Understanding reaction mechanisms from transition path sampling molecular dynamics simulations

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Transition path sampling (TPS) is an increasingly prominent simulation method for exploring processes that are triggered by large activation barriers. By efficiently tackling the inherent time-length scale problem, TPS molecular dynamics simulations allow very detailed insights into the mechanisms of reactions, phase transitions, structural reorganization and other kinds of barrier crossing events.

The method is particularly suited to the investigation of complex systems, in which the guessing of model reaction coordinates is likely to bias the simulation results. TPS represents a Monte-Carlo iteration in the trajectory space of reactive events and hence converges to the preferred mechanisms in an unprejudiced manner. Thus, initial pathways -which are needed as prerequisites- may be chosen essentially arbitrarily.

The method and its implementation aspects are illustrated by the example of reactions, phase transitions and phase separation processes. In each case, we deliberately use ‘wrong’ reaction mechanisms for preparing a starting pathway and then demonstrate the evolution of trajectories in favor of the real mechanism.

Key references:

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