Molecular Dynamics in the NVT ensemble Peter Virnau, 06.12.2007

So far, we have only considered simulations in the microcanonical (NVE) ensemble. Sometimes, however, it is beneficial to simulate at constant temperature. For example, we might want to adjust the temperature of a system before starting an NVE production run, which is often better suited to study dynamics.

The Andersen thermostat (1980)

In the Andersen thermostat, thermalization is achieved by coupling the system to a stochastic heat bath. After each integration step, we choose particles at random, whose velocities are reset according to the Maxwell-Boltzmann distribution at temperature T_0 (→ MC step)

Example: Implementation with velocity Verlet integrator

Given: r(t), v(t), f(t)

1. $r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}\frac{f}{m}\Delta t^2$
2. $v' = v(t) + \frac{f(t)}{2m}\Delta t$
3. Determine forces f(t+Δt)
4. $v(t+\Delta t) = v' + \frac{f(t+\Delta t)}{2m}\Delta t$

} regular velocity Verlet

According to the Maxwell-Boltzmann distribution

$$P(v_i) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_i^2}{2k_B T}\right)$$

} new

5. Check for each particle if velocity is adjusted
   (constant probability for adjustment → draw random number …)
   YES? Draw new velocity according to Maxwell-Boltzmann distribution

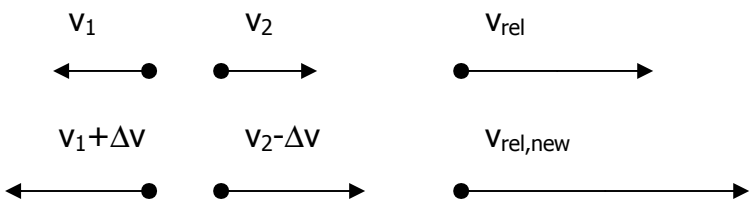
Problem: Momentum is not conserved (← stochastic kicks)
→ unrealistic dynamics, center of mass "diffuses"

However, the algorithm is well-suited to study static properties of the system and to adjust the temperature for a subsequent NVE simulation. In the following we'll discuss an extension which conserves momentum.

The Lowe-Andersen thermostat (1999)

Idea: Change relative velocities of particle pairs (according to the Maxwell-Boltzmann distribution) without changing momentum.

Example:



Alternatives: Stochastic: Langevin (→ problem set),
Extended Lagrangian: Nose-Hoover, DPD

Hybrid Monte Carlo – "bad MD, good MC"

Advantage MC: Unphysical moves are allowed, but collective molecular motions are not well-represented (f.i. in a local update only one particle is moved although we need to calculate the interactions with all surrounding particles.)

Advantage MD: Superior collective (local) dynamics, but energy needs to be conserved (NVE ensemble) → rather small time steps.

Idea: Evolve system with a series of MD steps (velocities are randomized), accept/reject with Metropolis criterion.