



Complementarity relation for irreversible processes near steady states



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HIGHLIGHTS

- We show an inequality, connecting work and experimental time, for QS processes.
- We deduce the second law for QS processes with a 1st order correction.
- We analyze the stretching of an RNA molecule and the drag of a dipolar particle.

ARTICLE INFO

Article history:

Received 29 December 2012

Received in revised form 10 May 2013

Available online 24 June 2013

Keywords:

Stochastic energetics

Langevin equation

Thermodynamics

Fluctuation phenomena

ABSTRACT

A relation giving a minimum for the irreversible work in quasi-equilibrium processes was derived by Sekimoto et al. [K. Sekimoto, S. Sasa, J. Phys. Soc. Japan 66 (1997) 3326] in the framework of stochastic energetics. This relation can also be written as a type of “uncertainty principle” in such a way that the precise determination of the Helmholtz free energy through the observation of the work $\langle W \rangle$ requires an indefinitely large experimental time Δt . In the present article, we extend this relation to the case of quasi-steady processes by using the concept of non-equilibrium Helmholtz free energy. We give a formulation of the second law for these processes that extends that presented by Sekimoto [K. Sekimoto, Prog. Theoret. Phys. Suppl. No. 130 (1998) 17] by a term of the first order in the inverse of the experimental time. As an application of our results, two possible experimental situations are considered: stretching of a RNA molecule and the drag of a dipolar particle in the presence of a gradient of electric force.

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1. Introduction

In recent years, there has been a growing interest in studying small mesoscopic systems, immersed in different substrates, such as colloidal particles, nanoparticles in solutions, or biological systems, all of which are dominated by fluctuations. The principal interest is motivated due to recent experimental breakthroughs and technical applications. Thermodynamic notions, such as applied work, dissipated heat and entropy, have been used successfully to analyze processes, in which single

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colloidal particles or biomolecules are manipulated externally [1]. In this area, it is possible to find several studies that have focused on the generation of non-equilibrium situations, from a time-dependent potential, manipulated externally to model the effect of moving laser traps, micropipettes, or atomic force microscopic tips. In all these cases, it is straightforward to find a clear identification of external work, internal energy and dissipated heat, whose consistency has been proven in many experiments, going from the micro to the nano world [2–8].

Several authors have also established a connection between the phenomena related to non-equilibrium steady states and the thermodynamic laws for slow processes connecting different steady states [9–15]. The main objective of this paper is to shed some light on this last point, by addressing the analysis of a quasi-steady process, consisting of a particle in contact with a single bath at temperature T , while some control parameter changes slowly.

The dynamics of this particle can be modeled by a Langevin equation in the framework of Stochastic Energetics (SE) (see below).

According to thermodynamics, if we consider a system in contact with a heat bath and control parameters changes quasi-statically, the work W (done on the system) needed for the change is equal to the variation of Helmholtz free energy, ΔF :

$$W = \Delta F, \quad (1)$$

being ΔF composed by the sum of the reversible heat released to the heat bath, Q_{rev} and the change of internal energy, ΔE : $\Delta F = Q_{rev} + \Delta E$. If the change of the control parameters is not quasi-static, then the necessary work W is larger than the reversible one

$$W - \Delta F = Q_{irr} \geq 0, \quad (2)$$

where Q_{irr} is the irreversible heat that is equal to the difference between the released heat Q and the reversible heat: $Q_{irr} = Q - Q_{rev}$. The released heat Q satisfies the first law:

$$Q + \Delta E = W. \quad (3)$$

In this definition we have adopted that if $Q > 0$ the system dissipates energy to the environment.

In order to obtain the released heat Q for a given protocol of control parameters, it is necessary to have both a dynamical model of the system and a kinematical interpretation of the heat released by the system. An approach was introduced to obtain Q for systems whose dynamics are described by Langevin equations which are now known as *stochastic energetics* [16–18]. It constitutes an intermediary level of description that lies between Hamiltonian dynamics including all degrees of freedom of the concerned system, and thermodynamics where the system is controlled by external agents. In the framework of this approach, for a system that follows a quasi-static isothermal process, a complementarity relation giving a minimum for the product of the irreversible heat times the experimental time, $Q_{irr} \Delta t \geq k_B T \delta_{min}$, was demonstrated in Ref. [9] and an expression for the second law with a first order correction was obtained in Ref. [19]. An extension of the stochastic energetics to the case of quasi-steady (QS) processes and an expression for the second law to zero-th order were presented in Ref. [19]. In the present letter we continue, in one sense, the work initiated in Ref. [19] by generalizing the approach used in Ref. [9]. We are able to show a complementarity relation that is valid for QS processes together with an expression for the second principle with a first order correction. We propose two possible experimental situations in order to discuss the relevance of our results. They are the stretching of a RNA molecule and the drag of a dipolar particle subjected to a gradient of electric field. For the last we detect a difference in the irreversible heat given by a temperature-dependent term, which appears only in one case, i.e. when the stiffness constant is varied too.

This work is organized as follows: in the next section we apply the approach of SE to the case of the QS processes followed by a system satisfying a Langevin equation (already used in Ref. [19] but with slightly more general expression for the applied forces). At the same time, we sketch the principal steps of SE. We obtain our results and then in Section 3 we exemplify them by studying a simple model. In Sections 5 and 6 we illustrate the results in two models of possible applications related to the stretching of a RNA molecule and to the drag of a dipolar particle in the presence of a electric gradient. The next section is for the conclusions. Some computing is included in the [Appendices A](#) and [B](#), in order not to deviate the text from the principal line of reasoning.

2. Stochastic energetics. The case of irreversible processes near steady states. The second principle

We are going to extend the approach followed in Ref. [9] for irreversible processes near equilibrium states, to the case of irreversible processes near steady states. To that end we consider a generalization of the model studied in Ref. [19, Section 5], which exhibits the features of a QS process. We study the response of a system in contact with a single bath, at temperature T , in the limit of very strong friction. Let $\mathbf{x} = \{x_1, \dots, x_n\}$ representing the state of the fluctuating system and $\mathbf{b} = \{b_1, \dots, b_r\}$ the parameters that control the system through the potential $U(\mathbf{x}(t); \mathbf{a}(t); \mathbf{b}(t)) = U(\mathbf{x}(t) - \mathbf{a}(t); \mathbf{b}(t))$. The quantity $\mathbf{a}(t)$ is another parameter that models a conservative force. We consider the QS state where $\dot{\mathbf{a}} = \mathbf{v}$, with \mathbf{v} a constant velocity and, for simplicity, we can take $\mathbf{a}(0) = 0$. Besides the conservative forces arising from the potential $U(\mathbf{x} - \mathbf{a}; \mathbf{b}(t))$, we can perturb the particle by a direct force \mathbf{f} which we assume constant. This force may include all the conservative and non-conservative contributions that do not depend on \mathbf{a} . We describe the stochastic particle motion through the Langevin equation as follows:

$$\Gamma \cdot \frac{d\mathbf{x}}{dt} = -\frac{\partial U}{\partial \mathbf{x}}(\mathbf{x}; \mathbf{a}; \mathbf{b}) + \xi(t) + \mathbf{f} \quad (4)$$

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