

Nonequilibrium dynamics of reacting network system

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Abstract

As a first step to understand nonequilibrium dynamics of reacting network system, we propose a model of reacting network system in which reaction rates are determined by a simple dynamics of energy flow.

1 Introduction

A great variety of plants and animals have been living on earth, and we are living and evolving by absorbing energy from the sun, and at the same time dissipating them. By the development of molecular biology in 20th century, its activities are found to be supported by complex reaction networks. However, temporal understandings of nonequilibrium reacting networks are far behind for understanding the life.

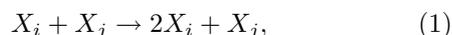
Phenomenological studies based on differential equations have been mainly done so far, however, we do not have enough understandings why the system choose to let parameters in the equations have the values. Next step will be to include additional variables to understand how the value of parameters are determined, and most appropriate one would be energy which flows through the system in various forms such as substances, ATP, light, and so on. Recently, we propose a simple model in which energy flow is included and reaction proceed depending on the variable[1].

In this paper, we applied the model in which reaction paths form random networks.

2 Model

2.1 Reactions

We consider s chemicals X_i ($i = 1, \dots, s$) are inside the system. The following reactions will occur in the system,



which means that new X_i will be produced by catalysis of X_j . We construct random network of catalytic relations. For every chemical, density of path of reactions is fixed to ρ , so that every chemical has $s\rho$ catalyst on average.

2.2 Dynamics of energy flow

We assume a homogeneous system and that frequency of reactions are proportional to the multiplier of concentrations of reactants $c_i c_j$ where c_i denote the number of X_i divided by total number of molecules N_T . Therefore, the increase of X_i can be written as

$$\Delta N_i = \gamma_i \frac{N_i}{N_T} \frac{N_j}{N_T}. \quad (2)$$

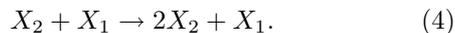
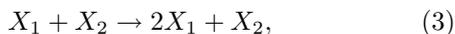
where γ_i denote rate constant for X_i . We do not give values of γ_i as parameters. Instead, following dynamics are introduced in the system. We introduce a new quantity J which represents resources to produce new molecules such as substances, light, ATP and so on. We refer to J as energy in this paper, and we also assume J is a single quantity for whole of the system. We assume that J is flowing into the system so that J increase constantly by ΔJ whether reactions occur or not. We determine E for every reaction that is necessary amount of J to proceed the reaction. We progress the reaction if the amount of J is greater than E in the system. These dynamics determine the rate constant.

The simulations are carried out as follows. We introduce discrete simulation steps. In every step, we pick up two molecules randomly from the system. If there is a reaction path between the two molecules, reaction may occur. If not, we just put them back to the system. When there is a reaction path between the two, and at the same time, if J is greater than E for the reaction, we add new particle as eq.(1). As a cell division, if the total number of molecules N_T exceed a threshold N_{max} , we randomly remove half of them from the system. We also add ΔJ to J in every step whether reactions occur or not.

3 Results

3.1 In case of two species[1]

First of all, we consider two species case $s = 2$,



We denote the necessary amount of J for these reactions as E_1 and E_2 , respectively. In case of $E_1 = E_2 = E$, we can calculate the rate constant γ in a steady state as $\gamma = 4\Delta J/E$. However, in asymmetric case $E_2 > E_1$, interesting behavior is observed in a steady state. Rate constant for X_2 shows not only the Arrhenius type $\gamma_2 \sim \exp(-E_2/\alpha\Delta J^2)$ but also non-trivial power-law dependence on E_2 as ΔJ is fixed to be greater value. Further, we also observe crossover behavior that the power changes from $-1/2$ to -1 at some large value of E_2 . Details of results and analysis are in Ref.[1].

3.2 Random network case

We simulate a random network case. We construct the random reaction paths and we also determine the value of E for every reaction randomly between 0 and E_{max} . It is noted that in the case, mutually catalytic reaction paths are eliminated. We fix parameters as $N_{max} = 16000$, $\rho = 0.1$, $E_{max} = 30$ and $\Delta J = 1$. Further, initial number of chemical species s is chosen as $s = 200$.

3.2.1 Steady states and fluctuations

The system attains a steady state in which several chemicals are survived as shown in Fig. 1

It is noteworthy that the survived chemicals can be different for every simulation even if the parameters are the same. This implies that a condition whether some chemicals can be survived depends on generations of random numbers. We will not discuss which chemicals or networks can survive, but examine the properties of the survived networks.

In the reaction network, every chemical is catalyzed by other chemicals in the network and the chemical also catalyze other chemicals. Thus, the survived chemicals form a cycle like shown in Fig. 2.

As a general feature of replicating system with catalytic networks, it is known that fluctuations of the number of chemicals which are peripheral to but catalyzed by the core cycle are log-normal

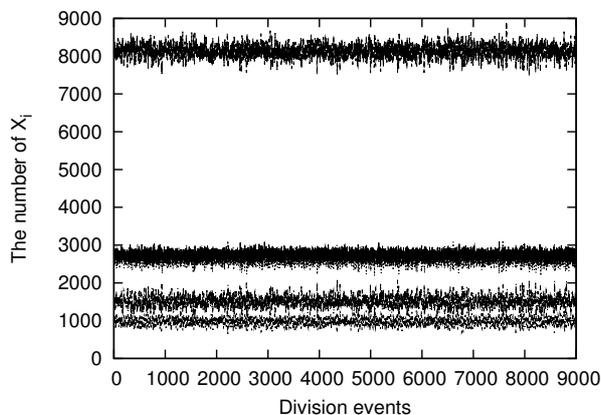


Figure 1: Number of each chemicals in the system. Several chemicals survived and they continues to reproduce theirselves.

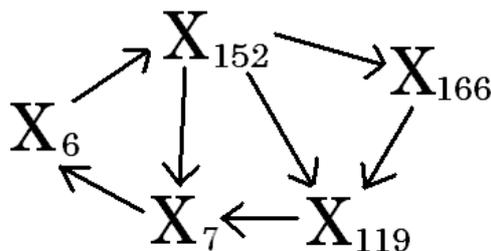


Figure 2: The survived reaction network in our simulation. The number denotes a chemical and arrow from chemical X_i to X_j denotes that X_i catalyzes X_j . The reaction energies of the surviving chemicals are $E_6 = 11.45$, $E_7 = 6.31$, $E_{119} = 7.37$, $E_{152} = 2.65$ and $E_{166} = 0.18$.

distributions[2]. The log-normal distribution is represented by a normal distribution of $\log(N_i)$ as

$$P(N_i) \approx \exp\left(-\frac{(\log(N_i) - \mu)^2}{2\sigma^2}\right),$$

where μ and σ denote the mean and the standard deviation, respectively. The log-normal distributions of the number of chemicals are found experimentally in some cellular reactions[3]. In this model, the fluctuations of the components of the core cycle 6, 7, 152 are small, but fluctuations of the chemicals which are peripheral to but catalyzed by the core cycle, 119 and 166 shows log-normal distributions[4].

3.2.2 Dynamics of energy resources

We examine the microscopic dynamics of J in the surviving cycle. We represent the distributions of J as P_J . We also represent q_i as

$$q_i = \left(\sum_k \frac{N_k}{N_t}\right) \frac{N_i}{N_t},$$

where k is summed up through chemicals which the chemical X_i catalyze. Thus, the master equation of P_J is written as follows,

$$P_J(t+1) = P_{J-\Delta J}(t) \left(1 - \sum_i q_i\right) + \sum_i P_{J+\tilde{E}_i-\Delta J}(t) q_i, \quad (5)$$

where t denotes the simulation step, and \tilde{E}_i is written as

$$\tilde{E}_i = \begin{cases} E_i & (J \geq E_i) \\ 0 & (J < E_i). \end{cases}$$

We obtain the steady state solution P_J by a condition $P_J(t+1) = P_J(t)$ numerically. For simplicity, we assume that values of J are multiples of ΔJ . First, we assume that

$$P_J = k \times P_{J-\Delta J},$$

for $J > E_{max}$ where k satisfies the following equation,

$$k = \left(1 - \sum_i q_i\right) + \sum_i q_i k^{E_i/\Delta J}. \quad (6)$$

Based on the master eq. (5) and the values of P_J for $J > E_{max}$, we obtain P_J for $J < E_{max}$. Figure 3 shows the distributions of J obtained from the original model and the master eq. (5). It is confirmed that the value of the original model agrees with that of the random walk analysis.

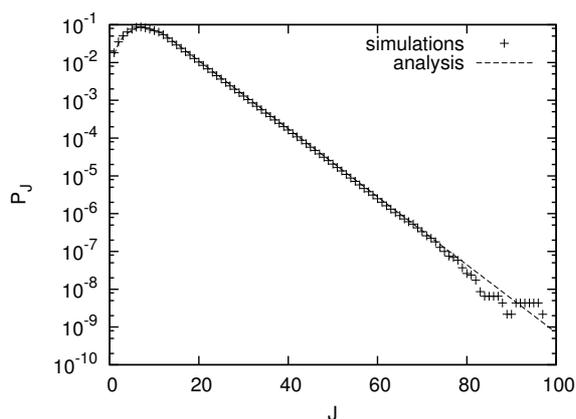


Figure 3: Distribution of J represented as P_J in the steady state. The points represented as “simulations” show the results of the original simulations, and the dotted line as “analysis” show that of the random walk analysis with $k = 0.813$.

Consequently, we can derive the rate constants γ_i for chemical X_i as

$$\gamma_i = \sum_{J > E_i} P_J. \quad (7)$$

3.2.3 Rate of Replicating “Heavy” Chemicals

In the previous subsection, we have shown that the random walk analysis explained the distribution of J and the rate constant of the survived chemicals.

As noted in the previous subsection, the survived chemicals comprises the self-sustaining cycles. In this subsection, we examine how the rate constant depends on the reaction energy in case that the system should possess a “heavy” chemical which means that the chemical needs a very large energy E to reproduce. In our model, the “heavy” chemical cannot survive by itself in general because there is usually an alternative cycle in which chemicals reproduce themselves more easily.

However, it is possible that the chemical plays an essential role in the system such as DNA even if the chemical is difficult to obtain. Therefore, we consider the case that the system should possess the “heavy” chemical. It is obvious that chemicals should comprise the self-sustaining hypercycle for its survival. As a simplest case in our model, the cycle is composed by three chemicals, say A, B , and C . We refer to the “heavy” chemical as A . B is a chemical which is catalyzed by A . Finally, C is a chemical which is cat-

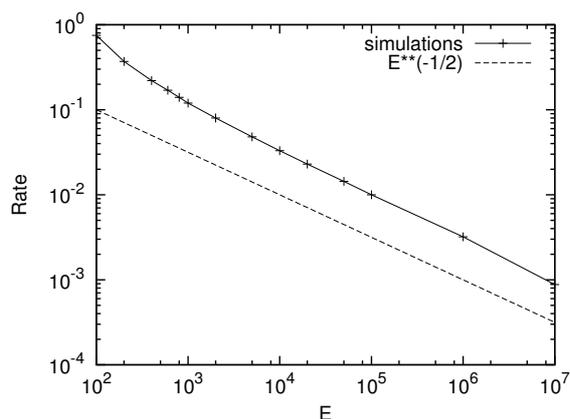


Figure 4: Rate constant vs. reaction energy E of the “heavy” chemical. The line $E^{-1/2}$ is also drawn.

alyzed by B and it also catalyzes A .

It is obvious that the cycle is advantageous for its survival when the values of energy E to obtain the chemicals B and C are small. Thus we assume that the values of E to obtain B and C are small compared to that of A .

We simulate the system and show the dependence of rate of replicating A on the reaction energy in Fig. 4. It is clear that the rate constant have power-law dependence with regard to the reaction energy and the power is $-1/2$.

This behavior is explained by the macroscopic relations of the system. In the steady state, the following relations hold in the system: the conservation of energy in each step,

$$\Delta J = E_A \Delta N_A + E_B \Delta N_B + E_C \Delta N_C, \quad (8)$$

the condition of steady state about the number

$$\frac{N_i + \Delta N_i}{N_t + \Delta N_t} = \frac{N_i}{N_t}, \quad (9)$$

where Δ indicates the expecting increase of each number in one step, the index i represents every chemical A, B , and C , and N_t denotes the total number of molecules. Furthermore, ΔN_i is written as

$$\Delta N_i = \frac{N_i}{N_t} \frac{N_{(i)}}{N_t} \gamma_i, \quad (10)$$

where (i) indicates a chemical which catalyzes chemical i , and γ_i is the rate constant.

When we assume that γ_B and γ_C is fixed to one, we obtain from eqs. (8) to (10)

$$(\Delta J - E_B) \gamma_A^3 + (5\Delta J - 2E_A - E_B) \gamma_A^2 + (8\Delta J - 2E_C) \gamma_A + 4\Delta J = 0. \quad (11)$$

If we remind ourselves that the value of E_A is large compared with the other parameters and only the second term of left-hand-side of the equation includes the E_A , we roughly observe that

$$E_A \gamma_A^2 \approx 1. \quad (12)$$

Therefore, the rate constant have a power-law dependence $E_A^{-1/2}$.

4 Summary

We have studied a reacting model of catalytic network. By introducing energy flux which is acquired from the outside, the rate is determined by the model itself. We study the dependence of rate constant on reaction energy, and the behavior is explained by the asymmetric random walk model. We have found the same dependences in a situation that the system should possess a “heavy” chemical as observed in mutually catalytic system.

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