Thermodynamic cost of external control

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Abstract

Artificial molecular machines are often driven by the periodic variation of an external parameter. This external control exerts work on the system of which a part can be extracted as output if the system runs against an applied load. Usually, the thermodynamic cost of the process that generates the external control is ignored. Here, we derive a refined second law for such small machines that include this cost, which is, for example, generated by free energy consumption of a chemical reaction that modifies the energy landscape for such a machine. In the limit of irreversible control, this refined second law becomes the standard one. Beyond this ideal limiting case, our analysis shows that due to a new entropic term unexpected regimes can occur: the control work can be smaller than the extracted work and the work required to generate the control can be smaller than this control work. Our general inequalities are illustrated by a paradigmatic three-state system.

1. Introduction

 Thermodynamic systems driven by external periodic control that reach a periodic steady state constitute a main class of systems out of equilibrium. Such systems are also known as ‘stochastic pumps’ [1] or ‘pulsating ratchets’ [2] in the context of Brownian motors. For these systems an external protocol for the periodic variation of energies and energy barriers can lead to a net current. Recent theoretical results for such systems include no-pumping theorems [3–7], a general theoretical framework for systems with periodic temperature (and other parameters) variations [8, 9], a mapping between periodic steady states and nonequilibrium steady states [10], the relation between cost and precision in Brownian clocks [11], the analysis of stochastic protocols [11, 12], limits on thermodynamic efficiency [13], generation of current with a hidden pump [14], and the study of large fluctuations [15].

 On the experimental side, synthetically made molecular machines constitute a promising field for future applications [16]. In particular, net motion in a given direction due to external control has been achieved in several experiments [17–19]. Interestingly, more recently an autonomous synthetic molecular machine that leads to rotation of a small ring on a larger ring of a catenane has been realized experimentally [20]. In this case, the control, i.e., the periodic change of energies and energy barriers, is exerted by bulky groups that can attach to and detach from the larger ring blocking transitions between a link. These chemical reactions leading to attachment and detachment consume free energy. Such an autonomous synthetic machine is more similar to biological motors, which, typically, consume ATP.

 In standard thermodynamics, the deterministic variation in time of an external parameter leads to work exerted on the system. This control work is given by the average change in the energy of the system due to changes of the external parameter [21]. Part of this control work can be extracted as output if an external load is applied to the system. For this well known situation the energetic cost of generating the external control does not appear in the second law. However, for an autonomous machine, illustrated in figure 1, where a thermodynamically consistent external control is generated by the free energy difference in a chemical reaction, the second law has to include this cost.

 In this paper, we obtain generalized second law inequalities that incorporate the cost of external control in a thermodynamically consistent way. Our inequalities relate the work to generate the external control, the work
done on the system through external control, the extracted work, and an entropic term that quantifies correlations between the dynamics of the internal system and the state of the external control.

There is a particular limit, in which our new results have to become the known inequality for systems driven by periodic control, which is the statement that the control work is larger than the extracted work. In this limit, which we call the limit of irreversible control, the external control moves the parameters unidirectionally leading to a cost of external control that formally diverges. It is then reasonable to expect that the cost to generate the control is larger than the control work done on the system. Furthermore, due to the statement of the second law for this known case of irreversible control, it is also reasonable to expect that the extracted work is smaller than the control work. We show that due to the presence of a new entropic term these expectations are not necessarily correct for the realistic case of a thermodynamically consistent control, which cannot be fully irreversible. The cost to generate the control can then be smaller than the control work and the extracted work can be larger than the control work, which can be even negative.

From a conceptual perspective, our results show that the standard periodically driven steady states can be seen as a particular limit of a bipartite system. Indeed, our refined second law inequalities that account for the cost of external control follow from the theoretical framework for bipartite systems [22–26]. We note that in a recent related study a bound on ‘dissipation’ that considers the entropic term to drive the external control has been obtained in [27].

The paper is organized in the following way. In section 2 we introduce our main result with a simple model. Our main result for the general setup is derived in section 3. We illustrate our refined inequalities with a three-state model in section 4. We conclude in section 5.

2. Illustrative example

Our main result, which is equation (3) below, can be illustrated with a simple model for a small machine driven by external control shown in figure 2. The magenta particle can be in three different positions, each representing a different state of the internal system. We assume that our model has Markovian dynamics with the particle jumping between these three positions. For instance, the three positions could be three different states of an enzyme $M_1$, $M_2$, and $M_3$, with the change between two states corresponding to a rotation of 120° of the enzyme, similar to the case of F1-ATPase, see, e.g., [28] and references therein. The green position represents a state with
energy \( E \), whereas the other two black positions represent states with energy 0. The red line represents an infinite energy barrier that does not allow transitions between the respective states.

The external control is represented by the green arrows in figure 2. Changes in the control state leads to changes in the energies of the internal states and in the energy barriers between internal states. These changes can happen at fixed times for a deterministic protocol or at exponentially distributed waiting times for a stochastic protocol [11, 12]. An internal current, i.e., net movement of the particle in the circle, in the clockwise direction can be induced by the external control in figure 2. If the particle is moving against a load that leads to a thermodynamic force \( A_{\text{out}} \) in the anticlockwise direction, the system can do work against this force at a rate \( \omega_{\text{out}} \). This load would be the torque for an enzyme that rotates. The second law for this system with this irreversible control implies the inequality

\[
\omega_{\text{con}} \geq \omega_{\text{out}},
\]

where \( \omega_{\text{con}} \) is the control power exerted on the internal system.

For a stochastic protocol, the green arrows represent transitions between states of the full system composed of the three-state ring and the external control. We call irreversible control the limit for which the transition rates represented by the brown dotted arrows in figure 2 vanish. However, if we want to have a protocol that is thermodynamically consistent, we have to consider the possibility of reversed transitions. A physical model for irreversible control implies the inequality

\[
3.1. \text{Second law for the full system}
\]

We consider a bipartite Markov process in a stationary state [22–26]. States of the internal system are denoted by Roman letters \( i \) and \( j \) and states of the external protocol by Greek letters \( \alpha \) and \( \beta \). The transition rate from state \((i, \alpha)\) to state \((j, \beta)\) is

\[
w_{ij}^{\alpha \beta} \equiv \begin{cases} w_{ij}^{\alpha \beta} & \text{if } i = j \text{ and } \alpha = \beta, \\ w_{ij}^{\alpha} & \text{if } i = j \text{ and } \alpha = \beta, \\ 0 & \text{if } i = j \text{ and } \alpha \neq \beta. \end{cases}
\]

Transitions that change the state of the internal system and the state of the external protocol simultaneously are not allowed.
The transition rates are related to the free energies and thermodynamic affinities. The free energy of an state \((i, \alpha)\) is denoted \(F_i^\alpha\), the affinity that drives the external protocol is denoted \(A_{\text{gen}}\) and the affinity of the internal process is denoted \(A_{\text{out}}\). The generalized detailed balance relation [29] for transitions that change the internal states reads
\[
\ln \frac{w_{ij}^\alpha}{w_{ji}^\alpha} = F_i^\alpha - F_j^\alpha - A_{\text{out}} d_{ij},
\]
where we are assuming an isothermal system with \(k_B T = 1\) throughout. For transitions that change the external protocol, this relation is
\[
\ln \frac{w_{ij}^{\alpha \beta}}{w_{ji}^{\alpha \beta}} = F_i^{\alpha} - F_j^{\beta} + A_{\text{gen}} d_{ij}.
\]

The quantities \(d_{ij}\) and \(d_{ij}^{\alpha \beta}\) are generalized distances. If \(A_{\text{gen}}\) is a chemical potential difference, then \(d_{ij}^{\alpha \beta}\) is the number of substrate molecules consumed in the transition from \(\alpha\) to \(\beta\). If \(A_{\text{out}}\) is a torque, then \(d_{ij}\) is an angle difference between \(i\) and \(j\).

The power required to generate the control is defined as
\[
\omega_{\text{gen}} \equiv A_{\text{gen}} \sum_i \sum_{\alpha < \beta} f_i^{\alpha \beta} d_{ij}^{\alpha \beta},
\]
where \(f_i^{\alpha \beta} \equiv P_i^\alpha w_{ij}^{\alpha \beta} - P_j^\beta w_{ji}^{\alpha \beta}\) and the sum \(\sum_{\alpha < \beta}\) is over all external links. The rate of extracted work is given by
\[
\omega_{\text{out}} \equiv A_{\text{out}} \sum_{i < j} f_{ij} d_{ij},
\]
where \(f_{ij} \equiv P_i^\alpha w_{ij}^\alpha - P_j^\alpha w_{ji}^\alpha\) and the sum \(\sum_{i < j}\) is over all internal links. The entropy production of the full system is
\[
\sigma \equiv \sum_i P_i^\alpha \sum_{\beta < \alpha} w_{ij}^{\alpha \beta} \ln \frac{w_{ij}^{\alpha \beta}}{w_{ji}^{\alpha \beta}} + \sum_i P_i^\alpha \sum_{\beta > \alpha} w_{ij}^{\alpha \beta} \ln \frac{w_{ij}^{\alpha \beta}}{w_{ji}^{\alpha \beta}} = \omega_{\text{gen}} - \omega_{\text{out}} \geq 0,
\]
where the second equality follows from equations (7) and (8). The inequality above is the standard second law from stochastic thermodynamics for the full bipartite process. In this paper, we restrict to the case \(\omega_{\text{gen}} \geq 0\). If \(\omega_{\text{gen}}\) is negative, then the internal system plays the role of an external protocol and the external protocol plays the role of an internal system.

A key quantity for a system driven by external control that does not appear in this standard second law (9) is the rate of work done on the system by external control, i.e., the control power
\[
\omega_{\text{con}} \equiv \sum_i \sum_{\beta < \alpha} f_{ij}^{\alpha \beta} (F_i^\beta - F_j^\beta) = \sum_{\alpha} \sum_{j < i} f_{ij}^{\alpha \beta} (F_i^\beta - F_j^\beta).
\]
The second equality comes from the conservation law \(\sum_{\beta} \sum_{i < j} f_{ij}^{\alpha \beta} F_i^\beta = 0\). Hence, \(\omega_{\text{con}}\) does not appear in the entropy production (9) because the terms leading to free energy changes due to jumps that change the external control cancels the terms due to internal jumps.

### 3.2. Refined second law
The external protocol and internal system are two subsystems that form the full system. For a bipartite system, there are also second law inequalities for these subsystems [24, 25]. The rate of entropy production associated only with the jumps that change the external protocol is given by
\[
\sigma_{\text{gen}} \equiv \sum_i P_i^\alpha \sum_{\beta < \alpha} w_{ij}^{\alpha \beta} \ln \frac{w_{ij}^{\alpha \beta} P_i^\alpha}{w_{ji}^{\alpha \beta} P_j^\beta} \geq 0.
\]

Using equations (7) and (10), this second law for the external control alone reads
\[
\sigma_{\text{gen}} = \omega_{\text{gen}} - \omega_{\text{con}} + \mathcal{I} \geq 0,
\]
where
\[
\mathcal{I} \equiv \sum_i \sum_{\beta < \alpha} f_{ij}^{\alpha \beta} \ln \frac{P_i^\beta}{P_j^\beta}.
\]
This entropic rate is the rate at which jumps of the external control decrease the static mutual information (or increase the conditional Shannon entropy) [24, 25, 30]. If \(\mathcal{I}\) is positive, then the dynamics of the external control decreases the correlation between the subsystems. Bipartite systems have the following entropic conservation law: the rate at which jumps of the internal system increase the static mutual information is exactly \(\mathcal{I}\). If \(\mathcal{I}\) is negative, the dynamics of the internal system decreases the correlation between the subsystems.
The rate of entropy production due to jumps related to the internal system is
\[ \sigma_{\text{int}} = \sum_{k, \alpha} P_k^\alpha \sum_{j, \beta} w_{ij}^\alpha \ln \frac{w_{ij}^\beta P_j^\beta}{w_{ij}^\alpha P_j^\alpha} \geq 0. \] (14)

For the internal subsystem the second law reads
\[ \sigma_{\text{int}} = \omega_{\text{con}} - S - \omega_{\text{out}} \geq 0, \] (15)
where we used equations (8) and (10). With equations (12) and (15), we obtain
\[ \omega_{\text{gen}} \geq \omega_{\text{con}} - S \geq \omega_{\text{out}}, \] (16)
which is our refined second law in equation (3). We note that here we consider an internal affinity \( A_{\text{out}} \) that is independent of \( n \). For the case of several internal affinities that can depend on the external control, which is the case of a model that displays a phenomena known as negative mobility [31, 32], there will be different terms from those terms contained in equation (16). In principle, our theoretical framework should be generalizable to a case where the cost of such external control would be relevant.

### 3.3. Limit of irreversible control

The external protocol becomes unaffected by the dynamics of the internal system in the following limit [12]. The free energy difference is written as
\[ F_i^\beta - F_i^\alpha = E_i^\beta - E_i^\alpha + E_{j,i}^{\beta,\alpha}, \] (17)
where \( E_i^\alpha \) is the energy of the state \( \alpha \) of the external protocol and \( E_{j,i}^{\beta,\alpha} \) is the interaction energy. From the generalized detailed balance relation (6) we obtain \( w_{ij}^{\beta,\alpha} \approx w_{ij}^{\alpha,\beta} \), if this energy difference fulfills \( E_i^\beta - E_i^\alpha > E_{j,i}^{\beta,\alpha} \). For such transition rates the external protocol alone is a Markov process with dynamics unaffected by the state of the internal system.

Even though \( w_{ij}^{\beta,\alpha} \approx w_{ij}^{\alpha,\beta} \), we have to account for the contribution coming from the interaction energy difference in the inequalities (16). In particular, using equation (17), the control power in equation (10) becomes
\[ \omega_{\text{con}} = \sum_{\beta < \alpha} j_{ij}^{\alpha,\beta} (E_j^\beta - E_j^\alpha) + \sum_{\beta < \alpha} j_{ij}^{\beta,\alpha} (E_{j,i}^{\beta,\alpha} - E_{j,i}^{\alpha,\beta}) = \sum_{\beta < \alpha} j_{ij}^{\alpha,\beta} (E_j^\beta - E_j^\alpha), \] (18)
where \( j_{ij}^{\beta,\alpha} = \sum_{\beta < \alpha} j_{ij}^{\alpha,\beta} \). The term \( \sum_{\beta < \alpha} j_{ij}^{\beta,\alpha} (E_j^\beta - E_j^\alpha) = 0 \) because the dynamics of the external protocol alone is Markovian.

The limit of irreversible control corresponds to irreversible rates for jumps of the external protocol. If the external protocol has \( N \) states, \( \alpha = 1, 2, \ldots, N \) and then we write the rates as \( w^{\alpha,\alpha+1} = \gamma_\alpha \) and \( w^{\alpha+1,\alpha} = 0 \), with \( \alpha + 1 = 1 \) for \( \alpha = N \). Such irreversible rates correspond to a formally divergent affinity \( A_{\text{gen}} \) in (6), leading to \( \omega_{\text{gen}} \to \infty \). Therefore, in this limit of irreversible control the refined second law (16) leads to
\[ \omega_{\text{con}} \geq \omega_{\text{out}} + S \geq \omega_{\text{out}}, \] (19)
where we used the fact that \( S \geq 0 \) for transition rates \( w^{\alpha,\beta} \) independent of \( i \) [26].

### 4. Three-state model and time-scale separation

#### 4.1. Illustration of the refined inequalities

We now consider a more general version of the model in figure 2, with arbitrary energies and energy barriers. The three internal states are three different rotation angles of the enzyme \( i = 1, 2, 3 \) and the three states of the external protocol are \( M_i, M_{i+1}, \) and \( M_{i+2} \), which correspond to \( \alpha = 1, 2, 3 \), respectively. The total Markov process of internal system and external protocol together has then nine states. The transition rates for an internal change are set to
\[ w_{i,i+1}^{\alpha} = ke^{E_i^{\alpha} - E_i^{\alpha+1}}, \] (20)
for a clockwise rotation,
\[ w_{i+1,i}^{\alpha} = ke^{A_{\text{out}}/2}e^{E_i^{\alpha+1} - E_i^{\alpha}} \] (21)
for an anti-clockwise rotation. The quantities \( B_i^{\alpha} \) represent energy barriers between states. The transition rates for a change in the external protocol are given by
\[ w_{i,i+1,\alpha}^{\alpha,\alpha+1} = \gamma_\alpha, \] (22)
and
\[ w_{i,i+1,\alpha}^{\alpha+1,\alpha} = \gamma e^{-A_{\text{out}}/2}e^{E_i^{\alpha} - E_i^{\alpha+1}}. \] (23)
The parameter \( k \) characterizes the speed of internal transitions and the parameter \( \gamma \) characterizes the speed of changes in the external protocol.

A symmetric protocol is obtained with the energies and energy barriers given by

\[
F_i^\alpha = F_i - \alpha + 1, \tag{24}
\]

and

\[
B_i^\alpha = B_i - \alpha + 1, \tag{25}
\]

where we assume periodic boundary conditions for the subscript \( i - \alpha + 1 \). With this symmetric choice we can reduce the stochastic matrix for the full Markov process with dimension nine to a stochastic matrix with dimension three \([11]\). This reduction facilitates the analytical calculation that leads to a stationary distribution with quite long expression in term of the parameters for the general case. The model shown in figure 2 corresponds to the choice \( F_1 = E, \ B_3 \to \infty \) and \( F_2 = F_3 = B_1 = B_2 = 0 \).

In figure 3 we illustrate the major role played by the entropic rate \( \mathcal{I} \) for a thermodynamically consistent external control. Due to this entropic contribution two somewhat surprising situations can happen. First, in figure 3(a), we show that the power to generate the external control \( \mathcal{W}_{\text{gen}} \) can be smaller than the control power exerted on the system \( \mathcal{W}_{\text{con}} \). Second, in figure 3(b), we show that the extracted power \( \mathcal{W}_{\text{out}} \) can be larger than the control power \( \mathcal{W}_{\text{con}} \) which can be negative.

From the second law inequalities in equation (16) we can define the efficiencies \( \eta \equiv \mathcal{W}_{\text{out}} / \mathcal{W}_{\text{gen}} \) and \( \eta_{\text{int}} \equiv \mathcal{W}_{\text{int}} / \mathcal{W}_{\text{con}} \). The first efficiency \( \eta \) is the standard efficiency for a nonequilibrium steady state \([33]\) corresponding to the full bipartite process. This efficiency compares the extracted power with the full cost to generate the external control. The second efficiency \( \eta_{\text{int}} \) gives the fraction of the power to generate the external control that is transformed into control power minus the entropic rate \( \mathcal{I} \).

Interestingly, in the limit of irreversible control the ratio \( \mathcal{W}_{\text{out}} / \mathcal{W}_{\text{con}} \) is an efficiency that quantifies the amount of the control work that is transformed into extracted work \([13]\). For the general case, \( \mathcal{W}_{\text{out}} / \mathcal{W}_{\text{con}} \) becomes a pseudo-efficiency since it can be larger than one. For a thermodynamic consistent control the third efficiency \( \eta_{\text{int}} \) should rather be used to characterize the performance of the machine to convert ‘control power’ into output power.

4.2. Time-scale separation

If there is time-scale separation then, with a few assumptions, we can show that the second law inequality (15) for the internal subsystem is saturated. The internal rates \( \omega_{ij}^\alpha \) are assumed to be of order \( k \) and the external rates \( \omega_{ij}^{\alpha\beta} \) are assumed to be of order \( \gamma \), with \( k \gg \gamma \). In this case, the power to drive the control \( \mathcal{W}_{\text{gen}} \gg 0 \) is of order \( \gamma \). If we impose that \( \mathcal{W}_{\text{out}} \gg 0 \), then from the standard second law (9), \( \mathcal{W}_{\text{out}} \) must also be of order \( \gamma \).

Since \( \mathcal{W}_{\text{out}} \) is of order \( \gamma \), it is reasonable to expect that the internal currents \( J_{ij}^\alpha \) that appear in equation (8) are also of order \( \gamma \). In this case, form equation (15) we obtain

![Figure 3](image-url)
\[ \omega_{\text{con}} - \mathcal{I} - \omega_{\text{out}} = \sum_{a} \sum_{j<i} r_{ij} \ln \frac{W_{\ell}^{a} P_{\ell}^{a}}{W_{\mu}^{a} P_{\mu}^{a}} = \sum_{a} \sum_{j<i} r_{ij} \ln \left(1 + \frac{f_{ij}^{a}}{W_{\ell}^{a} P_{\ell}^{a}}\right) = \gamma \left(\frac{2}{k}\right). \]  

Hence, in the limit where changes in the external protocol are infinitely slower than the internal transitions the second inequality in (16) is saturated, i.e., \( \omega_{\text{con}} - \mathcal{I} = \omega_{\text{out}} \). This equality is illustrated with the three-state model in figure 3(a).

The typical case of irreversible control with a deterministic protocol can be recovered if we consider a stochastic protocol with a large number of jumps \( N \) and a rate \( \gamma \) for a change of the external protocol that scales with \( N \). In this case, the entropic rate \( \mathcal{I} \) goes to zero and we obtain \( \omega_{\text{con}} = \omega_{\text{out}} \) with the separation of time scales in equation (26), a known result in thermodynamics.

5. Conclusion

We have obtained refined second law inequalities for machines driven by periodic external control that take the thermodynamic cost to generate the external control into account. Our inequalities establish a relation between the cost to generate external control, the control work exerted on the internal system, and the extracted work. In particular, we have shown that the cost for external control can be smaller than the control work and that the extracted work can be larger than the control work. These regimes result from the entropic term \( \mathcal{I} \) in equation (16) that quantifies correlations between the dynamics of the internal system and the state of the external control, which has to be stochastic for a thermodynamic consistent control.

From a conceptual perspective we have shown that systems driven by external control that reach a periodic steady state, which form a major class of nonequilibrium systems, can be seen as a particular limit of a steady state of a bipartite process. In this limit of irreversible control, the cost of control diverges and we are left only with the second inequality in equation (16). This result further demonstrates the power of the theoretical framework for bipartite systems developed in [24–26].

Our refined inequalities correspond to the appropriate statement of the second law for a machine driven by a thermodynamically consistent control. This kind of control occurs in particular if the system is driven by free energy consumption of a chemical reaction, as is the case of the catenane analyzed experimentally in [20]. We expect our formalism to play an important role for understanding and optimizing the operation of such autonomously driven machines.

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