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ORIGINAL PAPER

# On the flux-force partitioning and non-equilibrium thermodynamics near a steady state

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**Abstract** The flux-force linear relationship is a basic building block in the development of irreversible thermodynamics near equilibrium. Here, we explore the fate of this relationship near a steady state in a finer detail by partitioning the fluxes and the forces into time-independent and time-dependent components. To this end, we use a master equation approach without assuming the condition of detailed balance. The connection of the flux-force components with various state functions and path functions provides a detailed picture of the variations of such quantities in terms of the deviation of probabilities from the steady state. Pilot calculations on an exactly-solvable case furnish insights into the energy-balance mechanism for non-equilibrium systems, revealing additionally how an out-of-equilibrium scenario can be favorable in realizing a minimized free energy state.

**Keywords** Irreversible thermodynamics · Stochastic process · Steady state

## 1 Introduction

The field of irreversible thermodynamics, starting with the pioneering work of Onsager on the reciprocal relations in coupled irreversible processes close to equilibrium [1,2], have expanded rapidly over the years [3–6]. In the last two decades, a major focus has been on small systems where fluctuations play a vital role [7–9]. The kinetic and thermodynamic descriptions of such stochastic systems are shown to be satisfactorily provided by a master equation approach [10,11]. The key quantity in the characterization of the non-equilibrium thermodynamic behavior of a system is the total entropy production rate (EPR) [4,5]. Its primary role is to indicate the nature of a steady state

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(SS). A vanishing total EPR in the SS means the state is a true thermodynamic equilibrium (TE), arising in a closed system. On the other hand, a positive constant value of total EPR refers to a non-equilibrium steady state (NESS) [12] that can emerge in an open system. The total EPR is generally expressed as a sum of products of fluxes and their corresponding forces [3,4]. Taking a linear flux-force relationship, one studies the variation of total EPR near a TE. This obviously results in a quadratic form of total EPR in either the flux or the force, close to a TE.

With the above background, here we like to investigate how the linear dependence of fluxes on the conjugate forces gets modified near a SS where condition of detailed balance (DB) is violated. For an in-depth understanding of this issue, we split the fluxes and the corresponding forces into time-independent and time-dependent parts. This is similar in spirit to the partitioning of the total EPR into adiabatic and nonadiabatic contributions [13,14], obtained by splitting the force part, that produces a clear separation of a system's relaxation to a SS and subsequent sustenance of that SS [15]. The interrelations among the various parts of the flux and the force are thoroughly analyzed. This kind of partitioning provides a detailed understanding of the generic behavior of total EPR near a SS. More importantly, as a result of this splitting, the dependence of various state and path functions on deviations from SS probability distribution (PD) and DB gets revealed nicely.

## 2 Components of flux and force and their interrelations

For a stochastic system described by a Markov process, the master equation is written as [16]

$$\dot{p}_i = \sum_j \left( w_{ji} p_j(t) - w_{ij} p_i(t) \right) = \sum_j J_{ji}(t). \tag{1}$$

Here $p_i(t)$ is the probability to find the system in i-th state at time $t$, $w_{ij}$ is the time-independent $i \to j$ transition rate and $J_{ij}(t)$ is the flux associated with the transition defined as

$$J_{ij}(t) = w_{ij} p_i(t) - w_{ji} p_j(t) = -J_{ji}(t). \tag{2}$$

In the long-time limit, the system reaches a SS characterized by the PD $\{p_i^s\}$. We do not assume the condition of DB

$$w_{ij} p_i^s = w_{ji} p_j^s \tag{3}$$

at the outset. It is well-known in the field of stochastic non-equilibrium thermodynamics that the total EPR of such a system has the form (setting the Boltzmann constant $k_\mathrm{B} = 1$) [11]

$$\dot{S}_\mathrm{tot}(t) = \frac{1}{2} \sum_{i,j} \left( w_{ij} p_i(t) - w_{ji} p_j(t) \right) \ln \frac{w_{ij} p_i(t)}{w_{ji} p_j(t)} \geq 0. \tag{4}$$

The inequality in Eq. (4) holds for an NESS, while the equality is valid at TE where Eq. (3) holds. An alternative way is to write Eq. (4) as a product of fluxes $J_{ij}$ and their corresponding forces $X_{ij}$ [4,6,14]:

$$\dot{S}_{\mathrm{tot}}(t) = \frac{1}{2}\sum_{i,j} J_{ij}(t)\, X_{ij}(t), \tag{5}$$

where the logarithmic term in Eq. (4) refers to $X_{ij}(t)$.

Now, we define deviations in the state probabilities from their corresponding SS values by

$$\delta_i(t) = p_i(t) - p_i^s. \tag{6}$$

Using Eq. (6), one can split the flux $J_{ij}(t)$ into a time-independent part $\bar{J}_{ij}$ and a time-dependent part $\jmath_{ij}(t)$ as

$$J_{ij}(t) = \bar{J}_{ij} + \jmath_{ij}(t). \tag{7}$$

In Eq. (7)

$$\bar{J}_{ij} = w_{ij} p_i^s - w_{ji} p_j^s, \tag{8}$$

$$\jmath_{ij}(t) = w_{ij}\delta_i(t) - w_{ji}\delta_j(t). \tag{9}$$

It is interesting to see that $\bar{J}_{ij}$ vanishes when DB holds. Thus, $\bar{J}_{ij}$ represents the *steady* driving that is a characteristic of the NESS. At SS, it follows from Eq. (1) that

$$\sum_j \bar{J}_{ji} = 0 = \sum_j \bar{J}_{ij}. \tag{10}$$

Using Eq. (10), we obtain a very important property, *viz.*

$$\sum_{i,j} f_i(t)\bar{J}_{ij} = \sum_i f_i(t)\sum_j \bar{J}_{ij} = 0 = \sum_j f_j(t)\sum_i \bar{J}_{ij} \tag{11}$$

where $f_i(t)$ is any arbitrary quantity depending on the state-index i. As a corollary, we can write

$$\sum_{i,j} f_{ij}(t)\bar{J}_{ij} = 0 \tag{12}$$

whenever $f_{ij}(t)$ satisfies

$$f_{ij}(t) = \alpha f_i(t) + \beta f_j(t), \tag{13}$$

with any constants $\alpha$, $\beta$. We will see the significance of Eqs.(11) and (12) later that also provides a sound motivation behind the decomposition of the total flux. The time-dependent part of the flux, $\jmath_{ij}(t)$, represents the irreversible approach of the system towards the SS and vanishes at the SS irrespective of whether it is an NESS or a TE.

In a similar manner, the force $X_{ij}$ can be decomposed into time-independent and time-dependent parts as

$$X_{ij}(t) = \bar{X}_{ij} + \chi_{ij}(t) \tag{14}$$

where

$$\bar{X}_{ij} = \ln \frac{w_{ij} p_i^s}{w_{ji} p_j^s}, \tag{15}$$

$$\chi_{ij}(t) = \ln \frac{p_i(t) p_j^s}{p_j(t) p_i^s} = \ln \frac{1 + \delta_i / p_i^s}{1 + \delta_j / p_j^s}. \tag{16}$$

The final step of Eq. (16) is obtained by using Eq. (6). It follows that, when DB holds, $\bar{X}_{ij} = 0$ by virtue of Eq. (3). Hence, the *steady* driving is due to this part of the total force. So, it is naturally the conjugate force of the flux $\bar{J}_{ij}$. Similarly, $\chi_{ij}(t)$ is the conjugate force of the flux $\jmath_{ij}(t)$ and vanishes at any SS. We may mention here that the partitioning in Eq. (14) is similar in spirit to the splitting of the total force into adiabatic and nonadiabatic contributions in presence of zero or a constant external driving [14].

Let us now ask: Are the two components of flux linearly related to their corresponding components of force, *even* when one is near SS? To explore, we define a parameter $\epsilon'_{ij}$ as

$$\epsilon'_{ij} = \frac{w_{ij} p_i^s}{w_{ji} p_j^s} = 1 + \epsilon_{ij}. \tag{17}$$

When DB holds, one gets $\epsilon'_{ij} = 1, \forall\, i, j$, from Eq. (3). Thus, $\epsilon'_{ij}$ measures the extent of DB violation. A few important results now follow:

A. Choose first the case of time-independent flux and force. Using Eqs. (8) and (17), $\bar{J}_{ij}$ can be expressed as

$$\bar{J}_{ij} = w_{ji} p_j^s \epsilon_{ij}. \tag{18}$$

From Eqs. (15), (17) and (18), one can write in a similar way

$$\bar{X}_{ij} = \ln(1 + \epsilon_{ij}) \approx \epsilon_{ij} \quad \text{for } \epsilon_{ij} \ll 1. \tag{19}$$

Now $\epsilon_{ij} \ll 1$ implies a small deviation from DB. Only under this condition, from Eqs. (18) and (19), we get

$$\bar{J}_{ij} = w_{ji} p_j^s \bar{X}_{ij}. \tag{20}$$

Otherwise, the simple linearity between $\bar{J}_{ij}$ and $\bar{X}_{ij}$ is *lost*.

B. Near a SS, from Eqs. (6) and (16), the time-dependent force $\chi_{ij}(t)$ can be written as

$$\chi_{ij}(t) \simeq \left( \delta_i / p_i^s - \delta_j / p_j^s \right). \tag{21}$$

Using Eqs. (9), (17) and (21), we get the desired relation between $\jmath_{ij}(t)$ and $\chi_{ij}(t)$ as

$$\jmath_{ij}(t) = w_{ji} p_j^s \chi_{ij}(t) + \frac{w_{ji} p_j^s \epsilon_{ij}}{p_i^s} \delta_i(t). \tag{22}$$

It suggests that, near a SS, $\jmath_{ij}(t)$ is *not* linearly proportional to $\chi_{ij}(t)$. It will be so only near a TE (where DB holds, *i.e.*, $\epsilon_{ij} = 0$).

C. From Eqs. (7), (14), (20) and (22), the total flux $J_{ij}(t)$ near a SS becomes

$$J_{ij}(t) = w_{ji} p_j^s X_{ij}(t) + \frac{w_{ji} p_j^s \epsilon_{ij}}{p_i^s} \delta_i(t). \tag{23}$$

Thus, $J_{ij}$ becomes linearly proportional to $X_{ij}$ *only* near a TE. The *breaking of linearity* near a SS is contained in the final term at the r.h.s. of Eq. (23) that gives the extent of DB violation.

## 3 Partitioning of total EPR

From Eqs. (4), (7) and (14), the total EPR can be expressed as

$$\dot{S}_{\text{tot}}(t) = \frac{1}{2} \sum_{i,j} \left( \bar{J}_{ij} \bar{X}_{ij} + \bar{J}_{ij} \chi_{ij}(t) + \jmath_{ij}(t) \bar{X}_{ij} + \jmath_{ij}(t) \chi_{ij}(t) \right), \tag{24}$$

where components of time-independent and time-dependent flux and force are explicitly seen. From Eqs. (8), (9), (15) and (16), the steady value of total EPR is given as

$$\dot{S}^s_{\text{tot}} = \frac{1}{2} \sum_{i,j} \bar{J}_{ij} \bar{X}_{ij} \geq 0. \tag{25}$$

Again, the inequality in Eq. (25) holds for an NESS and the equality holds for a TE. The following properties of the components are already known in the literature in the context of adiabatic and nonadiabatic EPRs [14]:

$$\sum_{i,j} \left( \bar{J}_{ij} + \jmath_{ij}(t) \right) \bar{X}_{ij} = \sum_{i,j} J_{ij}(t) \bar{X}_{ij} \geq 0. \tag{26}$$

$$\sum_{i,j} J_{ij}(t) \chi_{ij}(t) \geq 0. \tag{27}$$

We find from Eq. (16) that

$$\chi_{ij}(t) = \ln \frac{p_i(t)}{p_i^s} + \ln \frac{p_j^s}{p_j(t)}.$$

This is of the form given in Eq. (13) with $\alpha = \beta = 1$. Hence, we obtain

$$\sum_{i,j} \bar{J}_{ij} \chi_{ij}(t) = 0. \tag{28}$$

Then, from Eqs. (27) and (28), one finds

$$\sum_{i,j} J_{ij}(t)\chi_{ij}(t) \geq 0. \tag{29}$$

Now we shall study the behavior of the total EPR close to SS, taking the various flux-force products, as given at the r.h.s. of Eq. (24). Using Eqs. (9) and (22), one can write the fourth term of Eq. (24) as

$$\begin{aligned} J_{ij}(t)\chi_{ij}(t) &= \frac{J_{ij}^2(t)}{w_{ji}p_j^s} - \frac{\epsilon_{ij}J_{ij}}{p_i^s}\delta_i(t) \\ &= P_{ij}\delta_i^2(t) + Q_{ij}\delta_j^2(t) + R_{ij}\delta_i(t)\delta_j(t), \end{aligned} \tag{30}$$

where

$$P_{ij} = \frac{w_{ij}^2}{w_{ji}p_j^s} - \frac{w_{ij}\epsilon_{ij}}{p_i^s}, \tag{31}$$

$$Q_{ij} = \frac{w_{ji}}{p_j^s}, \tag{32}$$

$$R_{ij} = \frac{w_{ji}\epsilon_{ij}}{p_i^s} - \frac{2w_{ij}}{p_j^s}. \tag{33}$$

Hence, the term $J_{ij}(t)\chi_{ij}(t)$ is *quadratic* in the probability deviations $\delta_i(t)$ near a SS. Interestingly, it remains so *even* for $\epsilon_{ij} = 0$, *i.e.*, near a TE.

The third term in Eq. (24) can be rewritten as

$$J_{ij}(t)\bar{X}_{ij} = S_{ij}\delta_i(t) - T_{ij}\delta_j(t), \tag{34}$$

where we employ Eq. (9) and define

$$S_{ij} = w_{ij}\bar{X}_{ij}, \tag{35}$$

$$T_{ij} = w_{ji}\bar{X}_{ij}. \tag{36}$$

The r.h.s. of Eq. (34) is linear in the probability deviations $\delta_i(t)$. Note that, in writing Eq. (34), we *do not* require $\delta_i$ to be small. Actually, we consider the *near*-SS situation (*i.e.*, $\delta_i/p_i^s \ll 1$) *only* for those quantities which depend on $\chi_{ij}(t)$.

As the term $\bar{J}_{ij}\bar{X}_{ij}$ is time-independent, the total EPR comprises of a constant term, a linear one and a quadratic one in $\delta_i(t)$ near a SS. From Eqs. (24), (28), (30) and (34), the desired expression in terms of $\delta_i(t)$ is written as

$$\begin{aligned} \dot{S}_{\text{tot}}(t) = \frac{1}{2}\sum_{i,j} \Big[ \bar{J}_{ij}\bar{X}_{ij} + \big(S_{ij}\delta_i(t) - T_{ij}\delta_j(t)\big) \\ + \Big(P_{ij}\delta_i^2(t) + Q_{ij}\delta_j^2(t) + R_{ij}\delta_i(t)\delta_j(t)\Big)\Big]. \end{aligned} \tag{37}$$

The origin of each term is, by now, clear.

## 4 Behavior of state and path functions

When a system reaches a TE, we have $\bar{J}_{ij} = 0 = \bar{X}_{ij}$. Then, it follows from Eqs. (35), (36) and (37) that $\dot{S}_{\text{tot}}(t)$ is purely quadratic in $\delta_i(t)$ near a TE. Here, the whole contribution to $\dot{S}_{\text{tot}}(t)$ comes from the product of time-dependent fluxes and forces. As the total EPR for a system reaching TE multiplied by temperature T equals the negative of the rate of free energy change $\dot{F}(t)$ of the system, we can write

$$-\dot{F}(t) = \frac{T}{2}\sum_{i,j} \jmath_{ij}(t)\chi_{ij}(t). \tag{38}$$

Therefore, it follows from Eq. (30) that, $\dot{F}(t)$ is quadratic in $\delta_i(t)$ near a SS but it vanishes *at* the SS, as expected for a state function.

Next, we take the combination of the first and the third terms of total EPR at the r.h.s. of Eq. (24). It represents what is known in the literature as the adiabatic component of the total EPR and is identical to the 'housekeeping heat' when multiplied by the temperature $T$. With time-independent transition rates, the 'housekeeping heat' is the same as the rate of irreversible work done $w_{\text{irr}}(t)$ on the system to keep it away from any TE [15]. We thus get

$$w_{\text{irr}}(t) = \frac{T}{2}\sum_{i,j}\left(\bar{J}_{ij}\bar{X}_{ij} + \jmath_{ij}(t)\bar{X}_{ij}\right). \tag{39}$$

This result, along with Eq. (34), shows $w_{\text{irr}}(t)$ is *linear* in $\delta_i(t)$ and it is true for *all time*, since we do not assume $\delta_i(t)$ to be small in writing Eq. (34). The constant first term in $w_{\text{irr}}(t)$ gives its value at the SS. It is zero at a TE.

More commonly, the total EPR is split into system and medium contributions in the following way:

$$\dot{S}_{\text{tot}}(t) = \dot{S}_{\text{sys}}(t) + \dot{S}_{\text{m}}(t). \tag{40}$$

Here, the medium EPR is given by

$$\dot{S}_{\text{m}}(t) = \frac{1}{2}\sum_{i,j}\left(\bar{J}_{ij} + \jmath_{ij}(t)\right)\ln\frac{w_{ij}}{w_{ji}} = h_d(t)/T \tag{41}$$

where $h_d(t)$ is the heat dissipation rate. Note that, similar to $w_{\text{irr}}$, $h_d$ is also *linear* in $\delta_i(t)$ for *all time*. The constant part is the value of $h_d$ at the SS that vanishes at a TE. Using Eqs. (6) and (16), the system EPR becomes

$$\begin{aligned}\dot{S}_{\text{sys}}(t) &= \frac{1}{2}\sum_{i,j}\left(\bar{J}_{ij} + \jmath_{ij}(t)\right)\ln\frac{p_i(t)}{p_j(t)}\\ &= \frac{1}{2}\sum_{i,j}\left(\bar{J}_{ij}\ln\frac{p_i^s}{p_j^s} + \bar{J}_{ij}\chi_{ij}(t) + \jmath_{ij}(t)\ln\frac{p_i^s}{p_j^s} + \jmath_{ij}(t)\chi_{ij}(t)\right).\end{aligned} \tag{42}$$

On the basis of Eq. (12), the first term in the sum of Eq. (42) becomes zero, *i.e.*,

$$\sum_{i,j} \bar{J}_{ij} \ln \frac{p_i^s}{p_j^s} = 0. \tag{43}$$

This is expected because the system entropy is a state function, and so $\dot{S}_{\mathrm{sys}}$ must vanish at SS. It has already been shown that the second term of the sum in Eq. (42) is also zero by virtue of Eq. (28). Thus, the system EPR reduces essentially to

$$\dot{S}_{\mathrm{sys}}(t) = \frac{1}{2} \sum_{i,j} \left( j_{ij}(t) \ln \frac{p_i^s}{p_j^s} + j_{ij}(t) \chi_{ij}(t) \right). \tag{44}$$

From Eqs. (9) and (30), one now finds that $\dot{S}_{\mathrm{sys}}(t)$ has a linear as well as a quadratic term in $\delta_i$ near a SS, both of which vanish at SS. Also, using Eqs. (15) and (43) in Eq. (24), we get

$$\begin{aligned} \dot{S}_{\mathrm{tot}}(t) &= \frac{1}{2} \sum_{i,j} \left( \bar{J}_{ij} \ln \frac{w_{ij}}{w_{ji}} + j_{ij}(t) \ln \frac{w_{ij}}{w_{ji}} + j_{ij}(t) \ln \frac{p_i^s}{p_j^s} + j_{ij}(t) \chi_{ij}(t) \right) \\ &= \dot{S}_{\mathrm{m}}(t) + \dot{S}_{\mathrm{sys}}(t) \end{aligned} \tag{45}$$

where we have used Eqs. (41) and (44) in the last step. Equation (45) unifies the description of the various EPRs in terms of the time-dependent and time-independent fluxes and forces.

Finally, the rate of internal energy change $\dot{U}(t)$ of the system is obtained from $w_{\mathrm{irr}}$ and $h_d$ using a first-law like relation

$$\begin{aligned} \dot{U}(t) &= w_{\mathrm{irr}}(t) - h_d(t) \\ &= \frac{T}{2} \sum_{i,j} \left( \bar{J}_{ij} \ln \frac{p_i^s}{p_j^s} + j_{ij}(t) \ln \frac{p_i^s}{p_j^s} \right) = \frac{T}{2} \sum_{i,j} j_{ij}(t) \ln \frac{p_i^s}{p_j^s}. \end{aligned} \tag{46}$$

Here, in the final step, we have used Eq. (43). Thus, $\dot{U}(t)$ is linear in $\delta_i(t)$ for *all time* and becomes zero at any SS.

## 5 An application: a two-level system attaining NESS

A two-level system with multiple transition pathways is shown schematically in Fig. 1. The system can go from state 1 to state 2 via two routes having rate constants $k_1$ and $k_2$. The opposite transition also takes place via another two paths with rate constants $k_{-1}$ and $k_{-2}$. The kinetic equations of the state probabilities $p_i$ $(i = 1, 2)$ are given by

$$\dot{p}_1(t) = -(K_1 + K_2) p_1(t) + K_2 \tag{47}$$

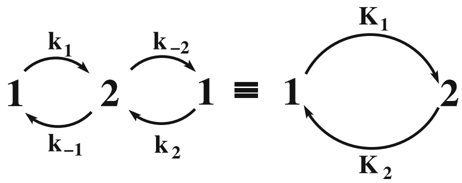


**Fig. 1** Schematic diagram of a two-level system that can support NESS

where $K_1 = k_1 + k_2$, $K_2 = k_{-1} + k_{-2}$ and we have used $p_2 = 1 - p_1$. Equation (47) is exactly solvable. For the initial condition $p_1(t = 0) = 1$, the solution is

$$p_1(t) = 1 - p_2(t) = \frac{1}{K}\left(K_2 + K_1 \mathrm{e}^{-Kt}\right). \tag{48}$$

Here $K = K_1 + K_2$. The system will reach NESS with a non-zero total EPR except when DB is satisfied with

$$\frac{k_1 k_{-2}}{k_{-1} k_2} = 1. \tag{49}$$

When Eq. (49) holds, the system attains the TE. At NESS, setting $\dot{p}_1 = 0$ in Eq. (47), we get

$$k_1 p_1^s - k_{-1} p_2^s = k_{-2} p_2^s - k_2 p_1^s = \bar{J}. \tag{50}$$

For this two-level system, the deviations of probabilities from their respective NESS values are given as

$$\delta_1(t) = p_1(t) - p_1^s = p_2^s - p_2(t) = -\delta_2(t) = \delta(t). \tag{51}$$

Since $p_1(t)$ decreases monotonically to $p_1^s$ [see Eq. (48)], $\delta(t) \geq 0$ in Eq. (51). The total EPR in this system is written as

$$\dot{S}_{\mathrm{tot}}(t) = \sum_{i=1,2} (k_i p_1(t) - k_{-i} p_2(t)) \ln \frac{k_i p_1(t)}{k_{-i} p_2(t)}. \tag{52}$$

Hence, by using Eqs. (50) and (51), the total EPR near NESS becomes

$$\dot{S}_{\mathrm{tot}}(t) = \bar{J} \ln \frac{k_1 k_{-2}}{k_{-1} k_2} + \left((k_1 + k_{-1}) \ln \frac{k_1 p_1^s}{k_{-1} p_2^s} - (k_2 + k_{-2}) \ln \frac{k_{-2} p_2^s}{k_2 p_1^s}\right) \delta$$
$$+ K \left(\frac{1}{p_1^s} + \frac{1}{p_2^s}\right) \delta^2. \tag{53}$$

This is in conformity with the general behavior found in Eq. (37). It is evident that when DB holds, the total EPR vanishes at NESS according to Eq. (49) and the system reaches TE. We also clarify that, as the system is exactly-solvable, all the thermodynamic quantities can be determined without any approximation. But, we consider the *near*-NESS situation to compare the results with those derived in previous sections for a general network.

The adiabatic component of the total EPR reads as

$$w_{\text{irr}}(t)/T = \bar{J}\ln\frac{k_1k_{-2}}{k_{-1}k_2} + \left((k_1+k_{-1})\ln\frac{k_1p_1^s}{k_{-1}p_2^s} - (k_2+k_{-2})\ln\frac{k_{-2}p_2^s}{k_2p_1^s}\right)\delta. \tag{54}$$

Equation (54) is valid for *all time*, as already pointed out. The rate of free energy change *near* NESS then becomes

$$-\dot{F}(t)/T = K\left(\frac{1}{p_1^s} + \frac{1}{p_2^s}\right)\delta^2. \tag{55}$$

Following a similar procedure, the medium EPR becomes

$$\dot{S}_{\text{m}}(t) = h_d(t)/T = \bar{J}\ln\frac{k_1k_{-2}}{k_{-1}k_2} + \left((k_1+k_{-1})\ln\frac{k_1}{k_{-1}} - (k_2+k_{-2})\ln\frac{k_{-2}}{k_2}\right)\delta \tag{56}$$

for *all time*. The system EPR *near* NESS is written as

$$\dot{S}_{\text{sys}}(t) = \left(K\ln\frac{p_1^s}{p_2^s}\right)\delta + K\left(\frac{1}{p_1^s} + \frac{1}{p_2^s}\right)\delta^2. \tag{57}$$

Thus, the rate of internal energy change for *all time* becomes

$$\dot{U}(t)/T = w_{\text{irr}}(t)/T - h_d(t)/T = \left(K\ln\frac{p_1^s}{p_2^s}\right)\delta. \tag{58}$$

Analyzing these results, we summarize below our observations:

A. When DB holds, we get

$$\dot{S}_{\text{tot}}(t) = -\dot{F}(t)/T = K\left(\frac{1}{p_1^s} + \frac{1}{p_2^s}\right)\delta^2. \tag{59}$$

B. From Eq. (50), if $\bar{J} > 0$ then $k_1p_1^s > k_{-1}p_2^s$, $k_{-2}p_2^s > k_2p_1^s$. Similar results hold for $\bar{J} < 0$. So, the first and the second terms in the coefficient of $\delta$ in Eq. (53) are either both positive or both negative. Hence, the coefficient itself can be positive or negative. With $\delta \geq 0$, there is scope for the total EPR to get decreased from its NESS value. The same is true for $w_{\text{irr}}(t)$ given in Eq. (54).

C. Inspection of Eq. (48) reveals that, for $K_1 < K_2$, the curve of $p_1(t)$ versus $t$ cannot intersect that of $p_2(t)$ versus $t$. Then, $p_1^s > p_2^s$ and, from Eq. (58), we get $\dot{U}(t) \geq 0$. In this case, a part of the irreversible work done on the system increases its internal energy and the rest gets dissipated as heat to the medium. However, for $K_1 > K_2$, the curves do cross, so $p_1^s < p_2^s$ and $\dot{U}(t) \leq 0$. Here, the heat dissipation to the medium is greater than the irreversible work done on the system and the energy balance occurs by reduction of the internal energy of the system.

D. When $p_1^s = p_2^s = 1/2$, *i.e.*, we have a uniform SS distribution, Eqs. (55), (57) and (58) lead us to

$$\dot{S}_{\text{sys}}(t) = -\dot{F}(t)/T = 4K\delta^2, \tag{60}$$

$$\dot{U}(t)/T = w_{\text{irr}}(t)/T - h_d(t)/T = 0. \tag{61}$$

Hence, in this case, the irreversible work done on the system gets totally dissipated as heat and system's internal energy remains unchanged. Also, for a uniform steady distribution, the entropy change of the system is maximum and the free energy change is minimized. In the following, we will discuss when such a situation can arise.

(i) Equation (48) yields the condition $K_1 = K_2$ for the NESS with a uniform distribution. From their definitions, we find that *three* rate constants out of four can be varied *independently*.
(ii) The uniform distribution can also occur at any TE when $k_{-1} = k_1$, $k_{-2} = k_2$ [see Eqs. (49), (50)]. This means, there are *two* independent rate constants for the system. However, the conditions on the backward rate constants to be identical with the corresponding forward ones are highly restrictive and seem accidental for processes involving chemical reactions. Thus, a uniform distribution with maximum entropy production and minimum free energy change is much more likely to occur in a non-equilibrium set up.

## 6 Conclusion

Starting from a master equation description of the system without assuming DB, here we have decomposed the fluxes and the corresponding forces into time-independent and time-dependent portions. The relationships among these components near any arbitrary NESS are in general, nonlinear. We have shown that (i) both the time-dependent and time-independent parts of the flux are *linearly proportional* to their conjugate parts of the force only near a TE [Eqs. (20), (22), (23)]. (ii) The total EPR consists of direct and cross-products of these fluxes and forces. Analysis of their behavior provides a thorough understanding on the evolution and sustenance of irreversibility in the system. (iii) A clear identification of the components of flux and force with certain state functions and path functions of the system is possible [Eqs. (38), (39), (41), (42) and (46)]. More importantly, we have determined how these functions will vary as one moves away from a SS. (iv) Although we have focused on a near-SS situation, the variations of the rate of irreversible work done, the heat dissipation rate and the rate of internal energy change turn out to be *independent* of the extent of deviation from the SS. Incidentally, all these three quantities emerge from the *first law* of thermodynamics.

Applying our methodology to a two-level system sustaining NESS, we have found how the system parameters govern the utilization of the irreversible work done on the system. This is indeed linked with the heat dissipation to the medium and internal energy change of the system. Depending on the relative magnitudes of the transitions rates, the internal energy change can either be positive or negative. This helps us in understanding the mechanism of energy expenditure. We have also shown the advantage of a non-equilibrium scenario in the context of realizing a minimized free energy state.

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