Proper Statistical Sampling in Isothermal-Isobaric Discrete-Time Molecular Dynamics

Abstract: Molecular Dynamics simulations always involve a discretization of time, but the discrete-time behavior is increasingly different from that of the continuous-time physical equations as the time step is increased. This fact creates a dilemma for any simulation of a dynamical system: Use a small time step, resulting in dynamics that resemble continuous-time behavior at the expense of efficiency; or use a large time step that makes the simulation finish sooner at the expense of meaningful evolution. It is, therefore, essential to understand the features of different algorithms, such that optimal properties can be chosen for a given set of problems and objectives.

Our aim is to investigate and improve Molecular Dynamics simulation techniques for systems in thermal equilibrium. I will present our recent simple derivation [1] of a stochastic Stormer-Verlet algorithm for the evolution of Langevin equations. The method, which is as simple as conventional Verlet schemes, has been numerically tested on both low-dimensional nonlinear systems as well as more complex molecular ensembles with many degrees of freedom [2]. In light of the fundamental artifacts introduced by discrete time to dynamical simulations, I will provide a simple intuitive picture of the unique benefits of our algorithm that, unlike other algorithms, preserves proper configurational sampling (diffusion and Boltzmann distribution) in discrete time. I will then introduce a new companion algorithm for controlling pressure in molecular ensembles, i.e., a barostat for NPT simulations [3]. Drawing on the idea of Andersen, we consider a global variable (a piston), which emulates the dynamics of the simulated volume in systems with periodic boundary conditions. However, our description of the dynamics is defined differently from previous work and, thus, leads to a very simple set of discrete-time equations that is easily implemented, tested for statistical accuracy, and show favorable comparisons against state-of-the-art algorithms when simulating molecular ensembles at constant pressure and temperature.

[1] Gronbech-Jensen & Farago, Molecular Physics Vol.111, 983 (2013).
[2] Gronbech-Jensen, Hayre, & Farago, Computer Physics Communications, Vol.185, 524 (2014).
[3] Gronbech-Jensen & Farago, ``Constant pressure and temperature discrete-time Langevin molecular dynamics", arXiv:1408.2151, to appear in J. Chem. Phys.