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Entropy Production along Dominant Pathway of Nonequilibrium Phase Transition in Mesoscopic Chemical System

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We consider a bistable mesoscopic chemical reaction system and calculate entropy production along the dominant pathway during nonequilibrium phase transition. Using probability generating function method and eikonal approximation, we first convert the chemical master equation into the classical Hamilton-Jacobi equation, and then find the dominant pathways between two steady states in the phase space by calculating zero-energy trajectories. We find that entropy productions are related to the actions of the forward and backward dominant pathways. At the coexistence point where the stabilities of the two steady states are equivalent, both the system entropy change and the medium entropy change are zero; whereas at non-coexistence point both of them are nonzero.

Key words: Entropy production, Mesoscopic chemical reaction, Nonequilibrium phase transition

I. INTRODUCTION

Equilibrium statistical physics plays an important role in the fields of physics, chemistry, and biology. However, most of systems around us are in nonequilibrium condition [1]. Examples are ubiquitous including from mesoscopic chemical reactions in living systems to the evolution of biological population. Albeit stochastic fluctuations in mesoscopic systems are inevitable, such systems are capable of reaching a nonequilibrium steady state following Klein's concise terminology [2]. While for a nonlinear system, it is possible that there exist more than one steady state under the same condition, wherein each stable steady state corresponds to a peak in the stationary probability distribution, while an unstable steady state corresponds to a saddle [3, 4]. In this situation, fluctuations can induce the system from one stable steady state to another one, which is similar to a first-order phase transition in equilibrium systems [5–8].

On the other hand, stochastic thermodynamics of chemical reaction systems has gained much attention recently [9–15]. The non-equilibrium steady state can be characterized by a non-zero entropy production rate. Recent developments in the area have highlighted the importance of entropy production and its relationship with the irreversible nature of a system. In particular, ever since the pioneer work of Seifert and co-workers

[16], it is possible to define a kind of dynamic entropy production along a stochastic trajectory. Therefore, a natural question arises: whether does entropy production along a fluctuation-induced transition pathway between two nonequilibrium stable steady states predict the relative stability of each state or not?

In this work, we use a bistable mesoscopic chemical reaction system that can possess two stable steady states and one unstable one. This system can conveniently illustrate the aforementioned idea. To obtain the transition pathway between the two stable steady states, we use probability generating function method and eikonal approximation to convert the chemical master equation into the classical Hamilton-Jacobi equation, and then get the dominant pathways in the phase space in terms of zero-energy trajectories.

II. CALCULATION

We consider an autocatalytic trimolecular reaction, first proposed by Schlögl [17],



Let a and b denote the concentrations of the chemicals A and B, respectively, which are both constants in the system. Let x be the concentration of the dynamic chemical X. The system is assumed to be homogeneous

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in space, and the volume of the system will be denoted as V .

At the macroscopic level, the time evolution of the system's dynamics is described by the deterministic equation:

$$\frac{dx}{dt} = k_1ax^2 - k_2x^3 - k_4x + k_3b \quad (3)$$

Depending on the system's parameters, the system can have one or two stable steady states [18]. In this work, we want to study the transition between two stable steady states. To the end, $k_1=3.0$, $k_2=0.6$, $k_3=0.25$, $k_4=2.95$ and $a=1.0$ keep unchanged, and b varies between 0 and 3.0, in which there are two stable steady states separated by an unstable steady state, *i.e.*, the bistable case.

III. RESULTS AND DISCUSSION

At the mesoscopic level, however, molecular fluctuations are important and the reactive events are stochastic. Accordingly, the reactions are described as a birth-death stochastic process for the number of the species X, $n(t)$. The dynamics is then ruled by the chemical master equation for the probability $P_n(t)$ that the system contains the n X molecules at time t ,

$$\frac{dP_n(t)}{dt} = W_+(n-1)P_{n-1}(t) + W_-(n+1)P_{n+1}(t) - [W_+(n) + W_-(n)]P_n(t) \quad (4)$$

$$W_+(n) = \frac{k_1an(n-1)}{V} + k_3bV \quad (5)$$

$$W_-(n) = \frac{k_2n(n-1)(n-2)}{V^2} + k_4n \quad (6)$$

where $W_+(n)$ and $W_-(n)$ are the birth and death rates of X molecules for a given number n , respectively. Generally, the chemical master equation cannot be solved analytically. However, it provides the basis for the stochastic simulation algorithm proposed by Gillespie [19]. The main idea of Gillespie's algorithm is to randomly determine what the succeeding reaction step is and when it will happen according to the transition probabilities $W_{\pm}(n)$. A long-time simulation trajectory is shown in Fig.1, from which one can observe that the value of n jumps between a low-value state and a high-value state due to fluctuation. To observe these transitions, a long waiting time is desirable, especially for a larger V .

In order to get the dominant pathway of these nonequilibrium transitions, we shall adopt the method proposed by Elgart and Kamenev by using probability generation function and eikonal approximation [20, 21]. Let us now define the generating function of $P_n(t)$ as

$$G(p, t) = \sum_{n=0}^{\infty} p^n P_n(t) \quad (7)$$

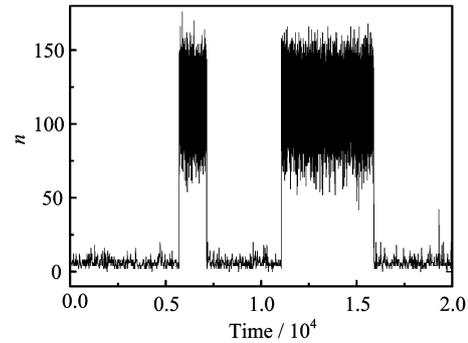


FIG. 1 A long-time simulation trajectory of the number n of X molecules generated by Gillespie's algorithm. The parameters are $k_1=3.0$, $k_2=0.6$, $k_3=0.25$, $k_4=2.95$, $a=1.0$, $b=1.6$, and $V=30$.

Knowing the generating function, one may find a probability of having n molecules at time t as:

$$P_n(t) = \frac{\partial_p^n G(p, t)|_{p=0}}{n!} \quad (8)$$

In addition, $p=1$ plays a special role in this formulation. Firstly, the conservation of probability demands the fundamental normalization condition, $G(1, t) \equiv 1$. Secondly, the moments of the $P_n(t)$ can be expressed through derivatives of the generating function at $p=1$, *e.g.*,

$$\langle n(t) \rangle \equiv \sum_n n P_n(t) = \partial_p G(p, t)|_{p=1} \quad (9)$$

According to the generating function, the master Eq.(4) may be identically rewritten as

$$\frac{\partial G}{\partial t} = \hat{H}G \quad (10)$$

with the effective Hamiltonian operator

$$\hat{H} = (p-1) \left(-\frac{k_2}{V^2} p^2 q^3 + \frac{ak_1}{V} p^2 q^2 - k_4 q + bk_3 V \right) \quad (11)$$

where $q = \partial / \partial p$ is an auxiliary operator.

Using the eikonal ansatz $G(p, t) = \exp[-S(p, t)]$, we arrive at a Hamilton-Jacobi equation $\partial_t S + H = 0$, where S is the classical action. Knowing the canonical equation $\dot{q} = \partial H / \partial p$, and letting $p \equiv 1$, we obtain

$$\dot{q} = \frac{ak_1}{V} q^2 - \frac{k_2}{V^2} q^3 + bk_3 V - k_4 q \quad (12)$$

The Eq.(12) coincides with the mean-field equation Eq.(3). Therefore, we have $q = \langle n \rangle$. Eq.(12) possesses three stationary states, q_0 , q_1 , and q_2 . Two of them, q_1 and q_2 are stable states, and q_0 is unstable state.

To find the dominant pathway of nonequilibrium phase transitions between q_1 and q_2 , we need a phase

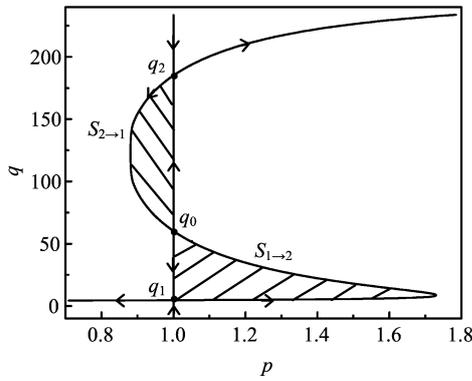


FIG. 2 The phase portrait of the bistable reaction process. The lines correspond to zero-energy trajectories, $H(p, q)=0$. Fat dots are fixed points. The shaded areas denote the actions of the dominant pathways between q_1 and q_2 . Line $p=1$ gives the mean-field dynamics.

portrait of the system. It contains two lines of zero energy: the mean-field line $p=1$, and the non-mean-field line,

$$-\frac{k_2}{V^2}p^2q^3 + \frac{ak_1}{V}p^2q^2 - k_4q + bk_3V = 0 \quad (13)$$

which can be determined by numerical calculation. These lines determine the topology of the phase diagram, as shown in Fig.2, where the arrows show the positive time direction. The dominant pathway from q_1 to q_2 starts along the non-mean-field line to reach q_0 , and then go along the mean-field line. The action along the dominant pathway is denoted by $S_{1 \rightarrow 2}$. The dominant pathway from q_2 to q_1 takes a similar way and the corresponding action is denoted by $S_{2 \rightarrow 1}$. Correspondingly, the transition rates are $R_{1 \rightarrow 2} \approx \exp(-S_{1 \rightarrow 2})$ and $R_{2 \rightarrow 1} \approx \exp(-S_{2 \rightarrow 1})$, respectively.

In Fig.3, we plot $S_{1 \rightarrow 2}$ and $S_{2 \rightarrow 1}$ as a function of the volume of the system V for $b=1$, in which we can find that both $S_{1 \rightarrow 2}$ and $S_{2 \rightarrow 1}$ linearly increase with V . This implies that the stability of the two stable states increase with the system's volume. In the limit $V \rightarrow \infty$, as described by the mean-field Eq.(3), the transition events between two stable states can not occur. In order to validate the results, we use a recent developed rare-event sampling method, forward flux sampling (FFS) [22], to calculate the transition rate from q_2 to q_1 . FFS method can be used to calculate the rate of rare events both in and out of equilibrium systems. For comparison, in Fig.3 we also plot the logarithm of $R_{2 \rightarrow 1}$, $\ln R_{2 \rightarrow 1}$, for some different V . It is clearly observed that the data from FFS are in agreement with those through calculating the action of the dominant pathway.

In Fig.4, we show that $S_{1 \rightarrow 2}$ and $S_{2 \rightarrow 1}$ as a function of b for a fixed $V=50$. With the increment of b , $S_{1 \rightarrow 2}$ monotonically decreases and $S_{2 \rightarrow 1}$ monotonically increases, and the two lines coincide at $b \simeq 1.5$. This indicates that the stability of q_1 is weakened as b increases,

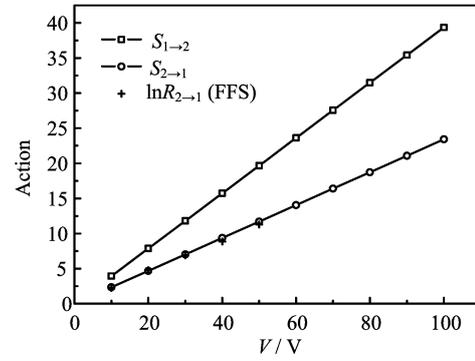


FIG. 3 The action of the dominant pathway from q_1 to q_2 , $S_{1 \rightarrow 2}$, and that from q_2 to q_1 , $S_{2 \rightarrow 1}$, as a function of the system's volume V for a fixed $b=1$. The crosses are the results of $\ln R_{2 \rightarrow 1}$ obtained by FFS. Other parameters are the same as those in Fig.1.

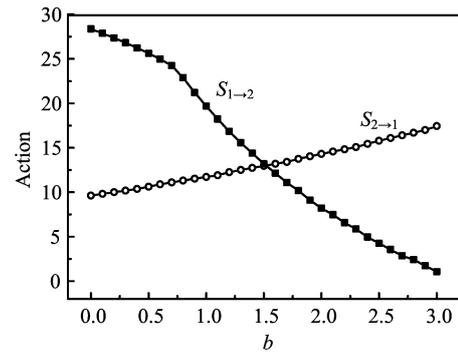


FIG. 4 The action of the dominant pathway from q_1 to q_2 , $S_{1 \rightarrow 2}$, and that from q_2 to q_1 , $S_{2 \rightarrow 1}$, as a function of b for a fixed $V=50$. Other parameters are the same as those in Fig.1.

while stability of q_2 is strengthened with b . The stabilities of q_1 and q_2 are the same at $b \simeq 1.5$. From the thermodynamic point of view, the two stable states co-exist only at $b \simeq 1.5$.

Recently, Seifert introduced the concept of entropy production along a stochastic trajectory, which makes it possible to define a kind of dynamic entropy production based on a path [16]. According to Seifert's definition, the total entropy change along the path is the sum of the system entropy change and the medium entropy change as follows

$$\Delta s_{\text{tot}} = \Delta s + \Delta s_{\text{m}} \quad (14)$$

$$\Delta s = \ln \frac{P_{q_1}(0)}{P_{q_2}(t)} \quad (15)$$

$$\Delta s_{\text{m}} = \sum_j \ln \frac{W_+(j-1 \rightarrow j)}{W_-(j \rightarrow j-1)} \quad (16)$$

Under the steady condition, we have

$$P_{q_1}^s R_{1 \rightarrow 2} = P_{q_2}^s R_{2 \rightarrow 1} \quad (17)$$

or equivalently,

$$P_{q_1}^s \exp(-S_{1 \rightarrow 2}) = P_{q_2}^s \exp(-S_{2 \rightarrow 1}) \quad (18)$$

Thus, we get

$$\begin{aligned} \Delta s(q_1 \rightarrow q_2) &= \ln \frac{P_{q_1}^s}{P_{q_2}^s} = S_{1 \rightarrow 2} - S_{2 \rightarrow 1} \quad (19) \\ \Delta s_m(q_1 \rightarrow q_2) &= \sum_{j=q_1}^{q_2} \ln \frac{W_+(j \rightarrow j+1)}{W_-(j+1 \rightarrow j)} \\ &= \sum_{j=q_1}^{q_2} \ln \frac{\exp[-S(j \rightarrow j+1)]}{\exp[-S(j+1 \rightarrow j)]} \\ &= \left(\sum_{j=q_1}^{q_0-1} + \sum_{j=q_0}^{q_2} \right) \ln \frac{\exp[-S(j \rightarrow j+1)]}{\exp[-S(j+1 \rightarrow j)]} \\ &= \sum_{j=q_1}^{q_0-1} \ln \frac{\exp[-S(j \rightarrow j+1)]}{1} + \\ &\quad \sum_{j=q_0}^{q_2} \ln \frac{1}{\exp[-S(j+1 \rightarrow j)]} \\ &= -S_{1 \rightarrow 2} + S_{2 \rightarrow 1} \quad (20) \end{aligned}$$

Similarly, we have $\Delta s(q_2 \rightarrow q_1) = S_{2 \rightarrow 1} - S_{1 \rightarrow 2}$ and $\Delta s_m(q_2 \rightarrow q_1) = -S_{2 \rightarrow 1} + S_{1 \rightarrow 2}$. The total entropy change is $\Delta s_{\text{tot}} = 0$. An direct conclusion is that at the coexistence point ($S_{1 \rightarrow 2} = S_{2 \rightarrow 1}$), $\Delta s = \Delta s_m = 0$, while at the non-coexistence point ($S_{1 \rightarrow 2} \neq S_{2 \rightarrow 1}$), $\Delta s = -\Delta s_m \neq 0$.

IV. CONCLUSION

Using a mesoscopic chemical reaction system that can possess two stable steady states, we have investigated entropy production along the dominant transition pathway from one stable state to the other one and its backward dominant pathway. By probability generating function method and eikonal approximation, we have converted the chemical master equation to the classical Hamilton-Jacobi equation. In the phase space, we have identified the dominant pathways between two steady states by calculating zero-energy trajectories. We find that entropy productions are related to the actions of the forward and backward dominant pathways. At the coexistence point where the stabilities of the two steady states are equivalent, both the system entropy change and the medium entropy change are zero, while at non-coexistence point both of them are nonzero. Therefore, one may use entropy production along the dominant pathways of nonequilibrium phase transitions to determine the dynamical stabilities of nonequilibrium steady

states, and thus establish a possible relation between thermodynamics and dynamics.

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- [1] R. Zwanzig, *Nonequilibrium Statistical Mechanics*, New York: Oxford University Press, (2001).
- [2] M. J. Klein, *Phys. Rev.* **97**, 1446 (1955).
- [3] X. J. Zhang, H. Qian, and M. Qian, *Phys. Rep.* **510**, 1 (2012).
- [4] H. Ge, H. Qian, and M. Qian, *Phys. Rep.* **510**, 87 (2012).
- [5] L. Schimansky-Geier and W. Ebeling, *Annalen der Physik* **495**, 10 (1983).
- [6] H. Ge and H. Qian, *Phys. Rev. Lett.* **103**, 148103 (2009).
- [7] H. Ge and H. Qian, *J. R. Soc. Interface* **8**, 107 (2011).
- [8] X. F. Guo, D. J. Liu, and J. W. Evans, *J. Chem. Phys.* **130**, 074106 (2009).
- [9] C. Bustamante, J. Liphardt, and F. Ritort, *Phys. Today* **58**, 43 (2005).
- [10] U. Seifert, *J. Phys. A* **37**, 517 (2004).
- [11] P. Gaspard, *J. Chem. Phys.* **120**, 8898 (2004).
- [12] T. Schmiedl and U. Seifert, *J. Chem. Phys.* **126**, 044101 (2007).
- [13] T. J. Xiao, Z. H. Hou, and H. W. Xin, *J. Chem. Phys.* **129**, 114506 (2008).
- [14] T. J. Xiao, Z. H. Hou, and H. W. Xin, *J. Phys. Chem. B* **113**, 9316 (2009).
- [15] T. Rao, T. J. Xiao, and Z. H. Hou, *J. Chem. Phys.* **134**, 214112 (2011).
- [16] U. Seifert, *Phys. Rev. Lett.* **95**, 040602 (2005).
- [17] F. Schlögl, *Z. Physik* **253**, 147 (1972).
- [18] M. Vellela and H. Qian, *J. R. Soc. Interface* **6**, 925 (2009).
- [19] D. T. Gillespie, *J. Comput. Phys.* **22**, 403 (1976).
- [20] V. Elgart and A. Kamenev, *Phys. Rev. E* **70**, 046106 (2004).
- [21] V. Elgart and A. Kamenev, *Phys. Rev. E* **74**, 041101 (2006).
- [22] R. J. Allen, P. B. Warren, and P. R. ten Wolde, *Phys. Rev. Lett.* **94**, 018104 (2005).