Sampling trajectory space and finding order-disorder transitions in constrained dynamical systems

David Chandler

University of California, Berkeley
Department of Chemistry
Berkeley, California 94720 USA

Abstract

Statistical mechanics of trajectory space of classical systems provides a thermodynamic-like formalism of space-time. The partition functions are path integrals or sums over histories (i.e., trajectories) that are weighted by probability functionals for trajectories. Associated free energies as functions of discriminating field variables exhibit singularities at conditions of coexistence between extensively different sub-ensembles of trajectories. In equilibrium statistical mechanics, coexistence can be gleaned numerically from applications of Monte Carlo sampling of micro-states. A corresponding technique for trajectory space is the method of transition path sampling. This lecture describes this method and applications of it to study kinetically constrained models of structural glass forming materials. For these models, the glass transition is associated with phase coexistence between dynamically active and inactive phases.