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Stability, Accuracy and Cost of NEB and String Methods

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Abstract. In this paper, the zero-temperature string method and the nudged elastic band method for computing the transition paths and transition rates between metastable states are investigated. The stability, accuracy as well as computational cost of the two methods are discussed. The results are verified by numerical experiments.

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Key words: Transition path, transition state, string method, nudged elastic band method, stability, accuracy and cost.

1 Introduction

The string method [4,5] and the nudged elastic band (NEB) method [9] have been widely used in the study of transition paths and transition rates between metastable states. Both methods have been successfully applied to continuous models, empirical potential models and first-principles calculations, see [4, 10, 18–20] for the string method, and [2, 8, 12, 13, 21–23] for the NEB method.

In this paper, we focus on the zero-temperature string (ZTS) method and the NEB method. The ZTS method and the NEB method have some similarities. First, both methods evolve a chain of images of the system between the initial state and the final state. Second, the potential forces are decomposed into components normal and tangential to the path in both methods. Third, both methods minimize the energy in the plane normal to the path at each image. On the other hand, the two methods are different in several aspects. In the NEB method, extra spring interaction between the adjacent images is added to ensure continuity of the path. The systems move in a force field which is a combination of the normal component of the potential force and the tangential component of the

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spring force. In the ZTS method, the images are points on a string, i.e., a smooth curve with intrinsic parametrization such as arc length or energy-weighted arc length, which connects two metastable states. The string evolves to the minimal energy path (MEP) under the normal component of the potential force subject to some constraint.

We give a detailed theoretical analysis of the ZTS and the NEB methods, including the stability, accuracy and computational cost. An adaptive time step is obtained from the stability conditions for each method. Then the computational cost is estimated. A good choice for the elastic constant is obtained for the NEB method. These choices of the parameters make the methods more efficient or more accurate. As for the accuracy of the transition path, both methods have first order accuracy under L_2-norm and L_∞-norm. Two techniques to improve the accuracy at the transition state are discussed.

The rest of this paper is organized as follows: In Section 2, the ZTS method and the NEB method are briefly reviewed. In Section 3, the stability conditions of the ZTS method and the NEB method are provided. We analyze the accuracy in Section 4. Estimates of the computational cost of the two methods are presented in Section 5. We conclude the paper in Section 6.

2 ZTS method and NEB method

In this section, we briefly review the ZTS method and the NEB method (see [4,9] for more details).

2.1 ZTS method

Consider the example of a system modelled by the following stochastic equation

$$\dot{X}^\varepsilon = -\nabla V(X^\varepsilon) + \sqrt{2\varepsilon}\dot{W}, \tag{2.1}$$

where $V(X)$ is the potential energy of the system, $\dot{W}$ is a white noise, and ε is a parameter representing the strength of the white noise. Suppose the potential energy has two minima A and B. Let φ be a smooth curve, i.e., a string, connecting the two minima of the potential energy , A and B. By definition, φ is a MEP if

$$0 = (\nabla V(\varphi))^\perp, \tag{2.2}$$

where

$$(\nabla V(\varphi))^\perp = \nabla V(\varphi) - (\nabla V(\varphi)\cdot\hat{\tau})\hat{\tau},$$

with $\hat{\tau} = \varphi_\alpha / |\varphi_\alpha|$ being the unit tangent vector along φ, and α the intrinsic parameter of the string. Equivalently, the MEP φ is a curve that minimizes V in the hyperplane normal to itself. One way of finding solutions of Eq. (2.2) is to follow the dynamics determined by

$$\varphi_t = -(\nabla V(\varphi))^\perp + \gamma\hat{\tau}, \tag{2.3}$$