OPTIMIZATION CRITERIA AND EFFICIENCIES OF ISOTHERMAL MOLECULAR MACHINES

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ABSTRACT

In this work we present the efficiency performance for an isothermal molecular machine under maximum conditions for a figure of merit representing a compromise between useful energy and lost energy (the Ω criterion). This represents the best compromise between energy benefits and losses for a specific job and neither an explicit evaluation of entropies nor the consideration of environmental parameters are required. Such a regime has been invoked as optimum not only in macroscopic heat engines but also in some molecular motors. We compared our results with previous ones for the same model obtained by Van den Broeck, *et al.* PRL 108, 210602 (2012), where the efficiency is considered at maximum power conditions. The motion of a molecule, is very different from a macroscopic heat engine; to understand how molecular motors operate requires mechanical concepts such as force, elasticity, damping and work but it is necessary to consider special events such as highly damped and diffusive effects. In this work we studied a protein machine managed by a chemical force, where two chemical reaction rate theories were considered: the Eyring rate theory, where the reaction is assumed to correspond to the break-down of a single quantum-mechanical vibration of the protein, and the Kramers rate theory, where a global protein conformational changes, and the more physically realistic model is this rate theory. Then, we investigated the asymptotic behaviour of efficiencies at small global reaction chemical potential gap (ε), expanding them up to the third-order term of ε. This points to a number of revealing observations: the three first expansion terms are the prediction of linear irreversible thermodynamics of efficiency for the same optimization criteria under certain conditions. We also derive upper and lower bounds for the efficiency of an isothermal molecular machine operating at Omega function. The upper bound is reached when the activated state is close to the fuelling or reactant state (Eyring-like), while the lower bound is reached when the activated state is close to the product state (Kramers-like).

INTRODUCTION

Molecular motors [1] are biological molecular machines being the essential agents of movement in living organisms. In general terms, a motor may be defined as a device that consumes energy in one form and converts it into motion or mechanical work; for example, motor proteins are molecular machines that convert the chemical energy derived from the hydrolysis of ATP into a mechanical work used to power cellular motility [2; 3]. Molecular motors are an assembly of mechanical parts-springs, levers, swivels, and latches- that move in a coordinate fashion and as ATP is hydrolized a directed motion is produced. However, proteins and other biomolecules are so tiny that the inertial forces are comparatively small and can usually be ignored, whereas the viscous forces from the surrounding fluid, at constant temperature, are usually large and dominate the mechanical responses. In contrast with heat engines limited by Carnot's theorem [4], the upper value of thermodynamic efficiency of isothermal motors is 1. Similar to heat engines, however, operating at the upper bound comes at the price of zero power, since it requires infinitely slow driving. Searching the efficiency at maximum power (EMP) is most interesting [5; 6].

For heat engines this issue has been profoundly studied since the publication of the Curzon and Ahlborn paper [7], opened the perspective of establishing more real theoretical bounds for a real heat engine. The Curzon and Ahlborn paper gave rise to the birth and development of finite-time thermodynamics (FTT), a branch of thermodynamics devoted to extend classical reversible thermodynamics to include more realistic finite-time and finite-size (irreversible) processes [8; 9; 10; 11; 12; 13; 14; 15; 16].

The main goal of FTT is to ascertain the best operating mode of heat devices with finite-time cycles. Basically, finite-rate constraints arising from several sources of irreversibility are modelled and then a suitable function is optimized with respect to the involved parameters. In principle, one has the freedom to choose such a function. This has lead to the proposal of a great variety of criteria based on thermodynamic, economic, compromise, and sustainability considerations [17; 18; 19] in this context the so-called Ω criterion was presented by [20] and this represents a compromise between energy benefits and losses for a specific job. It is easy to apply in any energy converter (isothermal or non-isothermal) because it does not require the explicit evaluation of the entropy generation and it is independent of environmental parameters. It follows then that we present this criterion applied to isothermal molecular machine in this present work.

Already the efficiency of molecular motors has been discussed [21; 22; 23; 24], the problem of EMP or under other optimum condition, has received much less attention for machines working under isothermal conditions [25; 26]. For molecular motors, a case study has shown values well above the linear re-

sponse result $1/2$ [27]

In this work we address the issue of efficiency under Omega criterion for a model of molecular motor, the work is organized in the following way, in the section 1 the theoretical model of a molecular motor is presented, in section 2 we present the efficiencies of molecular motor in optimum conditions (EMP and Omega), finally en section 3 some discussions are enunciated.

1 MODEL FOR A MOLECULAR MOTOR

We first consider a generic model for a molecular motor, presented in [5], namely, a two-state machine operating along a one-dimensional reaction coordinate, see Fig. 1. The states correspond to two minima of an appropriate free energy landscape. While a physical energy landscape is expected to be very complicated and high dimensional, the thermally activated transitions between the two states will typically follow a preferred pathway that connects these states via the lowest lying saddle point, the so-called activated state. One can project the motion on this pathway and introduce a one-dimensional reaction coordinate x with corresponding effective free energy potential $G(x)$. The two rest states of the machine, that is, the minima in the absence of external forces, correspond to, say, locations

$$x = 0 \text{ and } x = L$$

The activated state lies at an intermediate position

$$x_a = \lambda L \ni \lambda \in [0,1]$$

In the unperturbed phase there are no net transitions, and the states 1 and 2 have the same baseline potential value,

$$G_0(x=0) = G_0(x=L) = 0$$

The potential has a maximum

$$G(x=\lambda L) = G_a$$

at the activated state, whose value is typically much larger than the thermal energy $\beta^{-1} = k_B T$(T being the temperature and k_B the Boltzmann constant).

In this rest state, the rates, when potential is minimum, k_0^{+1} from 1 to 2 and k_0^{-1} from 2 to 1, are equal and given by

$$k_0^{+1} = k_0^{-1} \equiv k_0 = \kappa exp(-\beta G_a),$$

where the pre-exponential factor κ is considered constant.

In the presence of external forces, states 1 and 2 can be identified as fuel and product states, respectively. To transform fuel into product, the machine is subject to a driving force F_1 which allows it to overcome an opposing but weaker loading force $-F_2$, with $F_2 \leq F_1$. These forces can be of various physical origins, including chemical, electrical or mechanical. The combined effect of driving and loading is a tilding of the potential towards the product state 2, that is,

$$G(x) = G_0(x) - Fx$$

with $F = F_1 - F_2 \geq 0$.

In a transition from state 1 to state 2, a input energy $\varepsilon_1 =_2 L$ is transformed into a output energy $\varepsilon_2 = \beta F_2 L$.

The efficiency of this conversion of energy is given by

$$\eta = \frac{\varepsilon_2}{\varepsilon_1} = \frac{F_2}{F_1}. \qquad (1)$$

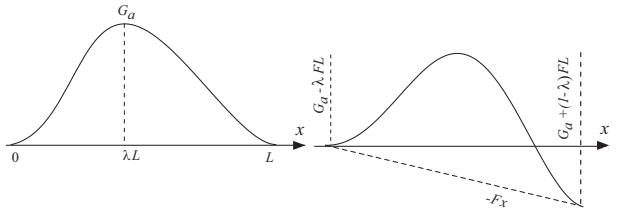

Figure 1. Schematic free energy potential $U_0(x)$ for a two-state molecular engine described by a reaction coordinate x under the net load force $F = F_1 - F_2 \geq 0$.

Equation (1) indicates how efficiently the energy is converted in the system in the process of doing work against the load. The maximum value of efficiency is $\eta = 1$, this is reached when the loading force F_2 approaches to the driving force F_1, and the transition from 1 to 2 is taken in infinity time, that is, in a reversible manner and therefore with zero power.

1.1 Rate Theories of Chemical Reactions

The Eyring and Kramers rate theories [1] represent two extreme views of the mechanism of global conformational changes of proteins. In the **Eyring** model, the transition state is like the initial state. A sudden, local chemical change creates a highly strained protein that then relaxes into a new stable conformation. The activated state is very close to the fuel state 1; *i.e.*, λ is close to zero. The perturbation $-Fx$ barely affects the height of the activation barrier that needs to be crossed to go from state 1 to 2. The rate also remains essentially unaffected, $k^+ \approx k_0$. However, a maximum barrier increase of FL occurs for the backward transition, resulting in a rate $k^- \approx k_0 exp(-\beta FL)$ (assuming $FL << G_a$). In the **Kramers** view, a protein undergoes a global diffusion into the activated state. When a sufficiently large conformational change has been achieved, the protein converts to the final state, at this scenario scenario $\lambda \approx 1$, $k_0^+ exp(\beta FL)$, while $k^- \approx k_0$ remains essentially unaffected. For a barrier at $x_a = \lambda L$, one has $k^+ = k_0 exp(\lambda\varepsilon)$ and $k^- = k_0 exp[-(1-\lambda)\varepsilon]$, where $\varepsilon = \varepsilon_1 - \varepsilon_2 = \beta FL$ is the energy loss. βF is a proper thermodynamics force that appears in the entropy production and is thus a measure of the distance from equilibrium.

2 MAXIMUM POWER AND OMEGA CRITERION

2.1 Maximum power output

With the explicit expressions for the rates, it is possible to write the output power P, given by the output energy ε_2 multiplied by its net rate of productions, that is, $P = k\varepsilon_2$, with $k = k^+ - k^- = k(\varepsilon) = k_0[e^{\lambda\varepsilon} - e^{-(1-\lambda)\varepsilon}]$. To specify the condition of maximum power it is necessary to solve next equation

$$\frac{\partial P}{\partial \varepsilon_2} = 0,$$

which yields the solution

$$\varepsilon_2 = \frac{1 - e^{-\varepsilon}}{\lambda(1 - e^{-\varepsilon}) + e^{-\varepsilon}}. \qquad (2)$$

Substituting this expression in Eq.(1), it is possible to get the EMP, given by,

$$\eta_{MP} = \frac{e^{\varepsilon} - 1}{(\lambda\varepsilon + 1)(e^{\varepsilon} - 1) + \varepsilon} \tag{3}$$

or,

$$\eta_{MP} = \frac{1}{2} + \frac{1 - 2\lambda}{8}\varepsilon + \frac{1 - 12\lambda + 12\lambda^2}{96}\varepsilon^2 + O(\varepsilon^3) \tag{4}$$

written in an expansion of Taylor series. In the next subsection we present the same procedure but under Omega criterion.

2.2 Omega function

Now we present the analysis of efficiency for the model of isothermal molecular engine, under de so-called Ω function, which represents a compromise between energy benefits and losses for a specific job; it is easy to apply in any energy converter, and it is independent on environmental parameters. The details of this optimization criterion is presented in [20].

For isothermal engine the Ω criterion reads as

$$\Omega = \frac{2\eta - 1}{\eta} P. \tag{5}$$

To find the efficiency under condition of maximum Omega we get,

$$\frac{d\Omega}{d\varepsilon_2} = 0, \tag{6}$$

this equation is solved where,

$$\varepsilon_2 = \frac{(e^{\varepsilon} - 1)(2 + \lambda\varepsilon) + \varepsilon}{\lambda(e^{\varepsilon} - 1) + 1}. \tag{7}$$

Substituting this expression in the expression for the efficiency eq. (1), we get the efficiency under Omega criterion condition, that is,

$$\eta_{\Omega} = \frac{\varepsilon_2}{\varepsilon_2 + \varepsilon} = \frac{(2 + \lambda\varepsilon)(e^{\varepsilon} - 1) + \varepsilon}{2[(1 + \lambda\varepsilon)(e^{\varepsilon} - 1) + \varepsilon]}. \tag{8}$$

Expanding this in a Taylor series around zero we get,

$$\eta_{\Omega} = \frac{3}{4} + \frac{1}{16}(1 - 2\lambda)\varepsilon + \frac{1}{192}(1 - 12\lambda + 12\lambda^2)(\varepsilon)^2 + O((\varepsilon)^3) \tag{9}$$

3 CONCLUSIONS

In this work we presented the efficiency of a model of molecular motor, under maximum power output conditions previously found by Broeck *et al*., We also presented a new result, the efficiency under Omega criterion, we can note that the behaviour observed for thermal heat engines, working between two heat reservoir [28], is similar for this isothermal model presented here. It could be interesting to check with experimental verification if molecular motors works closer to EMP or any other regime, like Omega criterion.

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