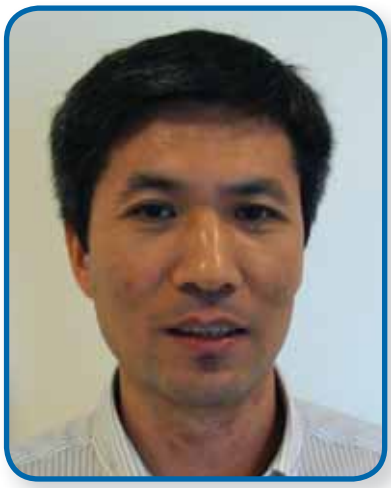
Understanding Complex Energy Landscapes and Rare Events

Assoc Prof Ren Weiqing
Department of Mathematics



Assoc Prof Ren Weiqing

Academic Profile:

A/P Ren obtained his PhD from the Courant Institute of Mathematical Sciences at New York University in 2002. He was a member of the Institute for Advanced Study at Princeton (2002-2003) and an instructor at Princeton University (2003-2005) before joining the faculty of Courant Institute as an assistant professor in 2005. In 2011, he joined the National University of Singapore as an Associate Professor of Mathematics and the Institute of High Performance Computing as a senior scientist.

Research Interests:

- Computational mathematics and scientific computing
- Analysis and algorithms for multiscale problems
- Complex energy landscapes and rare events
- Multi-phase flow and moving contact lines

Contact Details:

Department of Mathematics
National University of Singapore
Block S17, 10 Lower Kent Ridge Road
Singapore 119076

Telephone : (+65) 6516-8756
E-mail : matrw@nus.edu.sg
Website : http://www.math.nus.edu/~matrw

Introduction

Many problems arising from applied sciences can be abstractly formulated as a system navigating over a complex energy landscape. Well-known examples include conformational changes of bio-molecules, chemical reactions, nucleation events during phase transitions, etc. The dynamics proceeds by long waiting periods around metastable states followed by sudden jumps or transitions from one state to another. These transition events happen infrequently compared with the relaxation time scale of the system. However, when they do happen, they usually happen rather quickly and have important consequences. Typically a small amount of noise is present in the system and it is this that drives these rare events. For such an event to happen, the system has to wait for a long time in metastable states until the different components of the noise work together to bring the system over some energy barrier or go through a sequence of correlated changes.

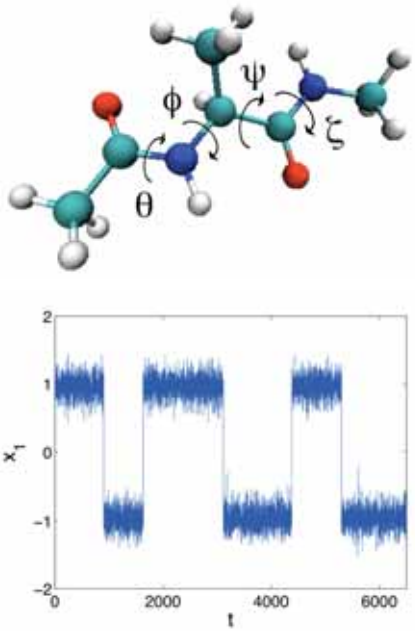


Figure 1: Alanine dipeptide (upper) and the time history of the (normalized) torsion angle (lower panel).

For illustration purposes, let us consider the dynamics of a small molecule, the alanine dipeptide, at room temperature. The molecule in vacuum has two main meta-stable configurations, which can be characterized by different values of the torsion angles along the backbone. Figure 1 shows the time history of one of the torsion angles obtained from the Langevin dynamics. It is seen that the system spends most of time in the two metastable states, with infrequent transitions (conformational changes) from one to the other.

It should be noted that the rare events that we are interested in are not really unusual. For example, conformational changes of biomolecules as in the above example usually happen on the time scale of microseconds or milliseconds. These events are rare on the time scale of molecular vibration (which is typically on the order of femtoseconds, s), but they are not rare on the time scale of our daily lives, which is often measured in minutes, hours or days. After all, all biological processes are driven by such events.

Our objective here is not to keep track of the detailed dynamics of the system but rather to capture statistically the sequence of transitions between different metastable states. This means that, effectively, the dynamics of the system is modeled by a Markov chain: the metastable states are the states of the chain and the hopping rates are transition rates between different metastable states. Therefore the main objects we need to compute are the transition pathways and the transition rates. The computation of these quantities represents one of the major challenges in computational science. The difficulty is mainly due to the disparity of time scales involved in the system, which makes conventional simulation techniques (e.g. the direct simulation of the Langevin dynamics or molecular dynamics, Monte Carlo simulations, etc.) prohibitively expensive. Indeed, one has to use a very small time step and resolve the relaxation time scale in Langevin dynamics or molecular dynamics for numerical stability, thus it takes a huge

number of time steps on average to observe a transition event in these simulations.

My work on modeling rare events (joint with Weinan E and Eric Vanden-Eijnden) has centered on developing the string method, which is now quite popular in computational chemistry and materials science, as well as the minimum action method for analyzing transition events in non-gradient systems (i.e. systems without an underlying energy landscape).

The minimum action method [1]

The Freidlin-Wentzel theory of large deviation is a rigorous mathematical theory for analyzing rare events. It provides an estimate for the probability of the transition events between metastable states in terms of an action functional. In view of this, finding the path with maximum probability becomes a problem of finding the path with minimum action subject to the constraint that the two end points of the path are fixed at two metastable states. Based on the large deviation theory, we developed the minimum action method for analyzing transition events in dynamical systems driven by small noise. The method has been successfully applied to a variety of problems, including the finite-time switching in a Ginzburg–Landau system, the Lorenz system, the Kardar-Parisi-Zhang equation for interface growth, and transitions in the Kuramoto-Sivashinsky equation.

Smooth energy landscapes and the zero-temperature string method [2,3]

For gradient systems with a smooth energy landscape in which the metastable states are separated by a few isolated barriers, the key objects are the transition states, which are saddle points on the potential energy landscape that separate the metastable states. The relevant notion for the transition pathways is that of minimum energy paths (MEPs). MEPs are the paths in configuration space that connects the metastable states along which the potential force is parallel

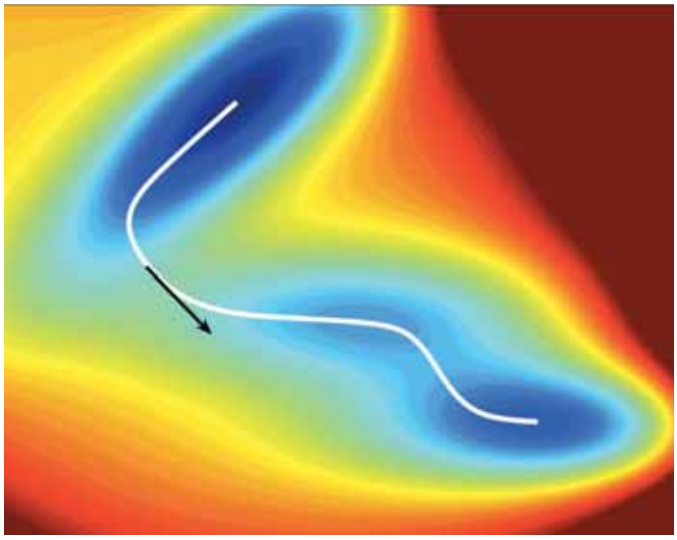


Figure 2: A smooth energy landscape and the minimum energy path.

to the tangent vector (see Figure 2). MEP allows us to identify the relevant saddle points which act as bottlenecks for a particular transition. The zero-temperature string method is designed to compute MEPs. It finds the MEP by evolving a string using the steepest descent dynamics in the path space.

As an interesting application, we used the string method to study the switching of micro-magnetic thin films [4]. Submicro-sized magnetic elements have found a wide range of applications in science and technology, particularly as storage devices. As the elements get smaller, the effect of thermal noise and the issue of data retention time become a major concern. For this reason, thermally activated switching has attracted considerable attention in the magnetics community. From the viewpoint of fundamental sciences, thermally activated switching of micro-sized magnetic elements is an example of rare events that drive a relatively complex system. Figures 3 and 4 show the critical points along two MEPs that were obtained using the string method. More details can be found in Reference 4.

Figure 3: The critical points along a minimum energy path (path a) followed by the magnetization during the switching of the element. The color code indicates the direction of the magnetization.

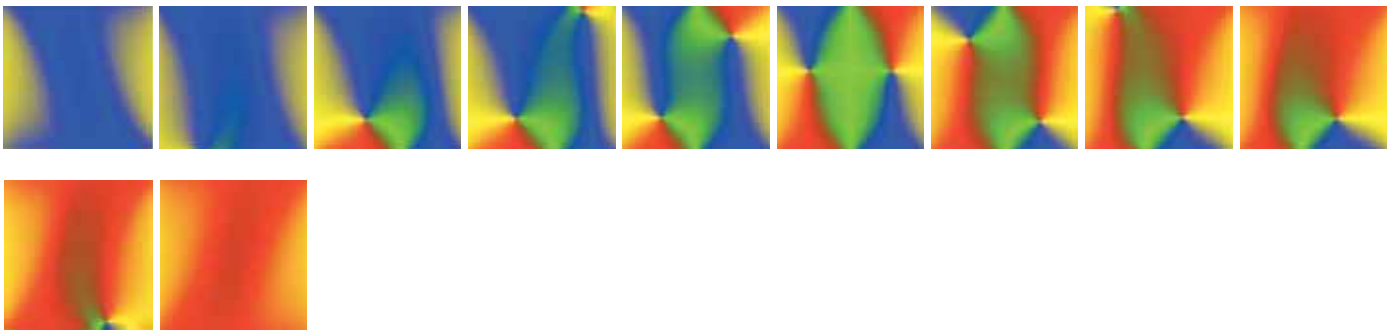


Figure 4: The critical points along a minimum energy path (path b) followed by the magnetization during the switching of the element. The color code indicates the direction of the magnetization.

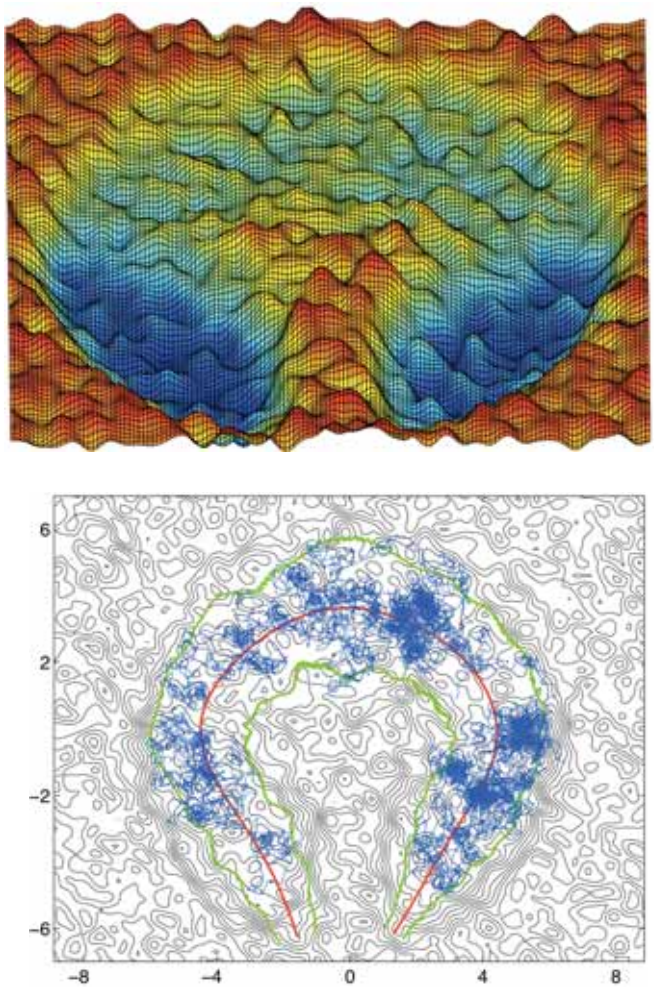


Figure 5: A rough energy landscape (upper) and the transition tube (lower panel).

Rough energy landscapes and the finite-temperature string method [5,6,7]

The situation is quite different for systems with rough energy landscapes, as is the case for typical chemical reactions of solvated systems. An example of rough energy landscape is shown in Figure 5. In this case, traditional notions of transition states have to be reconsidered since there may not exist specific microscopic configurations that identify the bottleneck of the transition. Instead the potential energy landscape typically contains numerous saddle points, most of which are separated by barriers that are less than or comparable to the noise, and therefore do not act as barriers. There is not a unique most probable path for the transition. Instead, a collection of paths is important.

In view of this, we developed the finite-temperature string method for analyzing transitions in complex systems with rough energy landscapes. The key objects in the finite-temperature string method are the transition tube and the transition state ensemble, which are defined with the help of the so-called committor function – the solution of the backward Kolmogorov equation in the configuration space with appropriate boundary conditions. Under the assumption that the transition paths are localized, we first use a variational formulation to reduce the backward Kolmogorov equation in the large dimensional configuration space to a large coupled system in one-dimensional space, then use an iterative procedure to identify the transition tube. An example of the transition tube computed using the string method is shown in Figure 5.

The numerical tools we have developed have been successfully applied to many problems arising from various disciplines, including conformational changes of biomolecules, switching of micro-magnetics thin films, phase transitions of complex fluids, dislocation dynamics in crystalline solids, etc. More information on these numerical methods and their applications can be found on the website: http://www.math.nus.edu/~matrw. ■

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