ID: 10.1a

Title: Crystal nucleation kinetics revealed by the reweighted path ensemble

Name: Bolhuis, Peter

Affiliation: University of Amsterdam

Numerical studies of rare events in high-dimensional complex systems, such as chemical reactions in solution, protein conformational changes, or crystal nucleation, often employ biasing along a predefined reaction coordinate to compute the free energy, compute the rate constants, and explore the mechanism. However, the choice of such a low-dimensional collective variable can be very delicate and often influences the results. If chosen poorly, the prediction of the transitions states and mechanisms might be completely wrong. Moreover, instead of imposing a reaction coordinate one would like to extract it from the simulation itself. The transition path sampling framework allows to do this, but does not immediately yield the free energy and rates. We introduce a novel reweighting scheme to unbias the path ensembles in the transition interface sampling framework. This reweighted path ensemble allows a full non-linear description of reaction coordinate, and directly yields projections of the free energy, committor and transmission coefficient landscapes in arbitrary collective variable spaces. While developed for use with path sampling, these analysis methods can also be applied to regular molecular dynamics trajectories. We illustrate the methodology on the mechanism of the homogeneous crystal nucleation from the supercooled liquid to the crystal phase in the Gaussian core model. We find that the size of the cloud of prestructured particles surrounding the crystalline nucleus enhances the description of the transition. Further, we show that the rearrangement of the inner core of the nucleus according to Ostwald?s step rule is a separate process, independent of the growth of the nucleus.