Heat Dissipation and Nonequilibrium Thermodynamics of Quasi-Steady States and Open Driven Steady State

Hao Ge[1,2*] and Hong Qian[3†]

[1]*School of Mathematical Sciences and Centre for Computational Systems Biology,
Fudan University, Shanghai 200433, PRC.* [2]*Department of Chemistry and Chemical Biology,
Harvard University, Cambridge, MA 02138, USA.* [3]*Department of Applied Mathematics,
University of Washington, Seattle, WA 98195, USA.*

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We develop a comparative thermodynamic theory, based on master-equation description of driven chemical reactions, for quasi-steady-state (QSS) and open-system nonequilibrium steady-state (NESS) sustained by chemical potential difference. The two processes have identical kinetics but different thermodynamics: Using motor protein as an example, we find that the difference in heat dissipation is the minimum work that needed for an external energy regenerating system that keeps the NESS (*e.g.*, sustains constant concentrations of ATP, ADP and Pi). The entropy production rate in the NESS equals to the rate of decreasing free energy in the QSS of the corresponding closed system. For systems approaching an NESS, the non-negativity of the rate of relative entropy change gives rise to the concept of *housekeeping heat*. This theory shows consistency and contradistinctions in thermodynamics of energy transduction and heat dissipation in the two different perspectives of nonequilibrium systems, *à la* Clausius and Kelvin. Furthermore, it suggests new thermodynamic ingredients of self-organization in driven systems.

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Statistical thermodynamics is the mathematical foundation of our material world in terms of classical physics, on which modern chemistry and biology stand [1]. To address the fundamental issues in complex living organisms such as a cell, there are currently two different perspectives: A classical physicist maintains a world following the Second Law of Thermodynamics and considers a living organism as a *subsystem* in a quasi-stationary state, due to the the slow changing nature of its environment; engineers and cellular biologists consider the complex systems in a sustained environment which has to be maintained. How to maintain such environment, however, is not a concern to someone who is interested in the internal, complex dynamics.

This distinction can be best illustrated by two types of laboratory experiments on a motor protein [2], which convert chemical energy from ATP hydrolysis to mechanical work. In the first type, the amount of ATP, ADP and Pi are not controlled. However, due to the excess nature of their amount in solution, their concentrations can be considered approximately constant over the entire duration of a single-molecule experiment. Nevertheless, if an experiment is prolonged for a sufficiently long time, the ATP and ADP+Pi will eventually reach their chemical equilibrium, and the motor protein will cease to execute a directional motion. In the second type of experiments, an ATP-regenerating system is coupled to the motor protein [3]. In this case, the motor protein, as an open chemical system, can reach a nonequilibrium steady state (NESS) while continuously move along its track, even with a constant load [4, 5].

In the past, this experimental distinction has not attracted much consideration from theorists since in the kinetic theories of motor proteins [2], both QSS and NESS treatments assume time-independent, constant concentrations of ATP, ADP and Pi, leading to identical predictions.

However, the thermodynamics of the two setups are different: In the QSS, the heat associated with each ATP hydrolysis is its ΔH; i.e., enthalpy (or internal energy for system with constant volume) change. But in the NESS, the amount heat dissipated is the ΔG of ATP hydrolysis! A consistent thermodynamic theory, thus, is needed to clarify the issues. The theory will naturally deduce NESS thermodynamics of an open system from thermodynamics of quasi-stationary transient processes in a closed system. A comparative study of QSS and NESS nonlinear dynamics can be found in [6].

A simple cyclic reaction system coupled with a regenerating system — Fig. 1 shows a simple biochemical reaction cycle $B \to C \to B$ coupled to ATP hydrolysis. The ATP, ADP and Pi concentrations are maintained by an "external" regenerating system:

$$B + ATP \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + ADP, \quad C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B + P_i. \qquad (1)$$

After completing a reaction cycle (1), the net effect is one ATP being hydrolyzed to ADP+Pi. At the meantime, the regenerating system would convert ADP+Pi back to ATP externally. This is the essential difference between NESS and QSS which results in one ATP hydrolysis after one cycle. Standard thermodynamics tells

*Electronic address: gehao@fudan.edu.cn
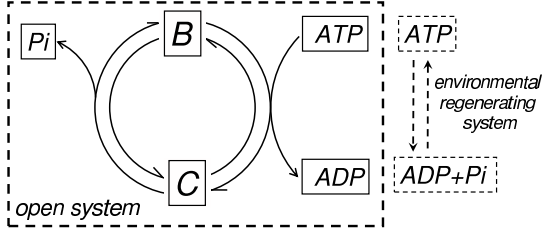†Electronic address: qian@amath.washington.edu

FIG. 1: The thermodynamics of spontaneous ATP hydrolysis and related ATP regenerating process. For net ATP hydrolysis reaction, $\Delta\mu = \Delta h^o - T\Delta s^o + k_B T \ln \frac{[ADP][Pi]}{[ATP]} = -k_B T \ln\gamma < 0$. Each hydrolysis reaction absorbs the amount of heat of Δh^o. In general, reaction Δh^o can be either positive (endothermic) or negative (exothermic). Associated with the reaction is also the change of configurational entropy Δs^o between a molecule ATP and the products ADP and Pi. The last term is entropy change associated with changing concentrations. Because of $\Delta\mu < 0$, the regenerating process can not be spontaneous. In fact, a minimal amount of work, $-\Delta\mu$ is required to synthesis an ATP from $ADP + P_i$, at the given concetrations. Furthermore due to energy conservation, this synthesis process also release amount of heat $T\Delta s^o + k_B T \ln \frac{[ATP]}{[ADP][P_i]}$. The entire cycle, therefore, has an $-\Delta\mu > 0$ amount of work input and the same amout of heat dissipated.

us the chemical potentials of each species are defined as

$$\mu_B = \mu_B^o + k_B T \ln[B], \quad \mu_C = \mu_C^o + k_B T \ln[C],$$
$$\mu_{ATP} = \mu_{ATP}^o + k_B T \ln[ATP],$$
$$\mu_{ADP} = \mu_{ADP}^o + k_B T \ln[ADP],$$
$$\mu_{P_i} = \mu_{P_i}^o + k_B T \ln[P_i]. \tag{2}$$

At chemical equilibrium, $\mu_B + \mu_{ATP} = \mu_C + \mu_{ADP}$ and $\mu_B + \mu_{P_i} = \mu_C$, i.e. $k_1[B]^{eq}[ATP]^{eq} = k_{-1}[C]^{eq}[ADP]^{eq}$ and $k_2[C]^{eq} = k_{-2}[B]^{eq}[P_i]^{eq}$, which also leads to the thermodynamic relations

$$\mu_B^0 + \mu_{ATP}^0 - \mu_C^0 - \mu_{ADP}^0 = k_B T \ln(k_1/k_{-1}), \tag{3}$$
$$\mu_C^0 - \mu_B^0 - \mu_{P_i}^0 = k_B T \ln(k_2/k_{-2}). \tag{4}$$

Each intrinsic chemical potential can be decomposed into $\mu^0 = h^0 - Ts^0$, where h^0 and s^0 are the intrinsic enthalpy and entropy respectively. Then for a single occurrence of the hydrolysis cycle in Fig. 1, the heat dissipation is

$$h_d = (h_B^0 + h_{ATP}^0 - h_C^0 - h_{ADP}^0) + (h_C^0 - h_{P_i}^0 - h_B^0)$$
$$= h_{ATP}^0 - h_{ADP}^0 - h_{P_i}^0. \tag{5}$$

There is an "external step" for the regenerating system converting ADP+Pi back to ATP after each completion of a cycle. The minimum work it has to do is the free energy difference between ADP+Pi and ATP, i.e.

$$W_{min} = \mu_{ATP} - \mu_{ADP} - \mu_{P_i}, \tag{6}$$

with corresponding enthalpy changes from $h_{ADP}^0 + h_{P_i}^0$ to h_{ATP}^0. Therefore, the energy dissipation of this external step in the environment, in the form of heat, is

$$h_d^{ext} = W_{min} - (h_{ATP}^0 - h_{ADP}^0 - h_{P_i}^0). \tag{7}$$

We note that h_d^{ext} is just the entropy change for the ATP hydrolysis.

Hence the total heat dissipation of a single forward biochemical cycle in a drive system with regeneration is

$$h_d + h_d^{ext} = W_{min} = \mu_{ATP} - \mu_{ADP} - \mu_{P_i} = k_B T \ln\gamma,$$

where $\gamma = \frac{k_1 k_2 [ATP]}{k_{-1} k_{-2}[ADP][P_i]} > 1$ is the affinity for the reaction cycle. The affinities has a clear thermodynamic meaning in such a driven cycle, and all the external work is dissipated while the system remaining steady.

We see the central importance of cycle kinetics from this simple example. Before a completion of a cycle, the regenerating system needs not to do anything to maintain the environment, and all the work done to "the system" is potentially reversible. This has been emphasized by T.L. Hill; a similar argument was put forward by Landauer for the thermodynamics of computation [7].

Master equation model and thermodynamic constrains — The above analysis for a single biochemical cycle can be generalized to dynamical models with master equations: Let us consider a motor protein with N different conformations $R_1, R_2, \cdots, R_N$. Suppose that the system is kept in a close contact with a large heat bath with constant temperature T and volume V, i.e., the system considered is in an isothermal surrounding with fixed volume. For simplicity, the concentration of every substance is assumed to be independent of its position, and there is no external input or output of mechanical energy.

Let k_{ij} be the first-order, or pseudo-first-order rate constants for reaction $R_i \to R_j$. Assume one of them is involved in the energy source, i.e., ATP and ADP:

$$ATP + R_1 \underset{\tilde{k}_{21}}{\overset{\tilde{k}_{12}}{\rightleftharpoons}} ADP + R_2,$$
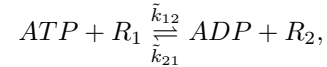
where $\tilde{k}_{12}$ and $\tilde{k}_{21}$ are both second-order reaction constants, and $k_{12} = \tilde{k}_{12}[ATP]$, $k_{21} = \tilde{k}_{21}[ADP]$ are pseudo-first-order rate constants.

Let c_i be the concentration of R_i. Then by the law of mass action, such a linear system could be described in terms of a mathematical model

$$\frac{dc_i(t)}{dt} = \sum_j (c_j k_{ji} - c_i k_{ij}). \tag{8}$$

If there is no external mechanism to keep the concentrations of ATP and ADP, then the time evolution of $[ATP]$ and $[ADP]$ is

$$\frac{dc_T}{dt} = -\frac{dc_D}{dt} = -\tilde{k}_{12} c_T c_1 + \tilde{k}_{21} c_D c_2. \tag{9}$$

Classical equilibrium thermodynamics for closed chemical system tells us that there is a unique dynamic and chemical equilibrium $\{c_1^{eq}, c_2^{eq}, \cdots, c_N^{eq}, c_T^{eq}, c_D^{eq}\}$ which satisfies the detailed balance condition $c_i^{eq} k_{ij} = c_j^{eq} k_{ji}$, where $k_{12} = \tilde{k}_{12} c_T^{eq}$ and $k_{21} = \tilde{k}_{21} c_D^{eq}$.

Each species has a chemical potential $\mu_i(c_i) = \mu_i^0 + kT \ln c_i$, and when a system reaches chemical equilibrium, the chemical potentials of different components are the same, i.e. $\mu_i(c_i^{eq}) = \mu_j(c_j^{eq})$, and $\mu_1(c_1^{eq}) + \mu_T(c_T^{eq}) = \mu_2(c_2^{eq}) + \mu_D(c_D^{eq})$, where $\mu_T(c_T) = \mu_T^0 + kT \ln c_T$ and $\mu_D(c_D) = \mu_D^0 + kT \ln c_D$ are the chemical potentials of ATP and ADP respectively. μ_i^0 is the internal chemical potential of species R_i and obeys the Boltzmann's law $\mu_i^0 = -kT \ln c_i^{eq} + $const.

Detailed balance gives the relation between μ^o's and k_{ij}'s of the system

$$\mu_i^0 - \mu_j^0 = kT \ln \frac{k_{ij}}{k_{ji}}, \quad \mu_T^0 - \mu_D^0 = kT \ln \frac{c_D^{eq}}{c_T^{eq}},$$

$$\mu_1^0 + \mu_T^0 - \mu_2^0 - \mu_D^0 = kT \ln \frac{\tilde{k}_{12}}{\tilde{k}_{21}}.$$

Thermodynamics of nonequilibrium driven system— With the presence of an external regenerating mechanism, the concentrations of ATP and ADP would be kept invariant. The system is not at equilibrium in general [8]. Recall that each μ^0 could be decomposed into $h^0 - Ts^0$, hence for each individual occurrence of the transition $R_i \to R_j$, the heat dissipation is $h_i^0 - h_j^0$ which is not related to the regenerating system. However, for the real driven reaction $ATP + R_1 \rightleftharpoons ADP + R_2$, the total heat dissipation should be $(h_1^0 + \mu_T) - (h_2^0 + \mu_D)$ following the above analysis.

Therefore the heat dissipation rate in such a driven open system is

$$\tilde{h}_d^{open}(t) = \sum_{i>j} (c_i(t)k_{ij} - c_j(t)k_{ji})(h_i^0 - h_j^0)$$
$$+ (c_1(t)k_{12} - c_2(t)k_{21})(\mu_T - \mu_D). \quad (10)$$

Furthermore, in the stationary NESS:

$$\tilde{h}_d^{ness} = \sum_{i>j} (c_i^{ss}k_{ij} - c_j^{ss}k_{ji})(\mu_i^0 - \mu_j^0)$$
$$+ (c_1^{ss}k_{12} - c_2^{ss}k_{21})(\mu_T - \mu_D)$$
$$= \sum_{i>j} (c_i^{ss}k_{ij} - c_j^{ss}k_{ji}) \ln \frac{k_{ij}}{k_{ji}}. \quad (11)$$

The rigorous derivation of (12) is based on the fact that in an NESS, its kinetics and thermodynamics can be decomposed into different cycles [1, 4, 9]. As we have stated, the regenerating system would not really do any irreversible work unless there is a completion of a driven cycle. The amount of minimum work that should be done for each internal cycle $c = \{i_0 \to i_1 \to i_2 \cdots \to i_n \to i_0\}$ is just

$$W_{min} = \ln \frac{k_{i_0 i_1} k_{i_1 i_2} \cdots k_{i_n i_0}}{k_{i_0 i_n} k_{i_n i_{n-1}} \cdots k_{i_1 i_0}}.$$

For each state i, the internal entropy $Ts_i^0 = h_i^0 - \mu_i^0$. Thus the entropy of the open system could be defined as

$\tilde{S}^{open} = S^0 + S^{open}$, where $S^0 = \sum_i Ts_i^0 c_i$ and $S^{open} = -\sum_i c_i \ln c_i$. Then the evolution of entropy becomes

$$\frac{d\tilde{S}^{open}}{dt} = e_p^{open} - \tilde{h}_d^{open}, \quad (12)$$

where $e_p^{open} = \sum_{i>j} (c_i k_{ij} - c_j k_{ji}) \ln \frac{c_i k_{ij}}{c_j k_{ji}}$ is the entropy production rate [1, 4, 9]. Thus the free energy

$$\tilde{F}^{open} = H^0 - \tilde{S}^{open} = \mu^0 - S^{open},$$

where $H^0 = \sum_i h_i^0 c_i$ is the enthalpy, and $\mu^0 = \sum_i \mu_i^0 c_i$ is the internal (conditional) free energy of the system.

We note that no matter how large the entropic component of μ_i^o is, s_i^o enters both H^o and $\tilde{S}^{open}$ and they compensate, leaving $\tilde{F}^{open}$ invariant [10]. If we know that $\Delta \mu_{ij}^0 = \ln(k_{ij}/k_{ji})$ does not depend on temperature, i.e. s^0 is exactly the same for each state, or we do not know the temperature dependence of $\{k_{ij}\}$, then we can operationally define "heat" for such a driven system as

$$h_d^{open} = \sum_{i>j} (c_i k_{ij} - c_j k_{ji}) \ln \frac{k_{ij}}{k_{ji}}. \quad (13)$$

Note that $\tilde{h}_d^{open}$ and h_d^{open} are the same at NESS, which imply the heat dissipation in an NESS does not rely on measurements based on different resolutions [11].

Using Eq. (13) and the definitions given for S^{open} and e_p^{open}, the fundamental entropy balance equation of nonequilibrium thermodynamics is recovered [1, 12, 15]:

$$\frac{dS^{open}}{dt} = e_p^{open} - h_d^{open}. \quad (14)$$

The difference between Eqs. (12) and (14) is that the latter is completely independent of the any details on the regenerating system, albeit the meaning of "heat" is a little obscured without knowing more about temperature dependence. This is analogous to an equilibrium ensemble based on the potential of mean force or conditional free energy without the knowledge of their temperature dependence [10].

QSS in a large closed system with detailed balance — In this case, the concentrations of ATP and ADP are very slowly changing; the whole system is closed; its dynamical equilibrium is a chemical equilibrium. The total free energy of the system is

$$F^{close} = \sum_i c_i \mu_i + c_T \mu_T + c_D \mu_D$$
$$= \sum_i c_i \ln \frac{c_i}{c_i^{eq}} + c_T \ln \frac{c_T}{c_T^{eq}} + c_D \ln \frac{c_D}{c_D^{eq}},$$

and which always decreases until it reaches to its minimum at equilibrium:

$$\frac{dF^{close}(t)}{dt} = -\sum_{i>j} (c_i k_{ij} - c_j k_{ji}) \ln \frac{c_i k_{ij}}{c_j k_{ji}} \leq 0. \quad (15)$$

Being a QSS, the $F^{close}(t)$ decreases very slowly. The term $f_d^{close} = -dF^{close}(t)/dt$ is called *free energy dissipation rate* [12].

Furthermore, the entropy of the whole closed system is defined as $S^{close} = \sum_i [-c_i \ln c_i] - c_T \ln c_T - c_D \ln c_D$. Then,

$$\frac{dS^{close}}{dt} = e_p^{close} - h_d^{close}, \qquad (16)$$

where $h_d^{close} = \frac{1}{2}\sum_{ij}(c_i k_{ij} - c_j k_{ji})(\mu_i^0 - \mu_j^0) + (c_1 k_{12} - c_2 k_{21})(\mu_T^0 - \mu_D^0)$ is the heat dissipation, and the *entropy production rate* $e_p^{close} = f_d^{close}$. The entropy of the system increases due to entropy generated in spontaneous processes and decreases when heat is expelled into the surrounding.

One could easily notice, from (12), that $e_p^{open} = e_p^{close} = f_d^{close}$. This reflects the different perspective of Boltzmann/Gibbs and Prigogine: Gibbs states free energy never increase in a closed, isothermal system; while Prigogine states that the entropy production is non-negative in an open system. They are equivalent.

Relative entropy and housekeeping heat in nonequilibrium open driven system — So far, based on existing classical thermodynamics, we have obtained a consistent picture for NESS and QSS. In fact, one can see a distinction between Clausius' and Kelvin's historical statements on the 2nd law: The former is about the spontaneity of a transient process, i.e. the non-negativity of f_d^{close}, while the latter is about a cyclic process with non-negative e_p^{open} in a NESS.

Recently, a more general nonequilibrium thermodynamic theory has been put forward for Markov processes including master equation systems [12]. For an open, driven system, one has the relative entropy [9, 12]

$$H\left(\{c_i\}\|\{c_i^{ness}\}\right) = \sum_i c_i \ln\left(c_i/c_i^{ness}\right), \qquad (17)$$

where c_i^{ness} is the unique steady state concentrations of the system (8). Interestingly, one has several new mathematical inequalities [12]: $H\left(\{c_i\}\|\{c_i^{ness}\}\right) \geq 0$; it time derivative

$$f_d = -\frac{d}{dt}H\left(\{c_i(t)\}\|\{c_i^{ness}\}\right) \geq 0; \qquad (18)$$

and a decompisition $f_d = e_p - Q_{hk}$ in which Q_{hk} is called *housekeeping heat* [12, 13]:

$$Q_{hk}(t) = \frac{1}{2}\sum_{ij}(c_i k_{ij} - c_j k_{ji})\ln\left(\frac{c_i^{ness}k_{ij}}{c_j^{ness}k_{ji}}\right) \geq 0. \quad (19)$$

For master equation with detailed balance, which correspond to closed system, $Q_{hk} = 0$ and the H in (17) is precisely the free energy deviation from the equilibrium [14], and Eq. (18) is reduced to (15), with $f_d = e_p$.

The novel mathematical results (18) and (19) beg for a thermodynamics interpretations in the simple example of motor protein. We have stated the regenerating system perform the W_{min} amount of work toward the system for each internal kinetic cycle. This is a consequence of 1st and 2nd laws of thermodynamics. One can in fact distribute the work input to the system as $W_{min}^{ij} = \ln(\phi_i k_{ij}/\phi_j k_{ji})$ for each transition $i \to j$, i.e. substitute $\{c_i^{ness}\}$ with any other distribution $\{\phi_i\}$ in Eq. 17. Any set of $\{\phi_i\}$ gives the same W_{min} over a cycle and NESS work input; $\phi_i = \pi_i$, however, is the only choice which yields $H\left(\{c_i(t)\}\|\{\phi_i\}\right) = 0$ at the NESS and thus being a minimum with respect to variations in $\{c_i\}$. Therefore, the Eqs. (18) and (19) implies a *principle of minimal H* for an NESS. This minimal principle requires the work input per transition in the specific form of

$$W_{min}^{ij} = \ln\left(c_i^{ness}k_{ij}/c_j^{ness}k_{ji}\right). \qquad (20)$$

The corresponding work input for an ensemble is then the Q_{hk} in (19). In the past, we have suggested to call H the *free energy* of a driven system with respect to its NESS [10, 12].

Summarize — A consistent thermodynamic analysis is carried out to illustrate the difference between closed-system QSS and open-system NESS perspectives of nonequilibrium systems. Taking a motor protein as an example, the former expects the heat dissipation as the Δh^o of ATP hydrolysis while for the latter it is the $\Delta\mu$. We have shown that the difference of heat dissipations between these two perspectives is just the minimum work needed for the regenerating system that sustains the NESS. The 2nd law in the former is expressed as free energy decreasing $f_d^{close} \geq 0$, and in the latter is $e_p^{open} \geq 0$.

One can also introduce a "free energy" like H function for open, driven systems. It decreases in a system's self-organization toward its NESS. The thermodynamic concepts of dissipation and housekeeping heat in driven system have been proposed for master equation systems.

[1] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977); T.L. Hill, *Free Energy Transduction in Biology* (Acad. Press, New York, 1977); D.A. Beard and H. Qian, *Chemical Biophysics* (Cambridge Univ. Press, U.K., 2008).

[2] H. Noji, R. Yasuda, M. Yoshida, and K. Kinosita, Nature **386**, 299 (1997); H. Wang and G. Oster, Appl. Phys. A **75**, 315 (2002); H. Qian, J. Phys. Cond. Matt. **17**, S3783

(2005); A.B. Kolomeisky and M.E. Fisher, Annu. Rev. Phys. Chem. **58**, 675 (2007).

[3] G. Wettermark, E. Borglund and S.E. Brolin, Anal. Biochem. **22**, 211 (1968); H. Liu, et. al. Nature Materials **1**, 173 (2002).

[4] D.-Q. Jiang, M. Qian and M.-P. Qian, *Mathematical Theory of Nonequilibrium Steady States*, LNM vol. 1833, (Springer-Verlag, Berlin, 2004).

[5] H. Qian, J. Phys. Chem. **110**, 15063-15074 (2006); Annu. Rev. Phys. Chem. **58**, 113-142 (2007); H. Qian and D.A. Beard, Biophys. Chem. **114**, 213-220 (2005).

[6] Y. Li, H. Qian and Y. Yi, J. Chem. Phys. **129**, 154505 (2008); J. Dyn. Diff. Eq. **22**, 491-507 (2010).

[7] T.L. Hill, Biochem. **14**, 2127-37 (1975); Proc. Natl. Acad. Sci. USA, **80**, 2922-2925 (1980); R. Landauer, IBM J. Res. Dev. **5**, 183-191 (1961).

[8] If ATP and ADP concentrations are sustained at their equilibrium values, this setting is known as *semi-grand ensemble* which is canonical for the motor protein but grand-canonical for the ligands.

[9] J. Schnakenberg, Rev. Mod. Phys. **48**, 571–585 (1976).

[10] M. Santillán and H. Qian, Phys. Rev. E. **83**, 041130 (2011); H. Qian and J.J. Hopfield, J. Chem. Phys. **105**, 9292-9296 (1996).

[11] R.M. Noyes, J. Chem. Phys. **34**, 1983-1985 (1961).

[12] H. Ge and H. Qian, *Phys. Rev. E* **81**, (2010); M. Esposito and C. van den Broeck, Phys. Rev. Lett. **104**, 090601 (2010); H. Ge, *Phys. Rev. E.* **80**, 021137 (2009); M. Esposito, U. Harbola and S. Mukamel, Phys. Rev. E. **76**, 031132 (2007).

[13] Y. Oono and M. Paniconi, Prog. Theor. Phys. Suppl. **130**, 29–44 (1998).

[14] H. Qian, Phys. Rev. E. **63**, 042103 (2001).

[15] U. Seifert, Phys. Rev. Lett. 95, 040602 (2005)