Taking a short stroll in the hills of molecular dynamics

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Abstract

The aim of molecular dynamics is to study the time-evolution of a microscopic system of N particles in order to deduce various of its macroscopic properties, like its energy, or its temperature. To do so, one needs to be able to sample the *Boltzmann-Gibbs measure* $\mu_V \propto exp(-\beta V)$ where V is the system's potential energy and β is the thermodynamic beta. A classical stochastic process used in this scope is the overdamped Langevin dynamics:

$$\mathrm{d}X_t = -\nabla V(X_t)\mathrm{d}t + \sqrt{2\beta^{-1}}\mathrm{d}W_t, \tag{1}$$

where $(W_t)_{t\geq 0}$ is a classical d-dimensional Brownian motion, and $\mathcal{F} = -\nabla V$ is the interaction force. A force which is the gradient of a potential energy V is said to be *conservative*. Note that from a PDE point of view, the law of the process $(X_t)_{t\geq 0}$ satisfies a nonlinear Fokker-Planck equation.

Such a process has good theoretical properties, but one practical issue arises, that of *metastability*: the system may remain trapped in potential wells for long periods of time, and the system's law's relaxation towards the equilibrium can be far too slow. In order to avoid metastability, one can rely on a *reaction coordinate*, namely a function ξ of the position which gives a low-dimensional representation of the system. Given this coordinate, one can then consider the *Adaptive Biasing Force* (ABF) method [1, 2], which consists in biasing the force $\mathcal{F}$ in the direction of ξ, with an adaptive bias B_t, and prove the longtime convergence –in a sense to be precised– of the algorithm[4]. One can also consider the *Projected Adaptive Biasing Force* (PABF) method, whose convergence has been proven in [3]. A good property of both methods is the *flat histogram property*: the energy landscape is flattened in the direction of ξ. In this talk, I will present a theoretical introduction to the ABF algorithm, and review its potential use in treating alchemical reactions.

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