USING THE METROPOLIS MONTE CARLO METHOD TO EXTRACT REACTION KINETICS FROM EQUILIBRIUM DISTRIBUTIONS OF STATES

SERGEI F. CHEKMAREV, *Laboratory of Modeling, Institute of Thermophysics, SB RAS, Novosibirsk, Russia*.

Both in experiment and simulations, the kinetics of the mutual interconversion of states in a complex many-body system are usually much more difficult to determine than the equilibrium distribution of states (EDSs). Therefore, it is tempting to find out whether the knowledge of the EDS of a system allows us to obtain information about its kinetics, and if so, to what extent. For this, it is proposed to use the Metropolis Monte Carlo (MMC) method. The EDS plays a roles of the potential of mean force that determines the acceptance probabilities of new states in the MMC simulations.

The approach is illustrated by the protein folding/unfolding reaction. Specifically, two proteins are considered - a model β-hairpin and helical $\alpha_3 D$ protein. For β-hairpin, the free-energy surfaces and free-energy profiles for a set of temperatures are used as the EDSs. It has been found that the rate constants and first-passage time (FPT) distributions obtained in the MMC simulations change with temperature in good agreement with those obtained from molecular dynamics simulations. For $\alpha_3 D$, whose equilibrium folding/unfolding was studied by single-molecule FRET (Chung et al., J. Phys. Chem. A, 115, 2011, 3642), the experimental FRET-efficiency histograms at different denaturant concentrations were used as the EDSs. The rate constants for folding and unfolding obtained in the MMC simulations have been found to change with denaturant concentration in reasonable agreement with the rate constants extracted from the photon trajectories on the basis of theoretical models.

The promising feature of the present approach is that it does not require introducing any additional parameters to perform simulations, which suggests its applicability to other complex systems.