Commun. Comput. Phys.
doi: 10.4208/cicp.220212.030812a

Vol. **14**, No. 2, pp. 265-275
August 2013

Optimization-Based String Method for Finding Minimum Energy Path

Amit Samanta[1,*] and Weinan E[2,3]

[1] *Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey, USA.*
[2] *Department of Mathematics and Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey, USA.*
[3] *Beijing International Center for Mathematical Research, Peking University, Beijing, China.*

Received 22 February 2012; Accepted (in revised version) 3 August 2012

Communicated by Wei Cai

Available online 27 November 2012

Abstract. We present an efficient algorithm for calculating the minimum energy path (MEP) and energy barriers between local minima on a multidimensional potential energy surface (PES). Such paths play a central role in the understanding of transition pathways between metastable states. Our method relies on the original formulation of the string method [Phys. Rev. B, **66**, 052301 (2002)], i.e. to evolve a smooth curve along a direction normal to the curve. The algorithm works by performing minimization steps on hyperplanes normal to the curve. Therefore the problem of finding MEP on the PES is remodeled as a set of constrained minimization problems. This provides the flexibility of using minimization algorithms faster than the steepest descent method used in the simplified string method [J. Chem. Phys., **126**(16), 164103 (2007)]. At the same time, it provides a more direct analog of the finite temperature string method. The applicability of the algorithm is demonstrated using various examples.

AMS subject classifications: 37C10

Key words: Rare events, string method, minimum energy path, dislocation nucleation.

1 Introduction

The dynamics of complex systems often involve thermally activated barrier-crossing events that allow the system to move from one local minimum of the energy surface

*Corresponding author. *Email addresses:* asamanta@math.princeton.edu (A. Samanta), weinan@math.princeton.edu (W. E)

to another. At finite temperatures, the total kinetic energy accessible to the system is on the order of Nk_BT, where N is the number of degrees of freedom, k_B is the Boltzmann constant and T is the temperature of the system. However, this huge amount of energy is distributed over the whole system. Consequently, it fails to cross over the free energy barrier (generally an index-1 saddle point) and move to a different basin of attraction. A system can overcome a free energy barrier only when sufficient energy is localized on an activated region of the system. The activated region is the volume of the sample where bond breaking/formation, atomic re-arrangements etc. take place [1, 2]. It is of great theoretical and practical interest to develop algorithms that can enable us to efficiently compute the most probable pathways for such transition events. For systems with relatively smooth energy landscapes, it can be shown that the most probable pathways are the minimum energy paths (MEP). Minimum energy paths are physically relevant in the low temperature dynamics of a system and provides information only about the energy barrier involved in a thermally activated event without any consideration of the width of the channel near the saddle point or other entropic effects. Further, at high temperature, the energy surface becomes rugged due to thermal fluctuations and the presence of multiple peaks of $\mathcal{O}(k_BT)$ makes the concept of MEP irrelevant. However in such a scenario the MEP can still correspond to the path with the maximum likelihood [3, 4].

The problem of finding the MEP and the bottlenecks for transition events can be broadly categorized into two classes depending on the initial conditions: (a) when only the initial point is known, and (b) when both the initial and final points on the energy surface are available. In the former case, one can resort to methods like gentlest ascent dynamics [5], dimer method [6], etc. to explore the energy surface. For the second category, the most notable examples include the string method [7–10] and the nudged elastic band method [11–13]. In this case, we are given the initial and final states of the system, and our aim is to find the MEP connecting these states. Since there can be multiple paths joining the end points, the converged MEP is dependent on the choice of the initial path. In the original string method, a path γ evolves as:

$$\dot{\gamma} = -\nabla V(\gamma)^{\perp} + r\hat{t}, \tag{1.1}$$

where, $\dot{\gamma}$ is the time derivative of γ, $\nabla V^{\perp} = \nabla V - (\nabla V, \hat{\tau})\hat{\tau}$ is the gradient of the potential perpendicular to γ, $\hat{\tau}$ is the unit vector parallel to the tangent to γ and r is a Lagrange multiplier used to enforce a particular parametrization of the string.

The string method is easy to implement and works well even if the initial and the final states are not local minimum [7]. This advantage has led to a class of algorithms called growing string method that have been tested for real systems using quantum mechanical tools [14–16]. Further, if one is solely interested in knowing the free energy barrier and the configuration at the saddle point, the end of the string need not be a local minimum but some intermediate configuration lying in a basin other than that of the initial point.

The string method is based on the idea of moving curves by using a steepest descent-type of dynamics. It should be emphasized that even though the dynamics used in the string method has very strong steepest decent flavor, the method does not amount to