Abstract

The nonequilibrium thermodynamics feature of a Brownian motor operating between two different heat baths is explored as a function of time $t$. Using the Gibbs entropy and Schnakenberg microscopic stochastic approach, we find exact closed form expressions for the free energy, the rate of entropy production and the rate of entropy flow from the system to the outside. We show that when the system is out of equilibrium, it constantly produces entropy and at the same time extract entropy out of the system. Its entropy production and extraction rates decrease in time and saturate to constant value. In long time limit, the rate of entropy production balances the rate of entropy extraction and at equilibrium both entropy production and extraction rates become zero. Furthermore, via the present model, not only many thermodynamic theories can be checked but also the wrong conclusions that are given due to lack of exact analytic expressions will be corrected.

1 Introduction

Equilibrium thermodynamics is well established and intensively studied discipline. However, its application is limited since most systems in nature
are far from equilibrium and this warrant the need to advance the nonequilibrium thermodynamics. On other hand, nonequilibrium thermodynamics deals with systems which are nonhomogeneous where the systems thermodynamic quantities such as entropy, and free energy strictly rely on the system parameters in complicated manner. As a result nonequilibrium thermodynamics is still under investigation. In the last few decades several studies have been conducted to explore the nonequilibrium features of systems out of equilibrium [1, 2, 3, 4]. Particularly for system where its dynamics is governed by a master equation, Boltzmann-Gibbs nonequilibrium entropy along with the entropy balance equation serves as a basic tool to understand the nonequilibrium thermodynamic features [1, 2, 3].

Recent study by Schnakenberg also reveals that various thermodynamics quantities such as entropy production rate can be rewritten in terms of local probability density and transition probability rate [3]. Based on this microscopic stochastic approach, many theoretical studies have been conducted [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. These theoretical works confirmed that systems which are out of equilibrium constantly produce entropy and at the same time extract entropy out of the system. In long time limit, the rate of entropy production balances the rate of entropy extraction and at equilibrium both entropy production and extraction rates become zero. However, most of these previous studies focused on exploring the thermodynamic properties of the nonequilibrium system at steady state [1, 2]. In this work we present a simple model which serves as a basic tool for a better understanding of the nonequilibrium statistical physics not only in the regime of nonequilibrium steady state (NESS) but also at any time \( t \). We explore the short time behavior of the system either for isothermal case with load or in general for nonisothermal case with or without load. Many mathematical theories can be independently checked via the present model [1]. For instance, we show that the entropy balance equation always satisfied for any parameter choice. Moreover, the first and second laws of thermodynamics are rewritten in terms of the model parameters. Several thermodynamic relations are also uncovered based on the exact analytic results.

At this point we want to stress that in this work, we extend (reconsider) the previous work [17] and uncover far more results. We find exact closed form expressions for the free energy dissipation rate \( F \), the rate of entropy production \( \dot{c}_p \), and the rate of entropy flow from the system to the outside \( \dot{h}_d \). The dependence for the change in total entropy, free energy and entropy production on model parameters is studied. Since closed form expressions
are obtained for all thermodynamic quantities which are under consideration, we are able to extract thermodynamic information at any time \( t \). We believe that even though, a specific model system is considered, the result obtained in this work is generic and advances nonequilibrium thermodynamics.

Moreover it is found that the entropy \( S \) attains a zero value at \( t = 0 \); it increases with \( t \) and then attains an optimum value. It then decreases as \( t \) increases further. In the limit \( t \to \infty \), \( S \) approaches a certain constant. Far from equilibrium, in the presence of nonuniform temperature or non-zero load, \( \dot{e}_p \) and \( \dot{h}_d \) decrease with time and approach their steady state value. At steady state, \( \dot{e}_p = \dot{h}_d > 0 \). At equilibrium, (for isothermal case and zero load), \( \dot{e}_p = \dot{h}_d = 0 \). Moreover, when the heat exchange via kinetic energy is included, we show that even at quasistatic limit \( \dot{e}_p \neq 0 \) or \( \dot{E}_p \neq 0 \). This also implies that since the motor is arranged to undergo a biased random work on spatially arranged thermal background, Carnot efficiency or Carnot refrigerator is unattainable; there is always an irreversible heat flow via the kinetic energy [17, 18, 19, 20, 21].

The rest of paper is organized as follows: in Section II, we present the model. In Section III, we derive the expressions the rate of entropy production \( \dot{e}_p \) and the rate of entropy flow from the system to the outside \( \dot{h}_d \). In section IV we explore the free energy \( F \) as a function of \( t \). The role of particle recrossing on the entropy production rate will be studied in section V. Section VI deals with summary and conclusion.

![Figure 1: (Color online) Schematic diagram for a Brownian particle walking in a discrete ratchet potential with load. Sites with red circles are coupled to the hot reservoir (\( T_h \)) while sites with blue circles are coupled to the cold reservoir (\( T_c \)). Site 2 is labeled explicitly and \( d \) is the lattice spacing.](image)
2 The model

Consider a single Brownian particle that hops along one dimensional discrete ratchet potential with load \[13\]

\[ U_i = E[i \text{mod} 3 - 1] + ifd \]  

(1)

that coupled with the temperature

\[ T_i = \begin{cases} T_h, & \text{if } E[i \text{mod} 3 - 1] = 0; \\ T_c, & \text{otherwise}; \end{cases} \]  

(2)

as shown in Fig. 1. The potential \( E > 0 \), \( f \) denotes the load and \( i \) is an integer that runs from \(-\infty\) to \(\infty\). \( T_h \) and \( T_c \) denote the temperature for the hot and cold reservoirs, respectively. Moreover, the one dimensional lattice has spacing \( d \) and in one cycle, the particle walks a net displacement of three lattice sites.

The jump probability for the particle to hop from site \( i \) to \( i + 1 \) is given by

\[ \Gamma e^{-\Delta E/k_B T_i} \]

where \( \Delta E = U_{i+1} - U_i \) and \( \Gamma \) is the probability attempting a jump per unit time. \( k_B \) designates the Boltzmann constant and hereafter \( k_B, \Gamma \) and \( d \) are considered to be a unity. When the particle undergoes a biased random walk, it is assumed that first it decides which way to jump (backward or forward) with equal probability obeying the metropolis algorithm. Accordingly, when \( \Delta E \leq 0 \), the jump the jump definitely takes place while \( \Delta E > 0 \) the jump takes place with probability \( \exp(-\Delta E/T_i) \).

The model exhibits identical behavior with a spin-1 particle system \[17\]. The master equation which governs the system dynamics is given by

\[ \frac{dP_n}{dt} = \sum_{n \neq n'} (P_{nn'}p_{n'} - P_{n'n}p_n), \quad n, n' = 1, 2, 3 \]  

(3)

where \( P_{n'n} \) is the transition probability rate at which the system, originally in state \( n \), makes transition to state \( n' \). Here \( P_{n'n} \) is given by the Metropolis rule. For instance, \( P_{21} = \frac{1}{2}e^{-(E+f)/T_c}, \quad P_{12} = \frac{1}{2}, \quad P_{32} = \frac{1}{2}e^{-(E+f)/T_h} \) and \( P_{23} = \frac{1}{2} \). The rate equation for the model can then be expressed as a matrix equation \( \frac{d\vec{p}}{dt} = \mathbf{P}\vec{p} \) where \( \vec{p} = (p_1, p_2, p_3)^T \). \( \mathbf{P} \) is a 3 by 3 matrix which is given by

\[ \mathbf{P} = \begin{pmatrix} -\frac{\mu \alpha^2 - \mu^2}{2a} & \frac{1}{2} & \frac{1}{2} \\ \frac{\mu \alpha}{2a} & -\frac{1}{2} & \frac{1}{2} \\ \frac{\mu^2}{2a} & \frac{\nu \beta}{2} & -1 \end{pmatrix} \]  

(4)
as long as $0 < f < 2E/d$. Here $\mu = e^{-E/T_c}$, $\nu = e^{-E/T_h}$, $a = e^{-f d/T_c}$ and $b = e^{-f d/T_h}$. Note that the sum of each column of the matrix $P$ is zero, $\sum_m P_{mn} = 0$ which reveals that the total probability is conserved: 

\[
(d/dt) \sum_n p_n = d/dt(1^T \cdot p) = 1^T \cdot (P \vec{p}) = 0.
\]

For the particle which is initially situated at site $i = 2$, by solving Eq. (3), we find the time dependent normalized probability distributions for $p_1(t)$, $p_2(t)$ and $p_3(t)$ as shown in Appendix A. The expression for the velocity $V(t)$ at any time $t$ as well as the rate of heat flow from the hot reservoir $\dot{Q}_h(t)$ and the rate of heat flow into the cold reservoir $\dot{Q}_c(t)$ are also given in Appendix A.

Hereafter all figures are plotted by taking dimensionless quantities $\epsilon = E/T_c$, $\lambda = f d/T_c$ and $\tau = T_h/T_c - 1$. We also introduce dimensionless time $\bar{t} = \Gamma t$ and after this the bar will be dropped.

3 Derivation of Entropy and entropy production

The relation between the internal energy $U(t)$, entropy $S(t)$ and free energy $F(t)$ is well known for isothermal system (uniform temperature $T$) which satisfies detailed balance condition, and can be written as

\[
\dot{U}[p_i(t)] = -T \dot{h}_d(t) = -\dot{H}_d(t) \tag{5}
\]

\[
= -T \sum_{i>j} (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right),
\]

\[
\dot{F}[p_i(t)] = -T \dot{e}_p(t) = -\dot{E}_P(t) \tag{6}
\]

\[
= -T \sum_{i>j} (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{p_i P_{ji}}{p_j P_{ij}} \right),
\]

and the corresponding fundamental entropy balance equation is given by

\[
\dot{S}(t) = e_p(t) - h_d(t) \tag{7}
\]

where $S$ is the Gibbs entropy given by

\[
S[p_i(t)] = - \sum_{i=1}^{N} p_i \ln p_i. \tag{8}
\]
Here $\dot{h}_d(t)$ and $\dot{e}_p(t)$ designate the term which is related to the heat dissipation rate and the instantaneous entropy production ($\dot{e}_p > 0$), respectively. The entropy balance equation (7) can be rewritten as $\dot{S}^T(t) = \dot{E}_p(t) - \dot{H}_d(t)$ where $S^T(t) = TdS(t)/dt$. Recently for isothermal system which is driven out of equilibrium, the above relations have been extended via phonological approach [1].

Next, we examine whether the well-known thermodynamic relations, which are valid for equilibrium system, are still obeyed for the model system which is driven out of equilibrium due to inhomogeneous thermal arrangement $T_h \neq T_c$ or non-zero external load $f \neq 0$. For the three state model we present,

$$S[p_i(t)] = -\sum_{i=1}^{3} p_i \ln p_i, \quad (9)$$

$$\dot{h}_d = \sum_{i>j}(p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right)$$

$$= (-p_1 P_{21} + p_2 P_{12}) \ln \left( \frac{P_{12}}{P_{21}} \right) +$$

$$(-p_2 P_{32} + p_3 P_{23}) \ln \left( \frac{P_{23}}{P_{32}} \right) +$$

$$(p_3 P_{13} - p_1 P_{31}) \ln \left( \frac{P_{13}}{P_{31}} \right) \quad (10)$$

and

$$\dot{e}_p = \sum_{i>j}(p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{p_i P_{ji}}{p_j P_{ij}} \right)$$

$$= (-p_1 P_{21} + p_2 P_{12}) \ln \left( \frac{p_2 P_{12}}{p_1 P_{21}} \right) +$$

$$(-p_2 P_{32} + p_3 P_{23}) \ln \left( \frac{p_3 P_{23}}{p_2 P_{32}} \right) +$$

$$(p_3 P_{13} - p_1 P_{31}) \ln \left( \frac{p_3 P_{13}}{p_1 P_{31}} \right) \quad (11)$$

where the indexes $i = 1...3$ and $j = 1...3$. It is important to note that via the expressions $p_1(t)$, $p_2(t)$ and $p_3(t)$ that are shown in Appendix A and using
the rates (see Eq. (4)),
\[ P_{21} = \frac{1}{2} e^{-(E+f)/T_c}, \quad P_{12} = \frac{1}{2}, \quad P_{32} = \frac{1}{2} e^{-(E+f)/T_h} \]
\[ P_{23} = \frac{1}{2}, \quad P_{13} = \frac{1}{2}, \quad P_{31} = \frac{1}{2} e^{-(2E-f)/T_c} \]
(12)
the thermodynamic quantities which are under investigation can be evaluated.

For our nonequilibrium system where \( T_h \neq T_c \) and \( f \neq 0 \), regardless of our parameter choice, we find that the fundamental entropy balance equation
\[ \dot{S}(t) = \dot{\epsilon}_p(t) - \dot{h}_d(t) \]
(13)
is always satisfied at any time \( t \). Moreover \( \dot{h}_d(t) \) is found to satisfy the relation
\[ \dot{h}_d(t) = \frac{-\dot{Q}_h(t)}{T_h} + \frac{\dot{Q}_c(t)}{T_c}. \]
(14)
Next we study how \( S, \dot{S}, \) and \( \dot{\epsilon}_p \) and \( \dot{h}_d \) vary in time.

Entropy. — The entropy of the system exhibits an intriguing parameter dependence. Exploiting Eq. (9) one can see that (for any parameter choice) when \( t \to 0, S \to 0 \). As time increases \( S \) increases and attains an optimum value. As \( t \) further increases, \( S \) decreases. In the limit \( t \to \infty \), the total entropy approach its steady state value \( S \to -\sum_{i=1}^{3} p_i \ln p_i \). Particularly, for the case where \( f = 0 \), one can get a simplified expression by expanding \( S \) in small \( t \) regime and after some algebra one gets
\[ S = \frac{1}{2} e^{-\frac{U_0}{T_h}} (1 + \frac{U_0}{T_h} + \frac{U_0}{T_h} \ln[2])t \]
\[ -\frac{1}{2} e^{-\frac{U_0}{T_h}} (\ln[\frac{e^{-\frac{U_0}{T_h}}}{2}] - \ln[t] - e^{-\frac{U_0}{T_h}} \ln[t])t. \]
(15)
Eq. (15) clearly depicts that in the limit \( t \to 0, S \to 0 \). In Fig. 2a, we plot the entropy \( S \) as a function of \( t \) for parameter choice of \( U_0 = 2.0, \tau = 2 \) and \( \lambda = 0 \) (red line) and \( \lambda = 0.5 \) (black line). The figure once again shows that the entropy attains an optimum value at particular time \( t \).

One can note that the system sustains a non-vanishing current (the system is out of equilibrium) as long as \( T_h \neq T_c \) and \( U_0 \neq 0 \) both in the presence
or in the absence of load. For isothermal case, the system is driven out of equilibrium only in the presence of load \( f > 0 \). This implies that the system relaxes to equilibrium in the absence of load and when \( T_h = T_c \). In the absence of both external load and bistable potential \( U_0 = 0 \), the particle undergoes a random walk on lattice. In long time limit, the system may approach equilibrium as long as the heat exchange via kinetic energy is neglected (even if a distinct temperature difference is retained between the hot and cold reservoirs). Thus when \( f = 0 \) and in the limit \( U_0 \rightarrow 0 \) (approaching equilibrium), Eq. (9) converges to

\[
S(t) = \frac{1}{3} e^{-\frac{3t}{\tau}} (-2(-1 + e^{\frac{3t}{\tau}}) \ln \left( \frac{1}{3} - \frac{e^{-\frac{3t}{\tau}}}{3} \right)) \\
-\frac{1}{3} e^{-\frac{3t}{\tau}} (2 + e^{\frac{3t}{\tau}}) \ln \left( \frac{1}{3} + \frac{2}{3} e^{-\frac{3t}{\tau}} \right)).
\]  

(16)

As it can be seen from Eq. (16), in the limit \( S \rightarrow 0 \) as \( t \rightarrow 0 \) and when \( t \rightarrow \infty \), \( S \rightarrow \ln[3] \). Note that at stationary state, \( S \) is constant implies that \( \Delta S = 0 \).

![Figure 2](image1.png)

**Figure 2:** (Color online) (a) Total entropy \( S(t) \) versus \( t \) for a given \( \epsilon = 2 \), \( \tau = 2.0 \) and \( \lambda = 0 \). (b) Plot of \( \dot{S}(t) \) (dotted green line), \( \dot{e}_p(t) \) (dashed red line) and \( \dot{h}_d(t) \) (black solid line) as a function of \( t \) for a given \( \epsilon = 2 \), \( \tau = 2.0 \) and \( \lambda = 0 \).

**Entropy production rate.** — Let us focus on the rate of entropy production \( \dot{e}_p \), the rate of total entropy \( \dot{S}(t) \) and the rate of entropy flow from the system to the outside \( \dot{h}_d(t) \). The plot of \( \dot{S}(t) \) (dotted green line), \( \dot{e}_p(t) \) (dashed red line) and \( \dot{h}_d(t) \) (solid black line) as a function of \( t \) is depicted in Fig. 2b for a given values of \( \epsilon = 2 \), \( \tau = 2.0 \) and \( \lambda = 0 \). The figure indicates that \( \dot{e}_p \) and \( \dot{h}_d(t) \) decrease to their steady state values \( \dot{e}_p = \dot{h}_d > 0.04 \) as time
Figure 3: (Color online) (a) Plot of $\dot{S}(t)$ (green line), $\dot{e}_p(t)$ (dashed red line) and $\dot{h}_d(t)$ (solid line) as a function of $t$ for a given $\epsilon = 2$, $\tau = 2.0$ and $t = 10^6$ (steady state). Here $\dot{e}_p(t) = \dot{h}_d(t)$.

progress. Exploiting Eqs. (10), (11) and (13), one can also see that far from equilibrium $\dot{e}_p > 0$ and $\dot{h}_d > 0$. When $t \to 0$, $\dot{e}_p$ becomes much greater than $\dot{h}_d(t)$ and as time increases, in a certain time interval, $\dot{h}_d(t) > \dot{e}_p$. In general, as time progresses $\dot{e}_p$ and $\dot{h}_d$ decrease and approach their steady state value. At steady state, $\dot{e}_p = \dot{h}_d > 0$. At equilibrium, for isothermal case and zero load, $\dot{e}_p = \dot{h}_d = 0$. Particularly expanding $\dot{e}_p$ and $\dot{h}_d(t)$ in the small time regime, we find

$$\dot{e}_p = \frac{1}{2} e^{-\frac{U_0}{\tau h}} (\ln[\frac{2}{\theta}] - e^{-\frac{U_0}{\tau h}} \ln[\frac{e^{-\frac{U_0}{\tau h}}}{2}] - (e^{-\frac{U_0}{\tau h}}) \ln[t])$$ \hspace{1cm} (17)

and

$$\dot{h}_d = -\frac{1}{2} \ln[\exp{-\frac{U_0}{\tau h}}] - \frac{1}{2} e^{-\frac{U_0}{\tau h}} \ln[\exp{\frac{U_0}{\tau h}}].$$ \hspace{1cm} (18)

On the other hand in the limit $U_0 \to 0$ and $f = 0$ (approaching equilibrium), $\dot{h}_d = 0$ for any $t$ while

$$\dot{e}_p = -e^{-\frac{U_0}{\tau}} \ln[\frac{-1 + e^{\frac{U_0}{\tau}}}{2 + e^{\frac{U_0}{\tau}}}] \hspace{1cm} (19)$$

Here $\dot{e}_p > 0$ for small $t$ and decreases (the system relaxes to equilibrium) as time increases. In the limit $t \to \infty$, $\dot{e}_p = \dot{h}_d = 0$.

The quasistatic limit of the system corresponds to the case where the velocity approaches zero $V(t) = 0$ in the vicinity of the stall force or in the absence of load when $U_0 \to 0$. The general expression for the stall force
is lengthy and will not be presented. However, at steady state, the stall force reduces to \( f = E\left(\frac{T_h}{T_c} - 1\right)/\left(2\frac{T_h}{T_c} + 1\right) \). At quasistatic limit, regardless of any parameter choice, we find \( \dot{e}_p = \dot{h}_d(t) = 0 \). This can be appreciated by plotting \( \dot{e}_p \) or \( \dot{h}_d(t) \) as a function of load in long time limit. Figure 3 exhibits that both \( \dot{e}_p \) and \( \dot{h}_d(t) \) decrease as the load increases and attain a zero value at stall force \( \lambda = 0.4 \). As the load further increases, \( \dot{e}_p \) and \( \dot{h}_d(t) \) step up. On the contrary, \( \dot{S} \) decreases with time. At stall force, \( \dot{S} = 0 \).

![Figure 4](image-url)

Figure 4: (Color online) (a) Plot of \( \Delta e_p = e_p(t) - e_p(0) \) (red line) and \( \Delta h_d = h_d(t) - h_d(0) \) (Black line) as a function of \( t \) for a given \( \epsilon = 2, \tau = 2.0 \) and \( \lambda = 0 \). (b) \( \Delta S(t) = S(t) - S(0) \) versus \( t \) for a given \( \epsilon = 2, \tau = 2.0 \) and \( \lambda = 0 \).

Since closed form expressions for \( \dot{S}(t), \dot{e}_p(t) \) and \( \dot{h}_d(t) \) are obtained for any time \( t \), the analytic expressions for the change in entropy production, heat dissipation and the change in the total entropy can be found analytically via

\[
\Delta h_d = \int_{t_0}^{t} \left( \sum_{i>j} (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right) \right) dt, \quad (20)
\]

\[
\Delta e_p = \int_{t_0}^{t} \left( \sum_{i>j} (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right) \right) dt \quad (21)
\]

and

\[
\Delta S = \int_{t_0}^{t} \left( \sum_{i>j} (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right) \right) dt
\]

\[
= - \sum_{i=1}^{3} p_i(t) \ln p_i(t) + \sum_{i=1}^{3} p_i(0) \ln p_i(0) \quad (22)
\]
where $\Delta S = \Delta e_p - \Delta h_d$ and the indexes $i = 1...3$ and $j = 1...3$. The expressions for $\Delta h_d$, $\Delta S$ and $\Delta e_p$ are lengthy.

Here care must be taken since $\dot{e}_p(t) > 0$ or $\dot{h}_d(t) > 0$ does not imply that $\Delta h_d = h_d(t) - h_d(t_0) > 0$, $\Delta S = S(t) - S(t_0) > 0$ or $\Delta e_p = e_p(t) - e_p(t_0) > 0$. Rather since $\dot{h}_d$, $\dot{S}$ and $\dot{e}_p$ are decreasing function of $t$, $\Delta h_d$, $\Delta S$ and $\Delta e_p$ can take even negative values depending on the interval between $t_0$ and $t$. If the system reaches at steady state or stationary state and if the change in these parameters are taken at the steady state regime, then $\Delta h_d = 0$, $\Delta S = 0$ or $\Delta e_p = 0$. However this does not indicate that second law of thermodynamics is violated.

In fact the second law of thermodynamics is always preserved as it can be seen by exploiting the exact analytic expressions (Eqs. (20-22). In reality, once the motor starts operating, entropy will be accumulated in the system starting from $t = 0$ and as time progresses, more entropy will be stored in the system even though some entropy is extracted out of the system. Hence if the change in these parameters is taken between $t = 0$ and any time $t$, always the inequality $\Delta h_d = h_d(t) - h_d(0) > 0$, $\Delta S = S(t) - S(0) > 0$ or $\Delta e_p = e_p(t) - e_p(0) > 0$ holds true and as time progresses the change in this parameters increases as shown in Fig. 4a. As a matter of fact, in small $t$ regimes, $\dot{e}_p$ becomes much greater than $\dot{h}_d(t)$ (see Fig. 2b) revealing that the entropy production is higher (than entropy extraction) in the first few period of times. As time increases, more entropy will be extracted $\dot{h}_d(t) > \dot{e}_p$. Over all, since the system produces enormous amount of entropy in initial times, in latter time or any time $t$, $\Delta e_p > \Delta h_d$ and hence $\Delta S > 0$ (see Fig. 4).

4 Free energy dissipation rate and Free energy

In order to relate the free energy dissipation rate with $\dot{E}_p(t)$ and $\dot{H}_d(t)$ let us now introduce $\dot{H}_d(t)$ for the model system we considered. The heat dissipation rate is given by $\dot{H}_d(t) = -\dot{Q}_h(t) + \dot{Q}_c(t)$. Using Eqs. (56) and (57), one finds

$$
\dot{H}_d(t) = -\dot{Q}_h(t) + \dot{Q}_c(t)
= \sum_{i>j} T_j (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right).
$$
Equation (23) is notably different from Eq. (10) due to the term $T_j$. Similar relation has been used by Hao. et al for the isothermal case \[1\]. We rewrite Eq. (23) as

$$\dot{H}_d(t) = \sum_{i>j} T_j(p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right)$$

(24)

where

$$\dot{E}_p(t) = \sum_{i>j} T_j(p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{p_i P_{ji}}{p_j P_{ij}} \right)$$

(25)

and

$$\dot{S}^T(t) = \sum_{i>j} T_j(p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{p_i}{p_j} \right).$$

(26)

Here the indexes $i = 1 \ldots 3$ and $j = 1 \ldots 3$. Now we have entropy balance equation $\dot{S}^T(t) = \dot{E}_p(t) - \dot{H}_d(t)$ for our model system. Note that for isothermal case Eqs. (24), (25) and (26) converge to $T \dot{h}_d(t)$, $T \dot{e}_p(t)$ and $T \dot{S}^T(t) = T \dot{S}(t)$, respectively. All the above analysis indicates that $\dot{E}_p(t)$, $\dot{H}_d(t)$ and $\dot{S}^T(t)$ contain a term $(p_2 P_{32} - p_3 P_{23})$ which is associated with the rate of heat taken out of the hot reservoir and two terms $(p_2 P_{12} - p_1 P_{31})$ and $(p_3 P_{13} - p_1 P_{31})$ which are associated with the rate of heat given to the cold reservoir.

One notable difference between $\dot{e}_p(t)/\dot{h}_d(t)$ and $\dot{E}_p(t)/\dot{H}_d(t)$ is that $\dot{e}_p(t)/\dot{h}_d(t)$ always approaches unity in long time limit while $\dot{E}_p(t)/\dot{H}_d(t)$ approaches unity only for isothermal cases with or without load as shown in Fig. 5. Figure 5a depicts the plot of $\dot{e}_p(t)/\dot{h}_d(t)$ as a function of $t$ for a given $\epsilon = 2$, $f = 0.8 \tau = 2.0$ (red line) and $\tau = 1.0$ (black line). Figure 5b shows the Plot of $\dot{E}_p(t)/\dot{H}_d(t)$ as a function of $t$ for a given $\epsilon = 2$, $f = 0.8$ and $\tau = 2.0$ (red line) and $\tau = 1.0$ (black line).
The second law of thermodynamics can be written \( \Delta S^T = \Delta E_p - \Delta H_d \) where \( \Delta S^T \), \( \Delta E_p \), and \( \Delta H_d \) are very lengthy expressions which can be evaluated via

\[
\Delta H_d = \int_{t_0}^{t} \left( \sum_{i>j} T_j (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{P_{ji}}{P_{ij}} \right) \right) dt, \quad (27)
\]

\[
\Delta E_p = \int_{t_0}^{t} \left( \sum_{i>j} T_j (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{p_i P_{ji}}{p_j P_{ij}} \right) \right) dt \quad (28)
\]

and

\[
\Delta S^T = \int_{t_0}^{t} \left( \sum_{i>j} T_j (p_i P_{ji} - p_j P_{ij}) \ln \left( \frac{p_i}{p_j} \right) \right) dt. \quad (29)
\]

In Fig. 6a, we plot \( \Delta E_p = E_p(t) - E_p(0) \) (red line), \( \Delta H_d(t) = H_d(t) - H_d(0) \) (green line) and \( \Delta S^T(t) = S^T(t) - S^T(0) \) (black line) as a function of \( t \) for given \( \epsilon = 2 \), \( f = 0.8 \) and \( \tau = 2.0 \). The figure exhibits that as long as \( t > 0 \), \( \Delta E_p > \Delta H_d \) and hence \( \Delta S^T > 0 \).

On the other hand, the total internal energy \( U(t) \) is the sum of the internal energies

\[
U[p_i(t)] = \sum_{i=1}^{3} p_i u_i = p_1(t)(-E) + p_3(t)(E) \quad (30)
\]
Figure 6: (Color online) (a) Plot of $\Delta E_p(t)$ (red line) $\Delta H_d(t)$ (green line) and $\Delta S^T(t)$ (black line) as a function of $t$ for a given $\epsilon = 2$, $f = 0.8$ and $\tau = 2.0$ (red line). (b) Plot of $\dot{U}(t)$ as a function of $t$ for a given the same parameter choice.

while the change in the internal energy is given by

$$\Delta U = U[p_i(t)] - U[p_i(0)] = E(p_3(t) - p_3(0) + p_1(0) - p_1(t)).$$

(31)

As the particle walks along the reaction coordinate, it receives some heat from the hot reservoir and gives part of it to the cold bath. The remaining heat will be spent to do some work $\dot{W}(t) = fV(t)$ against the external load. Hence we verify the first law of thermodynamics

$$\dot{U}[p_i(t)] = -\sum_{i>j}(p_i p_{ji} - p_j P_{ij}) (u_i - u_j)$$

$$= \dot{Q}_h(t) - \dot{Q}_c(t) - \dot{W}(t)$$

$$= -(\dot{H}_d(t) + fV(t)).$$

(32)

The change in the internal energy (Eq. (31)) can be also rewritten as

$$\Delta U = -\int_0^t \left( \dot{Q}_h(t) - \dot{Q}_c(t) - W(t) \right) dt$$

$$= \int_0^t \left( -(\dot{H}_d(t) + fV(t)) \right) dt$$

$$= \Delta Q_h - \Delta Q_c - \Delta W.$$  

(33)

Note that similar relation is derived in the work [23] for the isothermal case. Fig. 6b depicts the plot of $\dot{U}(t)$ as a function of $t$ for the same parameter
choice of $\epsilon = 2$, $f = 0.8$ and $\tau = 2.0$. The figure shows that as $t \to \infty$, $\dot{U}(t) \to 0$ as expected.

Next let us find the expression for the free energy dissipation rate $\dot{F}$. For the isothermal case, the free energy is given by $F = U - TS$ and we can still adapt this relationship to nonisothermal case to write

$$\dot{F}(t) = \dot{U} - \dot{S}^T(t).$$  \hspace{1cm} (34)

Substituting Eqs. (23) and (25) in Eq. (32) leads to

$$\dot{F}(t) + \dot{E}_p(t) = \dot{U}(t) + \dot{H}_d(t) = -fV(t)$$  \hspace{1cm} (35)

which is the second law of thermodynamics. Note that in the absence of load, $\dot{U}(t) = -\dot{H}_d(t)$ and consequently $\dot{E}_p(t) = -\dot{F}(t)$. The dependence of the free energy on time $t$ can be explored by exploiting Eq. (35). In general $\dot{F} < 0$ and approaches to zero in the long time limit (see Fig. 7a). In order to get a very simplified expression, let us expand Eq. (35) in small time regime for the case where $f = 0$ to get

$$\dot{F} = \frac{1}{2} e^{-\frac{U_0}{T_h}} \left( -T_h \ln|2| + e^{\frac{U_0}{T_h}} \ln[\frac{e^{-\frac{U_0}{T_c}}}{2}T_c] \right) + \frac{1}{2} e^{-\frac{U_0}{T_h}} (e^{\frac{U_0}{T_h} T_c \ln[t] + T_h \ln[t]}).$$  \hspace{1cm} (36)

When $t \to 0$, $\dot{F}$ diverges. On the other hand when $U_0 \to 0$ and $f = 0$
(approaching equilibrium), we get

\[ \dot{F} = e^{-\frac{3t}{T}} (T_c + T_h) \ln \left[ \frac{e^{\frac{3t}{T}} - 1}{2 + e^{\frac{3t}{T}}} \right]. \]  \hspace{1cm} (37)

As it can been seen in Eq. (37), in the limit \( t \to \infty \), \( \dot{F} \to 0 \) and when \( t \to 0 \), \( \dot{F} \) diverges.

The change in the free energy also is given by

\[ \Delta F = - \int_{t_0}^{t} \left( fV(t) + \dot{E}_p(t) \right) dt \]  \hspace{1cm} (38)

\[ = \int_{t_0}^{t} \left( \dot{U}(t) + \dot{H}_d(t) - \dot{E}_p(t) \right) dt \]

\[ = \Delta U + \Delta H_d - \Delta E_p. \]

At quasi-static limit where the velocity approaches zero \( V(t) = 0 \), \( \dot{E}_p(t) = 0 \) and \( \dot{H}_d(t) = 0 \) (see Fig. (7b)) and far from quasi-static limit \( E_p > 0 \) which is expected as the engine operates irreversibly. Far from stall force, \( \dot{E}_p(t) \neq \dot{H}_d(t) \) as long as a distinct temperature difference between the hot reservoirs is retained. However, for isothermal case, at steady state, \( \dot{E}_p(t) = \dot{H}_d(t) \) which implies \( \Delta F = \Delta U \).

Finally, in the work [1], the second law of thermodynamics is rewritten in terms of the housekeeping heat and excess heat by considering isothermal case. For the model system we consider, when the particle undergoes a cyclic motion, at least it has to get \( fV(t) \) amount of energy rate from the hot reservoir in order to keep the system at steady state. Hence \( fV(t) \) is equivalent to the housekeeping heat \( Q_{hk} \) and we can rewrite Eq. (35) as

\[ \dot{F}(t) + \dot{E}_p(t) - \dot{U}(t) + \dot{H}_d(t) = -fV(t) = -\dot{Q}_{hk} \]  \hspace{1cm} (39)

while the excess heat \( \dot{Q}_{ex} \) part is given by

\[ \dot{Q}_{ex} = \dot{H}_d - \dot{Q}_{hk}. \]  \hspace{1cm} (40)

For isothermal case, we can rewrite the second law of thermodynamics as

\[ S^T = \dot{E}_p - \dot{H}_d = -\dot{F} - \dot{Q}_{ex} \]  \hspace{1cm} (41)

and

\[ \dot{F} = \dot{Q}_{hk} - \dot{E}_p. \]  \hspace{1cm} (42)
5 Irreversibility due to particle recrossing along the boundaries

In the previous section we have seen that at quasistatic limit, the system is reversible and hence $\dot{e}_p = 0$ or $\dot{E}_p = 0$ even if $T_h \neq T_c$. However so far the rate of heat loss due to particle recrossing at the boundary between the hot and cold reservoirs is not included. If the heat exchange via kinetic energy is included, even at quasistatic limit $\dot{e}_p \neq 0$ or $\dot{E}_p \neq 0$. This also implies that since the motor is arranged to undergo a biased random work on spatially arranged thermal background, Carnot efficiency or Carnot refrigerator is unattainable; there is always an irreversible heat flow via the kinetic energy [17, 18, 19, 20, 21].

![Figure 8](image_url) (Color online) Plot of $\dot{E}_p(t)$ (dashed black line) and $\dot{E}_p^*(t)$ (red line) as a function of $\lambda$ for a given $\epsilon = 2$, $\tau = 2.0$ and $t = 10^6$.

When the particle by chance jumps from the cold to hot reservoir, it absorbs, $k_B(T_h - T_c)/2$ amount of heat from the hot bath. When it hops back to the cold reservoir, it dumps back this $k_B(T_h - T_c)/2$ amount of heat to the cold bath. This irreversible heat flow is always one way, i.e.; from the hot to the cold baths and it cannot be recovered. Hence we can conclude this heat transfer from the hot to cold reservoirs depends on how often the particle jumps from the cold to hot heat baths and it can be written as

$$\dot{Q}_{irr} = (p_1 P_{21} + p_3 P_{23}) (T_h - T_c)/2.$$  \hfill (43)

The heat exchange via kinetic energy does not affect $\dot{H}_d$ since the whole heat taken from the hot reservoirs goes to the cold reservoir. This also implies that the whole heat dumped to the cold reservoirs contributes to the internal
entropy production and hence for any parameter choice \( \dot{E}_p \geq 0 \) as long as \( T_h \neq T_c \). The heat loss due to particle recrossing only contributes to the internal entropy production and we infer the new entropy production rate to be

\[
\dot{E}_p^* = \dot{E}_p + \dot{Q}_{irr}.
\]  

(44)

One can then rewrite the thermodynamic relations that derived in the previous section in terms of \( \dot{E}_p^* \). Here \( \dot{E}_p^* = 0 \) only when \( T_h = T_c \). \( \dot{E}_p^* \) as a function of the load \( \lambda \) is plotted in Fig. 8. The figure depicts that even at quasistatic limit \( \dot{e}_p^* \neq 0 \). The same figure shows that if the heat exchange via kinetic energy is omitted, \( \dot{E}_p = 0 \) at stall force \( \lambda = 0.4 \). Note that when \( U_0 \) and \( f = 0 \), the particle undergoes unbiased random walk problem. Its average velocity is zero but its speed is nonzero. If the particle by chance hops from the cold to hot reservoirs, it absorbs an energy and latter dumps this energy to cold bath. So even in this case the system is far from equilibrium.

6 summary and conclusion

In this work we present a paradigmatic model which serves a basic tool for a better understanding of the nonequilibrium statistical physics not only in the regime of nonequilibrium steady state (NESS) but also at any time \( t \). Not only the long time behavior of the system is explored but also we investigate the short time behavior of the system either for isothermal case with load or in general for nonisothermal case with or without load.

Based on the Gibbs entropy and Schnakenberg microscopic stochastic approach, we get exact analytic expressions for the thermodynamic quantities that are under investigations. We show that whenever the system is out of equilibrium, it constantly produce entropy and at the same time extract entropy out of the system. At steady state, the rate of entropy production balances the rate of entropy extraction and at equilibrium both entropy production and extraction rates become zero. Moreover we show that the entropy balance equation \[22\] always satisfied for any parameter choice. Furthermore, the first and second laws of thermodynamics are rewritten in terms of the model parameters. Several thermodynamic relations are also uncovered based on the exact analytic results.

The exact analytic expressions are also obtained for the free energy dissipation rate \( \dot{F} \), the rate of entropy production \( \dot{e}_p \) and the rate of entropy flow
from the system to the outside \( \hat{h}_d \). Particularly, the analytical study reveals that the entropy \( S \) attains a zero value at \( t = 0 \); it increases with \( t \) and then attains an optimum value. It then decreases as \( t \) increases further. In the limit \( t \to \infty \), \( S \) approaches a certain constant. Far from equilibrium, in the presence of nonuniform temperature or non-zero load, \( \dot{e}_p \) and \( \dot{h}_d \) decrease with time and approach their steady state value. At steady state, \( \dot{e}_p = \dot{h}_d > 0 \). At equilibrium, for isothermal case and zero load, \( \dot{e}_p = \dot{h}_d = 0 \). Moreover, when the heat exchange via kinetic energy is included, we show that even at quasistatic limit \( \dot{e}_p \neq 0 \) or \( \dot{E}_p \neq 0 \). This also implies that since the motor is arranged to undergo a biased random work on spatially arranged thermal background, Carnot efficiency or Carnot refrigerator is unattainable; there is always an irreversible heat flow via the kinetic energy.

In conclusion, in this work we present a simple model which serves as a basic tool for better understanding of the nonequilibrium statistical physics not only in the regime of nonequilibrium steady state (NESS) but also at any time \( t \). The present model also serves as a tool to check many elegant thermodynamic theories. Based on this exactly solvable model, we uncovered several thermodynamic relations. We believe that even though, a specific model system is considered, the result obtained in this work is generic and advances nonequilibrium thermodynamics.

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**Appendix A**

In this Appendix we will give the expressions for \( p_1(t) \), \( p_2(t) \) and \( p_3(t) \) as well as \( V(t) \), \( \dot{Q}_h(t) \) and \( \dot{Q}_c(t) \). For the particle which is initially situated at site \( i = 2 \), the time dependent normalized probability distributions after solving
Eq. (3) are

$$p_1(t) = c_1 \frac{a(2 + \nu b)}{\mu (\mu + (a^2 + \mu) \nu b)} + c_2 e^{-\frac{(a^2 + \mu + \nu b)}{2a} \left( -1 + \frac{a(-1 + a\mu)}{-\mu^2 + a\nu b} \right)}, \quad (45)$$

$$p_2(t) = -c_3 e^{\frac{a(2 - \nu b)}{2a}} - c_2 \frac{a e^{-\frac{(a^2 + \mu + \nu b)}{2a} \left( -1 + a\mu \right)} + c_1}{-\mu^2 + a\nu b} + c_2 e^{-\frac{(a^2 + \mu + \nu b)}{2a} \left( -2 - \nu b \right)}, \quad (46)$$

$$p_3(t) = c_1 + c_2 e^{-\frac{(a^2 + \mu + \nu b)}{2a} \left( -1 + a\mu \right)} + c_3 e^{\frac{a(2 - \nu b)}{2a}}, \quad (47)$$

where

$$c_1 = \frac{\mu (\mu + (a^2 + \mu) \nu b)}{(a + a^2 \mu + \mu^2) (2 + \nu b)}, \quad (48)$$

$$c_2 = \frac{a}{(a + a^2 \mu + \nu b) \left( -1 + \frac{a(-1 + a\mu)}{-\mu^2 + a\nu b} \right)}, \quad (49)$$

$$c_3 = -\frac{\mu (\mu + a^2 \nu b + \mu \nu b)}{(a + a^2 \mu + \mu^2) (2 + \nu b)} + \frac{a}{(a + a^2 \mu + \mu^2) \left( -1 + \frac{a(-1 + a\mu)}{-\mu^2 + a\nu b} \right)}, \quad (50)$$

The $\sum_{i=1}^{3} p_i(t) = 1$ revealing the probability distribution is normalized. In the limit of $t \to \infty$, we recapture the steady state probability distributions

$$p_1^s = \frac{a}{a + a^2 \mu + \mu^2}, \quad (51)$$

$$p_2^s = \frac{\mu (2a^2 + \mu)}{(a + a^2 \mu + \mu^2) (2 + \nu b)}, \quad (52)$$

$$p_3^s = \frac{\mu (\mu + b(a^2 + \mu) \nu)}{(a + a^2 \mu + \mu^2) (2 + \nu b)} \quad (53)$$

shown in the work [13].
The velocity $V(t)$ at any time $t$ is the difference between the forward $V^+_i(t)$ and backward $V^-_i(t)$ velocities at each site $i$

$$V(t) = \sum_{i=1}^{3} (V^+_i(t) - V^-_i(t))$$

(54)

$$= \left(p_1P_{21} - p_2P_{12}\right) + \left(p_2P_{32} - p_3P_{23}\right) + \left(p_3P_{13} - p_1P_{31}\right).$$

Exploiting Eq. (14), one can see that the particle retains a unidirectional current when $f = 0$ and $T_h > T_c$. For isothermal case $T_h = T_c$, the system sustains a non-zero velocity in the presence of load $f \neq 0$ as expected. Moreover, when $t \to \infty$, the velocity $V(t)$ increases with $t$ and approaches to steady state velocity

$$V^s = 3\frac{\mu \left(ba\nu - \frac{\mu}{a}\right)}{2(2 + \nu b) \left(1 + a\mu + \frac{\mu^2}{a}\right)}$$

(55)

The heat per unit time taken from the hot reservoir has a form

$$\dot{Q}_h(t) = (E + f)(p_2P_{32} - p_3P_{23})$$

$$= T_h(p_2P_{32} - p_3P_{23}) \ln\left(\frac{P_{32}}{P_{23}}\right).$$

(56)

On the other hand, the heat per unit time given to cold reservoir is given by

$$\dot{Q}_c(t) = (E + f)(p_2P_{12} - p_1P_{21}) + (2E - f)(p_3P_{13} - p_1P_{31})$$

$$= T_c(p_2P_{12} - p_1P_{21}) \ln\left(\frac{P_{12}}{P_{21}}\right) + T_c(p_3P_{13} - p_1P_{31}) \ln\left(\frac{P_{13}}{P_{31}}\right).$$

(57)

As $t \to \infty$, both $\dot{Q}_h(t)$ and $\dot{Q}_c(t)$ evolve in time to their corresponding steady state values

$$\dot{Q}_h^s = (E + f)\frac{\mu \left(ba\nu - \frac{\mu}{a}\right)}{2(2 + \nu b) \left(1 + a\mu + \frac{\mu^2}{a}\right)}$$

(58)

and

$$\dot{Q}_c^s = (E - 2f)\frac{\mu \left(ba\nu - \frac{\mu}{a}\right)}{2(2 + \nu b) \left(1 + a\mu + \frac{\mu^2}{a}\right)}.$$ 

(59)
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