Molecular Dynamics in non-NVE ensembles

Simplest case: constant-$T$, $N$ MD

Isolated system

What do we mean by constant temperature?

Maxwell-Boltzmann distribution of velocities:

$$P(v) = \left( \frac{B}{2\pi m} \right)^{3/2} \exp \left[ -\frac{Bv^2}{2m} \right]$$

The average kinetic energy

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3kT}{2}$$

Can be used to define the "instantaneous" kinetic temperature, $T_k = \frac{m}{3k} \frac{\sum v^2}{N}$

But this quantity fluctuates even in the $NVT$ ensemble:

$$\langle v^2 \rangle = \frac{3kT}{m} = \frac{3}{8m}$$

$$\langle v^4 \rangle = \int dv v^4 P(v) = \frac{15}{(8m)^2} \langle T_k \rangle$$

$$\langle v^4 \rangle = \frac{15-9}{9N} = \frac{2}{3N}$$
In early days of MD simulation (~60's, 70's) an "ad hoc" velocity rescaling was often used to "keep the temperature constant" - this is incorrect, as the kinetic temperature should fluctuate as shown on the previous page.

Two rigorous methods for sampling the NVT ensemble in MD (41 common ad hoc method).

A. The Andersen Thermostat


⇒ Stochastic impulsive forces acting on randomly selected particles

Probability of a stochastic collision of a particle at time interval Δt is \(v \Delta t\), where \(v\) is an (arbitrary) collision frequency that controls the rate of heat transfer between heat bath and system.

1. Start with initial positions + velocities, integrate

2. For every time step, check for probability of collision \(v \Delta t\); if there is a collision, new velocity for a randomly selected particle is drawn from the Maxwell-Boltzmann distribution.
Consequences:

+ Energy is no longer conserved
+ Dynamics are affected; Randomization of velocities leads to rapid loss of correlations / decay of velocity autocorrelation

B. Noé-Hoover Thermostat


Deterministic MD with an extended Lagrangian

\[ L = \sum_{i=1}^{N} \frac{m_i}{2} \left( \frac{\dot{\vec{r}}_i}{s^2} \right)^2 + U(\vec{r}_i) + \frac{m_s}{2} s^2 - \frac{g}{\beta} \ln s \]

- \( s \): extra variable (scales time)
- \( m_s \): effective "mass" for \( s \)
- \( g \): to be determined so that system follows canonical ensemble \((=3N+1)\)

Momenta conjugate to \( \vec{r}_i, s \):

\[ \vec{p}_i = \frac{\partial L}{\partial \dot{\vec{r}}_i} = m_i s^2 \dot{\vec{r}}_i \]

\[ \vec{p}_s = \frac{\partial L}{\partial \dot{s}} = m_s \dot{s} \]

\[ H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i s^2} + U(\vec{r}_i) + \frac{\vec{p}_s^2}{2m_s} + \frac{g}{\beta} \ln s \]

For a system of \( N \) atoms, \( H \) generates a microcanonical ensemble distribution of \( 6N+2 \) degrees of freedom:
\[ Q = \frac{1}{N!} \int \sum_{i} d\mathbf{p}_i^N d\mathbf{r}_i^N \delta (E - \mathcal{J}) = \]
\[ = \frac{1}{N!} \int \sum_{i} d\mathbf{p}_i^N d\mathbf{r}_i^N S^N \delta (E - \mathcal{J}) \text{, where} \]
\[ \mathbf{p}_i' = \mathbf{p}_i / s \]

It can be shown that by choosing \( g = 3N + 1 \) the extended ensemble in the "scaled" variables follows the canonical distribution.

Physically, primed variables are "real", unprimed are "virtual" - simulation is done in either set of coordinates, with

\[ r' = r \]
\[ p' = p / s \]
\[ s' = s \]
\[ \Delta t' = \Delta t / s \text{ = real time step fluctuates} \]

The Hoover formulation of the equations of motion is the one usually implemented:

\[ \frac{\dot{r}_i}{p_i} = \frac{\mathbf{p}_i}{m_i} \quad (1) \]
\[ \frac{\dot{p}_i}{p_i} = - \frac{\partial U(\mathbf{r}_i^N)}{\partial \mathbf{r}_i} - 3 \mathbf{p}_i \quad (2) \]
\[ \mathbf{\dddot{s}} = \left( \sum \frac{p_i^2}{m_i} - \frac{3N}{6} \right) / m_s \quad (3) \]

Extra equation to check for consistency

\[ \frac{d \mathbf{s}}{d t} = \mathbf{\dddot{s}} \quad (4) \]
Consequence:
* Dynamics only mildly perturbed
* ms influences response to perturbation
* Thermostat "chains" needed for systems w/ no external forces
* Method can be extended for cons.-P, controlling polarizability etc.

Bersundsen thermostat / Barostat


This common approach is also not rigorous, but results in a better approximation of real dynamics than Andersen thermostat.

Eg. for cons.-P simulations,

couple to external "pressure reservoir" at $P_0$ by extra term in equations of motion, so that

$$\frac{dP}{dt} = \frac{(P_0 - P)}{t_p}$$

$\rightarrow$ time constant

$\rightarrow$ desired value of pressure

At each step, volume of simulation box is scaled by a factor $\chi$ and the coordinates:

$$r^2' = \chi^{1/3} r^2$$

where

$$\chi = 1 - \frac{3 t_p \Delta t}{t_p} (P_0 - P)$$

where $t_p \approx 0.01 \text{ ps}$ to $0.1 \text{ ps}$