Thermodynamics of a stochastic twin elevator

Niraj Kumar,[1] Christian Van den Broeck,[2] Massimiliano Esposito,[3] and Katja Lindenberg[1]

[1]*Department of Chemistry and Biochemistry and BioCircuits Institute, University of California San Diego,*
9500 Gilman Drive, La Jolla, California 92093-0340, USA
[2]*Hasselt University, B-3590 Diepenbeek, Belgium*
[3]*Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, CP 231, Campus Plaine, B-1050 Brussels, Belgium*

We study the nonequilibrium thermodynamics of a single particle with two available energy levels, in contact with a classical (Maxwell-Boltzmann) or quantum (Bose-Einstein) heat bath. The particle can undergo transitions between the levels via thermal activation or deactivation. The energy levels are alternately raised at a given rate regardless of occupation by the particle, maintaining a fixed energy gap equal to ε between them. We explicitly calculate the work, heat, and entropy production rates. The efficiency in both the classical and the quantum case goes to a limit between 100 and 50% that depends on the relative rates of particle transitions and level elevation. In the classical problem we explicitly find the large deviation functions for heat, work, and internal energy.

I. INTRODUCTION

Over the past decade, there has been growing interest in the stochastic energetics of small systems. This interest is driven in part by the impressive experimental and technological progress in bio- and nanotechnology. At the same time, the study of small-scale systems has led to spectacular developments in nonequilibrium statistical mechanics and thermodynamics. Brownian motors and refrigerators [1], work and fluctuation theorems [2,3], and stochastic thermodynamics [4,5] provide prominent examples of these developments. Among the issues of specific interest are the thermodynamic properties of small-scale stochastic systems and, in particular, the efficiency of interconverting different forms of energy. For classical heat engines, a certain degree of universality has been identified for the transformation of heat into work. In particular, the efficiency η at maximum power is found to be half of Carnot efficiency in the regime of linear response [6]. This result has been illustrated by explicit calculations for several small-scale engines [7–9]. However, many artificial and most biological engines operate in an isothermal environment [10]. They transform one form of energy (e.g., chemical or electrical) into another form (e.g., mechanical or optical). Thermodynamics prescribes that the efficiency of this transformation is at most 100%, a limit again reached for a reversible, hence zero-power transformation. Concerning the efficiency at maximum power, it appears that there is again universality at the lowest order, i.e., in the regime of linear response $\eta = 1/2$ [11]. This result is reminiscent of the so-called maximum power transfer theorem from electrical engineering [12], enunciated by Moritz von Jacobi around 1840: Maximum power is achieved when the load resistance is equal to the source resistance, with corresponding efficiency equal to 50%. The issue of universality beyond linear response is currently under debate [13].

The standard way to apply external work in statistical mechanics is to systematically move (modulate) energy levels or to modulate the potential energy. Unfortunately, the analytic treatment of even the simplest case, namely, modulating a single energy level, appears to be extremely difficult; see, for example, Refs. [8,9,14,15]. The main purpose of this paper is to introduce an exactly solvable toy model that can be solved

in full analytic detail, in both a classical and a quantum setting. We will call it the stochastic twin elevator. We present explicit results for the rates of work, heat, and entropy production. The efficiency of conversion of external work into internal energy is found to vary between 100 and 50%. For the case of a classical bath we also derive the analytic expressions for the large deviation functions [16] that characterize the statistics of the accumulated stochastic work, heat, and internal energy and show that a heat fluctuation theorem is satisfied in the steady state. Such an explicit calculation is the exception rather than the rule [17].

The paper is organized as follows. In Sec. II we introduce the stochastic twin elevator model and present the evolution equations and associated rates of heat, work, internal energy, and entropy production, as well as the results for the efficiency of the energy conversion process. In Sec. III we concentrate on the classical bath and derive the steady-state fluctuation theorem for heat. We also explicitly calculate the large deviation functions for the heat, work, and internal energy. We conclude with a brief summary in Sec. IV.

II. STOCHASTIC TWIN ELEVATOR MODEL

The model is defined as follows. A single particle, in contact with a heat bath, can reside in one of two available energy levels separated by a fixed energy gap equal to $\varepsilon \equiv \epsilon/k_B T$. Here k_B is the Boltzmann constant and T is the temperature of the bath. Thus ε is the energy in units of $k_B T$; all energies will be expressed in these units. The levels are alternately and instantaneously raised at random times at a rate k_c, while maintaining the fixed energy gap ε between them. When the particle occupies the level that is raised, the external agent must perform an amount of work equal to 2ε on the system. If the level that is raised is unoccupied, the external work is zero. Note that this raising of the levels is a disturbance that drives the system away from equilibrium. Due to its contact with the heat bath, the particle can at any time make a thermal transition from the level it is occupying to the other level, absorbing from the bath (if the transition is uphill) or releasing to the bath (for downhill transitions) an amount of heat equal to

to ε. In this way, work and heat can be monitored. At the same time, the entropy produced in the process is known from stochastic thermodynamics; see below for more details.

The technical simplicity of the stochastic twin elevator is due to the following mapping onto a four-state Markovian model. Let us arbitrarily call one of the elevator levels "1" and the other "2." The system can be in one of the four states $\{(1,1),(1,2),(2,1),(2,2)\}$, the first index indicating which state is the lower and the second indicating which state holds the particle. Thus, for example, the state label (1,2) means that level 1 is below level 2, and that the particle occupies level 2 (the higher one in this case). The system undergoes stochastic transitions between the four states. For example, lifting of the lower level in the state (1,1) corresponds to a transition to the state (2,1); see Fig. 1. Similarly, if the particle in state (1,1) makes a thermal jump to the other energy level, the state changes to (1,2). These transitions all take place randomly in time, so that the probability distribution vector **P** with elements

$$\mathbf{P} = \begin{bmatrix} P(1,1) \\ P(1,2) \\ P(2,1) \\ P(2,2) \end{bmatrix} \tag{1}$$

evolves according to the master equation

$$\frac{d\mathbf{P}}{dt} = \mathbf{M}\mathbf{P}. \tag{2}$$

The analysis of the properties of the system is thus reduced to matrix algebra involving a time-independent 4×4 matrix.

Whether the bath is classical or quantum mechanical, the rates for thermal transitions of the particle obey the detailed balance condition

$$\frac{W_{h \to l}}{W_{l \to h}} = e^{\varepsilon}, \tag{3}$$

where W stands for the transition rate, and h and l stand for higher and lower energy levels, respectively.

A. Classical bath

Consider first the case of a classical heat bath, and let k be the transition rate from the higher to the lower energy level in a given configuration. The transition rate from the lower to the higher is $ke^{-\varepsilon}$ (in general, k could depend on temperature):

$$W_{(1,1) \to (1,2)} = W_{(2,2) \to (2,1)} = ke^{-\varepsilon},$$
$$W_{(1,2) \to (1,1)} = W_{(2,1) \to (2,2)} = k. \tag{4}$$

As mentioned before, k_c is the rate of lifting the lower energy level. We conclude that the transition matrix is given by the following expression:

$$\mathbf{M} = \begin{bmatrix} -(ke^{-\varepsilon} + k_c) & k & k_c & 0 \\ ke^{-\varepsilon} & -(k + k_c) & 0 & k_c \\ k_c & 0 & -(k_c + k) & ke^{-\varepsilon} \\ 0 & k_c & k & -(ke^{-\varepsilon} + k_c) \end{bmatrix}$$

$$= k \begin{bmatrix} -(e^{-\varepsilon} + \xi) & 1 & \xi & 0 \\ e^{-\varepsilon} & -(1 + \xi) & 0 & \xi \\ \xi & 0 & -(1 + \xi) & e^{-\varepsilon} \\ 0 & \xi & 1 & -(e^{-\varepsilon} + \xi) \end{bmatrix}, \tag{5}$$

where we have introduced the dimensionless parameter $\xi = k_c/k$. We will exhibit results in terms of the three parameters ε, ξ, and k. We will focus on the steady-state properties. The steady-state probabilities $P(1,1)$, $P(1,2)$, $P(2,1)$, $P(2,2)$, with $P(1,1) + P(1,2) + P(2,1) + P(2,2) = 1$, are found as the components of the right eigenvector of the matrix **M** associated with the zero eigenvalue. Explicitly,

$$P(1,1) = P(2,2) = \frac{e^{\varepsilon}(1 + \xi)}{2[1 + e^{\varepsilon}(1 + 2\xi)]},$$
$$P(1,2) = P(2,1) = \frac{1 + \xi e^{\varepsilon}}{2[1 + e^{\varepsilon}(1 + 2\xi)]}. \tag{6}$$

In the absence of driving, $k_c = 0$, the current between any two states vanishes. However, this is no longer so when $k_c > 0$. In this case the four steady-state currents between the states indicated by the subscripts are given by

$$I \equiv I_{(1,1) \to (1,2)} = I_{(1,2) \to (2,2)} = I_{(2,2) \to (2,1)} = I_{(2,1) \to (1,1)}$$
$$= P(1,1)ke^{-\varepsilon} - P(1,2)k = \frac{k\xi(1 - e^{\varepsilon})}{2[1 + e^{\varepsilon}(1 + 2\xi)]}. \tag{7}$$

Let us look more closely at the nonequilibrium thermodynamic properties. The heat flux to the system (recall that all energies are given in units of $k_B T$) is given by

$$\dot{Q} = \varepsilon [W_{11 \to 12} P(1,1) - W_{12 \to 11} P(1,2)]$$
$$- \varepsilon [W_{21 \to 22} P(2,1) - W_{22 \to 21} P(2,2)]$$
$$= k\varepsilon \left\{ e^{-\varepsilon} [P(1,1) + P(2,2)] - [P(1,2) + P(2,1)] \right\}. \tag{8}$$

The rate of change of the work, that is, the power delivered to the system, is

$$\dot{\mathcal{W}} = 2\varepsilon [W_{11 \to 21} P(1,1) + W_{22 \to 12} P(2,2)]$$
$$= 2\varepsilon k\xi [P(1,1) + P(2,2)], \tag{9}$$

which reflects the fact that work in the amount of 2ε is performed on the system when an occupied level is lifted. Using the First Law of Thermodynamics, the increase in the internal energy of the system per unit time is just the sum of these two contributions,

$$\dot{U} = \dot{\mathcal{W}} + \dot{Q}. \tag{10}$$

Finally, the rate of total entropy production associated with the master equation is given by [4]

$$\dot{S}_i = k_B \sum W_{v, j \to v', j'} P(v, j) \log \frac{W_{v, j \to v', j'} P(v, j)}{W_{v', j' \to v, j} P(v', j')}, \tag{11}$$

where the summation is over all possible states.

The thermodynamic quantities $\dot{Q}$, $\dot{\mathcal{W}}$, $\dot{U}$, and $\dot{S}_i$ in nondimensional form $\dot{q}$, $\dot{w}$, $\dot{u}$, and $\dot{s}_i$ can be rewritten as

$$\dot{q} = \frac{\dot{Q}}{k\xi} = \frac{\varepsilon(1 - e^{\varepsilon})}{1 + e^{\varepsilon}(1 + 2\xi)}, \tag{12}$$

$$\dot{w} = \frac{\dot{\mathcal{W}}}{k\xi} = \frac{2\varepsilon e^{\varepsilon}(1 + \xi)}{1 + e^{\varepsilon}(1 + 2\xi)}, \tag{13}$$

$$\dot{u} = \frac{\dot{U}}{k\xi} = \dot{w} + \dot{q} = \varepsilon, \tag{14}$$

and

$$\dot{s}_i = \frac{\dot{S}_i}{k} = \xi \dot{q}. \tag{15}$$
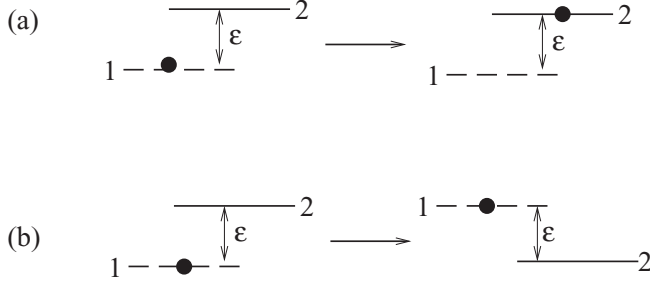
FIG. 1. Schematic representation of the two configurations of the twin elevator. The dotted line represents level 1, while the solid one is level 2. (a) Hopping of particle in configuration 1 from the lower level to the higher level leading to a transition from state (1,1) to (1,2). (b) Transition from configuration 1 to 2 due to lifting of the lower energy level by 2ε thus changing the state from (1,1) to (2,1).

We have plotted the results for the entropy production rate as a function of ε and of ξ in the two left panels of Fig. 2. Note that equilibrium can be reached in two different ways, namely, with $\varepsilon \to 0$ or with $\xi \to 0$. In these limits $\dot{s}_i$ goes to zero. When the system is out of equilibrium, $\dot{s}_i$ increases when ε or ξ increase. (The right panels will be discussed in the next subsection.)

Finally, we turn to the efficiency of the system, which quantifies how efficiently the work done on the system is utilized in increasing its internal energy and is given as

$$\eta = \frac{\dot{U}}{\dot{W}} = \frac{1 + e^\varepsilon(1 + 2\xi)}{2e^\varepsilon(1 + \xi)}. \quad (16)$$

In the two left panels of Fig. 3 we have plotted the results for efficiency as a function of ε and of ξ (the right panels will be discussed in the next subsection). We observe that η decreases
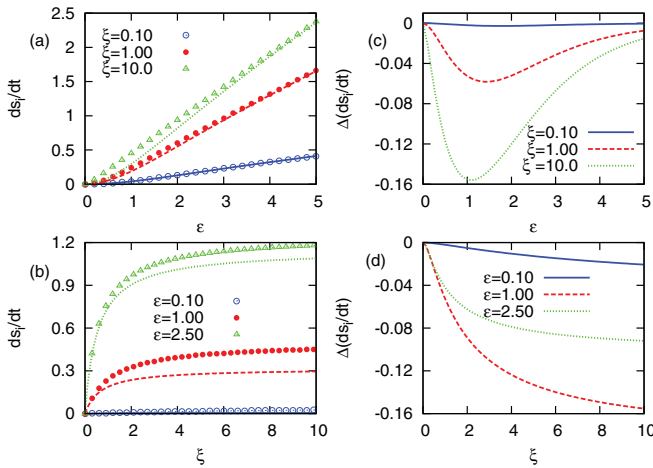

FIG. 2. (Color online) (a) Entropy production rate $\dot{s}_i$ as a function of ε for different values of ξ. The lines are for a classical bath and the symbols for a quantum bath. (b) $\dot{s}_i$ vs ξ for various values of ε. The lines are for a classical bath and the symbols for a quantum bath. (c) Difference in entropy production rates between the classical and quantum bath cases as a function of ε for various values of ξ. (d) Difference in entropy production rates between the classical and quantum bath cases as a function of ξ for various values of ε.
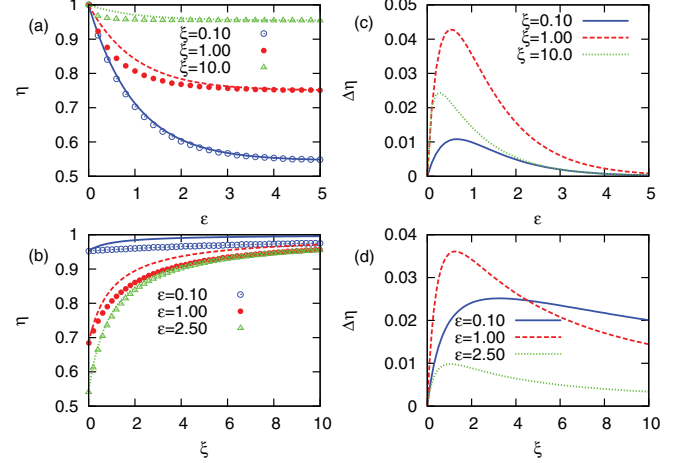

FIG. 3. (Color online) (a) Efficiency η as a function of ϵ for different values of ξ. The lines are for a classical bath and the symbols for a quantum bath. (b) η vs ξ for different values of ε. The lines are for a classical heat bath and the symbols for a quantum bath. (c) Difference of efficiencies between the classical and quantum bath cases as a function of ε for various values of ξ. (d) Difference of efficiency between the classical and quantum bath cases as a function of ξ for various values of ε.

with increasing values of ε [see Fig. 3(a)] and increases with increasing values of ξ [see Fig. 3(b)]. We further note that:

(1) For $\varepsilon \to 0$, $\eta \to 1$. In this limit, all the four states have equal probability equal to 1/4, and so the efficiency $\eta = 1$.

(2) In the other extreme limit, i.e., $\varepsilon \to \infty$, we have

$$\eta \to \frac{1 + 2\xi}{2(1 + \xi)} \to \frac{1}{2}, \quad (17)$$

which decreases from 1 when $\xi \to \infty$ and goes to 1/2 when $\xi \to 0$.

(3) In general, there is a balance between the rate associated with configuration changes and that associated with particle transitions. If the configuration changes very quickly compared to k, the efficiency of the system increases.

B. Quantum bath

The difference between the classical and the quantum versions of our toy model lies in the nature of the bath. In the former, the bath is described by Maxwell-Boltzmann statistics. In the latter, where, for example, the bath excitations might be phonons or photons, the statistics are Bose-Einstein. The rates at which the particle makes a transition between the two levels in a given configuration involve the emission or absorption of these excitations by the bath and are now given by

$$W_{(1,1)\to(1,2)} = W_{(2,2)\to(2,1)} = kn(\varepsilon),$$
$$W_{(1,2)\to(1,1)} = W_{(2,1)\to(2,2)} = k[1 + n(\varepsilon)], \quad (18)$$

where, as before, ε is the energy difference between the levels in units of the thermal energy, $n(\varepsilon) = (e^\varepsilon - 1)^{-1}$ is the Bose-Einstein distribution function, and k is a rate coefficient. Note that these transition elements obey the

detailed balance condition Eq. (3). As in the classical case, the stochastic evolution of the system is described

by the master equation (2), but now with the transition matrix

$$\mathbf{M} = k \begin{bmatrix} -[n(\varepsilon) + \xi] & [n(\varepsilon) + 1] & \xi & 0 \\ n(\varepsilon) & -[1 + n(\varepsilon) + \xi] & 0 & \xi \\ \xi & 0 & -[1 + n(\varepsilon) + \xi] & n(\varepsilon) \\ 0 & \xi & [n(\varepsilon) + 1] & -[n(\varepsilon) + \xi]. \end{bmatrix}. \tag{19}$$

The master equation leads to the steady-state solution for the probabilities

$$P(1,1) = P(2,2) = \frac{e^{\varepsilon}(1 + \xi) - \xi}{2(2e^{\varepsilon}\xi + e^{\varepsilon} - 2\xi + 1)},$$
$$P(1,2) = P(2,1) = \frac{e^{\varepsilon}\xi + 1 - \xi}{2(2e^{\varepsilon}\xi + e^{\varepsilon} - 2\xi + 1)}. \tag{20}$$

Following our earlier rules for the classical case, we can write the rates of heat, work, and internal energy influx into the system. In adimensional form we find

$$\dot{q} = \frac{\varepsilon(1 - e^{\varepsilon})}{2e^{\varepsilon}\xi + e^{\varepsilon} - 2\xi + 1}, \quad \dot{w} = \frac{2\varepsilon(e^{\varepsilon}\xi + e^{\varepsilon} - \xi)}{2e^{\varepsilon}\xi + e^{\varepsilon} - 2\xi + 1},$$
$$\dot{u} = \dot{w} + \dot{q} = \varepsilon, \quad \dot{s}_i = -\xi\dot{q}. \tag{21}$$

In the left panels of Fig. 2 we show the entropy production rate as a function of ε (upper panel, symbols) and of ξ (lower panel, symbols). In the right-hand panels of Fig. 2 we show the difference between the classical and quantum entropy production rates, in panel (c) as a function of ε for different values of ξ, and in panel (d) as a function of ξ for different values of ε. The classical and quantum entropy production rates are equal in the limits $\varepsilon \to 0$ and $\varepsilon \to \infty$, but between these two limits the quantum entropy production rate is everywhere greater than in the classical case. As a function of ξ for fixed ε, the two again become equal as $\xi \to 0$. As $\xi \to \infty$ the difference goes to the limit $-\varepsilon e^{-\varepsilon}/2$.

Finally, we calculate the efficiency of the system:

$$\eta = \frac{\dot{U}}{\dot{W}} = \frac{2e^{\varepsilon}\xi + e^{\varepsilon} - 2\xi + 1}{2(e^{\varepsilon}\xi + e^{\varepsilon} - \xi)}. \tag{22}$$

The efficiency as a function of ε and of ξ are shown by the symbols in the left-hand panels of Fig. 3. We show the difference between the classical and quantum efficiencies (classical minus quantum) in the right-hand panels of Fig. 3 for a number of parameter values. In the limits $\varepsilon \to 0$ and $\varepsilon \to \infty$ the difference between the two goes to zero, as seen in panel (c), as it should. In the limit $\varepsilon \to \infty$ we find

$$\eta = \frac{2\xi + 1}{2\xi + 2}, \tag{23}$$

again exactly as in the classical case. The approach of the classical and quantum results to one another with increasing ε is seen in panel (c) of the figure. For all values of ε between these limits the efficiency is higher in the classical case. As in the classical case, there is in the quantum case a balance between the rate associated with configuration changes and

that associated with particle transitions; if the configuration changes very quickly compared to k, the efficiency of the system increases. In panel (d) we show the difference between classical and quantum efficiencies as a function of ξ for various values of ε. Again, the efficiencies are equal when $\xi = 0$, as they should be. As ξ increases, the difference goes through a maximum (it is always higher in the classical case) and goes to zero again as $\xi \to \infty$ and both efficiencies go to unity.

III. FLUCTUATION THEOREM AND LARGE DEVIATION FUNCTIONS FOR CLASSICAL BATH

We now turn to the classical case to explicitly calculate a number of other thermodynamic properties for the twin elevator system, in particular, the large deviation function and the steady-state fluctuation theorem for heat, as well as the large deviation functions for work and internal energy.

A. Fluctuation theorem for Q

Let Q be the accumulated heat transferred to the reservoir up to time t. Since the transition of the particle between the levels is stochastic, the total accumulated heat Q is also stochastic. Let $P(i,Q,t)$ be the probability that the system is in state i at time t and the heat transferred to the reservoir is Q. The evolution of $P(i,Q,t)$ follows from the equation

$$P(i,Q,t+dt) = \sum_j W_{j\to i} dt \, P(j,Q - \Delta Q_{j\to i},t)$$
$$+ \left(1 - \sum_j W_{i\to j} dt\right) P(i,Q,t). \tag{24}$$

Here $\Delta Q_{j\to i}$ is the amount of heat transferred to the reservoir as a result of a transition of the particle between the levels in state j, the resultant state being state i, with rate $W_{j\to i}$. As always, the quantities $\Delta Q_{j\to i}$ and Q are in units of $k_B T$. The differential form of the evolution equation follows from the master equation (2),

$$\frac{\partial P(i,Q,t)}{\partial t} = \sum_j W_{j\to i} P(j,Q - \Delta Q_{j\to i},t)$$
$$- \sum_j W_{i\to j} P(i,Q,t). \tag{25}$$

We solve the above equation using the characteristic function (the subscript q labels this as the characteristic function for the heat),

$$\rho_q(i,\lambda,t) = \int_{-\infty}^{\infty} dQ\, e^{-\lambda Q} P(i,Q,t), \quad (26)$$

whose evolution equation is obtained directly from Eq. (25),

$$\frac{\partial \rho_q(i,\lambda,t)}{\partial t} = \sum_j W_{j\to i} e^{-\lambda \Delta Q_{j\to i}} \rho_q(j,\lambda,t)$$
$$- \sum_j W_{i\to j} \rho_q(i,\lambda,t). \quad (27)$$

In matrix notation, it can be written as

$$\frac{\partial \rho_q}{\partial t} = \mathbf{M}_q(\lambda)\rho_q, \quad (28)$$

where $\mathbf{M}_q(\lambda)$ is

$$\mathbf{M}_q(\lambda) = k \begin{bmatrix} -(e^{-\varepsilon}+\xi) & e^{-\lambda\varepsilon} & \xi & 0 \\ e^{(\lambda-1)\varepsilon} & -(1+\xi) & 0 & \xi \\ \xi & 0 & -(1+\xi) & e^{(\lambda-1)\varepsilon} \\ 0 & \xi & e^{-\lambda\varepsilon} & -(e^{-\varepsilon}+\xi) \end{bmatrix}, \quad (29)$$

and ρ_q is a column matrix with four components. In writing the above matrix we make use of the fact that during an upward transition of the particle in a given configuration the reservoir loses heat to the system and so q is $-\varepsilon$, and when the particle makes a downward transition heat flows to the reservoir, i.e., $q = +\varepsilon$. We also note that the matrix $\mathbf{M}_\lambda$ and its adjoint $\mathbf{M}_\lambda^\dagger$ satisfy the symmetry relation [18]

$$\mathbf{M}_q(\lambda) = \mathbf{M}_q^\dagger(1-\lambda). \quad (30)$$

The matrix $\mathbf{M}_q(\lambda)$ has four eigenvalues, and the general solution of Eq. (28) is written as a linear combination of the four independent associated eigenvectors. However, the large t behavior of ρ_q is dominated by its largest eigenvalue, i.e.,

$$\langle e^{-\lambda Q} \rangle = \int_{-\infty}^{\infty} dQ\, e^{-\lambda Q} P(Q,t) \sim e^{tf_q(\lambda)}, \quad (31)$$

where $f_q(\lambda)$ is the largest eigenvalue of the matrix $\mathbf{M}_q(\lambda)$, which we find to be

$$f_q(\lambda) = \frac{ke^{-\varepsilon}}{2}[-(2\xi e^\varepsilon + e^\varepsilon + 1)$$
$$+ \sqrt{4\xi e^\varepsilon(\xi e^\varepsilon + e^{\lambda\varepsilon} + e^{(1-\lambda)\varepsilon}) + (1+e^\varepsilon)^2}]. \quad (32)$$

We observe that the eigenvalue $f_q(\lambda)$ obeys the symmetry relation

$$f_q(\lambda) = f_q(1-\lambda), \quad (33)$$

which is a direct consequence of the symmetry relation (30) for the matrix $\mathbf{M}_q(\lambda)$. The above symmetry relation for

the maximum eigenvalue reflects the steady-state fluctuation theorem [2], i.e.,

$$\frac{P(Q)}{P(-Q)} \sim e^Q. \quad (34)$$

It is easy to verify that the average heat per unit time released to the reservoir is given in terms of the first derivative of the maximum eigenvalue evaluated at $\lambda = 0$, i.e.,

$$\langle \dot{Q} \rangle = -\frac{df_q(\lambda)}{d\lambda}\bigg|_{\lambda=0} = \frac{k\xi\varepsilon(e^\varepsilon-1)}{1+e^\varepsilon(1+2\xi)}. \quad (35)$$

We note that the magnitude of $\langle \dot{Q} \rangle$ is the same as that given in Eq. (12) (where the average is understood).

We next turn to the explicit evaluation of the large deviation properties. For this we need to find the probability $P(Q,t)$ for long times. The heat Q is expected to grow linearly in time. We thus introduce the variable $\phi = Q/t = \dot{Q}$, which is the heat flux. The flux ϕ can be positive as well as negative due to gain or loss of heat. According to large deviation theory [16], the probability $P(Q,t)$ at long times can be written as

$$P(Q,t) \sim e^{-tg_q(\phi)}, \quad (36)$$

where $g_q(\phi)$ is the large deviation function. To find the relation between $f_q(\lambda)$ and $g_q(\phi)$, we implement the change of variables from Q to ϕ in the integrand of Eq. (31), which immediately allows us to identify $f_q(\lambda)$ with the extremum of $-[g_q(\phi) + \lambda\phi]$ with respect to ϕ. That is, invoking large deviation theory we see that the maximum eigenvalue $f_q(\lambda)$ and the large deviation function $g_q(\phi)$ are related by a Legendre transformation, leading to

$$g_q(\phi) = -[f(\lambda_\phi) + \phi\lambda_\phi], \quad (37)$$

where λ_ϕ is the solution of

$$f_q'(\lambda_\phi) + \phi = 0, \quad (38)$$

the prime denoting differentiation with respect to λ. We find that the large deviation function $g_q(\phi)$ is given by (see the Appendix)

$$g_q^\pm(\phi) = \frac{ke^{-\varepsilon}}{2}\Bigg\{(2\xi e^\varepsilon + e^\varepsilon + 1)$$
$$- \sqrt{4\xi^2 e^{2\varepsilon} + (1+e^\varepsilon)^2 + 4\xi e^\varepsilon\left[\gamma^\mp(\phi) + \frac{e^\varepsilon}{\gamma^\mp(\phi)}\right]}\Bigg\}$$
$$- \frac{\phi}{\varepsilon}\ln\gamma^\mp(\phi), \quad (39)$$

where we have introduced the distinct notation $g_q(\phi) \equiv g_q^+(\phi)$ when $\phi > 0$ and $g_q(\phi) \equiv g_q^-(\phi)$ when $\phi < 0$, and

$$\gamma^\mp(\phi) = \tfrac{1}{2}[p(\phi) \mp \sqrt{p^2(\phi) - 4e^\varepsilon}], \quad (40)$$

with

$$p(\phi) = \frac{\sqrt{4k^4\xi^2\varepsilon^4 e^{-\varepsilon} + 4k^2\varepsilon^2\phi^2\xi^2 + k^2\varepsilon^2\phi^2 e^{-2\varepsilon}(1+e^\varepsilon)^2 + 4\phi^4} + 2\phi^2}{k^2\varepsilon^2\xi e^{-\varepsilon}}. \quad (41)$$
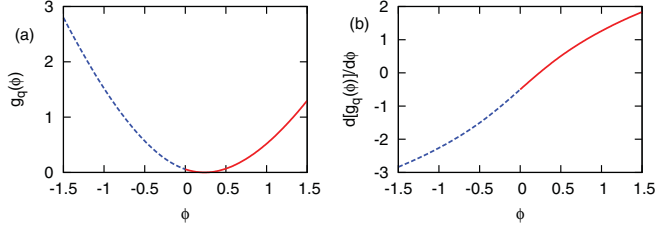
FIG. 4. (Color online) Large deviation function $g_q(\phi)$ and its derivative as a function of ϕ for $\varepsilon = 1$, $\xi = 2$, $k = 1$. The solid line is for $g_q^+(\phi)$, and the dashed line is for $g_q^-(\phi)$. The value of ϕ where $g_q(\phi) = 0$ is 0.23552, which is the same as $\langle \dot{Q} \rangle$ obtained from Eq. (35).

In Fig. 4 we show the large deviation function and its derivative as a function of ϕ for particular parameter choices. We note that the functions $g_q^+(\phi)$ and $g_q^-(\phi)$ match smoothly at $\phi = 0$ as their values are the same at that point,

$$g_q^+(0) = g_q^-(0) = \tfrac{1}{2}ke^{-\varepsilon}[2\xi e^\varepsilon + e^\varepsilon + 1$$
$$- \sqrt{8\xi e^{3\varepsilon/2} + 4\xi^2 e^{2\varepsilon} + (1 + e^\varepsilon)^2}], \quad (42)$$

as are their first derivatives,

$$\frac{dg^+(0)}{d\phi} = \frac{dg^-(0)}{d\phi} = -\frac{1}{2}. \quad (43)$$

The higher order derivatives, however, do not coincide and the large deviation function is therefore not analytic in ϕ. We also note that $g_q(\phi)$ has a single minimum at $\phi = \langle \dot{Q} \rangle$, as given by Eq. (35), and at that point $g_q(\phi) = 0$. Although the large deviation function is a complicated nonlinear function of ϕ, the difference between $g_q^+(\phi)$ and $g_q^-(\phi)$ turns out to be a simple linear function. That is, for $\phi > 0$,

$$g_q(-\phi) - g_q(\phi) = g_q^-(-\phi) - g_q^+(\phi) = \phi, \quad (44)$$

which leads to the fluctuation theorem for heat as written in Eq. (34).

B. Large deviation function for $\mathcal{W}$

We next turn to large deviation function for the work $\mathcal{W}$ done on the system. Work is done on the system whenever the

filled lower energy level is lifted by energy 2ε. The process of lifting the level at rate k_c is a random Markov process. As time increases, the work $\mathcal{W}$ also increases. Let $P(i, \mathcal{W}, t)$ be the probability that the system is in state i at time t with total accumulated work $\mathcal{W}$. In analogy with the heat in Eq. (25), the Markovian nature of the evolution allows us to write

$$\frac{\partial P(i, \mathcal{W}, t)}{\partial t} = \sum_j W_{j \to i} P(j, \mathcal{W} - \Delta \mathcal{W}_{j \to i}, t)$$
$$- \sum_j W_{i \to j} P(i, \mathcal{W}, t). \quad (45)$$

Here $\Delta \mathcal{W}_{j \to i} = 2\varepsilon$ is the work done on the system when its state change from j to i at rate $W_{j \to i} = k_c$. The characteristic function is given by

$$\rho_w(i, \lambda, t) = \int_{-\infty}^{\infty} d\mathcal{W} e^{-\lambda \mathcal{W}} P(i, \mathcal{W}, t), \quad (46)$$

with subscript w standing for work. The evolution equation for $\rho_w(i, \lambda, t)$ is

$$\frac{\partial \rho_w(i, \mathcal{W}, t)}{\partial t} = \sum_j W_{j \to i} e^{-\lambda \Delta \mathcal{W}_{j \to i}} \rho_w(j, \lambda, t)$$
$$- \sum_j W_{i \to j} \rho_w(i, \lambda, t), \quad (47)$$

or, equivalently,

$$\frac{\partial \rho_w}{\partial t} = \mathbf{M}_w(\lambda) \rho_w, \quad (48)$$

where

$$\mathbf{M}_w(\lambda) = k \begin{bmatrix} -(e^{-\varepsilon} + \xi) & 1 & \xi & 0 \\ e^{-\varepsilon} & -(1 + \xi) & 0 & e^{-2\lambda\varepsilon}\xi \\ e^{-2\lambda\varepsilon}\xi & 0 & -(1 + \xi) & e^{-\varepsilon} \\ 0 & \xi & 1 & -(e^{-\varepsilon} + \xi) \end{bmatrix}. \quad (49)$$

Again, the large t behavior of ρ_w is dominated by the maximum eigenvalue, i.e.,

$$\langle e^{-\lambda \mathcal{W}} \rangle \sim e^{t f_w(\lambda)}, \quad (50)$$

where $f_w(\lambda)$ is the largest eigenvalue of the matrix $\mathbf{M}_w(\lambda)$,

$$f_w(\lambda) = \tfrac{1}{2}ke^{-\varepsilon}[-(2\xi e^\varepsilon + e^\varepsilon + 1) + e^{-\lambda\varepsilon}\sqrt{(4\xi e^\varepsilon + 1)e^{2\lambda\varepsilon} + e^{2(\lambda+1)\varepsilon} + 2e^{(2\lambda+1)\varepsilon} + 4e^{2\varepsilon}\xi + 4\xi^2 e^{2\varepsilon}}]. \quad (51)$$

We can verify that the average work done per unit time,

$$\langle \dot{\mathcal{W}} \rangle = -\frac{df_w(0)}{d\lambda} = \frac{2k\varepsilon e^\varepsilon \xi (1 + \xi)}{1 + e^\varepsilon(1 + 2\xi)}, \quad (52)$$

is the same as that obtained in Eq. (13).

Next we use the large deviation theory to shed more light on the probability distribution $P(\mathcal{W}, t)$, which allows one to write

$$P(\mathcal{W}, t) \sim e^{-t g_w(\phi)}, \quad (53)$$

where $g_w(\phi)$ is the large deviation function and ϕ is the flux of work ($\phi = \mathcal{W}/t = \dot{\mathcal{W}}$). Here we note that (contrary

to the case of heat) ϕ is always positive as the system always receives work so that $\mathcal{W}$ increases monotonically with time. The function $g_w(\phi)$ is again related to $f_w(\lambda)$ by its Legendre transform. Following the same steps as for the heat, we now find the large deviation function $g_w(\phi)$ to be given by

$$g_w(\phi) = \frac{1}{2\zeta_1} \left\{ ke^{-\varepsilon}[(2\xi e^\varepsilon + e^\varepsilon + 1)\zeta_1 - \zeta_2] - \frac{\phi}{\varepsilon} \zeta_1 \ln 2\zeta_1^2 \right\}, \quad (54)$$
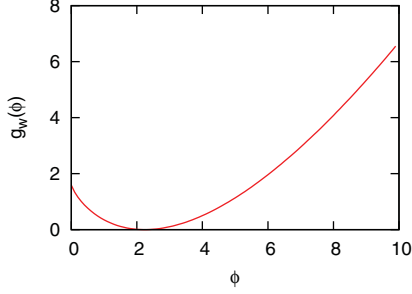
FIG. 5. (Color online) Large deviation function for work. Parameters are: $\varepsilon = 1, \xi = 2, k = 1$. The value of ϕ where $g_w(\phi) = 0$ is unique and its value is 0.23552, which is the same as that obtained from Eq. (52).

where

$$\zeta_1 = e^\varepsilon \sqrt{\frac{\xi(1+\xi)\{-\phi + \sqrt{k^2\varepsilon^2 e^{-2\varepsilon}[4\xi e^\varepsilon + (1+e^\varepsilon)^2] + \phi^2}\}}{[4\xi e^\varepsilon + (1+e^\varepsilon)^2]\phi}},$$

(55)

and

$$\zeta_2 = e^\varepsilon \sqrt{\frac{\xi(1+\xi)\{\phi + \sqrt{k^2\varepsilon^2 e^{-2\varepsilon}[4\xi e^\varepsilon + (1+e^\varepsilon)^2] + \phi^2}\}}{\phi}}.$$

(56)

In Fig. 5 we have plotted the large deviation function for work for a particular set of parameters. We see that it has a unique minimum and $g_w(\phi) = 0$ at $\phi = \langle \mathcal{W}/t \rangle$.

C. Large deviation function for the internal energy

Finally, we turn to the large deviation function for the internal energy. Following the procedure in the previous sections, we can write the evolution of the characteristic function,

$$\rho_u(i, \lambda, t) = \int_{-\infty}^{\infty} dU\, e^{-\lambda U} P(i, U, t)$$

(57)

(subscript u for internal energy), as

$$\frac{\partial \rho_u(i, U, t)}{\partial t} = \sum_j W_{j \to i} e^{-\lambda \Delta U_{j \to i}} \rho_u(j, \lambda, t)$$

$$- \sum_j W_{i \to j} \rho_u(i, \lambda, t).$$

(58)

Here ΔU is the change in internal energy when the system undergoes a transition from one state to the other either due to a jump of the particle between the levels or by lifting the filled lower level. The above evolution equation can be rewritten as the matrix equation

$$\frac{\partial \rho_u}{\partial t} = \mathbf{M}_u(\lambda)\rho_u,$$

(59)

where

$$\mathbf{M}_u(\lambda) = k \begin{bmatrix} -(e^{-\varepsilon} + \xi) & e^{\lambda\varepsilon} & \xi & 0 \\ e^{-(\lambda+1)\varepsilon} & -(1+\xi) & 0 & e^{-2\lambda\varepsilon}\xi \\ e^{-2\lambda\varepsilon}\xi & 0 & -(1+\xi) & e^{-(\lambda+1)\varepsilon} \\ 0 & \xi & e^{\lambda\varepsilon} & -(e^{-\varepsilon} + \xi) \end{bmatrix}.$$
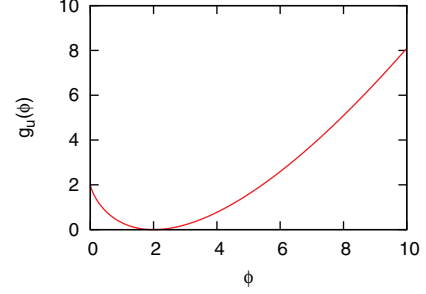
(60)

FIG. 6. (Color online) Large deviation function for the internal energy. Parameters are $\varepsilon = 1, \xi = 2, k = 1$. The value of ϕ where $g_u(\phi) = 0$ is unique and its value is 2, which is the same as that obtained from Eq. (63).

In writing the above matrix, we have made use of the fact that during an upward transition of the particle, there is a gain of internal energy ($\Delta U = \varepsilon$) and, during a downward transition, there is a loss ($\Delta U = -\varepsilon$). There are four such transitions where the system internal energy increases or decreases as a result of particle transitions between the levels. Similarly, when the lower level containing the particle is lifted, the internal energy of the system increases, $\Delta U = 2\varepsilon$. There are two such transitions that lead to an increase in the internal energy of the system by lifting. We are interested in the long-time behavior, and so we can write

$$\langle e^{-\lambda U} \rangle \sim e^{t f_u(\lambda)},$$

(61)

where $f_u(\lambda)$ is the largest eigenvalue of matrix $\mathbf{M}_u(\lambda)$ and is given as

$$f_u(\lambda) = k\xi(e^{-\lambda\varepsilon} - 1).$$

(62)

We verify that

$$\langle \dot{U} \rangle = -\frac{df_u(0)}{d\lambda} = k\xi\varepsilon,$$

(63)

in agreement with Eq. (14). Next, we use large deviation theory to write for the probability distribution for the internal energy

$$P(U, t) \sim e^{-t g_u(\phi)},$$

(64)

where $g_u(\phi)$ is the large deviation function for the internal energy and $\phi = U/t = \dot{U}$. The large deviation function and maximum eigenvalue are again related by a Legendre transform, from which we obtain

$$g_u(\phi) = \frac{1}{\varepsilon}\left[\phi \log\left(\frac{\phi}{k\varepsilon\xi}\right) + k\varepsilon\xi - \phi\right].$$

(65)

Note that the energy of the system is (aside from a finite term ε) determined by the number of configurational switches. The latter obeys Poisson statistics; hence the above result can also be obtained more directly from the large deviation properties of this process. In Fig. 6 we show the large deviation function for the internal energy for a particular set of parameter values. Again, we note that it has a unique minimum at $\phi = \langle \dot{U} \rangle$ where $g_u(\phi) = 0$.

IV. CONCLUSION

We have presented the stochastic thermodynamics of a single particle that can reside on one of two energy levels,

in contact with a classical or a quantum heat bath. The energy levels have a fixed energy separation, and the system is driven out of equilibrium by alternately and stochastically lifting one of the two energy levels. The particle can make upward or downward transitions between the energy levels mediated by the heat bath. At a given bath temperature, three parameters determine the behavior of the system: the energy separation between the levels, the transition rates for the particle to move between levels, and the rate at which the levels are stochastically raised. The interest of this toy model lies in the fact that we can obtain explicit analytic expressions not only for average quantities such as work and heat flux, rate of entropy production, and efficiency, but also of stochastic trajectory-dependent quantities including the steady-state fluctuation theorem for the heat and the large deviation properties of work, heat, and internal energy, both at the level of their characteristic function as well as in terms of the variables themselves.

Finally, we note the specific choices of parameters in this work, in particular, the equality of the rates of stochastic lifting and of the lifting magnitudes for the two levels. This renders the analytic diagonalization of our 4×4 matrix generator, and the resulting expressions for the attendant physical quantities, relatively simple. As pointed out by an anonymous referee, with these choices our four-state problem can be mapped into a two-state problem with two paths connecting them, one thermal and one mechanical. Without these parameter restrictions this mapping is no longer possible, and the 4×4 structure in indispensable. We have not explored the consequences of relaxing these conditions.

APPENIDX: LARGE DEVIATION FUNCTION

To find the large deviation function, using Eq. (38) we must solve the equation

$$\left[\frac{df_q(\lambda)}{d\lambda} \right]^2 = \phi^2. \tag{A1}$$

Differentiating $f_q(\lambda)$ with respect to λ gives

$$\frac{df_q(\lambda)}{d\lambda} = \frac{\xi \varepsilon k (e^{\lambda \varepsilon} - e^{-(\lambda-1)\varepsilon})}{\sqrt{4\xi^2 e^{2\varepsilon} + (e^\varepsilon + 1)^2 + 4\xi e^\varepsilon (e^{\lambda\varepsilon} + e^{(1-\lambda)\varepsilon})}}. \tag{A2}$$

Using Eq. (A2) in Eq. (A1), we get the following quadratic equation in p:

$$\xi^2 \varepsilon^2 k^2 p^2 - 4\xi e^\varepsilon \phi^2 p$$
$$- \{4\xi^2 \varepsilon^2 k^2 e^\varepsilon + \phi^2 [4\xi^2 e^{2\varepsilon} + (l + e^\varepsilon)^2]\} = 0, \tag{A3}$$

where

$$p = \gamma + \frac{e^\varepsilon}{\gamma}, \qquad \gamma \equiv e^{\lambda \varepsilon}. \tag{A4}$$

p is always positive since it is a sum of exponentials. We thus consider only the positive solution of Eq. (A3), which is given by Eq. (41). We note that p is an even function of ϕ, i.e., $p(\phi) = p(-\phi)$, and is an increasing function of ϕ. The limiting values of ϕ are

$$p(\phi) = 2e^{\varepsilon/2} \quad \text{for } \phi \to 0, \quad = \infty \quad \text{for } \phi \to \pm \infty. \tag{A5}$$

Using Eq. (A4), we get a quadratic equation in $\gamma(\phi)$ with two roots $\gamma^-(\phi)$ and $\gamma^+(\phi)$ as given by Eq. (40). The valid solution for $\gamma(\phi)$ must satisfy Eq. (38). That is, for $\phi > 0$, $df_q(\lambda)/d\lambda$ must be negative, which from Eq. (A2) requires that $e^{(2\lambda-1)\varepsilon} < 1$. Using the properties and limiting values of $p(\phi)$ as given in Eq. (A5), it turns out that this inequality is satisfied only if $\gamma(\phi) = \gamma^-(\phi)$. Similarly, for $\phi < 0$, $\gamma(\phi) = \gamma^+(\phi)$. Finally, using these values of $\gamma(\phi)$ in Eq. (37), we get the desired large deviation function $g_q(\phi)$ as given in Eq. (39).

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