Dynamical Foundation and Limitations of Statistical Reaction Theory

Akira Shojiguchi

Department of Physics, Nara women's university, Nara, 630-8501, Japan

Chun-Biu Li[b], Tamiki Komatsuzaki[b,c]

[b]*Department of Earth and Planetary Sciences, Kobe University, Nada, Kobe 657-8501, Japan*

[c]*Department of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

Mikito Toda

Department of Physics, Nara women's university, Nara, 630-8501, Japan

Abstract

We study the foundation and limitations of the statistical reaction theory. In particular, we focus our attention to the question of whether the rate *constant* can be defined for nonergodic systems. Based on the analysis of the Arnold web in the reactant well, we show that the survival probability exhibits two types of behavior: one where it depends on the residential time as the power-law decay and the other where it decays exponentially. The power-law decay casts a doubt on definability of the rate *constant* for nonergodic systems. We indicate that existence of the two types of behavior comes from sub-diffusive motions in regions where the Arnold web is sparse. Moreover, based on the analysis of nonstationary features of the trajectories, we can understand how the NHIM is connected with the Arnold web. We propose that the following two features play a key role in understanding the reactions where ergodicity is broken, i.e, whether the Arnold web is sparse and nonuniform or not, and how the NHIM is connected with the Arnold web.

Key words: Normally Hyperbolic Invariant Manifolds (NHIMs), Arnold webs, Lie Canonical Perturbation Theory (LCPT), Transition States (TSs), Rice-Ramsperger-Kessel-Marcus (RRKM) formula
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1 Introduction

Reaction processes are ubiquitous from microscopic phenomena such as nuclear and chemical reactions to macroscopic ones such as population dynamics. In the study of reaction processes, the rate equation of the type

$$\frac{d}{dt}P(t) = -kP(t), \tag{1}$$

is frequently used in the phenomenological treatment, where the rate *constant* k is supposed to describe how the density $P(t)$ of the reactant changes. Then, $P(t)$ obeys the exponential decay, and the inverse of the rate *constant* gives the characteristic time scale of the processes.

As for the foundation of the rate equation, we usually presuppose that the reaction processes take place statistically. In particular, for reaction processes in microscopic phenomena, the Rice-Ramsperger-Kessel-Marcus (RRKM) formula is employed to estimate the rate *constant* k. In deriving the RRKM formula, we need the following two assumptions; (1) The no-recrossing boundary exists between the reactant and the product, and we call it the transition state (TS). (2) The processes within the reactant well are ergodic so that the trajectories lose their memories of initial conditions when they exit from the well [1].

Suppose that we are given a distribution of initial conditions within the reactant well. Then, the first assumption means that the reaction rate can be estimated by simply counting the number of trajectories which cross the TS from the reactant to the product. The second assumption implies that the reaction rate thus estimated does not depend on the distribution of initial conditions within the well. In order for the second assumption to hold, the characteristic time scale for the system to react must be much longer than that to explore the phase space within the well. Then, starting from any distribution, it will spread into the whole region of the phase space within the well, before some of the trajectories go over the TS. Thus, the rate becomes independent of how we choose the distribution of initial conditions.

However, recent studies on reaction processes cast a doubt on the assumptions underlying the statistical reaction theory[2]. There are two problems on the assumptions; (1) whether we can have a mathematically sound definition of TSs, and (2) what if the processes within the well are not ergodic enough to guarantee the existence of the rate *constant*.

As for the first question, it is solved by the approach based on the geometric structures in the phase space called normally hyperbolic invariant manifolds (NHIMs). By applying the Lie canonical perturbation theory (LCPT)[3,4] to

the potential saddles of the index one, we can identify the geometric structures inherent to the saddle region, at least in the energy regime close to the energy of the saddle point [5]. This approach produces a large amount of applications for reaction processes ranging from atomic physics [6], cluster physics [7], to even celestial mechanics [8].

A NHIM is a manifold where the absolute values of the Lyapunov exponents along its normal directions are much larger than those along its tangential directions[9–11]. Its stable/unstable manifolds consist of those orbits which asymptotically approach or leave the NHIM, respectively. For saddles of the index one, these geometric structures enable us to identify the one-dimensional reaction coordinate as the normal direction to the NHIM, and thereby to define the TS as the the dividing hypersurface of co-dimension one locally near the saddle. The TS thus defined is free from the problem of recrossing orbits, and can decompose the phase space into the distinct regions of the reactants and the products [6,12–14] (See also the recent reviews[8,15–17] and the book[18].). Moreover, the stable/unstable manifolds of the NHIM provide us with the reaction conduit through which all the reactive trajectories pass from the reactant to the product or vice versa. Thus, these manifolds offer a crucial clue to understand controllability of the reaction.

On the other hand, the study on the foundation and limitations of the ergodicity assumption has been started. In particular, new approaches which do not rely on the ergodicity assumption have appeared recently. For example, a formula is found where the volume of phase space which contributes to the reaction is represented by the phase space average of the residential time, i.e., the duration for which each trajectory stays in the well [19]. Contrary to the RRKM formula, this one does not need the assumption of ergodicity. Then, the phase space average of the residential times in general depends on the distributions of initial conditions, leading to dependence of reaction rates on their choice. Moreover, the power-law decay of the survival probability $P(t)$ is found experimentally [20]. Recently, we have also obtained numerical results of classical mechanics showing that isomarization processes in HCN exhibit the power-law decay of the survival probability [21]. These results lead us to the following question; To what extent can we define the rate *constant* ?

This question is closely related to the problem of whether the transport coefficient can be defined by the linear response theory, when the system exhibits the long time tail [22–24]. In other words, when ergodicity is not satisfied, we face this problem. The long time tail is found in numerical simulations of Hamiltonian systems [25,26], water clusters [27], and ferro-magnetic spin systems [28]. Moreover, recent experiments show that proteins do exhibit long time memory [29]. Thus, the question of whether the rate *constant* can be defined or not has a far reaching importance in general.

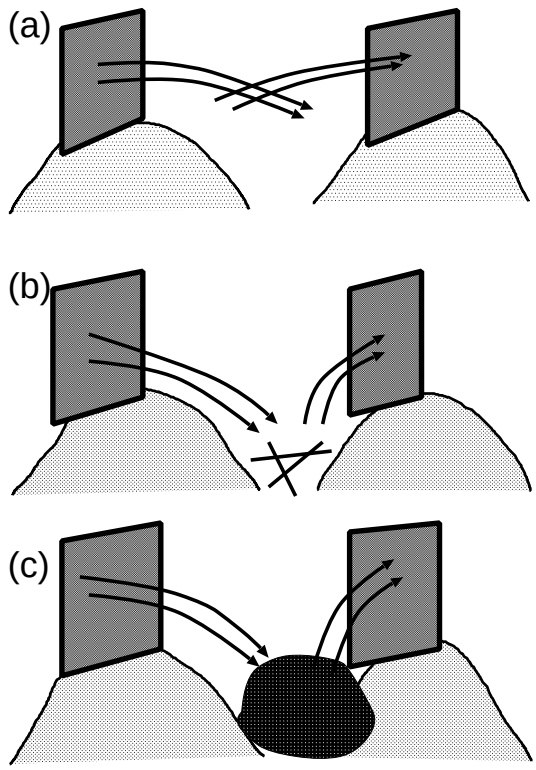

Fig. 1. Schematic pictures showing how NHIMs are connected by their stable and unstable manifolds. (a) Their stable and unstable manifolds have direct intersections without going deeply in the reactant well. (b) They land on the Arnold web in the well, where the web is sparse. (c) They land on the Arnold web in the well, where the web is dense.

In order to answer it, we need to understand the dynamical processes taking place in the reactant well, and see how their characteristics manifest themselves in the behavior of macroscopic quantities such as the reaction rate. We propose the following three scenarios concerning how the trajectories in the reaction conduit of the unstable manifold spend time in the well. One is to have direct intersection with the conduit of the stable manifold of the same (or another) NHIM. Then, the trajectories in the conduit stay in the well for a shorter time scale and exit. The others are to land on the Arnold web, i.e., the network of nonlinear resonances in the well [4]. Then, those trajectories wander around the Arnold web before they leave the well. Therefore, the time scale to exit the well is longer than the previous case. When the Arnold web is sparse, we will see nonergodic reaction processes. On the other hand, when the web is dense, we expect that statistical features will dominate the reaction processes. In the former case, the residential times of the trajectories vary depending on the initial conditions. Thus, in the analysis of reaction processes where ergodicity is broken, the distribution of the residential times is of our interest.

These scenarios are displayed by schematic pictures in Fig. 1, where the hills

indicate the potential barriers and the rectangles on the top of the hills show the NHIMs around the saddles. Their stable and unstable manifolds are shown by the arrows, respectively. In Fig. 1 (a), the stable and unstable manifolds have intersections without going deeply into the well. On the other hand, in Fig. 1 (b) and (c), they land on the Arnold web in the well. While, in Fig. 1 (b), the Arnold web is sparse, the web is dense in Fig. 1 (c). These characteristics of the web will manifest themselves in the distribution of the residential times, thereby leading to the difference in the statistical features of the reaction processes.

Thus, the dynamics in the Arnold web is crucial in judging the validity and limitations of the statistical reaction theory. However, there exist few studies concerning how the characteristic of the Arnold web affects the reaction processes [30]. In particular, those features of the Arnold web such as whether nonlinear resonances are dense or sparse, and whether they exist uniformly or not will be crucial for ergodicity of the processes in the well. Moreover, whether trajectories spend their times in those regions where nonlinear resonances are dense or not will affect their residential times in the well. Thus, characteristics of the Arnold web will play an important role in the problem of whether the rate *constant* can be defined.

In this paper, we study, using a simple model Hamiltonian, how characteristics of the Arnold web affect reaction processes. In particular, we focus our attention to the survival probability of trajectories within the reactant well. Thus, we shed light on how the reaction rate behaves for reaction processes where ergodicity is broken. The following is the content of this paper. In the section 2, we introduce our model Hamiltonian. In the section 3, the results of our study are discussed. In the section 4, the conclusions and future problems are discussed.

2 Model Hamiltonian

We consider a system of three degrees of freedom with a double-well potential. The system is regarded as a prototype of isomarization reactions. The model Hamiltonian is the following,

$$
\begin{aligned}
H &= H_0 + H_1, \\
H_0 &= \frac{p_1^2}{2} - \frac{\lambda^2 q_1^2}{2} + b q_1^4 + \sum_{i=2}^{3} \left(\frac{p_i^2}{2} + \frac{\omega_i^2 q_i^2}{2} + b q_i^4 \right), \\
H_1 &= \exp\left[-(q_1 - 1)^2/\sigma^2 \right] \left[a_1 q_2^2 q_3^2 + a_2 (q_1 - 1)^2 (q_2^2 + q_3^2) \right],
\end{aligned}
\tag{2}
$$

where q_1 is the reaction coordinate, and q_i $(i = 2, 3)$ are the bath coordinates. The parameters are $\omega_1 = 1.02,\ \omega_2 = 0.94,\ \omega_3 = 1.04,\ a_1 = 0.1,\ a_2 = 0.9$ and $b = 0.5$, where $\omega_1 = \lambda/\sqrt{2}$ is the unperturbed frequency at the bottom of the well $q_1 = 1$.

The unperturbed Hamiltonian of the bath coordinates $h_i = \frac{p_i^2}{2} + \frac{\omega_i^2 q_i^2}{2} + bq_i^4$ $(i = 2, 3)$ are nonlinear oscillators, respectively. They are integrable with the following constants of motion,

$$\begin{aligned} J_i(h_i) &= \frac{1}{2\pi} \oint dq_i p_i(q_i) \\ &= \frac{A}{3k^2} \left[(2k_i^2 - 1)E(k_i) + (1 - k_i^2)K(k_i) \right], \end{aligned} \tag{3}$$

where we use the notations $k_i^2 = \frac{\alpha_i^2}{\alpha_i^2+\beta_i^2}$, $\alpha_i^2 = \frac{-\omega_i^2+\sqrt{\omega_i^4+16bh_i}}{4b}$, $\beta_i^2 = \frac{\omega_i^2+\sqrt{\omega_i^4+16bh}}{4b}$ and $A_i = \frac{2\alpha_i^2}{\pi}\sqrt{2b(\alpha_i^2 + \beta_i^2)}$. Here, the elliptic functions are defined as $E(k) = \int_0^{\pi/2} d\phi \sqrt{1 - k^2 \sin^2 \phi}$ and $K(k) = \int_0^{\pi/2} d\phi \frac{1}{\sqrt{1-k^2 \sin^2 \phi}}$.

Expanding the Hamiltonian (2) by LCPT at the bottom of the well, we obtain the nonlinear frequencies for the bath coordinates, up to the first order of the action variables, as follows

$$\bar{\omega}_i(J_i) = \frac{\partial H_0}{\partial J_i} = \omega_i + \frac{3b}{\omega_i^2} J_i + O(J_i^2), \quad (i = 2, 3), \tag{4}$$

where we use the action variables Eq.(3). The reaction coordinate has the action variable in the well as follows

$$J_1(h_1) = \frac{\sqrt{2}\lambda}{3\pi}(\alpha_1 + \beta_1) \left[E(k_1) - \alpha_1\beta_1 K(k_1) \right], \tag{5}$$

where the unperturbed Hamiltonian of the reaction coordinate is expressed as $h_1 = \frac{p_1^2}{2} - \frac{\lambda^2 q_1^2}{2} + bq_1^4$ for the range $-\frac{\lambda^2}{4} < h_1 < 0$. Here, we use the notations $\alpha_1 = \sqrt{1 - \sqrt{1 + \frac{4h_1}{\lambda^2}}}$, $\beta_1 = \sqrt{1 + \sqrt{1 + \frac{4h_1}{\lambda^2}}}$ and $k_1 = \frac{\beta_1 - \alpha_1}{\beta_1 + \alpha_1}$. The nonlinear frequency of the reaction coordinate in the well is given, up to the first order of the action variable (5), by

$$\bar{\omega}_1 = \frac{\partial H_0}{\partial J_1} = \omega_1 - \frac{3}{4} J_1 + O(J_1^2). \tag{6}$$

Then, we can show that the system has the primary resonances given by

$$\bar{\omega}_1 = \bar{\omega}_2, \quad \bar{\omega}_1 = \bar{\omega}_3, \quad \bar{\omega}_2 = \bar{\omega}_3. \tag{7}$$

We will see that the Arnold web of the primary resonances is sparse. On the other hand, there exist regions where multiple resonances meet, i.e., resonance

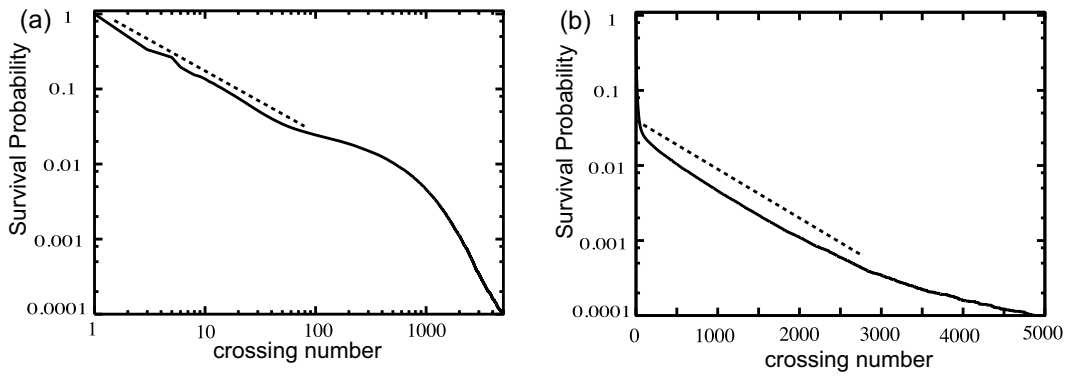

Fig. 2. Survival probability $P(n)$ as a function of the crossing number n is shown. (a) Log vs. log plot. The line indicates fitting with the function $n^{-\gamma}$. (b) Log vs. linear plot. The line indicates fitting with the function $\exp(-\alpha n)$.

junctions. Thus, the Arnold web has nonuniform features. These features will play an important role in the following results.

3 Results

In the following calculations, we choose initial conditions with their energy $E = 0.225$. Note that the potential energy at the saddle is $E = 0.125$. They leave the saddle to the reactant well, with all of the excess energy $\delta E = 0.1$ distributed randomly among the bath degrees of freedom. This distribution means that the initial conditions lie on the unstable manifold of the NHIM which exists around the saddle in phase space.

In order to estimate how long these trajectories stay in the well, we have calculated the residential time for each of the trajectories by counting the total number n of crossing points with the plane $q_1 = 1$ under the condition $p_1 > 0$, until it leaves the well. We call n the crossing number. By adding the number of trajectories with their crossing numbers from n to their maximum, we obtain the number of trajectories which remain in the well up to the crossing number n. The ratio of this quantity to the total number of the trajectories gives the survival probability $P(n)$.

In Fig.2, we show the survival probability $P(n)$ as a function of the crossing number n. There, two ranges of n exist where $P(n)$ behaves differently. One is the range where $P(n)$ varies as the power-law decay $n^{-\gamma}$, and the other where $P(n)$ changes exponentially as $\exp(-\alpha n)$. The range of the power-law decay extends from about $n = 10$ up to about $n = 100$ with $\gamma = 0.82$, and that of the exponential decay does from about $n = 100$ up to about $n = 5000$ with $\alpha = 0.0015$. Moreover, the Fourier spectra of the action variables correspondingly exhibit different characteristics [31]. For trajectories in the range of the power-

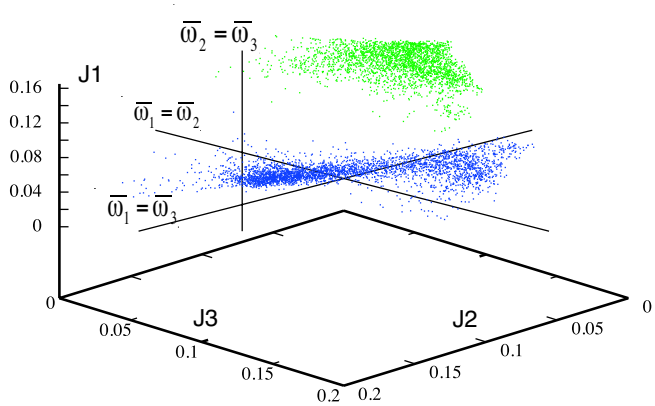

Fig. 3. The average locations of trajectories in the action space are plotted for initial conditions which are in the range of power-law (gray dots), and those in the range of exponential (black dots).

law decay, the Fourier spectrum exhibits $1/f$ dependence. On the other hand, it shows the Lorentzian feature for those in the range of the exponential decay. Based on the above results, we construct two ensembles of trajectories, one composed of the trajectories in the range where $P(n)$ shows the power-law decay, and the other composed of those in the range where $P(n)$ does the exponential decay.

From now on, we investigate the relation between those features of $P(n)$ and the characteristics of the Arnold web. In Fig.3, we plot the average location of the trajectory in the action space (J_2, J_3, J_1) for each initial condition. The location is estimated when the trajectory crosses the plane q_1=1, and the average is taken over its residential time. The figure reveals how the variance of $P(n)$ relate with the processes of energy exchange between the bath modes and the reaction coordinate. The gray (black) points are shown for those trajectories in the range where $P(n)$ changes as the power-law decay (exponentially). There, we also indicate the locations of the primary resonances for comparison.

First, we see in Fig.3 that the Arnold web of the primary resonances is sparse. Moreover, there exist resonance junctions. These features indicate that the Arnold web is nonuniform. Comparing these features with the distribution of the locations, we note the following. The gray points distribute only within a limited region. This suggests that there exist dynamical structures which prevent the trajectories from exploring the whole phase space. In particular, most of the points do not lie near the the primary resonances. This implies that the trajectories do not experience fully chaotic regions. On the other hand, the black points distribute in the resonance-overlap regions and around the resonance junctions, where multiple resonances meet. This means that the trajectories wander round fully chaotic regions.

In Fig.4, we draw the distance from the resonance line in the action space. The distance is calculated each time the trajectory crosses the place $q_1 = 1$,

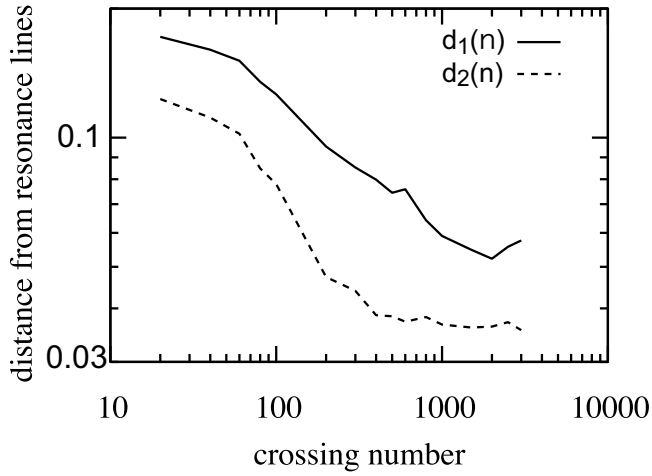

Fig. 4. The ensemble averages of the distances from the two resonance lines are shown as functions of the crossing number n with double logarithmic plot. The solid line (dashed line) indicates the distance from the resonance line with the condition $\bar{\omega}_1 = \bar{\omega}_2$ ($\bar{\omega}_1 = \bar{\omega}_3$).

and its values are averaged over time until the trajectory exits the well. The average is further taken over the trajectories with the crossing number n. Thus, we obtain the distance as a function of the crossing number. There, we show the average distance d_1 from the resonance $\bar{\omega}_1 = \bar{\omega}_2$, and the one d_2 from the resonance $\bar{\omega}_1 = \bar{\omega}_3$, respectively. Note that both of the resonances involve the reaction coordinate, thereby contributing to the processes when it loses (or obtains) its energy. There, we see that the distances decrease as the crossing number n increases. This means that the trajectories stay longer, as they wander around more deeply in the web, Moreover, for those with larger crossing numbers, both of the distances have smaller values. In particular, the values of d_2 drops around $n = 100$. This suggests that the trajectories in the range of the exponential decay migrate into the regions where the two resonances meet, i.e., the resonance junctions. These two figures indicate that the two ensembles of trajectories experience different parts of phase space.

These results imply the following. Those trajectories in the range of the power-law decay experience hierarchical structure of dynamical barriers, and keep a long time memory. On the other hand, those in the range of the exponential decay wander around more statistical regions.

Then, the next question is if the landing processes from the saddle to the Arnold web differ between the two ensembles of trajectories, that is, how the unstable manifold lands on the Arnold web. There are three cases for the landing processes. The first is that the unstable manifold lands on the Arnold web where the resonances are sparse. Then, the trajectories in the range of the exponential decay of $P(n)$ wander around the web and migrate into resonance junctions. The second is that the unstable manifold lands on the Arnold web where the resonances are dense such as resonance junctions.

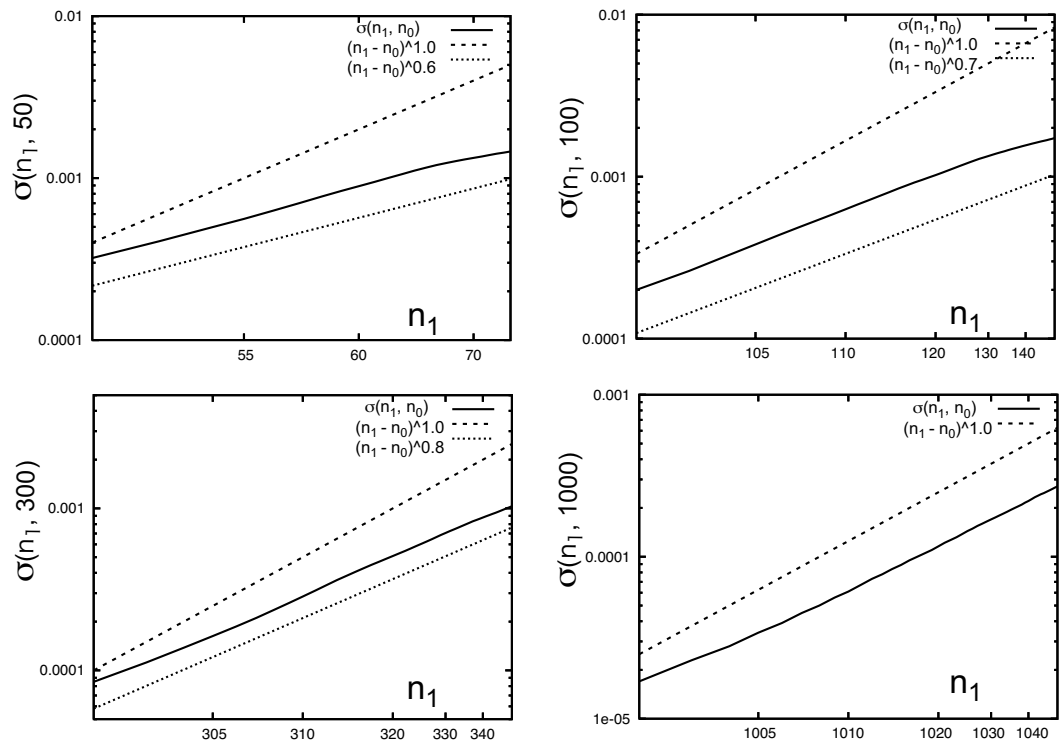

Fig. 5. $\sigma_1(n_1, n_0)$ with $n_0 = 50,\ 100,\ 300,\ 1000$ are plotted for trajectories in the range of the crossing number n between 2000 and 4000. The powers p of the growth of $\sigma_1(n_1, n_0)$ are $p = 0.6,\ 0.7,\ 0.8$, and 1.0 for $n_0 = 50,\ 100,\ 300$, and 1000, respectively.

Then, the trajectories in the range of the power-law decay of $P(n)$ wander around the web and migrate into the regions where the resonances are sparse. The last is that the unstable manifold spreads enough to cover both of the regions. Then, while the trajectories in the range of the power-law decay of $P(n)$ land on the sparse region, those in the range of the exponential decay do on the dense region.

In order to investigate which of the above is realized in our system, we study how the behavior varies for the trajectories in the range of the exponential decay as they wander around the web. In particular, we focus our attention to the initial, middle and last stages of their stay to see if their behavior changes as they experience the web. To find such nonstationary features, we estimate diffusion in the action scape as follows

$$\sigma_k(n_1, n_0) = \left\langle \left(J_k(n_1, i) - J_k(n_0, i)\right)^2 \right\rangle_i \tag{8}$$

where $J_k(n_0, i)$ is the value of the action J_k with $k = 1, 2, 3$ at the n_0th crossing with the plane $q_1 = 0$. We define $J_k(n_1, i)$ in a similar way. Here, the trajectories are indexed using i, and the average is taken over the trajectories in the range of the crossing number n between 2000 and 4000. By choosing both n_0 and n_1 so that the trajectories are in the initial, middle or last stages

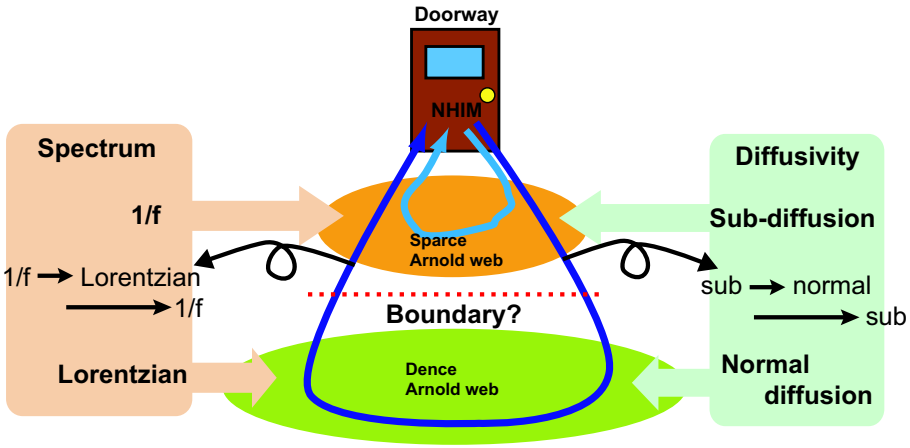

Fig. 6. We propose a working hypothesis.

of their stay, we can estimate how diffusion varies as the trajectories wander around the web.

In Fig.5, we show $\sigma_1(n_1, n_0)$ as a function of $n_1 - n_0$. These figures indicate that sub-diffusive behavior appears for the initial stage of their stay. This is revealed by the fact that $\sigma_1(n_1, n_0)$ varies as $(n_1 - n_0)^p$ with p less than 1. As the trajectories proceed in the web, the behavior comes closer to the normal diffusion. As for the last stage of their stay, the result at present is not conclusive.

We are also calculating the window Fourier spectrum to see if the above changes in the diffusion have corresponding features in the spectrum. Currently, we obtain results that, while the window Fourier spectra show $1/f$ dependence for the initial and last stages of their stay, they exhibit the Lorentzian feature in the middle [21].

These results strongly suggest that the trajectories in the range of the exponential decay also land on the regions where the web is sparse. After spending some time there, they migrate into the regions where the resonances are dense. When they leave, they migrate again to the regions where the web is sparse, and exit the well. These trajectories spend most of their times in the dense regions. Therefore, the dynamics there determine their statistical features. Based on the above idea, we draw a schematics picture in Fig.6 showing how the NHIM around the saddle is connected to the Arnold web by the unstable manifold.

4 Conclusion and Future Problems

In this paper, we have studied the reaction processes where ergodicity is broken in the reactant well. In particular, the question of whether the rate *constant* can be defined for nonergodic systems is investigated. By the analysis of the Arnold web in the reactant well, we have shown that the survival probability exhibits the two kinds of dependence on the residential time, i.e., the power-law and the exponential decays. The power-law decay casts a doubt on definability of the rate *constant* for nonergodic systems. The two kinds of dependence come from existence of regions in phase space where the sub-diffusive and normal diffusive motions are seen, respectively.

Analyzing the nonstationary features of the behavior, we suggest that the unstable manifold of the NHIM lands on the regions where the Arnold web is sparse. After landing, those trajectories in the power-law decay wander around the regions where the web is sparse. On the other hand, those in the exponential decay migrate into the regions where the web is dense. In leaving the well, they move again to the region where the web is sparse. Thus, we can understand how the NHIM around the saddle is connected with the Arnold web.

As for the future study, we raise the following two as urgent problems. First is to understand the phase space structure which gives rise to dynamical barriers in systems of more than two degrees of freedom. Second is to undertake similar analysis as is done in this paper to other systems.

As for the first, one may ask a possible relationship to the hierarchical structure of resonances. In the analysis of the Arnold web, we have only taken into account the locations of the primary resonances. For full understanding of the Arnold web, however, we have to to know whether higher order resonances remain there, and, if so, we need to estimate their locations. When higher order resonances remain, hierarchical structure of resonant tori exist there. However, tori per se do not constitute dynamical barriers in systems of more than two degrees of freedom. Therefore, their existence does not readily explain hierarchical structure of dynamical barriers as is revealed here. Thus, it is a challenging problem to understand the existence of dynamical barriers in systems of more than two degrees of freedom.

Second, we need to undertake similar analysis to other systems where the ergodicity assumption is broken. We think that such cases will also exist where the NHIM is connected to regions where the Arnold web is dense. Then, some of the trajectories migrate into regions where the web is sparse. For these cases, we suggest that the survival probability exhibit the exponential decay for shorter residential times, and the power-law decay for longer ones.

Thus, we can understand the foundation and limitations of the statistical reaction theory based on the analysis of the dynamical structures of phase space. In particular, the following two features play a key role in understanding the reaction processes, i.e., whether the Arnold web is sparse and nonuniform or not, and how the reaction conduits of the unstable/stable manifolds land on the Arnold web.

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