specific quantities, the result will be applicable to a large class of machines which turn out to fall into three regimes. In particular, we find that EMP is not bounded by 1/2. It can rather approach 1, which, however, requires some care in the design of the machine as well as a sufficiently large parameter space available for the maximization of power. In fact, for a severly restricted parameter space, EMP looses any universality.

Model.– We model the kinetics of the nano-machine as a Markov process in a heat bath of constant temperature [22–24]. At any time, the machine is in one of several possible states. A transition between state m and state n happens with a rate k_{mn}. Typically, in a transition, some (external) quantities d^{α}_{mn} later to be associated with the function of the machine change. Examples for such quantities could be (i) position along a linear track, (ii) rotation angle, (iii) number of consumed (or, if negative, produced) molecules of a certain species, or (iv) number of charges transported against an external field. For each such quantity, there exists a "conjugate" external field h^{α} with the property that the product $h^{\alpha}d^{\alpha}_{mn}$ is a (free) energy. Specifically, for the above cases, the conjugate field is (i) force f, (ii) torque N, and (iii) deviation $\Delta\mu^i$ of chemical potential of species i from its equilibrium value and (iv) potential difference $\Delta\phi$.

For the object to operate as a useful machine, at least two of the fields, an input field $h^{\rm in}$ and an output field $h^{\rm out}$, have to be set to non-zero values. For a rotary molecular motor like the F1-ATPase (see, e.g. [25, 26] and Refs. therein), one has to provide ATP at higher than equilibrium chemical potential, i.e., $h^{\rm in} = \Delta\mu^{\rm ATP}$. Hydrolysis of ATP can then be used to move against an external torque, i.e., $h^{\rm out} = N$. In contrast to macroscopic machines, the role of input and output is not unique but can be interchanged depending on the intended "purpose" of the machine. The ATPase can deliver mechanical work if fed with an excess of ATP molecules but can also synthesize ATP if pulled by an external torque in the opposite direction.

The external fields will affect the transition rates. Thermodynamic consistency requires a local detail balance (LDB) condition of the form

$$\frac{k_{mn}(h^{\rm in},h^{\rm out})}{k_{nm}(h^{\rm in},h^{\rm out})}=\left(\frac{k_{mn}}{k_{nm}}\right)_{\rm eq}\exp(h^{\rm in}d^{\rm in}_{mn}+h^{\rm out}d^{\rm out}_{mn}) \quad (1)$$

where $(k_{mn}/k_{nm})_{\rm eq}$ refers to the equilibrium ratio where all external fields are set to zero. Here, and throughout the paper, we measure energies in thermal units ($k_BT=1$). For constant external fields, $h^{\rm in}$ and $h^{\rm out}$, the machine reaches a steady state, i.e., will operate autonomously.

Unicyclic machines.– We first discuss unicyclic machines, for which the $m=1,...,M$ possible states are aligned in one cycle such that each state has two neighboring states. If the machine steps through the complete cycle in forward direction, it has consumed the work or (free) energy $w_{\rm in}=\sum_{m=1}^M h^{\rm in}d^{\rm in}_{m,m+1}$ and delivered the output $w_{\rm out}\equiv-\sum_{m=1}^N h^{\rm out}d^{\rm out}_{m,m+1}$ where $d^{\rm in}_{M,M+1}\equiv d^{\rm in}_{M,1}$. Likewise, had it stepped through the complete cycle in backward direction, it would have released $-w_{\rm in}$ to the input reservoir and consumed $-w_{\rm out}$ from the output reservoir. In order to work as a machine in the conceived sense, the mean time τ^+ it takes to complete the cycle in forward direction has to be smaller than the mean time τ^- for completing the cycle backwards. Both times can be expressed diagrammatically in terms of the transition rates but the explicit expressions will not be needed here [23]. The key point is that the ratio τ^+/τ^- is given by the ratio between the product of all backward rates and the product of all forward rates. With the local detail balance condition, eq. (1), and the identifications of input and output work just given, this ratio becomes

$$\tau^+/\tau^-=e^{w_{\rm out}-w_{\rm in}}. \quad (2)$$

Hence the power (or, more generally, the rate of "yield" if the output are chemical products) delivered by the machine in the steady state is

$$P_{\rm out}=w_{\rm out}(1/\tau^+-1/\tau^-)=w_{\rm out}[1-e^{w_{\rm out}-w_{\rm in}}]/\tau^+. \quad (3)$$

Likewise, the power used by the motor becomes

$$P_{\rm in}=w_{\rm in}(1/\tau^+-1/\tau^-)=w_{\rm in}[1-e^{w_{\rm out}-w_{\rm in}}]/\tau^+. \quad (4)$$

These transparent expressions for the power where the specific characteristics of the motor enter through the single quantity τ^+ constitute our first main result. In the regime $0<w_{\rm out}<w_{\rm in}$, the machine will work as intended. Its efficiency is simply given by $\eta\equiv P_{\rm out}/P_{\rm in}=w_{\rm out}/w_{\rm in}$ and is obviously bounded by thermodynamics through $0<\eta<1$. For $w_{\rm out}=w_{\rm in}$, the machine has optimal efficiency $\eta=1$ but does not deliver any power since it then cycles as often in forward as in backward direction.

The concept of EMP requires to identify the admissible variational parameters. Rather than starting with an arbitrary parameter set $\{\lambda_i\}$, the form of eq. (3) strongly suggest to focus first on the following three choices: (i) $w_{\rm out}$, (ii) $w_{\rm in}$, and (iii) $w_{\rm out}$ and $w_{\rm in}$. For each case, the crucial question becomes how the forward cycle time τ^+ depends on input and output. We will first assume that

$$x_{\rm out}\equiv-d\ln\tau^+/dw_{\rm out} \quad \text{and} \quad x_{\rm in}\equiv-d\ln\tau^+/dw_{\rm in}$$

are constants, i.e., that τ^+ depends mono-exponentially (with either sign) on input and output work as illustrated below with a specific example and later discuss the general case.

Maximization with respect to output $w_{\rm out}$.– For given input $w_{\rm in}$, the condition $dP_{\rm out}/dw_{\rm out}=0$ leads to the implicit relation

$$w_{\rm in}=w^*_{\rm out}+\ln\left(1+\frac{w^*_{\rm out}}{1+x_{\rm out}w^*_{\rm out}}\right) \quad (5)$$

for the optimal output $w^*_{\rm out}$ at fixed input $w_{\rm in}$. Consequently, we obtain for EMP under these conditions

$$\eta^*_{\rm out}\equiv\frac{w^*_{\rm out}}{w_{\rm in}}=\left[1+\frac{1}{w^*_{\rm out}}\ln\left(1+\frac{w^*_{\rm out}}{1+x_{\rm out}w^*_{\rm out}}\right)\right]^{-1}. \quad (6)$$

Two limit cases can be discussed analytically.

First, for small deviations from thermodynamic equilibrium, $w_{\rm in}\ll1$, expanding (5) and (6) leads to $w^*_{\rm out}\approx w_{\rm in}/2$ and to an efficiency at maximum power given by

$$\eta^*_{\rm out}=1/2+(x_{\rm out}+1/2)w_{\rm in}/8+O(w^2_{\rm in}).$$

For $x_{\rm out}>-1/2$, EMP increases if the machine operates beyond the linear response regime thus beating the bound 1/2 found in Ref. [18] under different conditions.

Second, for large $w_{\rm in}\gg1$, two cases must be distinguished. If $x_{\rm out}>0$, EMP, $\eta^*_{\rm out}\approx1-[\ln(1+1/x_{\rm out})]/w_{\rm in}$, approaches the thermodynamic upper bound 1. If $x_{\rm out}<0$, however, $w_{\rm out}\to1/|x_{\rm out}|$ for $w_{\rm in}\to\infty$ which implies $\eta^*_{\rm out}\approx1/|x_{\rm out}w_{\rm in}|$. In this case, efficiency at optimal power approaches 0 with increasing input since maximum power is reached for a finite $w^*_{\rm out}$.

Maximization with respect to input $w_{\rm in}$.– We now assume that the output $w_{\rm out}$ is given and search for the optimal input $w^*_{\rm in}(w_{\rm out})>w_{\rm out}$ maximizing the power. Two cases must be distinguished. (i) For $x_{\rm in}>0$, the power grows unbounded as $w_{\rm in}$ increases and hence EMP vanishes for all $w_{\rm out}$. (ii) For $x_{\rm in}<0$, the optimal input reads $w^*_{\rm in}=w_{\rm out}+\ln(1+1/|x_{\rm in}|)$ implying the EMP

$$\eta^*_{\rm in}=\frac{w_{\rm out}}{w^*_{\rm in}}=\left[1+\frac{1}{w_{\rm out}}\ln\left(1+1/|x_{\rm in}|\right)\right]^{-1}.$$

For $w_{\rm out}\ll1$, the efficiency $\eta^*_{\rm in}\approx w_{\rm out}/\ln\left(1+1/|x_{\rm in}|\right)$ differs from the linear response result derived above for output maximization since the optimal $w^*_{\rm in}$ is always a finite distance from $w_{\rm out}$ and hence no longer within

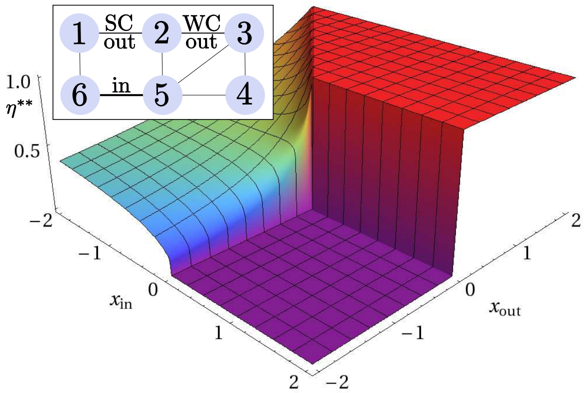

FIG. 1: Efficiency at maximum power $\eta^{**}(x_{\rm in}, x_{\rm out})$. Inset: Example of a multicyclic machine with 6 states, 6 cycles and the input transition (56). If (12) is the output transition (or, equivalently, (56) or (12)) the machine is strongly coupled (SC). For (23) as output transition, it is weakly coupled (WC). In the latter case, C_1 consists of cycles (123456) and (12356), $C_2 = \{(2345), (235)\}$, $C_3 = \{(1256)\}$, and $C_4 = \{(345)\}$.

the linear response regime. For $w_{\rm out} \gg 1$, one gets the asymptotics $\eta^*_{\rm in} \approx 1 - [\ln(1 + 1/|x_{\rm in}|)]w_{\rm out}$.

Maximization with respect to input and output.– This case, solved by $w^{**}_{\rm out}$ and $w^{**}_{\rm in}$, leads to three regimes for EMP, $\eta^{**} \equiv w^{**}_{\rm in}/w^{**}_{\rm out}$, shown in Fig. 1.

(i) For $x_{\rm out} > \max\{-x_{\rm in}, 0\}$, the power at optimal output increases exponentially with growing input. In this case, one has $w^{**}_{\rm in} \to \infty$ and $w^{**}_{\rm out} \to \infty$ with the finite difference $w^{**}_{\rm in} - w^{**}_{\rm out} \approx \ln(1 + 1/x_{\rm out})$ and hence $\eta^{**} = 1$. Such machines could be called "strong and efficient".

(ii) For $x_{\rm out} < 0$ and $x_{\rm in} > 0$, the power still increases with increasing input, and, hence $w^{**}_{\rm in} \to \infty$. The optimal output, however, in this limit remains finite at $w^{**}_{\rm out} = 1/|x_{\rm out}|$ which implies $\eta^{**} = 0$ for these "strong but inefficient" machines.

(iii) Finally, for $x_{\rm in} < \min\{-x_{\rm out}, 0\}$, the power peaks at a genuine maximum for $w^{**}_{\rm out} = 1/[-(x_{\rm in} + x_{\rm out})]$ and $w^{**}_{\rm in} = w^{**}_{\rm out} + \ln(1 + 1/|x_{\rm in}|)$ leading to

$$\eta^{**} = w^{**}_{\rm out}/w^{**}_{\rm in} = 1/\left[1 + |x_{\rm out} + x_{\rm in}| \ln(1 + 1/|x_{\rm in}|)\right].$$

Such machines could be called "balanced".

Example.– For a simple but still instructive specific example, we consider a one-state molecular motor for which hydrolysis of ATP leads to a forward step of length d along a linear track in the direction of an applied force f with rate $k^+ = 1/\tau^+ = k_0 \exp[\Delta\mu^{\rm ATP} + f\theta^+ d]$, where k_0 is the equilibrium rate. A backward step with rate and $k^- = 1/\tau^- = k_0 \exp[\Delta\mu^{\rm ADP} + \Delta\mu^{\rm P_i} - f\theta^- d]$, involves synthesis of ATP from ADP and $\rm P_i$. The load sharing factors θ^+ and θ^- with $\theta^+ + \theta^- = 1$ guaranteeing the LDB condition eq. (1) are related to the distance of the activation barrier in forward and backward direction, respectively [13]. The molecular architecture thus determines the sign of $x_{\rm out} = \partial_{w_{\rm out}} \ln k^+ = -\theta^+$ since $w_{\rm out} = -fd$.

The input $w_{\rm in} = \Delta\mu^{\rm ATP} - \Delta\mu^{\rm ADP} - \Delta\mu^{\rm P_i}$ can be changed in a variety of ways. The most obvious one, increasing $\Delta\mu^{\rm ATP}$, leads to $x_{\rm in} = 1$, whereas decreasing $\Delta\mu^{\rm ADP}$ leads to $x_{\rm in} = 0$. If both chemical potentials are changed simultaneously, any value for $x_{\rm in}$ can be reached, in principle. Thus, depending on the molecular architecture, in the EMP diagram, Fig. 1, this motor can either cross from balanced to strong and efficient (for $\theta^+ < 0$) or from balanced to strong and inefficient (for $\theta^+ > 0$) as the way the input power is delivered is changed.

Arbitrary unicyclic machines.– So far, the complete analysis benefitted from using two simplifying assumptions which will not always apply. First, we assumed the dependence of the forward cycle time τ^+ to be mono-exponential in both input and output. While each individual rate will typically depend mono-exponentially on $w_{\rm out}$ and $w_{\rm in}$, especially for intermediate values of $w_{\rm out}$ and $w_{\rm in}$ several rates may contribute comparably to τ^+. Then $x_{\rm out}$ becomes a function $x_{\rm out}(w_{\rm out}, w_{\rm in})$ where, e.g., for maximization with respect to output, $w_{\rm out}$ has to be determined self-consistently from eq. (5).

Correspondingly, in the analysis of the limiting values, the quantities $x_{\rm out}$ and $x_{\rm in}$ have then to replaced by their respective asymptotic limits. Generically, in a unicyclic machine consisting of several states, increasing the input will speed up one (or several) forward transitions. If at least one forward transition is not affected by the increasing input, it will act as a bottleneck for the whole cycle and, hence, $x_{\rm in} \approx 0$ for large $w_{\rm in}$. On the other hand, increasing the load, i.e., increasing $w_{\rm out}$ will typically slow down at least one forward transition now becoming the bottleneck and consequently $x_{\rm out} < 0$. Thus, generically, according to the EMP diagram, Fig. 1, such machines at maximum power will approach zero efficiency. In practice, increasing $w_{\rm in}$ will not lead to a significantly larger power since τ^+ will approach a limit value for large $w_{\rm in}$. At any finite $w_{\rm in}$, one may thus still reach a reasonable efficiency as given by eqs. (5) and (6) and miss maximum power by only a small amount.

The second major restriction so far was to focus on $w_{\rm in}$ and $w_{\rm out}$ as control parameters. For full generality, one should consider a set of arbitrary parameters $\{\lambda_i\}$. If the admissible range of these parameters spans the whole sector $0 < w_{\rm out} < w_{\rm in} < \infty$ (which will require at least two control parameters) then we are back at the case just discussed. On the other hand, if one has only one control parameter, or if only a limited part of the above sector can be coverered, EMP will become a strongly non-universal concept and its specific value will depend on the functional dependence of $w_{\rm out}, w_{\rm in}$ and τ^+ on $\{\lambda_i\}$.

Multicyclic machines.– In general, a nano-machine will contain several cycles. We will assume that the input affects only one transition, the "input transition" and that there is only one "output transition" which may or may not be the same as the input transition. Two generic cases, strong coupling (SC) and weak coupling (WC) should then be distinguished, see inset of Fig. 1.

(SC): If the input and the output transition are identical, or if there exists a direct connection between the two without any intermediate bifurcation, any cycle containing the input transition will also contain the output transition. For such strongly coupled machines exactly the same formalism as for unicyclic machines applies with the only caveat that τ^+ appearing there is now given by $1/\tau^+ \equiv \sum_i 1/\tau_i^+$ where the sum runs over all cycles that include input and output transition and the τ_i^+ are the corresponding forward cycle times. Thus, such strongly coupled machines obey the same relations for efficiency and EMP as discussed above for unicyclic machines. Note, however, that as the explicit expressions would show the τ_i^+ are affected by the rates contributing to the cycles not containing the input and output transition.

(WC): If the strong-coupling condition is not fulfilled, each cycle of the machine falls into one of four disjoint subsets C_1, C_2, C_3, C_4 containing, respectively, input and output transition, only the output transition, only the input transition, and neither one. Since only C_1 and C_2 contribute to the output, the power is given by

$$\begin{aligned} P_{\rm out} &= w_{\rm out}[(1/\tau_1^+ - 1/\tau_1^-) + (1/\tau_2^+ - 1/\tau_2^-)] \\ &= w_{\rm out}[(1-e^{w_{\rm out}-w_{\rm in}})/\tau_1^+ - (e^{w_{\rm out}}-1)/\tau_2^+], \end{aligned}$$

where $\tau_{1,2}^\pm \equiv \sum_{i\in C_{1,2}} 1/\tau_i^\pm$. For the second step, we have adapted the local detail balance constraint, eq. (1), and its consequence eq. (2) keeping in mind that the corresponding ratio for the C_2 cycles involves only the output transition. In fact, the presence of these cycle necessarily decreases the power. Moreover, stall conditions ($P_{\rm out} = 0$) are now reached at a maximum value $\widehat{w}_{\rm out}$ strictly smaller than $w_{\rm in}$. For the input power, one obtains similarly $P_{\rm in} = w_{\rm in}[(1-e^{w_{\rm out}-w_{\rm in}})/\tau_1^+ + (1-e^{-w_{\rm in}})/\tau_3^+]$, where $\tau_3^+ \equiv \sum_{i\in C_3} 1/\tau_i^+$. These expressions show that both, efficiency $\eta \equiv P_{\rm out}/P_{\rm in}$ and EMP $\eta^*_{\rm out}$, are even less universal than for strongly coupled machines. For the latter quantity, this fact becomes obvious by looking at the linear response regime. Expanding the above expressions for small $0 < w_{\rm out} < w_{\rm in} \ll 1$, one finds

$$\eta^*_{\rm out} = \frac{1/2}{1 + 2(\tau_1^+/\tau_2^+ + \tau_1^+/\tau_3^+ + \tau_1^{+2}/\tau_2^+\tau_3^+)} + O(w_{\rm in}),$$

with all cycle times evaluated in equilibrium. Thus, $\eta^*_{\rm out}$ is strictly smaller than $1/2$. Still, one should not conclude from this result that $\eta^*_{\rm out}$ necessarily remains bounded by $1/2$ with increasing $w_{\rm in}$.

Concluding perspective.– For soft machines working under isothermal steady state conditions, we have investigated EMP in the appropriate parameter space by varying output power, input power and both. For the first two cases, EMP is given by a one parameter function whereas in the third case machines universally fall into three classes. Our results hold for both unicyclic machines and strongly coupled multicyclic ones. Weakly coupled multicyclic machines are less efficient and their EMP is less universal. Our analytical results and the suggested classification provide not only a transparent theoretical framework but, in a longer term perspective, should also be helpful for designing efficient machines. From a theoretical point of view, as a next step, machines operating under periodically modulated fields should be analyzed similarly for EMP since the extant artificial machines typically still require such conditions.

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