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On the Stochastic Thermodynamics of Mesoscopic Electrochemical Reactions

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In this work, we discussed the stochastic thermodynamics of mesoscopic electron transfer reactions between ions and electrodes. With a relationship between the reaction rate constant and the electrode potential, we find that the heat dissipation βq equals to the dynamic irreversibility of the reaction system minus an internal entropy change term. The total entropy change Δs_t is defined as the summation of the system entropy change Δs and the heat dissipation βq such that $\Delta s_t = \Delta s + \beta q$. Even though the heat dissipation depends linearly on the electrode potential, the total entropy change is found to satisfy the fluctuation theorem $\langle e^{-\Delta s_t} \rangle = 1$, and hence a second law-like inequality reads $\langle \Delta s_t \rangle \geq 0$. Our study provides a practical methodology for the stochastic thermodynamics of electrochemical reactions, which may find applications in biochemical and electrochemical reaction systems.

Key words: Mesoscopic chemical reaction, Electron transfer, Electrode potential, Entropy production, Fluctuation theorem

I. INTRODUCTION

Stochastic thermodynamics (ST) has been a very active field in the modern statistic physics [1–4]. The fluctuations could be significant in mesoscopic systems, and hence various thermodynamic properties such as work, heat, and system entropy become stochastic variables [5–8]. One can introduce the system entropy s and the heat dissipation q or equivalently the medium entropy change $\Delta s_m = \beta q$ to characterize a stochastic system. A very important result from ST is that the total entropy change defined as $\Delta s_t = \Delta s + \Delta s_m$ may satisfy the fluctuation theorem $\langle e^{-\Delta s_t} \rangle = 1$, which leads to a second-law-like inequality $\langle \Delta s_t \rangle \geq 0$. Such a physical picture has been revealed in dissipative systems with Newtonian dynamics [9–12], the underdamped or overdamped Brownian particles [13–17] and the quantum systems [18, 19].

As a special case of the birth-death stochastic processes, chemical reactions have gained considerable attentions. In general, the state of a reaction system is described by the number vector \mathbf{X} of active species X , which could vary according to the reaction events. When the transition rates $W_{\pm\rho}(\mathbf{X})$ for a forward and a backward reaction are identified, the probability $p(\mathbf{X}; t)$ of variable \mathbf{X} evolves according to a master equation. Note that the heat dissipation of a reaction system is

known to have very subtle relationship with the transition rates [8, 20], a careful treatment of the heat dissipation is necessary. Previous studies on reaction network with elementary reactions $\sum_i r_\rho^i X_i \rightleftharpoons \sum_i p_\rho^i X_i$ demonstrate that the heat dissipation βq can be related to the quantity $\Sigma = \sum_i \ln \frac{W_{\rho_i}}{W_{-\rho_i}}$, so that the total entropy

change $\Delta s_t = \Delta s + \beta q$ would satisfy the fluctuation theorem [21, 22]. A key intermediate step to prove this relation is to use the relationship between the equilibrium constant and the chemical potential of the reactant and product species, which can either be found from the rate theory of gas phase reactions [23] or from the self-consistent thermodynamics constraints [22]. ST of simple reactions has been successfully applied to chemical reactions which are far away from equilibrium [24–29].

In this study, we focus on the electrochemical reactions where the electrons are transferred between ions and electrodes, and hence the electrode potential ψ plays a role. One may note that the electron transfer reactions have wide applications in sensing devices [30–32]. To the best of our knowledge, the effect of electric potential is not explicitly addressed in the previous studies of ST, so it would be useful to see how to incorporate the electrode potential into the ST of electrochemical reactions. Specifically, based on the constraints from thermodynamic self-consistency or the Marcus' theory of electron transfer reactions [33–36], a relation between the equilibrium constant and the electrode potential ψ is found. With this relation, we dem-

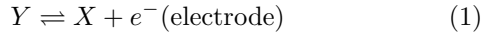
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onstrate that $\Sigma = \sum_i \ln \frac{W_{\rho_i}}{W_{-\rho_i}}$ equals to the heat dissipation βq minus an entropy change of the active species, so that the total entropy change defined as $\Delta s_t = \Delta s + \beta q$ satisfies the fluctuation theorem $\langle e^{-\Delta s_t} \rangle = 1$ and the second law reads $\langle \Delta s_t \rangle \geq 0$. For a reaction system with given propensity functions $\{W_{\pm\rho}\}$, the heat dissipation βq depends explicitly on the electrode potential as well as the internal entropy of the reactive species. When the electrode potential and the internal entropy of the system are not specified, βq is not well defined while the total entropy change Δs_t can be uniquely determined. Our finding implies that the ST of electron transfer reactions can be treated in the same way as ST of reactions without electron transfer.

In this work, a model electrochemical reaction system is first introduced. ST of electrochemical reactions is shown in a thermodynamic relationship between the reaction rate constant and the electrode potential is presented and the fluctuation theorem is discussed.

II. MODEL OF THE MESOSCOPIC ELECTROCHEMICAL SYSTEMS

Consider a model electrochemical reaction system with fixed volume V . The reaction system contacts to a heat bath with temperature T , and then the reduced inverse temperature can be defined as $\beta = 1/k_B T$. As an illustrative example, we consider an electrochemical reaction between an ion species Y and an electrode with electric potential ψ



where $Y = A^{n+}$ and $X = A^{(n+1)+}$ are the active species. Denote \mathbf{X} and \mathbf{Y} as the particle numbers of the X species and Y species. In the dilute limit, the reaction rate for elemental reactions satisfies the mass action law, where the reaction rates for the forward and backward reactions are given by [23]

$$\begin{aligned} W_+(\mathbf{X}) &= k_+ \mathbf{Y} \\ W_-(\mathbf{X}) &= k_- \mathbf{X} \end{aligned} \quad (2)$$

where k_+ and k_- are the reaction constant for the forward and backward reaction. The rate constant $K = k_+/k_-$ for electron transfer reactions is known to depend on the chemical potential of \mathbf{X} and \mathbf{Y} as well as electrode potential ψ [33, 36]. In the following section we will show that a simple relationship between the equilibrium constant K and the electrode potential ψ can be worked out.

The Y species is assumed to contact to a particle reservoir with chemical potential μ_Y and hence keeps its particle number fixed. Denote the probability distribution of the intermediate species X as $p(\mathbf{X}; t)$. The evolution of $p(\mathbf{X}; t)$ is governed by the master equation

as

$$\partial_t p(\mathbf{X}; t) = \sum_{\rho=\pm} [W_\rho(\mathbf{X} - v_\rho) p(\mathbf{X} - v_\rho; t) - W_\rho(\mathbf{X}) p(\mathbf{X}; t)] \quad (3)$$

where $v_+ = 1$ and $v_- = -1$ are the stoichiometric coefficients of X species for the forward and backward reactions, *i.e.*, the particle number changes from \mathbf{X} to $\mathbf{X} + v_+$ or $\mathbf{X} + v_-$ given a forward or a backward reaction happens. In the long time limit, the system could reach a stationary distribution $p_s(\mathbf{X}) = p(\mathbf{X}; t \rightarrow \infty)$, such that $\partial_t p_s(\mathbf{X}) = 0$.

III. STOCHASTIC THERMODYNAMICS IN THE SINGLE TRAJECTORY LEVEL

A. Single trajectory and dynamic irreversibility

For the reaction system, the reaction events change the state variable of the system and hence generate a stochastic trajectory. Denote $\mathbf{X}_j \equiv \mathbf{X}(t'' = t_j)$ as the particle number of species X at time $t'' = t_j$. A forward trajectory $\chi(t)$ consisted of n consecutive reactions is defined as

$$\begin{aligned} \chi(t) &= \{\mathbf{X}_0(t'' = t_0) \rightarrow \mathbf{X}_1(t'' = t_1) \rightarrow \dots \rightarrow \\ &\quad \mathbf{X}_{n-1}(t'' = t_{n-1}) \rightarrow \mathbf{X}_n(t'' = t_n) \rightarrow \\ &\quad \mathbf{X}_n(t'' = t)\} \end{aligned}$$

its conjugate backward trajectory $\chi^R(t)$ is defined as

$$\begin{aligned} \chi^R(t) &= \{\mathbf{X}_n(t'' = t'_0) \rightarrow \mathbf{X}_{n-1}(t'' = t'_1) \rightarrow \dots \rightarrow \\ &\quad \mathbf{X}_1(t'' = t'_{n-1}) \rightarrow \mathbf{X}_0(t'' = t'_n) \rightarrow \mathbf{X}_0(t'' = t)\} \end{aligned}$$

$\tau_j = t_j - t_{j-1}$ and $\tau'_j = t'_j - t'_{j-1}$ are two time interval parameters. The conjugate condition requires that $\tau_j = \tau'_{n+1-j}$. According to the Gillespie's method [37, 38], the conditional probability to find such a trajectory or its conjugated one reads

$$P[\chi(t)|\mathbf{X}_0] = \prod_{j=1}^n e^{-r(\mathbf{X}_{j-1})\tau_j} \frac{W_{\rho_j}(\mathbf{X}_{j-1})}{r(\mathbf{X}_{j-1})} e^{-r(\mathbf{X}_n)(t-t_n)} \quad (4)$$

$$P[\chi^R(t)|\mathbf{X}_t] = \prod_{j=1}^n e^{-r(\mathbf{X}_{j-1})\tau'_j} \frac{W_{-\rho_j}(\mathbf{X}_j)}{r(\mathbf{X}_{j-1})} e^{-r(\mathbf{X}_n)(t-t_n)} \quad (5)$$

where $r(\mathbf{X}_i) = \sum_{\rho=\pm} W_\rho(\mathbf{X}_i)$ is the total propensity function. With the log ratio of those two probabilities, one

can introduce a dynamic irreversibility term Σ as

$$\begin{aligned}\Sigma &\equiv \ln \frac{P[\chi(t)|\mathbf{X}_0]}{P[\chi^R(t)|\mathbf{X}_t]} \\ &= \sum_{j=1}^n \ln \frac{W_{\rho_j}(\mathbf{X}_{j-1})}{W_{-\rho_j}(\mathbf{X}_j)}\end{aligned}\quad (6)$$

For the simple reaction systems, the dynamic irreversibility Σ differs from βq by a term which depends on the degeneracy of particles [22], and the averaged change rate $\langle \dot{\Sigma} \rangle$ can be related to the entropy production defined as the product of the thermodynamic flux and the thermodynamic force [21]. In the following part, we will show that such relations are also valid for the reaction systems with electron transfer.

B. Energy balance in the single trajectory level

In order to study the energetics of the reaction system, we consider the thermodynamic properties. The chemical potential μ_i for the i -th active species with particle number N_i can be expressed as $\beta\mu_i(N_i) = \beta\mu_i^* + \ln N_i$, where $\beta\mu_i^*$ is the chemical potential of a reference state [23]. The entropy s_i and the internal energy ϵ_i of the species i are connected via the thermodynamic relation $\beta\epsilon_i = \beta\mu_i + s_i$ [23].

Denote $A(\mathbf{X})$ as the free energy of the reaction system in state \mathbf{X} . After a reaction of the ρ_j -th kind, the state varies from \mathbf{X}_{j-1} to $\mathbf{X}_j = \mathbf{X}_{j-1} + v_{\rho_j}$, then the free energy change $\beta\Delta A^j$, the internal entropy change ΔS_0^j and the internal energy change ΔU^j for the reaction system reads

$$\beta\Delta A^j = v_{\rho_j} [\beta\mu_X^* + \ln(X_{j-1} + v_{\rho_j})] \quad (7)$$

$$\Delta S_0^j = v_{\rho_j} s_X \quad (8)$$

$$\beta\Delta U^j = \beta\Delta A^j + \Delta S_0^j \quad (9)$$

In order to keep the particle number of Y of the reaction system unchanged, the amount of chemical work done by particle reservoirs is as the following

$$\begin{aligned}\beta w_{\text{chem}}^j &= -u_{\rho_j} \beta\mu_Y \\ &= -u_{\rho_j} (\beta\mu_Y^* + \ln \mathbf{Y})\end{aligned}\quad (10)$$

where $u_+ = -1$ and $u_- = 1$ are the stoichiometric coefficients of Y species for the forward and backward reactions. The electric work by the electrode reads

$$\beta w_{\text{ele}}^j = v_{\rho_j} e_0 \psi \quad (11)$$

where e_0 is the elemental charge.

Since the temperature T of the reaction system is fixed during the reaction process, the amount of energy $\beta w_{\text{chem}}^j + \beta w_{\text{ele}}^j - \beta\Delta U^j$ should be released to the heat bath as heat dissipation βq^j , so the energy balance equation can be written as

$$\beta q^j = \beta w_{\text{chem}}^j + \beta w_{\text{ele}}^j - \beta\Delta U^j \quad (12)$$

Along a single trajectory which consists of n reactions,

the heat dissipation $\beta q \equiv \sum_{j=1}^n \beta q^j$ reads

$$\begin{aligned}\beta q &= - \sum_{j=1}^n [u_{\rho_j} \beta\mu_Y^* + v_{\rho_j} \beta\mu_X^* + v_{\rho_j} e_0 \psi] \\ &\quad - \sum_{j=1}^n [u_{\rho_j} \ln \mathbf{Y} + v_{\rho_j} \ln (\mathbf{X}_{j-1} + v_{\rho_j})] \\ &\quad - \sum_{j=1}^n \Delta S_0^j\end{aligned}\quad (13)$$

which implies that the heat dissipation has a linear dependence on the electrode potential.

C. Dynamic-thermodynamic relation

Herein we demonstrate that the heat dissipation βq could be related to the dynamic irreversibility Σ based on the constraints from macroscopic equilibrium system. Denote the equilibrium concentration of species X and Y as \mathbf{x}_s and \mathbf{y} :

$$\mathbf{x}_s \equiv \lim_{V \rightarrow \infty} \frac{\mathbf{X}}{V} \quad (14)$$

$$\mathbf{y} \equiv \lim_{V \rightarrow \infty} \frac{\mathbf{Y}}{V} \quad (15)$$

The zero current condition in the equilibrium system is:

$$k_+ \mathbf{y} - k_- \mathbf{x}_s = 0 \quad (16)$$

or equivalently:

$$\ln K = \ln \frac{k_+}{k_-} = \ln \frac{\mathbf{x}_s}{\mathbf{y}} \quad (17)$$

The electric potential equilibrium condition reads:

$$\beta\mu_X(\mathbf{x}_s V) - \beta\mu_Y(\mathbf{y} V) + e_0 \psi = 0 \quad (18)$$

or equivalently:

$$u_+ \beta\mu_Y^* + v_+ \beta\mu_X^* + v_+ e_0 \psi = - \ln \frac{\mathbf{x}_s}{\mathbf{y}} \quad (19)$$

By comparing these two constraints, one can find that

$$\begin{aligned}\ln K &\equiv \ln \frac{k_+}{k_-} \\ &= -(u_+ \beta\mu_Y^* + v_+ \beta\mu_X^* + v_+ e_0 \psi)\end{aligned}\quad (20)$$

One may note that it is possible to derive this equation in a different way, *e.g.*, one can use the reaction rate constant k_{\pm} from Marcus' theory of electron transfer [33, 36] to derive Eq.(14). With Eq.(2), Eq.(6),

Eq.(13) and Eq.(20), it is straightforward to prove that

$$\beta q = \sum_{j=1}^n \ln \frac{W_{\rho_j}(\mathbf{X}_{j-1})}{W_{-\rho_j}(\mathbf{X}_j)} - \sum_{j=1}^n \Delta S_0^j$$

$$= \Sigma - \Delta S \quad (21)$$

$$\Delta S_0 \equiv \sum_j \Delta S_0^j \quad (22)$$

where ΔS_0 is the internal entropy change along the trajectory. Eq.(21) implies that the heat dissipation equals to the dynamic irreversibility minus the internal entropy change of the reaction system.

D. Entropy balance and the fluctuation theorem

For the reaction system along the single trajectory $\chi(t)$, one should note that the stochastic system entropy $s(t)$ consists of an internal entropy contribution S_0 and the Shannon entropy contribution $-\ln[p(\mathbf{X}_t; t)]$ [20, 21], *i.e.*,

$$s = S_0 - \ln[p(\mathbf{X}_t; t)] \quad (23)$$

The system entropy change can then be evaluated as

$$\Delta s = \Delta S_0 + \ln \frac{p(\mathbf{X}_0, t_0)}{p(\mathbf{X}_t; t)} \quad (24)$$

When the internal entropy term is evaluated analytically from the grand canonical ensemble, one can find that ΔS_0 reduces to the degeneracy entropy term introduced by Schmiedl and Seifert [20, 22]. As one can see, the reactive species which contact with particle reservoir would not contribute to the system entropy change as their particle numbers are constants during the reactions.

Using Eq.(21) and Eq.(24), the total entropy change Δs_t defined as $\Delta s_t \equiv \Delta s + \beta q$ can be rewritten as

$$\Delta s_t = \Sigma + \ln \frac{p(\mathbf{X}_0, t_0)}{p(\mathbf{X}_t, t)}$$

$$= \ln \frac{P(\chi)}{P(\chi^R)} \quad (25)$$

According to Eq.(25), the total entropy change is equal to the log ratio of the probability of a forward trajectory to that of a conjugate backward trajectory. Then following the standard procedure in the stochastic thermodynamics [3, 22], it is straightforward to prove that Δs_t satisfies the fluctuation theorem as

$$\langle e^{-\Delta s_t} \rangle = 1 \quad (26)$$

and then the second law of thermodynamics follows as $\langle \Delta s_t \rangle \geq 0$.

As one can see, the propensity function $\{W_\rho(X)\}$ is insufficient to define a chemical reaction system with

unique thermodynamic properties, *i.e.*, chemical reaction systems with fixed $\{W_\rho(X)\}$ may have different internal entropy $\{s_i\}$ and different chemical potential $\{\mu_i^*\}$. According to Eq.(21) and Eq.(25), these systems would have different heat dissipation βq and the same total dissipation Δs_t . Even though the heat dissipation βq does depend on the electrode potential ψ , the dynamic-thermodynamic relations $\beta q = \Sigma - \Delta S_0$ and the fluctuation theorem $\langle e^{-\Delta s_t} \rangle = 1$ are still valid. Our study implies that the ST of electrochemical reactions can be treated in the same way as ST of simple reactions. Note that the mass action law is the starting point of this study and is known to be valid for dilute reactants, one can expect that our theory is at least applicable to dilute solutions. For concentrated solutions where the mass action law fails, the ST of reactions remains an open question and deserves further investigations.

IV. CONCLUSIONS

In this study, we discussed the stochastic thermodynamics of electrochemical reactions, where the electrode potential plays a role. We find a relationship between the reaction constant $K = k_+/k_-$ and the electrode potential ψ . With such a relationship, one can discuss the energy balance in stochastic trajectory level, where the heat dissipation βq is found to be equal to the log ratio of the conditional probabilities for a forward and a backward trajectory minus an internal entropy change term. Even though the heat dissipation βq has a linear dependence on the electrode potential ψ , the total entropy change $\Delta s_t = \Delta s + \beta q$ satisfies the fluctuation theorem $\langle e^{-\Delta s_t} \rangle = 1$ and is similar to the case of simple reactions without electron transfer. Our study provides a practical methodology for the stochastic thermodynamics of mesoscopic electron transfer reactions, which may find applications in small biochemical and electrochemical reaction systems.

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