Minimum Free-Energy Path Calculated via Umbrella Sampling Simulations

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To improve the efficiency of a chemical reaction the knowledge of the detailed course can be an important help. Under thermodynamical conditions, the most probable reaction path is described by the minimum free-energy path, which leads from a minimum over a saddle pointto another minimum in the free-energy landscape. These points represent the reactant, transition, and product states.

Unfortunately, scanning the whole energy landscape is computationally expensive, at first because thermostatistical simulations need a certain amount of sampling in order to dominate noise and at second, because complex paths would require to cover a high-dimensional surface.

In the first part we present an efficient method based on umbrella integration and Newton-Raphson iteration to calculate the minimum free-energy paths. Umbrella integration is known as a novel method to calculate the gradient and Hessian of a free-energy landscape.[1,2] We use these for an iterative Newton-Raphson search of the saddle points. Thereupon the minimum free energy path can be reconstructed by step wise umbrella integration and following the gradient down to the minimum.

This reduces the problem from a multidimensional surface scan to a one dimensional problem. We demonstrate the algorithm for a simple biological system.[3]

In further studies we aim to develop a method which allows iterative optimization of a chain of states. Independent molecular dynamics simulations have to be done along that chain, and can be run in parallel. Further the first guess needed to start the simulation is often easier obtained for the reaction mechanism as for the saddle point. We already archive quadratic convergence of nudged elastic band optimizations within the potential energy surface for simple example systems.

[1] J. Kästner, J. Chem. Phys., 131, 034109 (2009).
[2] J. Kästner, J. Chem. Phys., 136, 234102 (2012)
[3] M.U. Bohner, J. Kästner, J. Chem. Phys., 137, 034105 (2012)