

Exploring Complex Dynamics with Transition Path Sampling

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Computational studies of processes occurring in complex systems are often complicated by a wide separation of time scales. Autoionization in liquid water, for instance, occurs on time scales many orders of magnitude larger than the typical time scale of molecular motion. Such processes can be studied with transition path sampling, a computational methodology capable of bridging this time scale gap. Transition path sampling is based on an importance sampling of reactive trajectories, the rare but important dynamical pathways that bridge stable states. I will discuss the statistical view of dynamics underlying the method. Within this perspective, ensembles of trajectories can be sampled and manipulated in close analogy to standard techniques of statistical mechanics. Particular attention will be directed towards the calculation of rate constants, which can be determined by, in effect, reversibly changing ensembles of trajectories.