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Rare transition event with self-consistent theory of large-amplitude collective motion

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ABSTRACT

A numerical simulation method, based on Dang et al.'s self-consistent theory of large-amplitude collective motion, for rare transition events is presented. The method provides a one-dimensional pathway without knowledge of the final configuration, which includes a dynamical effect caused by not only a potential but also kinetic term. Although it is difficult to apply the molecular dynamics simulation to a narrow-gate potential, the method presented is applicable to the case. A toy model with a high-energy barrier and/or the narrow gate shows that while the Dang et al. treatment is unstable for a changing of model parameters, our method stable for it.

1. Introduction

Transition events with long timescales are of great importance in many fields of molecular science. In particular, examples in biology range from conformational changes in proteins associated with ligand binding [1] to allosteric transitions that occur throughout the global protein domain [2,3]. Their typical timescales are the order of $10^{-5} - 1$ s [4]. Such rare transition events are due to the separation between the initial and final configurations in phase space. The separation is caused by the existence of a high energy barrier or a narrow gate in a potential energy surface; schematic examples of such separations are shown in Fig. 1.

Numerical simulation is an essential tool to elucidate the rare transition event and obtain the final configuration. There exist two kinds of approaches to the problem. The first one is to find a pathway

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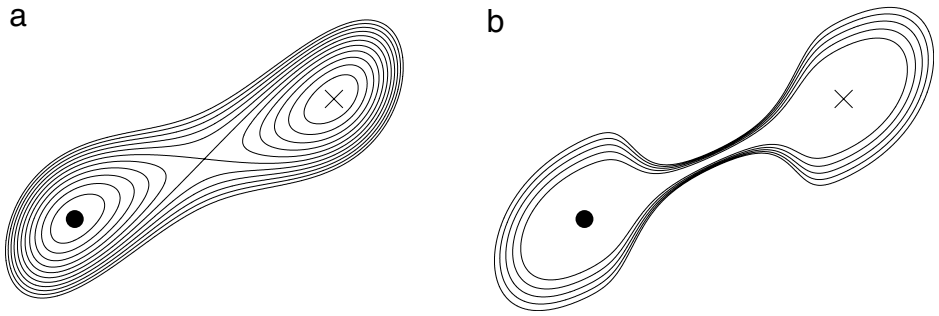

Fig. 1. Schematic examples of the separations in the potential energy surface. (a) A high energy barrier or (b) a narrow gate separates the initial and final configurations represented by the circle and cross, respectively. The thin lines denote the contours of the potential energy surfaces.

determined only by the geometrical feature of the potential energy together with some criteria. The second one is to obtain a trajectory which respects both the potential energy and the kinetic energy. In this work, we employ the latter one because the rare transition events are generated by the potential and kinetic effects.

A standard method for the latter one is molecular dynamics (MD). However, the computational time requirement of conventional MD makes this method insufficient for simulation of these rare transition events. A number of efficient methods that use artificial forces to overcome high energy barriers have been proposed [5–8]. Most of the previous methods, however, are not efficient for rare transition events caused by a narrow gate. This is because the transition rate through the narrow gate is determined by a frequency factor and has a weak (at most power-law) dependence on the magnitude of the artificial forces as shown in chemical kinetics. Both the high energy barrier and the narrow gate are of significance for rare transition events especially in biology [4].

In this paper, we describe the development of a method to simulate rare transition events caused by not only the high energy barrier but also the narrow gate; we are interested in transitions between local minima in a potential energy surface. Typical thermally fluctuating motions are confined in space near the initial configuration; the motions have complex multi-dimensional structures. On the other hand, the motion in the rare transition event moves along a simple sharp curve for the following reasons. For the narrow gate, coordinates of the system are limited to specific values as a result of the narrowness of the potential energy surface. For the high energy barrier, the coordinates must obtain large momenta to overcome the barrier, and the momenta restrict the direction of motion to a specific one. From this discussion, the method to be developed is one that can separate one relevant coordinate, which parametrizes the curve, from other coordinates orthogonal to the relevant one. We call the coordinate a *collective coordinate* and the curve a *collective path*. Many construction methods for the collective path have been proposed over the past five or more decades [9–19]. This approach includes both the potential energy and the kinetic energy as we shall see in Appendix A.

The self-consistent theory of large-amplitude collective motion developed by Dang et al. [15–18] is one of the powerful methods, which is a pioneering work in applications to molecular systems. Central to their theory are *decoupling conditions* given by four equations whose solution gives the collective path. Because exact decoupling is not anticipated for realistic systems, that is, the four equations cannot have a simultaneous solution in general, the problem becomes that of defining a constructive procedure for the approximate collective path. In Refs. [15–18], two approximations based on a subset of the four equations have been proposed.

However, which approximations in the theory of Dang et al. give a transition event between local minima in a potential energy surface depends highly on the details of the potential parameters, as will be demonstrated in Section 2.3. Owing to the lack of the robustness in the previous works, defining a unique approximation to the decoupling conditions and a method for evaluating the quality of it is a central issue for development of the collective path theory.