

S 7 Canonical Ensemble

Fixing energy is difficult (in reality), fixing temperature not so much.

$(E, V, N) \mapsto (T, V, N)$: Free energy $F(T, V, N) = E - TS$
via Legendre transfo

Let us soften the constraints a bit. We require only that the **average energy** is constant and allow fluctuations.

$$E = \int H(\underline{x}) S(\underline{x}) d^{6N} \underline{x} \quad (*)$$

How does $S(\underline{x})$ look like now?

$\lambda(\underline{x})$ is 2nd condition for the extremalization of the Gibbs entropy.

$$\delta \left\{ -k_B \int S \ln(S) d^{6N} \underline{x} + \lambda_1 \left[\int S d^{6N} \underline{x} - 1 \right] + \lambda_2 \left[\int H(\underline{x}) S d^{6N} \underline{x} - E \right] \right\} = 0$$

[...] Euler-Lagrange equation

$$-k_B \ln(S) - k_B + \lambda_1 + \lambda_2 H(\underline{x}) = 0$$

$$S(\underline{x}) = \frac{1}{C} \underbrace{\exp\left(\frac{\lambda_1 - k_B}{k_B}\right)}_{\frac{1}{Z}} \exp\left(\frac{\lambda_2}{k_B} H(\underline{x})\right)$$

$$= \frac{1}{C} \frac{1}{Z} e^{\frac{\lambda_2}{k_B} H(\underline{x})}$$

$\lambda_1(Z), \lambda_2$ can be determined from the constraints:

① Norm

$$\int \mathcal{S}(\underline{x}) d^{6N}x = \frac{1}{C} \frac{1}{Z} \int \exp\left(\frac{\lambda_2}{k_B} H(\underline{x})\right) d^{6N}x = 1$$

$$Z = \frac{1}{C} \int \exp\left(\frac{\lambda_2}{k_B} H(\underline{x})\right) d^{6N}x = e^{-\frac{\lambda_1 - k_B}{k_B}}$$

$$\lambda_1 - k_B = -k_B \ln(Z)$$

Multiply E-L by \mathcal{S} and integrate:

$$\underbrace{-k_B \int \mathcal{S} \ln(\mathcal{S}) d^{6N}x}_{S'} - (\lambda_B - \lambda_1) \underbrace{\int \mathcal{S} d^{6N}x}_{=1} + \lambda_2 \underbrace{\int H(\underline{x}) \mathcal{S} d^{6N}x}_E = 0$$

$$S - (\lambda_B - \lambda_1) + \lambda_2 E = 0$$

$$S - k_B \ln(Z) + \lambda_2 E = 0 \Rightarrow E - TS = F$$

$$S = k_B \ln(Z) - \lambda_2 E \Rightarrow S = -\frac{F}{T} + \frac{E}{T}$$

Compare: $\lambda_2 = -\frac{1}{T}$; $\frac{F}{T} = -k_B \ln(Z)$

$$\mathcal{S}(\underline{x}) = \frac{1}{Z} \frac{1}{C} e^{-\beta H(\underline{x})} \quad \beta = \frac{1}{k_B T}$$

and $Z = \frac{1}{C} \int e^{-\beta H(\underline{x})} d^{6N}x$ partition function

canonical distribution

$$F(T, V, N) = -k_B T \ln(Z)$$

§ 8 Thermostats

We have seen that, while the basic theory of Hamiltonian systems "corresponds" to MD simulations in the microcanonical ensemble (N, V, E), most 'real-world' applications deal with (at least) constant temperature setups, the canonical ensemble.

\Rightarrow biomolecules in your body.

Constant temperature in thermodynamic terms means that the system under study is not isolated but coupled to a heat bath.

Q : How do we translate this (and §7) into a MD simulation?
How do we fix the temperature?

How do we measure temperature, when all we know about are q and p ?

We did not discuss the virial theorem:

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij}$$

and from that the equipartition theorem

$$\underbrace{\left\langle \sum_{i=1}^N \frac{p_i^2}{2m_i} \right\rangle}_{\text{average of the kinetic energy}} = \frac{g}{2} k_B T \quad g: \text{degrees of freedom}$$

that links the temperature to the average kinetic energy.

8.1 Stochastic Collision Method

The coupling to the heat bath is represented by stochastic collisions that act on randomly selected particles.

Two parameters : T desired temperature

ω frequency of stochastic collisions
 $\hat{=}$ strength of the coupling to the heat bath

If successive collisions are uncorrelated, the distribution of time intervals is of Poisson form

$$P(t, \omega) = \omega e^{-\omega t}$$

procedure:

- integrate Hamiltonian equation until the time of next collision
- pick a particle, reset its momentum according to a Boltzmann distribution at T

$$\omega_i = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

It can be shown that Hamiltonian dynamics + stochastic collisions $\hat{=}$ MD simulation is a Markov process

- canonical distribution is invariant under repeated application of the procedure

time averages of this "Anderson trajectory" $\hat{=}$ canonical ensemble average

BUT

- velocities are randomly decorrelated
- dynamics are not physical!

\Rightarrow Nosé-Hoover thermostat is not good for dynamical properties

8.2 Extended System Method: Nose'-Hoover Thermostat

We start out from our usual system with N particles, coordinates q_i , masses m_i , and momenta p_i .

Now we introduce an additional variable (degree of freedom) s , representing how an external system acts on the simulated system.

and we write "new" variables (q'_i, p'_i, t')

$$q'_i = q_i$$

$$p'_i = s \cdot p_i$$

$$t' = \int_0^t \frac{dt'}{s} \quad \Rightarrow \quad dt = \frac{dt'}{s} \quad \text{transformation is}$$

"time scaling"

So we can express the "true" velocities as

$$\dot{q}_i = \frac{\partial q_i}{\partial t} = s \frac{\partial q_i}{\partial t'} = s \frac{\partial q'_i}{\partial t'}$$

The Hamiltonian needs: [...]

$$H_{\text{Nose}} = \sum_{i=1}^N \frac{p_i'^2}{2m_i s^2} + V(q) + \frac{p_s^2}{2Q} + g k_B T \ln(s)$$

Q : effective mass associated to s

g : # of degrees of freedom

This leads to extended Hamiltonian equations:

$$\frac{\partial H_{\text{Nose}}}{\partial p_i^*} = \frac{p_i^*}{m_i s^2} \quad - \frac{\partial H_{\text{Nose}}}{\partial q_i^*} = \text{grad } V(q^*) \quad \left\{ \begin{array}{l} \text{as} \\ \text{before} \end{array} \right.$$

$$\boxed{\frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} \quad - \frac{\partial H_{\text{Nose}}}{\partial s} = \frac{1}{s} \left(\sum_i \frac{p_i^*}{m_i s^2} - g k_B T \right)}$$

Consequences:

- This extended Hamiltonian H_{Nose} is conserved upon evolution according to the extended Hamiltonian equation
 \Rightarrow microcanonical ensemble of this extended system
- It can be shown that the microcanonical ensemble averages of the extended system are identical to the canonical ensemble averages of the original Hamiltonian (ensured by the choice of $g \ln(T/k_B)$)
- The time of the variable s depends on the choice of Q and can be interpreted as a coupling frequency.

8.3 Velocity Rescaling and Gaussian thermostat

The easiest: just rescale all velocities

$$p_i \mapsto \sqrt{\frac{T_0}{T}} p_i \quad \begin{array}{l} T_0: \text{desired temperature} \\ T: \text{the actual temp.} \end{array}$$

\Rightarrow ok, but leads to discontinuities in the momentum part of the phase space trajectory