Multiscale Dynamical Stochastic Techniques in various Thermodynamics Ensembles, & the Adiabatic Approximation

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Abstract

The realistic simulation of physico-chemical and biological systems at an atomic or molecular level where long time scales, and hundreds of thousands to several millions of atoms are present is an insurmountable challenge using brute force techniques alone. A variety of multiple time-scale techniques have been developed to try to render this problem more tractable, including rare-events methods such as meta-dynamics and temperature accelerated molecular dynamics (TAMD), each aiming to compute the free energy properties of relevant systems with respect to appropriate sets of collective variables, and where possible more general observables. The TAMD approach entails coupling harmonically the collective variables of the real system at a given temperature T to a set of auxiliary variables held at a fictitious temperature $\bar{T}$ high enough that all relevant free energy barriers can be overcome. The conditions for the validity of TAMD where the underlying stochastic dynamics realising thermostats T and $\bar{T}$ consists of **over-damped** *langevin equations have been established by Maragliano and Vanden Eijnden - in essence the changes of the real system wrought by the artificial system must be slow enough that the perturbation is in effect adiabatic. In particular, the langevin friction associated with the auxiliary thermostat must by far higher than that of the "real thermostat. However, for more general ensembles (e.g. isothermal-isobaric), and/or where the underlying stochastic dynamics is realised via* **under damped** *langevin equations, the role of viscosity as a parameter determining the strength of the perturbation is completely inverted, and overall the situation is murkier and more complex. This is perhaps important not least because most standard simulators use either under damped langevin dynamics, or the their "physical" equivalent, e.g. Nose-Hoover type dynamics. The aim of this presentation is to establish transparently the conditions of adiabaticity (or lack of it) , and how these are determined by the parameters of the auxiliary system, the real system,and their respective stochastic coupling. To this end, we will need to translate the TAMD stochastic differential equations to their corresponding Fokker Planck form, and rescale the ensuing variables borrowing an approach from non-adiabatic quantum classical dynamics. One pleasant result of the analysis will be that one of the conditions thought necessary for TAMD, but which make the adiabatic approximation far more difficult is superfluous if the equations are slightly modified.*