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Dynamical foundation and limitations of statistical reaction theory

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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 subdiffusive motions in remote regions from resonance overlap. Moreover, based on analysis of nonstationary features of trajectories, we can understand how the normally hyperbolic invariant manifold (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 nonuniform and how the NHIM is connected with the Arnold web.

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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 such as

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

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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 in unit time. Then, $P(t)$ obeys the exponential decay, and the inverse of the rate *constant* gives the characteristic time scale of the reaction processes. As for the foundation of the rate equation, it is implicitly supposed that the reaction processes take place statistically. For unimolecular reaction processes in microscopic phenomena, the Rice–Ramsperger–Kessel–Marcus (RRKM) formula [1] has been employed to estimate the rate *constant* k. The RRKM theory requires the following two assumptions: (1) The no-recrossing boundary exists between the reactant and the product, and chemists 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]. Given a distribution of initial conditions within the reactant well, 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 a specific 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.

Recently, however, theoretical [2–7] and experimental studies [8–11] have cast a doubt on the assumptions underlying the statistical reaction theory (see [12] for a review). There are two problems concerning the assumptions of the statistical reaction theory: (1) whether we can have the firm mathematical foundation 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 was 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) [13,14] 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 that of the saddle point [15]. Up to now, versatility of the no-return TSs has been well established in isomerization reactions of 6-atom clusters [16] and HCN [17,18], ionization of a hydrogen atom in crossed electric and magnetic fields [19], and also in the escape of asteroids from Mars [6]. 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 [20–22]. 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 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 [19,23–25] (see also recent reviews [26–29] and the book [30]). Moreover, the stable/unstable manifolds of the NHIM provide us with a 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 how reacting systems end up with the desired state. This is essential to study the question of how we can control the reaction.

However, only a few studies have considered the geometrical structure of the phase space inside the potential well. Recently, it is shown that 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 resides in the well [7]. Contrary to the RRKM formula, this relation holds irrespective of whether the reaction is ergodic or not. 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 the initial conditions. Moreover, the power-law decay of the survival probability has been observed experimentally [11]. Recently, we have also obtained numerical results of classical mechanics showing that isomerization processes in HCN exhibit the power-law decay of the survival probability [31]. 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 [32–34]. In other words, when ergodicity is not satisfied, we face this problem. The long time tail is found in numerical simulations of Hamiltonian systems [35,36], water clusters [37], and ferromagnetic spin systems [38]. Moreover, recent experiments show that proteins do exhibit long time memory [39]. Thus, the question of whether the rate *constant* can be defined or not has a far reaching importance in general.