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# Energetics of Brownian motors: a review

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**ABSTRACT** We review the literature on the energetics of Brownian motors, distinguishing between forced ratchets, chemical motors – driven out of equilibrium by differences of chemical potential, and thermal motors – driven by temperature differences. The discussion is focused on the definition of efficiency and the compatibility between the models and the laws of thermodynamics.

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## 1 Introduction

The term ‘thermal ratchet’ applies to a wide class of systems where thermal fluctuations are rectified resulting in a net current of particles [53]. These systems are in contact with one or several thermal baths (the source of thermal fluctuations) and are obviously out of equilibrium. In most cases, the source of nonequilibrium is supplying to the system some energy which is subsequently dissipated to the thermal bath(s) as heat.

If a small force, sometimes called load, is opposed to the current in a thermal ratchet, then particles will keep on moving, on average, against the force, performing some work. In these cases, part of the energy coming from the source of nonequilibrium is transformed into mechanical energy released to the load. We apply the term Brownian motor to this type of situation, i.e. a Brownian motor is nothing but a ratchet with a load<sup>1</sup>.

The aim of this paper is to explore the flow of energy between a Brownian motor and its surroundings and, in particular, its efficiency. The task highly depends on the physical nature of the mechanism driving the ratchet out of equilibrium, and therefore we have classified Brownian motors according to these mechanisms.

The study of the energetics of Brownian motors is relevant for several reasons. First, highly efficient motors are desirable in order to decrease the energy consumption and/or to decrease the heat dissipation. In fact, we think that the latter feature will be more relevant than the former in the two main fields where ratchets can be applied: cell biology and nanotechnology. It is generally believed that energy has not been a scarce resource for living beings. Therefore, one could think that evolution has no reason to favor efficient motors. Nevertheless, as occurs in modern computers, a high efficiency can be useful even if there is no need for energy saving, in cases where there are a lot of units in a small volume, a moderate temperature is required, and it is difficult to dissipate heat. This could be the case for the ion pumps spread along a cell membrane [10, 24], and the same problem will probably be faced by man-made Brownian motors.

Secondly, ratchets are related to fundamental problems of thermodynamics and statistical mechanics, such as the Maxwell demon and the trade-off between entropy and information. For instance, one of the first well-known Brownian motors was the ratchet-and-pawl setup studied by Feynman in his Lectures [23]. He calculated the efficiency of such an engine since his original purpose was to prove that an automatic demon cannot beat the second law of thermodynamics.

Thirdly, many models proposed in the literature are based on nonequilibrium fluctuations without specifying their source. On the other hand, the study of the energetics of such models requires a more precise formulation, since one has to determine the physical nature of the external agent and verify that the motor is consistent with the second law of thermodynamics. In this sense, some of the results of the present paper can also be considered as guidelines to find physical realizations (if any) of Brownian motors proposed in a purely theoretical context.

The paper is organized as follows. In Sect. 2 we introduce some basic concepts, such as the stopping force, and review some elementary results of thermodynamics and the theory of chemical reactions. Section 3 studies the energetics of one of the simplest Brownian motors: the flashing ratchet proposed by Ajdari and Prost [1]. In Sect. 4 we present a general theory of deterministically forced isothermal ratchets, which is complemented by Sect. 5, where the quasistatic limit is discussed. Section 6 reviews the literature on the energetics of rocking ratchets. Section 7 is an exhaustive treatment of chemical mo-

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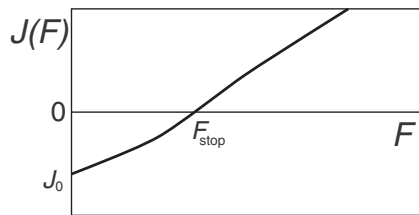
<sup>1</sup> The term ‘Brownian motor’ has been coined originally by Bartussek and Hänggi in an early feature article [13]. We should also notice that, in this paper, and in most of the subsequent literature, ‘Brownian motor’ is used as equivalent to thermal ratchet without requiring the presence of the load.

tors. Section 8 deals with thermal Brownian motors, such as the celebrated Feynman ratchet. In Sect. 9 we briefly discuss other models such as collective motors and quantum ratchets. Finally, in Sect. 10 we present our main conclusions.

## 2 Basic concepts

### 2.1 The stopping force

A ratchet is a system which can rectify thermal fluctuations and, as a consequence, exhibits a current of particles  $J_0$  in a given direction. If we add a force or load  $F$  in the opposite direction, then the current  $J(F)$  typically has the behavior depicted in Fig. 1. Its absolute value decreases and vanishes for a given value of the force  $F_{\text{stop}}$ , which is usually named stopping force.



**FIGURE 1** Current of particles in a ratchet as a function of the load. The ratchet works as a motor in the interval  $F \in [0, F_{\text{stop}}]$

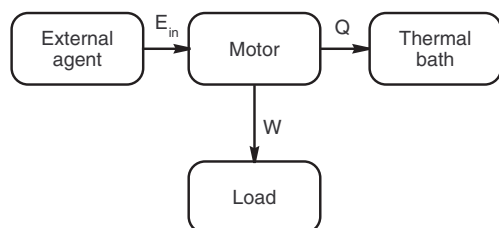
The ratchet works as a motor only in the interval  $F \in [0, F_{\text{stop}}]$ , since in this case  $FJ(F) < 0$  and particles move against the force performing some work. This work can be considered as a gain of potential energy of the particles or, alternatively, as an energy transfer from the motor to the system which exerts the force, i.e. to the load. We will follow the latter interpretation, which is more appropriate for motors.

### 2.2 A review of thermodynamics

An isothermal Brownian motor exchanges energy with three types of systems: the thermal bath, the load, and some external agent which is the source of nonequilibrium [48, 54]. Figure 2 presents the energy flows between the motor and its surroundings. If the sign of each energy transfer is the one indicated by the respective arrow, the laws of thermodynamics read:

$$E_{\text{in}} = Q + W \quad \text{First law,}$$

$$\Delta S_{\text{agent}} + \frac{Q}{T} = S_{\text{prod}} \geq 0 \quad \text{Second law,}$$



**FIGURE 2** Energy flows in an isothermal Brownian motor

where  $T$  is the absolute temperature,  $\Delta S_{\text{agent}}$  is the change of entropy in the external agent, and  $S_{\text{prod}}$  is the entropy production. We assume that the motor works either in a cycle or in a stationary regime and therefore its entropy does not change. All magnitudes, energy flows, and entropy changes are taken over a cycle or per unit of time, depending on the type of motor.

As will be clear throughout the paper, for a motor operating at constant pressure  $P$ , the proper definition of efficiency is

$$\eta \equiv \frac{W}{G_{\text{in}}}, \quad (1)$$

where  $G_{\text{in}}$  is the transfer of Gibbs free energy from the external agent to the system, i.e. the decrease of free energy of the external agent:

$$\begin{aligned} G_{\text{in}} &= -\Delta G_{\text{agent}} \\ &= -\Delta U_{\text{agent}} + T\Delta S_{\text{agent}} - P\Delta V_{\text{agent}} \\ &= E_{\text{in}} + T\Delta S_{\text{agent}}, \end{aligned} \quad (2)$$

where  $\Delta U_{\text{agent}}$  and  $\Delta V_{\text{agent}}$  are, respectively, the changes of internal energy and volume of the external agent. The decrease of the internal energy of the agent is used both to supply an energy  $E_{\text{in}}$  to the system and for a possible work of expansion  $P\Delta V_{\text{agent}}$ , which is nonzero only if there are changes of phase in some of the components of the external agent. Combining (2) with the two laws of thermodynamics, we obtain

$$G_{\text{in}} - W = TS_{\text{prod}} \geq 0. \quad (3)$$

This inequality reveals one of the most important interpretations of the Gibbs free energy: it is the maximum energy that can be converted into work. We cannot extract more work than the free energy lost by the external agent, and the free energy can be totally converted into work only under conditions of reversibility, when there is no entropy production.

For the efficiency, the above inequality implies that

$$\eta = 1 - \frac{TS_{\text{prod}}}{G_{\text{in}}} \leq 1, \quad (4)$$

and it attains its maximum value  $\eta = 1$  if and only if there is no production of entropy, i.e. in the case of motors working in a reversible way.

The use of the free energy  $G_{\text{in}}$  instead of  $E_{\text{in}}$  in the definition of efficiency has been widely applied for transduction of chemical energy [26], and introduced in the context of Brownian motors by Zhou and Chen [65] and later on by Jülicher et al. [32]. It is of extreme importance for chemical motors, since these motors can work by consuming some type of molecule, or fuel, which is degraded into another molecule with less energy and/or bigger entropy. For instance, this is the case of ATP in the cell metabolism [2, 17, 28]. In Sect. 7, we will present an example of a motor which works by increasing the entropy of the external agent but without taking any energy from it. A definition of efficiency which only takes into account the flow of energy,  $E_{\text{in}}$ , is meaningless in these cases. On the other hand, if the entropy of the external agent

does not change, then  $G_{\text{in}} = E_{\text{in}}$  and the definition of efficiency coincides with the one most commonly used in the literature.

For a motor working in contact with two thermal baths at different temperatures  $T_1 > T_2$ , the flow of energy is presented in Fig. 3. The laws of thermodynamics now read

$$Q_1 = Q_2 + W \quad \text{First law,}$$

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = S_{\text{prod}} \geq 0 \quad \text{Second law.}$$

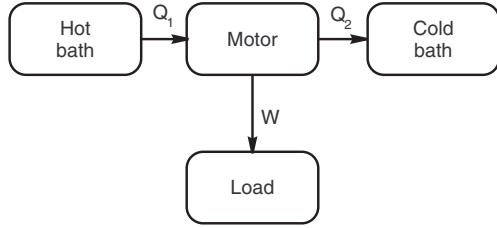


FIGURE 3 Energy flows in a thermal Brownian motor in contact with two thermal baths at temperatures  $T_1 > T_2$

The proper definition of efficiency is

$$\eta \equiv \frac{W}{Q_1}. \quad (5)$$

Combining the two laws of thermodynamics, we obtain

$$W = Q_1 \left( 1 - \frac{T_2}{T_1} \right) - T_2 S_{\text{prod}} \quad (6)$$

and

$$\eta = \eta_c - \frac{T_2 S_{\text{prod}}}{Q_1}, \quad (7)$$

where  $\eta_c \equiv 1 - T_2/T_1$  is the Carnot efficiency, which is attained only if there is no production of entropy, i.e. if the motor works in a reversible way.

Any physically meaningful model of a Brownian motor must be compatible with the limitations that the second law imposes on its efficiency. In fact, a major part of the present paper is devoted to prove this compatibility for wide classes of models, and to explore how the entropy production  $S_{\text{prod}}$  can be reduced in order to devise efficient motors.

Some authors [22, 64] have recently proposed an alternative definition of efficiency for particles moving in a fluid. In this definition the work done by the particles against the Stokes or friction force is added to the work released to the load. These authors claim that this new definition gives more information about the performance of some biological motors whose main task is to keep a finite velocity against the Stokes force. However, one has to be careful with this type of definition, since the work done against the friction is always dissipated as heat to the thermal bath. For instance, a body falling in the air at its terminal velocity is continuously transforming potential energy into heat by doing ‘work’ against the friction force, but it is hard to interpret this situation as a motor or a useful energy transducer.

### 2.3 Chemical potential and reaction kinetics

In a chemical motor the external agent is a chemical reaction kept out of equilibrium by means of a continuous supply of some of the reactants. For a full understanding of the energetics of chemical motors, it is worth reviewing the physical meaning of the chemical potential and the theory of chemical equilibrium and reaction kinetics [38]. The chemical potential is an indicator of equilibrium when the number of particles of a given species in a system can vary by chemical reactions, phase changes, or other mechanisms. For an ideal system at temperature  $T$ , with an average number of particles  $N$ , and occupying a volume  $V$ , the chemical potential reads

$$\mu = kT \ln \frac{N}{Z_1}, \quad (8)$$

where  $k$  is the Boltzmann constant and  $Z_1$  is the partition function for a single particle. Since the free energy of the system is given by  $F = -kT \ln(Z_1^N/N!)$ , one has the well-known relation

$$\mu = \frac{F + NkT}{N} = \frac{G}{N}, \quad (9)$$

where  $G$  is the Gibbs free energy. The chemical potential is usually split into an ‘internal’ part or standard chemical potential,  $\mu^0(T)$ , and a contribution due to the density of particles:

$$\mu = \mu^0(T) + kT \ln \frac{N}{V}, \quad (10)$$

where  $\mu^0(T)$  depends only on the temperature and can be interpreted, up to an additive constant, as the Helmholtz free energy  $E_{\text{int}} - TS_{\text{int}}$  of the internal degrees of freedom of the particles.

The equilibrium condition for an elementary reaction



is [38]

$$\Delta\mu = c\mu_C + d\mu_D - a\mu_A - b\mu_B = 0, \quad (12)$$

which, for ideal systems, reads

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = K(T), \quad (13)$$

where  $[\cdot]$  are the molar equilibrium concentrations and  $K(T) = \exp(-\beta\Delta\mu^0(T))$  is the so-called standard reaction equilibrium constant [38] with  $\beta = 1/(kT)$  and

$$\Delta\mu^0 = c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0. \quad (14)$$

Let us discuss the kinetics of reaction (11). If we assume that the rate of collisions between particles A and B, and C and D, is proportional to  $[A]^a [B]^b$  and  $[C]^c [D]^d$ , respectively, the evolution equation for the molar concentration  $[A](t)$  of particles A is

$$\partial_t [A](t) = a \left( \omega_- [C]^c [D]^d - \omega_+ [A]^a [B]^b \right), \quad (15)$$

where  $\omega_+$  and  $\omega_-$  are the transition rates at which the reaction (11) occurs to the right and left, respectively, for a single collision between reactants. To make compatible the reaction kinetics (15) with the equilibrium prescribed by (13), the rates must obey the detailed balance condition

$$\omega_+[A]^a[B]^b = \omega_-[C]^c[D]^d, \quad (16)$$

which implies that

$$\frac{\omega_+}{\omega_-} = K(T) = e^{-\beta\Delta\mu^0}. \quad (17)$$

#### 2.4 Reaction–diffusion equations and chemical potential

The above discussion can be extended to the case of an external potential  $V_\alpha(x)$  acting on the species  $\alpha$  and inducing a nonuniform concentration of particles. If  $\varrho_\alpha(x)$  is the local molar concentration, and if we assume local equilibrium, the chemical potential reads

$$\mu_\alpha(x, t) = \mu_\alpha^0(T) + V_\alpha(x) + kT \ln \varrho_\alpha(x, t). \quad (18)$$

Regarding chemical reactions, the rates in the presence of an external field can depend on the position, and the detailed balance condition becomes

$$\frac{\omega_+(x)}{\omega_-(x)} = e^{-\beta[\Delta\mu^0 + \Delta V(x)]}, \quad (19)$$

where

$$\Delta V(x) = cV_C(x) + dV_D(x) - aV_A(x) - bV_B(x). \quad (20)$$

The rate of reaction (11) at a point  $x$  is given by

$$\begin{aligned} r(x) &= \omega_+(x)\varrho_A(x)^a\varrho_B(x)^b - \omega_-(x)\varrho_C(x)^c\varrho_D(x)^d \\ &= \omega_+(x)\varrho_A(x)^a\varrho_B(x)^b [1 - e^{\beta\Delta\mu(x)}]. \end{aligned} \quad (21)$$

Notice that the rate  $r(x)$  and  $\Delta\mu(x)$  have opposite signs,  $r(x)\Delta\mu(x) \leq 0$  for all  $x$ . This inequality means that the reaction occurs, on average, towards the direction of decreasing chemical potential or, equivalently, the direction of decreasing Gibbs free energy.

On the other hand, the space-dependent chemical potential has the advantage of accounting for both spatial currents and rates of reaction. Consider a Brownian particle in a potential  $V(x)$  at a temperature  $T$  and subjected to a load  $F$ . If  $x(t)$  is the position of the particle, then the Langevin equation is

$$\dot{x}(t) = \kappa [-V'(x) + F + \xi(t)], \quad (22)$$

where the prime denotes a derivative with respect to  $x$  and  $\kappa = \beta D$ ,  $D$  being the diffusion coefficient<sup>2</sup>. Thermal fluctuations are represented by  $\xi(t)$ , a white Gaussian noise with zero mean and correlation given by

$$\langle \xi(t)\xi(t') \rangle = 2kT\kappa^{-1}\delta(t-t') = 2D\kappa^{-2}\delta(t-t'). \quad (23)$$

<sup>2</sup>The Einstein fluctuation–dissipation relation states that  $\kappa$  is equal to the inverse of the friction coefficient, i.e. the damping force is  $F_{\text{damp}} = -\dot{x}/\kappa$ .

The corresponding Fokker–Planck equation for the probability density can be written as

$$\partial_t \varrho(x, t) = -\partial_x J(x, t), \quad (24)$$

where the current is

$$J(x, t) = -\kappa \varrho(x, t) [\partial_x \mu(x, t) - F], \quad (25)$$

with  $\mu(x, t)$  given by (18). This dependence of the current on the gradient of the chemical potential will be extensively used throughout the paper. Notice also that a uniform chemical potential implies a zero current in the absence of load, i.e. mechanical equilibrium, whereas condition (12) implies chemical equilibrium at point  $x$ .

If the particle is involved in a chemical reaction, then a reaction term has to be added to the Fokker–Planck equation. For instance, if particles A in reaction (11) have a diffusion constant  $D_A = \kappa_A kT$ , the evolution equation for the concentration  $\varrho_A(x, t)$  is

$$\partial_t \varrho_A(x, t) = -\partial_x J_A(x, t) - ar(x), \quad (26)$$

where the current is given by (25) and the rate  $r(x)$  is given by (21).

### 3 The flashing ratchet

We start by studying the efficiency of one of the simplest Brownian motors and one of the first considered in the recent literature on ratchets [1, 7], namely, the flashing ratchet. It can be viewed as a Brownian particle in a flashing asymmetric and periodic potential. If  $x \in [0, L]$  is the position of the particle, then the Langevin equation reads

$$\dot{x}(t) = \kappa [-\zeta(t)V'(x) + F + \xi(t)], \quad (27)$$

where the potential  $V(x)$  is an asymmetric and piece-wise linear potential, as depicted in Fig. 4, and  $\zeta(t)$  is a dichotomous noise taking values 0 and 1 and therefore switching on and off the potential in a random way at rates  $\omega_{0 \rightarrow 1}$  and  $\omega_{1 \rightarrow 0}$ . These switches are nonequilibrium fluctuations induced by an external agent.

The joint probability distribution  $\varrho_\zeta(x, t)$  for the dichotomous noise and the position of the particle obeys the evolution equations

$$\begin{aligned} \partial_t \varrho_0(x, t) &= -\partial_x J_0(x, t) - r(x, t), \\ \partial_t \varrho_1(x, t) &= -\partial_x J_1(x, t) + r(x, t), \end{aligned} \quad (28)$$

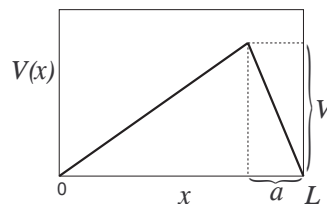


FIGURE 4 Potential of a flashing ratchet

where

$$\begin{aligned} J_\zeta(x, t) &= \kappa \left[ -\zeta V'(x) + F - kT\partial_x \right] \varrho_\zeta(x, t), \\ r(x, t) &= \omega_{0 \rightarrow 1} \varrho_0(x, t) - \omega_{1 \rightarrow 0} \varrho_1(x, t). \end{aligned} \quad (29)$$

These are the reaction–diffusion equations of a particle which can be in two states, corresponding to  $\zeta = 0$  and  $\zeta = 1$ , and randomly changes from one to the other. With this picture in mind,  $J_\zeta(x, t)$  is the current of particles in state  $\zeta$  at time  $t$  and position  $x$ , whereas  $r(x, t)$  is the reaction rate or the net flux of particles from state 0 to 1 at time  $t$  and position  $x$ .

It is well known that this system exhibits, in the stationary regime and for this particular choice of the potential, a current  $J = J_0(x) + J_1(x) < 0$  to the left for a load below the stopping force [1, 7]. The power of the motor, or work done per unit of time, is  $\dot{W} = -FJL$ , which is positive if  $F \in [0, F_{\text{stop}}]$ . This expression comes from the fact that a fraction  $J$  of particles crosses the interval per unit of time, each of them gaining an energy  $FL$ . We also assume that the external agent inducing the switching of the potential has no entropy. Then, the input of free energy equals the input of energy per unit of time:

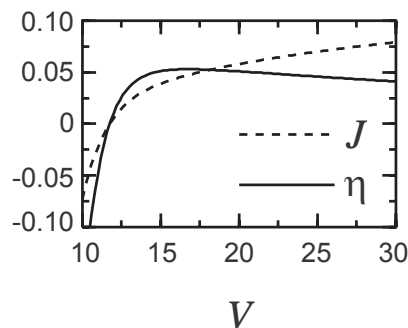
$$\dot{G}_{\text{in}} = \dot{E}_{\text{in}} = \int_0^L dx r(x) V(x), \quad (30)$$

since in each transformation from state 0 to state 1 at  $x$ , the particle gains an energy  $V(x)$  and there are, on average,  $r(x)$  transformations of this kind. Finally, following the prescriptions given in Sect. 1, the efficiency of the motor is

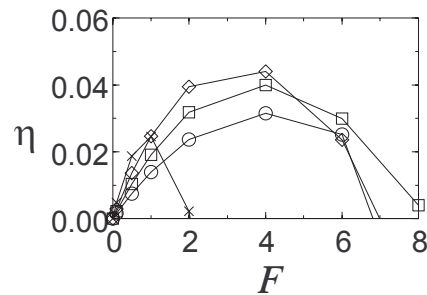
$$\eta = -\frac{JFL}{\dot{E}_{\text{in}}}. \quad (31)$$

Equations (28) can be solved analytically and the solution yields immediately the efficiency of the motor. This calculation has been done in [48]. In Fig. 5, we represent the efficiency of the flashing ratchet, as well as the current, for a set of values of the parameters yielding the maximum efficiency [48]. The low value of the efficiency indicates that the flashing ratchet works far from equilibrium. We also see that the current of particles increases with  $V$ , whereas the efficiency exhibits a maximum.

A periodic flashing instead of a random one does not sensitively increase the efficiency of the motor, as can be seen



**FIGURE 5** Efficiency of a randomly flashing ratchet as a function of the maximum height of the potential in Fig. 4. The rest of parameters are  $\omega_{1 \rightarrow 0} = 1.08$  and  $\omega_{0 \rightarrow 1} = 81.8$ ,  $a = 1/11$ ,  $F = 4.145$ , and  $\kappa = L = kT = 1$



**FIGURE 6** Numerical results for the efficiency of the ratchet consisting of the potential in Fig. 4 modulated by  $\zeta(t) = \cos^2(\pi t/\tau)$  as a function of the load  $F$  and for different values of the period  $\tau$ :  $\tau = 0.00125$  ( $\circ$ ),  $0.025$  ( $\square$ ),  $0.05$  ( $\diamond$ ), and  $0.25$  ( $\times$ )

in Fig. 6, where the efficiency of a deterministically flashing ratchet is depicted. It is not hard to understand the irreversibility of the flashing ratchet in this case: every time the potential is switched on and off, the probability distribution relaxes to the equilibrium profile, and entropy is produced in this relaxation.

In an attempt to increase the efficiency of the model, one could think of a slow modulation of the potential. However, this strategy does not work, as shown in Fig. 6. In fact, the efficiency vanishes when the period of the modulation tends to infinity. The reason will become clear in Sect. 5, when we study the general case of deterministically forced ratchets in the adiabatic limit.

So far we have not specified the physical nature of the external agent. Several interpretations have been given in the literature. Some of them consider the flashing ratchet as a thermal Brownian motor [48, 57] and will be discussed in Sect. 8. In Sect. 7 we give an alternative interpretation of the flashing ratchet as a chemical motor and prove that the model is compatible with the second law. It is also worth mentioning that the flashing ratchet with discrete states is more tractable from the analytical point of view and its energetics has been studied in [3, 57]. Finally, in an interesting work by Arizmendi and Family [5], the efficiency of the deterministically driven flashing ratchet is shown to be proportional to the Kolmogorov complexity of the position of the particle, revealing a deep connection between efficiency, entropy, and information.

#### 4 Deterministically forced ratchets I: general theory

##### 4.1 Energetics

In this section and the following we consider the most general case of an overdamped Brownian particle deterministically forced:

$$\dot{x}(t) = \kappa \left[ -V'(x, t) + F + \xi(t) \right], \quad (32)$$

where the potential  $V(x, t)$  is changed by the external agent. We consider a potential periodic both in time and space with periods  $\tau$  and  $L$ , respectively. Therefore, we are interested in motors working along cycles of period  $\tau$ . Particular examples of this type of ratchet can be found in [39, 48, 62].

The Fokker–Planck equation for the probability distribution  $\varrho(x, t)$  can be written as

$$\partial_t \varrho(x, t) = -\partial_x J(x, t), \quad (33)$$

where  $J(x, t)$  is the current:

$$J(x, t) = \kappa [-V'(x, t) + F - kT \partial_x] \varrho(x, t). \quad (34)$$

The distribution  $\varrho(x, t)$  must also satisfy the following boundary conditions:

$$\varrho(0, t) = \varrho(L, t); \quad J(0, t) = J(L, t). \quad (35)$$

Let us discuss the energetics of the system. As internal energy we only consider the periodic potential

$$\mathcal{U}(t) = \int_0^L dx V(x, t) \varrho(x, t). \quad (36)$$

The power, or work done by the particle against the load per unit of time, is the force times the mean velocity, i.e.

$$\dot{W}(t) = -F \langle \dot{x}(t) \rangle = - \int_0^L dx F J(x, t). \quad (37)$$

The input energy, i.e. the energy that the external agent puts into the system by modifying the potential, is given by

$$\dot{E}_{\text{in}}(t) \equiv \int_0^L dx \varrho(x, t) \partial_t V(x, t). \quad (38)$$

Finally, the heat, or transfer of energy from the system to the thermal bath, reads:

$$\dot{Q}(t) = - \int_0^L dx [V(x, t) \partial_t \varrho(x, t) - F J(x, t)]. \quad (39)$$

A more detailed justification of the above definitions of input energy (38) and heat (39) can be found in [50].

## 4.2 Thermodynamics

We will check in the following that the above definitions obey the two laws of thermodynamics as stated in Sect. 2.2. From the above definitions, it is straightforward to prove the first law:

$$\dot{E}_{\text{in}}(t) = \dot{Q}(t) + \dot{W}(t) + \frac{dU(t)}{dt} \quad \text{for all } t. \quad (40)$$

To derive the second law of thermodynamics, we will make use of the Shannon definition of the entropy of the motor:

$$S(t) \equiv -k \int_0^L dx \varrho(x, t) \ln \varrho(x, t) \quad (41)$$

and the chemical potential (the standard chemical potential  $\mu^0$  does not play any role in this case, since there is only one type of particle):

$$\mu(x, t) = V(x, t) + kT \ln \varrho(x, t), \quad (42)$$

whose average over  $\varrho(x, t)$  is

$$\int_0^L dx \varrho(x, t) \mu(x, t) = U(t) - TS(t). \quad (43)$$

Taking the time derivative of (43) and making use of the Fokker–Planck equation (33) and the relation between the current and the chemical potential (25), one finds [50]:

$$\frac{d}{dt} U(t) - T \frac{d}{dt} S(t) = -T \dot{S}_{\text{prod}}(t) + \dot{E}_{\text{in}}(t) - \dot{W}(t), \quad (44)$$

with

$$\dot{S}_{\text{prod}}(t) \equiv \frac{\kappa}{T} \int_0^L dx \varrho(x, t) [\partial_x \mu(x, t) - F]^2, \quad (45)$$

which is nonnegative. Using the first law (40), the above expression can be rewritten in a more familiar way as

$$\frac{d}{dt} S(t) + \frac{\dot{Q}(t)}{T} = \dot{S}_{\text{prod}}(t) \geq 0. \quad (46)$$

The l.h.s. of the equation contains two terms: the first one,  $dS/dt$ , is the increase of the entropy of the system; the second one,  $\dot{Q}/T$ , is the increase of the entropy of the thermal bath. Then, the sum  $\dot{S}_{\text{prod}}$  is the increase of the entropy of the universe or entropy production per unit of time, which has been proved to be positive.  $\dot{S}_{\text{prod}}$  vanishes only in equilibrium, i.e. only if both the external force  $F$  and the gradient of the chemical potential vanish. Notice also that the entropy production has the usual form in thermodynamics of irreversible processes [20]: it is the space integral of the product of the current  $J(x, t)$  times a thermodynamical force  $F - \partial_x \mu$  divided by the temperature.

To relate these results to the discussion in Sect. 2.2, let us consider the cyclic character of the model. The system, after a number of cycles, reaches a stationary regime where  $\varrho(x, t)$  and every state function, like the entropy  $S(t)$  or the internal energy  $U(t)$ , are periodic in time. Then, integrating over a period equations (40) and (46), we obtain

$$\begin{aligned} E_{\text{in}} &= Q + W \\ E_{\text{in}} - W &= TS_{\text{prod}}, \end{aligned} \quad (47)$$

where  $E_{\text{in}}$ ,  $W$ ,  $Q$ , and  $S_{\text{prod}}$  stand for the integral over a period of  $\dot{E}_{\text{in}}(t)$ ,  $\dot{W}(t)$ ,  $\dot{Q}(t)$ , and  $\dot{S}_{\text{prod}}(t)$ , respectively. Taking into account that, in a deterministically forced ratchet, the entropy of the external agent does not change and  $G_{\text{in}} = E_{\text{in}}$ , we recover the main result of Sect. 2.2, namely, (3), which implies in this case that there is an unavoidable dissipation of heat to the thermal bath (see Fig. 2) and, consequently, the efficiency of the motor cannot be bigger than one, and it reaches this value only if the entropy production is zero.

What we have presented is, in fact, a proof of the compatibility between the Langevin and Fokker–Planck formalisms of the Brownian motion and the two laws of thermodynamics. The same proof of compatibility, for  $F = 0$  and for underdamped particles, can be found in [55]. It is also worth

mentioning that inequality (46) can be violated if the external agent possesses information about the position of the particle and modifies the potential according to this information. This can happen in macroscopic systems undergoing symmetry-breaking phase transitions as we have shown in [47], in close relation with the Maxwell demon.

## 5 Deterministically forced ratchets II: the quasistatic limit

We mentioned in Sect. 3 that a possible strategy to decrease the entropy production, and consequently increase the efficiency of the motor, is to modify the potential very slowly. In this case, the probability density of the particle is always close to the equilibrium profile, and one expects a low entropy production. This is indeed the case. However, we will see in this section that only a certain class of ratchets can work arbitrarily close to equilibrium. Remarkably, ratchets consisting of slowly modulated potentials do not belong to this class.

This can be proved since the forced ratchet can be solved for an arbitrary potential  $V(x, t)$  in the quasistatic limit, i.e. when the potential  $V(x, t)$  changes infinitely slowly.

Let us start with  $F = 0$ . In this case, the work  $\dot{W}(t)$  is obviously zero, but we can still calculate the current  $J(x, t)$  which will be useful to obtain  $\dot{W}(t)$  later on.

At first sight, the adiabatic limit looks trivial. At any time  $t$ , the system is in equilibrium with the potential  $V(x, t)$ , i.e. the probability distribution is

$$\varrho_-(x, t) \equiv \frac{e^{-\beta V(x, t)}}{Z_-(t)}, \quad (48)$$

where  $Z_-(t)$  is a normalization constant (the subindex will be clear below). For this probability distribution the current vanishes. However, the integral of the current along the cycle can be different from zero in some cases [46, 48].

To prove this one has to solve the Fokker–Planck equation up to linear terms in  $\partial_t V(x, t)$ . The current at  $x = L$  can be found analytically [46, 50] and the result is

$$J(L, t) = \int_0^L dx \int_0^x dx' \varrho_+(x, t) \partial_t \varrho_-(x', t), \quad (49)$$

where  $\varrho_+(x, t)$  is a new probability distribution:

$$\varrho_+(x, t) \equiv \frac{e^{\beta V(x, t)}}{Z_+(t)}, \quad (50)$$

$Z_+(t)$  being a normalization constant.

In the quasistatic limit, the time derivative of  $\varrho_-(x, t)$  vanishes, and so does the current  $J(L, t)$ . However, the integral of  $J(L, t)$  along the cycle  $[0, \tau]$  can be, in some cases, different from zero. We define the integrated flow as

$$\phi_0 \equiv \int_0^\tau dt J(x, t), \quad (51)$$

which does not depend on the point  $x$ . Therefore,  $\phi_0$  can be calculated by integrating  $J(L, t)$  as given by (49). We have

called reversible ratchets those systems where the integrated flow is different from zero. They exhibit reversible, adiabatic, or quasistatic transport, i.e. the particle moves toward a direction and nevertheless is in equilibrium at any time.

As mentioned above, a slow modulation between two potentials  $V_A(x)$  and  $V_B(x)$ , i.e. if  $V(x, t) = \alpha(t)V_A(x) + [1 - \alpha(t)]V_B(x)$ , with  $\alpha(t)$  a periodic function oscillating between 0 and 1, can never be a reversible ratchet. This is proved by means of the change of variable  $t \rightarrow \alpha(t)$  in the integral (51). Notice that this is the case of the flashing ratchet [7]. In order to have a nontrivial reversible ratchet, the potential  $V(x, t)$  must depend on two or more parameters and must describe a loop in the space of parameters [46].

To build a Brownian motor from a reversible ratchet we must add a load  $F$ . The Fokker–Planck equation (33) can still be solved up to first order in  $F$  and  $1/\tau$ , and an explicit expression for the efficiency, exact in the quasistatic limit, is given in [48, 50]. In this case, the stopping force is of order  $1/\tau$ , since the force is acting along the whole cycle  $[0, \tau]$  and induces a current  $J(x, t)$  of order  $F$  at any time. This current, when integrated over the cycle, yields a contribution of order  $F\tau$ . Still, we can have a motor in the adiabatic limit if  $F$  goes to zero as  $1/\tau$ . Notice however that this is possible only for reversible ratchets, which can reach efficiencies arbitrary close to  $\eta = 1$ , whereas the efficiency of irreversible ratchets vanishes in the quasistatic limit (cf. Fig. 6). The previous theory has been applied to a model called sluice ratchet in [46] and [48], which has been proposed as a model for biological ion pumps [50]. Another example of reversible ratchet, based on a traveling potential, is studied in [39].

The theory of reversible ratchets can have some general consequences for protein motors, such as kinesins, myosins, or ion pumps in the cell membrane. They can be modeled as a single degree of freedom  $x(t)$  in a potential determined by the shape of a protein. Depending on the type of motor, the degree of freedom is the position of the protein itself or the position of an ion. ATP hydrolysis changes the shape of the protein and consequently changes the potential [2, 11, 17, 28, 37] as in the present model. The above conclusions indicate that the shape of the protein must change, describing a loop in some abstract space of parameters, if the interaction potential between the protein and the degree of freedom of the motor has to be a reversible ratchet. This is equivalent to saying that an efficient motor cannot work by jumps between only two states, but needs to perform some type of cycle with at least three states.

## 6 Rocking ratchets

A rocking ratchet can be briefly defined as a Brownian degree of freedom which exhibits a direct current (DC) when a purely alternating voltage (AC) is applied [40]. The Langevin equation reads

$$\dot{x}(t) = \kappa [-V'(x) + F_{AC}(t) + F + \xi(t)], \quad (52)$$

where  $F_{AC}(t)$  is a periodic forcing, with period  $\tau$  and zero time average, exerted by the external agent.

The input energy per unit of time is [54, 60]

$$\begin{aligned}\dot{E}_{\text{in}} &= - \int_0^\tau dt \int_0^L dx \varrho(x, t) x \frac{dF_{\text{AC}}(t)}{dt} \\ &= \int_0^\tau dt J(t) F_{\text{AC}}(t)\end{aligned}\quad (53)$$

with

$$J(t) \equiv \int_0^L dx J(x, t), \quad (54)$$

and again equals the supply of free energy,  $\dot{G}_{\text{in}} = \dot{E}_{\text{in}}$ , because the external agent carries no entropy. The efficiency can be written as

$$\eta = \frac{F \langle J(t) \rangle}{\langle F_{\text{AC}}(t) J(t) \rangle}, \quad (55)$$

where the brackets indicate a temporal average along a period.

In the quasistatic limit,  $J(t)$  is a function of  $F_{\text{AC}}(t)$ . For instance, for electrical devices, this is nothing but the characteristic function of the device, i.e. the relationship between current and voltage. Sokolov [60] has studied the efficiency of rocking ratchets in this quasistatic limit, finding that the efficiency can reach the thermodynamic upper bound  $\eta = 1$  if the rocking force is synchronized with the motion of the Brownian particle. Other works have investigated the dependence of the efficiency on the temperature  $T$  [34, 61]. It has been shown that, in the quasistatic limit, the efficiency of some rocking ratchets can be optimized at finite  $T$  [61]. Finally, Dan et al. [19] have studied the efficiency of rocking ratchets when the diffusion constant depends on the position of the particle, with similar conclusions.

## 7 Chemical motors

### 7.1 The flashing ratchet as a chemical motor

The flashing ratchet introduced by Ajdari and Prost [1] can be reinterpreted as a chemical motor, as suggested in [6, 7, 32]. Consider the following reaction in one dimension:



where A, B, and C feel potentials  $V_A(x)$ ,  $V_B(x)$ , and  $V_C(x)$ , respectively (this could be the case if, for instance, A and C are charged particles with opposite charge and B is neutral). The reaction–diffusion equations for the concentrations read

$$\begin{aligned}\partial_t \varrho_A(x, t) &= -\partial_x J_A(x, t) - r(x, t), \\ \partial_t \varrho_B(x, t) &= -\partial_x J_B(x, t) + r(x, t), \\ \partial_t \varrho_C(x, t) &= -\partial_x J_C(x, t) - r(x, t),\end{aligned}\quad (57)$$

where

$$\begin{aligned}J_\alpha(x, t) &= \kappa_\alpha [-V'_\alpha(x) + F - kT \partial_x] \varrho_\alpha(x, t) \\ &= -\kappa_\alpha \varrho_\alpha(x, t) [\partial_x \mu_\alpha(x, t) - F]\end{aligned}\quad (58)$$

are the spatial currents of each species, and

$$r(x, t) = \omega_+(x) \varrho_A(x, t) \varrho_C(x, t) - \omega_-(x) \varrho_B(x, t). \quad (59)$$

The reaction rates  $\omega_\pm$  obey the detailed balance condition (19). For zero load,  $F = 0$ , the stationary solution of this set of equations is the Gibbs state (which satisfies the equilibrium condition (12)):

$$\varrho_\alpha^{\text{st}}(x) = N_\alpha e^{-\beta(\mu_\alpha^0 + V_\alpha(x))}, \quad (60)$$

where  $N_\alpha$  are constants depending on the initial condition and satisfying  $N_A N_B / N_C = 1$ . We can now eliminate the species C in (57) and write an equation for the concentrations of A and B:

$$\begin{aligned}\partial_t \varrho_A(x, t) &= -\partial_x J_A - \hat{\omega}_+ \varrho_A + \hat{\omega}_- \varrho_B, \\ \partial_t \varrho_B(x, t) &= -\partial_x J_B + \hat{\omega}_+ \varrho_A - \hat{\omega}_- \varrho_B,\end{aligned}\quad (61)$$

where  $\hat{\omega}_+ = \varrho_C \omega_+$  and  $\hat{\omega}_- = \omega_-$  obey

$$\frac{\hat{\omega}_+(x)}{\hat{\omega}_-(x)} = e^{-\beta(\Delta\mu^0 + V_B(x) - V_A(x) - V_C(x) - kT \ln \varrho_C(x))}. \quad (62)$$

The system can be driven out of equilibrium by imposing a nonequilibrium concentration of C. For instance, to obtain  $\omega_+ = \omega_-$ , as in the original flashing ratchet, we need a concentration of C with a nonuniform chemical potential:

$$\mu_C(x) = V_B(x) - V_A(x) + \mu_B^0(T) - \mu_A^0(T). \quad (63)$$

What is the efficiency in this case? If we consider the C particles as the fuel of the motor, then the consumed free energy in a reaction occurring at  $x$  is  $\mu_C(x)$ . Therefore, the total Gibbs free energy consumption per unit of time is

$$\begin{aligned}\dot{G}_{\text{in}} &= \int dx r(x) \mu_C(x) \\ &= \int dx r(x) [V_B(x) - V_A(x)],\end{aligned}\quad (64)$$

where we have used the fact that the total rate  $r \equiv \int dx r(x)$  vanishes in the stationary regime. As introduced in Sect. 2.2, the efficiency of the engine is

$$\eta = - \frac{F(J_A + J_B)}{\dot{G}_{\text{in}}}. \quad (65)$$

Therefore, the definition of efficiency coincides with the one studied in Sect. 3, even though there we did not take into account the change of free energy in the external agent. The reason is that the number of C particles remains constant in the stationary regime ( $r = 0$ ) and, therefore, the external agent does not experience any change of entropy. We present in Sect. 7.3 a proof of the compatibility between a wide class of chemical motors and the second law of thermodynamics, which also applies to this interpretation of the flashing ratchet.



## 7.2 A chemical ‘Maxwell demon’

There is an alternative way of deviating a chemical system from equilibrium: to create a difference of chemical potential in a chemical cycle. This is the case considered extensively by Parmeggiani et al. [45] and by Zhou and Chen [65]. In fact, we believe that this type of chemical motors is more easily realizable than the one discussed above. Moreover, in this case the input of free energy can be different from the input of energy.

We first illustrate this type of motor with a simplified version of the models introduced in [45]. Consider the following flashing ratchet: a Brownian particle in a thermal bath at temperature  $T$  and confined in the interval  $[0, L]$ , with two different periodic potentials,  $V_A(x) = \delta(x)$  and  $V_B(x) = \delta(x - L/2)$ . If we add a load, the two potentials plus the potential energy due to the load are depicted in Fig. 7, where  $V_A(x)$  has been vertically shifted for clarity.

Let us suppose first a deterministic switching between the two potentials. It is easy to prove that a periodic switching produces no current for zero load. However, if the switching is activated depending on the location of the particle, then we can easily induce a current in any direction. For instance, if we switch from  $V_A$  to  $V_B$  at  $x = 3L/4$  and from  $V_B$  to  $V_A$  at  $x = L/4$ , then the particle will move to the right, even when the load is present. Moreover, in each switching the particle neither gains nor loses energy. Therefore, we can perform the switches with zero energy cost. The particle moves against the load performing some work, but the energy necessary to do this is taken entirely from the thermal bath. We have a true Maxwell demon. In fact, what the ratchet does is to wait until there is a fluctuation of the Brownian particle against the load and to place a barrier behind the particle. This system violates the second law of thermodynamics. The reason is that we are using information about the position of the particle, exactly as the Maxwell demon, and we have not included the energy or entropy cost of the acquisition of such information. The same conclusion could be reached for almost any flashing ratchet: information about the position of the particle could be used to increase the efficiency of the corresponding motor (see [5] for another account of the relationship between entropy, efficiency, and information in the flashing ratchet).

Nevertheless, we can reinterpret the above example as a chemical motor with localized transitions compatible with

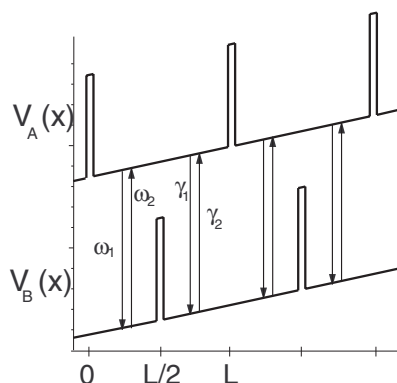
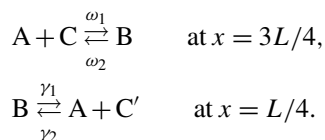


FIGURE 7 Two potentials and transitions in a chemical Maxwell demon

the second law. To do this, assume that the particle can be in either of two possible internal states A and B and that transitions between these internal states are carried out by chemical reactions localized in two active sites of the interval  $[0, L]$ :



Notice that the equilibrium condition of this chemical cycle implies  $\mu_C = \mu_{C'}$ . If we now drive the system out of equilibrium by imposing a difference of chemical potential:

$$\Delta\mu_{\text{fuel}} \equiv \mu_C - \mu_{C'}, \quad (66)$$

a current  $J$  is induced in the system. It is not difficult to solve the model analytically [31]. Although the expression for the current  $J$  is somewhat involved, the efficiency turns out to be quite simple. The input of free energy per unit of time is  $\dot{G}_{\text{in}} = r\Delta\mu_{\text{fuel}}$ , where  $r$  is the rate of either of the two reactions in (7). In the stationary regime, the rates of the two reactions are equal and they are also equal to the current,  $r = J$ . Therefore

$$\eta = \frac{|F|L}{\Delta\mu_{\text{fuel}}}. \quad (67)$$

From this equation it seems that we can again reach an efficiency greater than one by increasing the load  $|F|$ . However, this is not the case, because the stopping force is  $F_{\text{stop}} = \Delta\mu_{\text{fuel}}/L$ . Consequently, the maximum efficiency is  $\eta = 1$  and it is reached when the current vanishes, i.e. when the system works close to equilibrium.

Zhou and Chen [65] have considered a chemical motor consisting of a cycle but with delocalized reactions. Prost et al. [51], and subsequently Parmeggiani et al. [45], have also studied several models analogous to the one discussed here. They find a quite remarkable feature for some potentials: far from equilibrium the efficiency can increase with  $\Delta\mu_{\text{fuel}}$  and is even bigger than the efficiency in the limit  $\Delta\mu_{\text{fuel}} \rightarrow 0$ , i.e. when the system is close to equilibrium. This does not contradict the statements of Sect. 2.2, but indicates that in this limit the entropy production  $\dot{S}_{\text{prod}}$  and the input free energy  $\dot{G}_{\text{in}} = r\Delta\mu_{\text{fuel}}$  both vanish whereas the quotient tends to a finite value.

## 7.3 General theory for discrete chemical states

For a system with  $\alpha = 1, \dots, n$  species and  $\sigma = 1, \dots, s$  reactions, the equilibrium conditions are

$$\mu_\alpha(x) = \mu_\alpha \quad \text{Mechanical equil.},$$

$$\Delta\mu_\sigma(x) \equiv \sum_\alpha a_{\alpha,\sigma} \mu_\alpha(x) = 0 \quad \text{Chemical equil.}, \quad (68)$$

where  $a_{\alpha,\sigma}$  is the stoichiometric coefficient of species  $\alpha$  in reaction  $\sigma$  with the usual convention for the sign: the coefficient  $a_{\alpha,\sigma}$  is positive (negative) if  $\alpha$  appears in the r.h.s. (l.h.s.) of reaction  $\sigma$ . The first condition is equivalent to the absence of

spatial currents in the system for zero load, whereas the second condition is equivalent to the absence of a net reaction rate at point  $x$ .

As we have seen in the previous examples, one can drive the system out of equilibrium in several ways. The first consists of imposing a concentration of some species yielding a nonconstant chemical potential. The flashing ratchet considered above is an example. In the second we impose a chemical potential which is not compatible with the set of equations implying chemical equilibrium. The simplest way is to consider a cycle:



where  $A$  is a set of products,  $C$  is the fuel,  $C'$  is the degraded fuel, and the dashed arrow represents a set of chemical reactions. In the cycle, we can break the chemical equilibrium by imposing  $\mu_C - \mu_{C'} > 0$ .

We present now a general formalism which includes all these cases. Let us split the species into two sets:  $i = 1, \dots, m$  will denote the proper species of the motor, i.e. those whose current releases work to the load; and  $f = m + 1, \dots, n$  will denote the fuel molecules, i.e. those whose chemical potentials  $\mu_f(x)$  are imposed from outside. As before,  $\alpha = 1, \dots, n$  will denote the whole set of reactants, including motor molecules and fuel molecules. All the sums over  $\alpha, i$ , and  $f$  run over their respective ranges.

The evolution equations for the molar concentration of motor molecules are

$$\partial_t Q_i(x, t) = -\partial_x J_i(x, t) + \sum_{\sigma} a_{i,\sigma} r_{\sigma}(x), \quad (70)$$

where  $r_{\sigma}(x)$  is the rate of reaction  $\sigma$ . The reaction rates and the currents are related to the chemical potentials of the species by (21) and (25), respectively. In the stationary regime, the input free energy is

$$\dot{G}_{\text{in}} = -\sum_{f,\sigma} a_{f,\sigma} \int dx \mu_f(x) r_{\sigma}(x), \quad (71)$$

whereas the released work is

$$\dot{W} = -\sum_i \int dx J_i(x) F. \quad (72)$$

Using (25), we can write

$$\dot{W} = -\sum_i \int dx \left[ \frac{J_i(x)^2}{\kappa_i Q_i(x)} + J_i(x) \partial_x \mu_i(x) \right]. \quad (73)$$

Integrating by parts the second term and using (70), one has

$$\dot{W} = -\sum_i \int dx \left[ \frac{J_i(x)^2}{\kappa_i Q_i(x)} - \sum_{\sigma} a_{i,\sigma} r_{\sigma}(x) \mu_i(x) \right]. \quad (74)$$

$$\begin{aligned} T \dot{S}_{\text{prod}} &= \dot{G}_{\text{in}} - \dot{W} \\ &= \int dx \left[ -\sum_{\sigma} \Delta \mu_{\sigma}(x) r_{\sigma}(x) + \sum_i \frac{J_i(x)^2}{\kappa_i Q_i(x)} \right], \end{aligned} \quad (75)$$

which is a positive quantity, because reactions always flow in the direction of decreasing chemical potential and therefore  $\Delta \mu_{\sigma} r_{\sigma} < 0$  for any reaction  $\sigma$  (see (21)). The terms in the above expression have the usual form in linear irreversible thermodynamics: they are the product of a thermodynamical force ( $\Delta \mu_{\sigma}$  for the chemical reaction,  $\partial_x \mu_i(x) - F$  for the position) times a flow ( $r_{\sigma}(x)$  for the reaction,  $J_i(x)$  for the position) [20]. This is not surprising since the reaction–diffusion equations can be obtained in the framework of linear irreversible thermodynamics (although they can yield nonlinear relationships between the load, the chemical potential differences, the spatial current, and the reaction rate).

This theory could be extended to include a time dependence in the potentials. Work in this direction has been reported in [8, 9, 43], where the effects of an AC electric field on models of membrane proteins are investigated.

#### 7.4 General theory for continuous chemical coordinates

For continuous chemical coordinates, we restrict ourselves to chemical cycles, as given by (69). We partly follow an approach originally introduced by Magnasco [41] (see also [36]). Consider an overdamped Brownian particle whose internal state is described by a continuous chemical coordinate  $y$ . We can define a chemical potential  $\mu(x, y)$  which depends both on the position of the particle and on its internal state. Since we are considering cycles, the chemical coordinate is periodic or, equivalently, lies in the interval  $[0, 1]$  with periodic boundary conditions. If the chemical potential has several wells separated by activation barriers whose heights are much bigger than  $kT$ , then  $y$  is localized mostly around the minima of the wells and the model reduces to a set of cyclic chemical reactions such as (69) with reactions rates given by Kramer's theory [20, 25]. In equilibrium the chemical potential is periodic ( $\mu(x, y) = \mu(x + L, y + 1)$ ) and the joint probability density for the particle in  $\Omega = [0, L] \times [0, 1]$  will be

$$\varrho^e(x, y) = \frac{1}{Z} e^{-\beta \mu(x, y)}, \quad (76)$$

where  $Z$  is a normalization factor.

The system can be driven away from equilibrium by a load  $F$ , acting on coordinate  $x$ , and a difference of chemical potential  $\Delta \mu_{\text{fuel}}$ , acting on coordinate  $y$  and uniform along the spatial coordinate  $x$ . We assume an overdamped dynamics for the two coordinates of the particle. The corresponding Langevin equation is

$$\begin{aligned} \dot{x}(t) &= \kappa_x [F - \partial_x \mu(x(t), y(t)) + \xi_x(t)], \\ \dot{y}(t) &= \kappa_y [\Delta \mu_{\text{fuel}} - \partial_y \mu(x(t), y(t)) + \xi_y(t)], \end{aligned} \quad (77)$$

where  $\kappa_x$  and  $\kappa_y$  are the inverse of ‘friction’ coefficients and  $\xi_x(t)$ ,  $\xi_y(t)$  are Gaussian white noises which represent the interaction of the particle with the thermal bath. They satisfy

$$\begin{aligned} \langle \xi_x(t) \rangle &= \langle \xi_y(t) \rangle = 0, \\ \langle \xi_i(t) \xi_j(t') \rangle &= 2kT \kappa_i^{-1} \delta_{ij} \delta(t - t'), \end{aligned} \quad (78)$$

with  $i = x, y$ . The time-evolution equation for the probability density of the particle is

$$\partial_t \varrho(x, y, t) = -\nabla \mathbf{J}(x, y, t), \quad (79)$$

where  $\mathbf{J}(x, y, t) = (J_x, J_y)$  is a vector whose components are the spatial current and the rate of the reaction, respectively:

$$J_i(x, y, t) = \kappa_i [F_i - \partial_i \mu(x, y) - k_B T \partial_i] \varrho(x, y, t), \quad (80)$$

with  $F_x = F$  and  $F_y = \Delta \mu_{\text{fuel}}$ .

The free-energy consumption and work are

$$\begin{aligned} \dot{G}_{\text{in}} &= \int dx dy F_y J_y(x, y), \\ \dot{W} &= - \int dx dy F_x J_x(x). \end{aligned} \quad (81)$$

Therefore

$$T \dot{S}_{\text{prod}} = \dot{G}_{\text{in}} - \dot{W} = \int dx dy \mathbf{J}(x, y) \cdot \mathbf{F} \quad (82)$$

and, following similar steps as in Sect. 4, one can prove that, in the stationary regime:

$$T \dot{S}_{\text{prod}} = \int dx dy \varrho [\kappa_x (F - \partial_x \mu)^2 + \kappa_y (\Delta \mu - \partial_y \mu)^2], \quad (83)$$

which is positive.

In this type of motor, the chemical bias  $\Delta \mu_{\text{fuel}}$  creates both a spatial and a chemical current. The chemical current flows in the same direction as the bias and the spatial current persists for  $F < F_{\text{stop}}$ . The motor can of course work the other way around, i.e. transforming mechanical energy into chemical energy. This possibility has been explored in [32, 45].

### 7.5 Linear response theory

For a small load  $F$  and a small difference of chemical potential  $\Delta \mu_{\text{fuel}}$ , a linear response theory has been introduced by Jülicher et al. [32]. We follow the exposition made in [45]. The theory is valid both for continuous or discrete chemical coordinates, but only when the chemical bias is a single parameter  $\Delta \mu_{\text{fuel}}$ . The basic assumption is that the reaction rate  $r$  and the mean velocity  $v = \int dx J(x)$  depend linearly on the load and  $\Delta \mu_{\text{fuel}}$ , i.e.

$$\begin{aligned} v &= \lambda_{11} F + \lambda_{12} \Delta \mu_{\text{fuel}}, \\ r &= \lambda_{21} F + \lambda_{22} \Delta \mu_{\text{fuel}}. \end{aligned} \quad (84)$$

The second law implies that  $\lambda_{11} \lambda_{22} - \lambda_{12} \lambda_{21} > 0$ , which is equivalent to (82) and the positiveness of (83) or, in this new notation

$$vF + r \Delta \mu_{\text{fuel}} > 0 \quad (85)$$

for all  $F$  and  $\Delta \mu_{\text{fuel}}$ . Moreover, the Onsager reciprocity relations imply  $\lambda_{12} = \lambda_{21}$ . The efficiency is

$$\eta = - \frac{Fv}{r \Delta \mu_{\text{fuel}}} = - \frac{\lambda_{11} a^2 + \lambda_{12} a}{\lambda_{21} a + \lambda_{22}}, \quad (86)$$

with  $a = F / \Delta \mu_{\text{fuel}}$ . In [45], the above expression is discussed in detail. In particular, it is shown that the motor can work either by transforming chemical energy into mechanical energy or the other way around, and that the efficiency is singular and multivalued in the limit to equilibrium conditions,  $F, \Delta \mu_{\text{fuel}} \rightarrow 0$ . As mentioned before, a number of models beyond the regime of linear response is studied in [45].

## 8 Thermal Brownian motors

### 8.1 The Feynman ratchet

In his Lectures [23], Feynman presented a model of a rectifier of thermal fluctuations based on an idea originally proposed by Smoluchowski [56]. It consists of a ratchet forced by a pawl to turn only in a given direction and connected with vanes immersed in a fluid at temperature  $T_1$ . The vanes provide thermal fluctuations that are rectified by the ratchet and the pawl. Feynman showed that the ratchet and pawl must be at a temperature  $T_2 < T_1$ , i.e. they must be colder than the vanes to be able to rectify the fluctuations. Moreover, he proved that the efficiency of the engine is equal to the Carnot efficiency when operates quasistatically, i.e. when the load  $F$  approaches the stopping force  $F_{\text{stop}}$ .

However, some inconsistencies in Feynman's argument were found in [49]. In this paper, we showed that Carnot efficiency cannot be reached by the ratchet engine and, moreover, that the efficiency vanishes in the limit  $F \rightarrow F_{\text{stop}}$ , a feature that has been found later on in most Brownian motors. The reason is that in this limit the system is still out of equilibrium: the system is in contact with the thermal baths at different temperatures and the degree of freedom of the ratchet can transfer energy from one to the other, exhibiting a nonzero thermal conductivity [49]. Consequently, there is an entropy production whereas the work released tends to zero when  $F \rightarrow F_{\text{stop}}$ . Sekimoto [54] reached the same conclusions by numerical simulations and theoretical arguments, and so did Magnasco and Stolovitzky [42], who developed a novel analytical approach to solve the problem. Nevertheless, the statement that a single degree of freedom always exhibits a nonzero thermal conductivity has been qualified by Sokolov [59] (see below). On the other hand, Velasco et al. [63] have explored the consequences of the irreversibility of the Feynman ratchet and calculated the efficiency for maximum power, in the spirit of the so-called finite-time thermodynamics (FTT) [4].

### 8.2 Nonlinear resistors at different temperatures

Feynman's ratchet is closely related to the so-called Brillouin paradox [14]. Suppose an electrical circuit consisting of a diode in parallel with a resistor at temperature  $T$ . The thermal noise in the resistor generates a random voltage which, in principle, could be rectified by the diode resulting in a direct current able to perform work. The solution of the paradox is similar to Feynman's arguments: the diode loses its ability to rectify thermal fluctuations if it is at the same temperature as the source of the fluctuations.

However, the circuit works as a motor if the diode is colder than the resistor. This has been proved by Sokolov [58], using an effective Fokker-Planck equation for the probability distribution of the voltage. Moreover, in [59], he extended the theory to circuits with two diodes, finding that ideal diodes yield zero thermal conductivity.

Sokolov's treatment of nonlinear resistors could also be applied to mechanical degrees of freedom with nonlinear friction. In fact, Feynman's ratchet is nothing but a device with a high friction in one direction and a low friction in the other. However, there is no satisfactory theory of thermal fluctuations for nonlinear friction and there are even doubts that

a theory based on effective Fokker–Planck equations can consistently account for these fluctuations [35]. On the other hand, two thermal baths coupled to a single degree of freedom with linear friction cannot induce any current [49].

### 8.3 The flashing ratchet as a thermal motor

The flashing ratchet can also be interpreted as a system with two degrees of freedom in contact with thermal baths at different temperatures [12, 48, 57]. If the chemical coordinate which represents the two states of the particle is at infinite temperature, then the transition rates  $\omega_+$  and  $\omega_-$  are equal (see (19)). Therefore, the original flashing ratchet can be considered as a thermal Brownian motor working with a hot bath at infinite temperature and a cold bath at temperature  $T$ . The motor still works if the temperature of the hot bath is finite.

Another possibility is to interpret the deterministically flashing ratchet as a Brownian particle with a periodic modulation of the temperature [12, 57]. The absence of potential is here induced by a high temperature. As in the other models, the reported efficiencies are small compared with the upper bound given by Carnot. Finally, other thermal motors and heat pumps have been proposed in [21, 27, 30, 44].

## 9 Other types of Brownian motors

### 9.1 Collective motors

Collective ratchets constitute a field of increasing interest [53]. Some protein motors work in a collective way, such as myosins in the muscular tissue, and the interaction between many thermal ratchets has revealed surprising features like spontaneous symmetry breaking and absolute negative resistance (ANR).

However, the results on the energetics of these collective motors are still scarce. Jülicher and Prost [33] proposed one of the first models of a collective Brownian motor and studied its energetics. The efficiency reported there is rather high, and a novel feature appears: beyond a critical point the state of zero velocity becomes unstable and the stopping force is not defined.

Buceta et al. have proposed a model of a collective ratchet based on the rocking ratchet and exhibiting ANR [15], and have studied its energetics. The efficiency turns to be rather low, i.e. the system works far from equilibrium. Remarkably, its energetics is not sensitively affected by the presence of critical points. However, we believe that, in some cases, the divergence of the susceptibility at critical points should have some dramatic effects on the energetics of a motor. Further work is needed in this direction.

### 9.2 Quantum motors

Although quantum ratchets have been studied to some extent since the seminal work by Reimann et al. [52], the studies on the energetics of this kind of motors are scarce. Humphrey et al. [29] have proposed a model of a quantum Brownian motor consisting of two Fermi gases at different temperatures and with different chemical potentials. The motor can reach Carnot efficiency although there is a continuous transfer of particles from a hot to a cold bath. The reason is that

the transfer is filtered and only particles with energy  $\epsilon^*$  are allowed to pass from one gas to the other. This energy  $\epsilon^*$  is the one for which the two Fermi distributions for the gases intersect. Therefore, the distributions remain invariant throughout the transfer, which does not produce any entropy. Finally, the motor works slightly deviated from this pseudo-equilibrium situation, where the entropy production can be arbitrarily reduced. At first sight, this type of filter resembles a Maxwell demon. However, to our knowledge, such a filter does not violate the second law, as far as it acts in the same manner for both gases. This makes the idea of filtering particles a suitable strategy to devise efficient classical and quantum motors.

## 10 Conclusions

Throughout this paper we have reviewed the literature on the efficiency of Brownian motors, focusing on the compatibility with the laws of thermodynamics. Our aim was to present different physical realizations of Brownian motors and explore the energy flows in the motor operation.

We have discussed the energetics of forced ratchets, chemical motors, and thermal motors. Although forced ratchets are the simplest examples of Brownian motors, we believe that chemical motors are the most relevant in biology and nanotechnology.

With this idea in mind, we have presented a self-contained formulation of chemical Brownian motors based on space-dependent chemical potentials. We think that this concept will help to relate models proposed in the context of theoretical physics to those with a more biological orientation [2, 11, 17, 28, 36, 37]. The former often fail in specifying the source of nonequilibrium fluctuations, whereas the latter are based on chemical cycles but rarely detail the spatial motion of the involved species.

On the other hand, thermal Brownian motors can be of interest in the field of solar and thermoelectric cells where, obviously, efficiency is one of the most important issues and the efficiency of the available transducers is far from the thermodynamic upper bound.

Finally, we would also like to mention that, for the last few decades, there has been an active research line on irreversible motors, the so-called finite-time thermodynamics [4]. However, most of the motors considered by FTT are macroscopic and do not take into account fluctuations. Moreover, they are mostly endo-reversible, i.e. reversible motors where the only contribution to the entropy production is due to the interaction of the motor with its surroundings [16, 18]. Nevertheless, the concepts and strategies developed in FTT, such as calculating the efficiency in the regime of maximum power, will also be valuable for Brownian motors.

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