Rate constants from equilibrium simulations: a new method

Janos Daru[1,2], Andras Stirling[2]

[1] Eötvös Loránd University, Physical Chemistry Department, Hungary

[2] Research Centre for Natural Sciences, Institute of Organic Chemistry, Hungary

On the timescale of molecular simulations, reactions are rare-events. In most cases direct calculation of rate constants requires unaffordable computational costs. We have developed a theory and an algorithm to calculate rate constant from equilibrium simulations in a consistent and relatively cheap manner. The method requires the free energy profile of the reaction, implying that a suitable reaction coordinate is already identified. The ideas behind the method are to define the *Reactive Segment (RS)* within the reactant state and to recognize that the corresponding rate constant, k_{RS} can be calculated very efficiently. The phenomenological rate constant can be easily recovered by reweighing k_{RS} with the statistical weight of the selected *RS* within the full reactant state. If necessary the calculated rate constants can be used to derive activation free energies and related quantities. This can be useful to test the applicability of a kinetic model or to make contact with previous results.