

Hamilton Dynamics in Chemical Reactions: the Maupertuis Principle, Transition Paths and Energy Landscape

Yuan Gao* and Yufan Zhou

*Department of Mathematics, Purdue University, West Lafayette,
Indiana, USA.*

Received 22 April 2023; Accepted 3 May 2023

Abstract. In this paper, we explore the Hamilton structures in non-equilibrium chemical reactions, which is modeled as a random time-changed Poisson process on countable states. Transition paths between multiple steady states in a chemical reaction is a rare event that can be characterized via the large deviation principle. Compared with the Hamilton principle, we use the Maupertuis principle to compute the transition paths and the associated energy barriers, i.e., the rate function in the large deviation principle. Based on the corresponding stationary Hamilton-Jacobi equation, we select a proper stationary viscosity solution, which in general is not unique, to explicitly compute the energy barriers and the associated optimal control that realizes a transition path. Using one-dimensional example, we characterize the energy barriers for chemical reactions using a geometric quantity in the phase plane. We also compare the reaction barriers with the one in the diffusion approximation and show that the global energy landscape and energy barriers for non-equilibrium chemical reactions are quite different with its diffusion approximation.

AMS subject classifications: 49L99, 80A30, 49N99

Key words: Large deviation principle, thermodynamic limit, transition time, energy barriers, infinite time horizon.

*Corresponding author. *Email addresses:* gao662@purdue.edu (Y. Gao), zhou1187@purdue.edu (Y. Zhou)

1 Introduction

Chemical reactions are very important for living matters and also have many industry applications [1, 20, 31, 35, 36]. For various chemical reactions, the most important questions are how the reactions happen along a transition path and how fast they happen. Particularly, non-equilibrium chemical reactions have multiple steady chemical states and the global energy landscape is non-convex and unknown. Compared with equilibrium reactions, the most distinguished feature of non-equilibrium chemical reactions is the positive entropy production rate [30, 32], which can be used as the characterization of living cells. For those non-equilibrium chemical reactions, the above two questions are not only fundamental in the study of non-equilibrium physical processes [10, 30], but also mathematically challenging [2, 11].

A convenient stochastic model to describe a chemical reaction is a random time-changed Poisson process on countable states (see (2.3)) [1, 17, 25]. From this continuous time discrete state Markov process, there are many quantitative properties that can be characterized via the probability limiting theorems for the chemical reaction. For instance, the reaction rate equation, which was proposed in 1864 by Guldberg and Waage, can be viewed as an ensemble path following the law of large numbers. More importantly, the transitions from one stable chemical state to another stable chemical state can be viewed as rare events in the large deviation regime. Rare events happen with very small probability, but they are usually the most important events, for instance the transitions described above.

Based on the stochastic model for chemical reactions, one can further assume the container where chemical reaction happens is very large $V = 1/h \gg 1$. Thus in a macroscopic scale, we will give answers for how to find transition paths, how to compute the energy barrier for a transition path to happen, and what is the transition rate. First, to estimate the very small probability for transitions to happen, we explore the Hamiltonian structures in chemical reactions. Via WKB reformulations [12, 24], the Kolmogorov forward equation becomes a discrete Hamilton-Jacobi equation (HJE). If taking $V \rightarrow +\infty$, then the limiting HJE has an associated Hamiltonian $H(p, x)$ (see (2.8)). The Hamilton dynamics in terms of this Hamiltonian can be used to describe some least action trajectories in the state space [6]. Moreover, the reaction rate Eq. (2.2) can be viewed as a special trajectory for this Hamilton dynamics $p \equiv 0$. It has been proved that the rate function for the large deviation principle at fixed time of the chemical reactions can be computed via the dynamics solution to the corresponding HJE [16].

However, whether one should use the least action principle with a fixed terminal time (the Hamilton principle) or the least action principle with an undefined