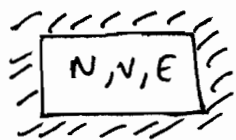
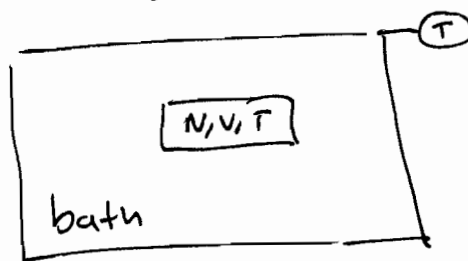


Molecular Dynamics in non-NVE ensembles

Simplest case: constant-T MD



Isolated system



What do we mean by constant temperature?

Maxwell-Boltzmann distribution of velocities:

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

The average kinetic energy $\frac{1}{2} m \langle v^2 \rangle = \frac{3 k T}{2}$



for monoatomic systems

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:

$$\left. \begin{aligned} \langle v^2 \rangle &= \frac{3kT}{m} = \frac{3}{Bm} \\ \langle v^4 \rangle &= \int dv v^4 P(v) = \frac{15}{(Bm)^2} \end{aligned} \right\} \frac{\langle T_k^2 \rangle - \langle T_k \rangle^2}{\langle T_k \rangle^2} = \frac{\langle v^4 \rangle - \langle v^2 \rangle^2}{N \langle v^2 \rangle^2}$$

$$= \frac{15 - 9}{9N} = \frac{2}{3N}$$

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 (+ 1 common ad hoc method).

A. The Andersen Thermostat

H.C. Andersen, MD @ const. T or P, J. Chem. Phys. 72:2384 (1980)

⇒ Stochastic impulsive forces acting on randomly selected particles

Probability of a stochastic collision of a particle at time interval Δt is $\nu \Delta t$, where ν 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 $\nu \Delta t$; 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. Nosé-Hoover Thermostat

References: JCP 81:511 (1984); Molec. Phys. 52:255 (1984)

Deterministic MD with an extended Lagrangian
 (Additional degrees of freedom)

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

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 :

$$\left. \begin{aligned} \vec{p}_i &= \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_i} = m_i s^2 \dot{\vec{r}}_i \\ p_s &= \frac{\partial \mathcal{L}}{\partial \dot{s}} = m_s \dot{s} \end{aligned} \right\} \Rightarrow \text{Hamiltonian } \mathcal{H}$$

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

For a system of N atoms, \mathcal{H} generates a microcanonical ensemble distribution of $3N+2$ degrees of freedom:

$$Q = \frac{1}{N!} \int dp_s ds d\vec{p}'^N d\vec{r}'^N \delta(E - \mathcal{H}) =$$

$$= \frac{1}{N!} \int dp_s ds d\vec{p}'^N d\vec{r}'^N s^{3N} \delta(E - \mathcal{H}) \quad , \text{ where } \vec{p}' = \vec{p}/s$$

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

$$r' = r$$

$$p' = p/s$$

$$s' = s$$

$$\Delta t' = \Delta t/s \quad \leftarrow \text{real time step fluctuates}$$

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

$$\dot{\vec{r}}_i = \vec{p}_i/m_i \quad (1)$$

$$\dot{\vec{p}}_i = - \frac{\partial u(\vec{r}^N)}{\partial \vec{r}_i} - \zeta \vec{p}_i \quad (2)$$

$$\dot{\zeta} = \left(\sum_i \vec{p}_i^2/m_i - \frac{3N}{B} \right) / m_s \quad (3)$$

Extra equation to check for consistency

$$\frac{d \ln s}{dt} = \zeta \quad (4)$$

- Consequences:
- * Dynamics only mildly perturbed
 - * m_s influences response to perturbations
 - * Thermostat "chains" needed for ^{some} systems w/ no external forces
 - * Method can be extended for const-P, controlling polarizability etc.

Berendsen thermostat / Barostat

J. Chem. Phys. 81:3684 (1984)

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

E.g. for const-P simulations,

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

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

↳ time constant
↳ desired value of pressure

At each step, volume of simulation box is scaled by a factor χ and the coordinates,

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

where

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

↳ isothermal compressibility of system
 $t_p \sim 0.01 \text{ ps to } 0.1 \text{ ps}$