

Course 06/1

Sampling the canonical ensemble.

- Temperature fluctuations in the canonical ensemble
- Extended Lagrangian of Nosé
- Sampling the canonical ensemble
- Average of physical quantity $A (\{ p \}, \{ r \})$

Constant temperature ?

Simple....., impose $T_{\text{inst}} = T_{\text{target}}$:

$$kT_{\text{inst}} = \frac{2 E_{\text{kin}}}{f} \quad \text{where} \quad E_{\text{kin}} = \sum_{I=1}^N \frac{1}{2} m v_I^2$$

Just scale all the velocities by an appropriate scaling factor α :

$$\vec{v}_I \rightarrow \alpha \vec{v}_I$$

However, this approach does not correspond to the canonical ensemble because the fluctuations of the temperature would be vanishing!

Temperature fluctuations in the canonical ensemble

The temperature is obtained as an average over the instantaneous temperature, which depends on the kinetic energy of the particles:

$$T = \langle T_{\text{inst}} \rangle \quad \text{where} \quad T_{\text{inst}} \propto \sum_i p_i^2$$

A measure of the fluctuations of the temperature is given by

$$\begin{aligned} \frac{\langle (T_{\text{inst}} - \langle T_{\text{inst}} \rangle)^2 \rangle}{\langle T_{\text{inst}} \rangle^2} &= \frac{\langle T_{\text{inst}}^2 \rangle - \langle T_{\text{inst}} \rangle^2}{\langle T_{\text{inst}} \rangle^2} = \frac{\langle (\sum_i p_i^2)^2 \rangle - (N \langle p^2 \rangle)^2}{(N \langle p^2 \rangle)^2} \\ &= \frac{\langle \sum_{i,j} p_i^2 p_j^2 \rangle - (N \langle p^2 \rangle)^2}{(N \langle p^2 \rangle)^2} \\ &= \frac{N \langle p^4 \rangle + N(N-1) \langle p^2 \rangle \langle p^2 \rangle - (N \langle p^2 \rangle)^2}{(N \langle p^2 \rangle)^2} = \frac{1}{N} \frac{\langle p^4 \rangle - \langle p^2 \rangle^2}{\langle p^2 \rangle^2} \end{aligned}$$

Temperature fluctuations in the canonical ensemble

$$\frac{\langle (T_{\text{inst}} - \langle T_{\text{inst}} \rangle)^2 \rangle}{\langle T_{\text{inst}} \rangle^2} = \frac{1}{N} \frac{\langle p^4 \rangle - \langle p^2 \rangle^2}{\langle p^2 \rangle^2}$$

Maxwell-Boltzmann distribution for the canonical ensemble:

$$\mathcal{P}(p) = \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp \left(-\frac{\beta p^2}{2m} \right) \quad \text{where } \beta = 1/(k_B T)$$

$$\left. \begin{aligned} \langle p^2 \rangle &= \int d\vec{p} \, p^2 \mathcal{P}(p) = \frac{3m}{\beta} \\ \langle p^4 \rangle &= \int d\vec{p} \, p^4 \mathcal{P}(p) = 15 \left(\frac{m}{\beta} \right)^2 \end{aligned} \right\} \frac{\langle (T_{\text{inst}} - \langle T_{\text{inst}} \rangle)^2 \rangle}{\langle T_{\text{inst}} \rangle^2} = \frac{2}{3N}$$

The fluctuations are finite and depend on the number of particles N !
Only for a very large system the temperature is truly a constant!

Comparison canonical vs microcanonical

Temperature fluctuations in the canonical ensemble:

$$\frac{\langle (T_{\text{inst}} - \langle T_{\text{inst}} \rangle)^2 \rangle}{\langle T_{\text{inst}} \rangle^2} = \frac{2}{3N}$$

Temperature fluctuations in the microcanonical ensemble:

$$\frac{\langle (T_{\text{inst}} - \langle T_{\text{inst}} \rangle)^2 \rangle}{\langle T_{\text{inst}} \rangle^2} = \frac{2}{3N} \left(1 - \frac{3k_B}{2c_v} \right)$$

Lebowitz, Percus & Verlet, *Phys. Rev.* **153**, 250 (1967)

where c_v is the specific heat at constant volume.

The temperature fluctuations are larger in the canonical ensemble than in the microcanonical one!

Sampling the canonical ensemble

- Extended Lagrangian S. Nosé, *Mol. Phys.* **52**, 255 (1984)
- Nosé-Hoover thermostat W. G. Hoover, *Phys. Rev. A.* **31**, 1695 (1985)

Goal

Calculation of averages over the canonical ensemble

$$\bar{A} = \langle A(\{r_i\}, \{p_i\}) \rangle = \frac{\int dp_i^N dr_i^N A(\{r_i\}, \{p_i\}) e^{-\beta H(\{r_i\}, \{p_i\})}}{\int dp_i^N dr_i^N e^{-\beta H(\{r_i\}, \{p_i\})}}$$

Alternatively, the thermal average can be obtained by a time average provided the evolution is ergodic:

$$\bar{A} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt A(\{r_i(t)\}, \{p_i(t)\})$$

Extended Lagrangian of Nosé

- Idea: rescaling the velocities $\dot{r}_i \rightarrow s \dot{r}_i$

where s is a dynamical variable, which evolves in time.

- Lagrangian including the variable s

$$\mathcal{L}_{\text{Nosé}}(\{r_i\}, \{\dot{r}_i\}, s, \dot{s}) = \sum_{i=1}^N \frac{1}{2} m_i s^2 \dot{r}_i^2 - U(r^N) + \underbrace{\frac{1}{2} Q \dot{s}^2}_{\text{kinetic energy of } s} - \underbrace{\frac{g}{\beta} \ln s}_{\text{potential energy of } s}$$

where Q is the inertial mass associated with s .

Problem of Nosé: finding a suitable potential energy that ensures that the physical variables occupy their phase space like in the canonical ensemble.

Our approach: We define the potential energy and show that the correct behavior is ensured, $\beta = 1/(k_B T)$ and g is a parameter that remains to be determined.

Hamiltonian associated to the Lagrangian of Nosé

Nosé Lagrangian

$$\mathcal{L}_{\text{Nosé}}(\{r_i\}, \{\dot{r}_i\}, s, \dot{s}) = \sum_{i=1}^N \frac{1}{2} m_i s^2 \dot{r}_i^2 - U(r^N) + \frac{1}{2} Q \dot{s}^2 - \frac{g}{\beta} \ln s$$

Definition of the momenta associated to the dynamical variables

$$p_i = \frac{\partial \mathcal{L}_{\text{Nosé}}}{\partial \dot{r}_i} = m_i s^2 \dot{r}_i \quad p_s = \frac{\partial \mathcal{L}_{\text{Nosé}}}{\partial \dot{s}} = Q \dot{s}$$

Definition of the associated Hamiltonian

There is no explicit time dependence in the Lagrangian

$$\mathcal{H}_{\text{Nosé}} = \sum_{i=1}^N \frac{p_i^2}{2m_i s^2} + U(r^N) + \frac{p_s^2}{2Q} + \frac{g}{\beta} \ln s$$

This is a conserved quantity (constant of motion)!

It corresponds to the energy of the extended system.

Partition function of extended Nosé system

We need to “integrate away” the unphysical variables...

Microcanonical partition function of the Nosé system

$$\begin{aligned} Q_{\text{Nosé}} &= \int dp_s ds dp_i^N dr_i^N \delta[\mathcal{H}_{\text{Nosé}}(p^N, r^N, s, p_s) - E] \\ &= \int dp_s ds dp_i^N dr_i^N \delta \left[\sum_{i=1}^N \frac{p_i^2}{2m_i s^2} + U(r^N) + \frac{p_s^2}{2Q} + \frac{g}{\beta} \ln s - E \right] \end{aligned}$$

From the expression of the kinetic energy, we see that we need to define “physical” variables for the momentum:

$$p' = p/s$$

We now distinguish the physical variables p' from the virtual (or Nosé) variables p .

Change of variable in the integral of the partition function

$$Q_{\text{Nosé}} = \int dp_s ds dp_i'^N dr_i^N s^{3N} \delta \left[\sum_{i=1}^N \frac{p_i'^2}{2m_i} + U(r^N) + \frac{p_s^2}{2Q} + \frac{g}{\beta} \ln s - E \right]$$

Partition function of extended Nosé system

$$Q_{\text{Nosé}} = \int dp_s ds dp_i'^N dr_i^N s^{3N} \delta \left[\sum_{i=1}^N \frac{p_i'^2}{2m_i} + U(r^N) + \frac{p_s^2}{2Q} + \frac{g}{\beta} \ln s - E \right]$$

Integration of δ function: we take the argument of the δ function as a function h of s :

$$\delta[h(s)] = \frac{\delta(s - s_0)}{|h'(s)|} \quad \text{where} \quad h'(s) = \frac{\partial h}{\partial s} = \frac{g}{\beta s}$$

and s_0 is determined by $h(s_0) = 0$:

$$s_0 = \exp \left[-\frac{\beta}{g} \left(\sum_{i=1}^N \frac{p_i'^2}{2m_i} + U(r^N) + \frac{p_s^2}{2Q} - E \right) \right]$$

The partition function becomes :

$$\begin{aligned} Q_{\text{Nosé}} &= \int dp_s ds dp_i'^N dr_i^N \frac{\beta s^{3N+1}}{g} \delta(s - s_0) \\ &= \int dp_s dp_i'^N dr_i^N \frac{\beta s_0^{3N+1}}{g} \end{aligned}$$

Partition function of extended Nosé system

$$\begin{aligned}
 Q_{\text{Nosé}} &= \int dp_s dp_i'^N dr_i^N \frac{\beta s_0^{3N+1}}{g} \\
 &= \int dp_s dp_i'^N dr_i^N \frac{\beta}{g} \exp \left[- \frac{(3N+1)\beta}{g} \left(\sum_{i=1}^N \frac{p_i'^2}{2m_i} + U(r^N) + \frac{p_s^2}{2Q} - E \right) \right] \\
 &\quad \underbrace{\hspace{10em}}_{\text{constant } C} \\
 &= \frac{\beta}{g} \exp \left[\frac{(3N+1)\beta}{g} E \right] \int dp_s \exp \left[- \frac{(3N+1)\beta}{g} \frac{p_s^2}{2Q} \right] \\
 &\quad \times \int dp_i'^N dr_i^N \exp \left[- \frac{(3N+1)\beta}{g} \mathcal{H}^{\text{PHYS}}(p'^N, r^N) \right]
 \end{aligned}$$

where

$$\mathcal{H}^{\text{PHYS}}(p'^N, r^N) = \sum_{i=1}^N \frac{p_i'^2}{2m_i} + U(r^N)$$

Average of a physical quantity $A(p', r)$

Partition function of extended Nosé system with fictitious variables integrated out

$$Q_{\text{Nosé}} = C \int dp_i'^N dr_i'^N \exp \left[-\frac{(3N+1)\beta}{g} \mathcal{H}^{\text{PHYS}}(p'^N, r^N) \right]$$

Ensemble average of $A(p', r)$

$$\langle A(p'^N/s, r^N) \rangle_{\text{Nosé}} = \frac{\int dp_i'^N dr_i'^N A(p'^N, r^N) \exp \left[-\frac{(3N+1)\beta}{g} \mathcal{H}^{\text{PHYS}}(p'^N, r^N) \right]}{\int dp_i'^N dr_i'^N \exp \left[-\frac{(3N+1)\beta}{g} \mathcal{H}^{\text{PHYS}}(p'^N, r^N) \right]}$$

physical variables

We obtain the correct canonical average for $g = 3N + 1$!!

Average of a physical quantity $A(p',r)$

In practice, the ensemble average is obtained through a time average achieved through molecular dynamics taking advantage of the ergodicity of the system

$$\bar{A} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} dt A(p^N(t)/s(t), r^N(t)) = \langle A(p^N/s, r^N) \rangle_{\text{Nosé}}$$

Nosé time

variables present in Nosé Lagrangian and following a deterministic evolution (virtual)

Control of temperature in MD

S. Nosé, *Mol. Phys.* **52**, 255 (1984)

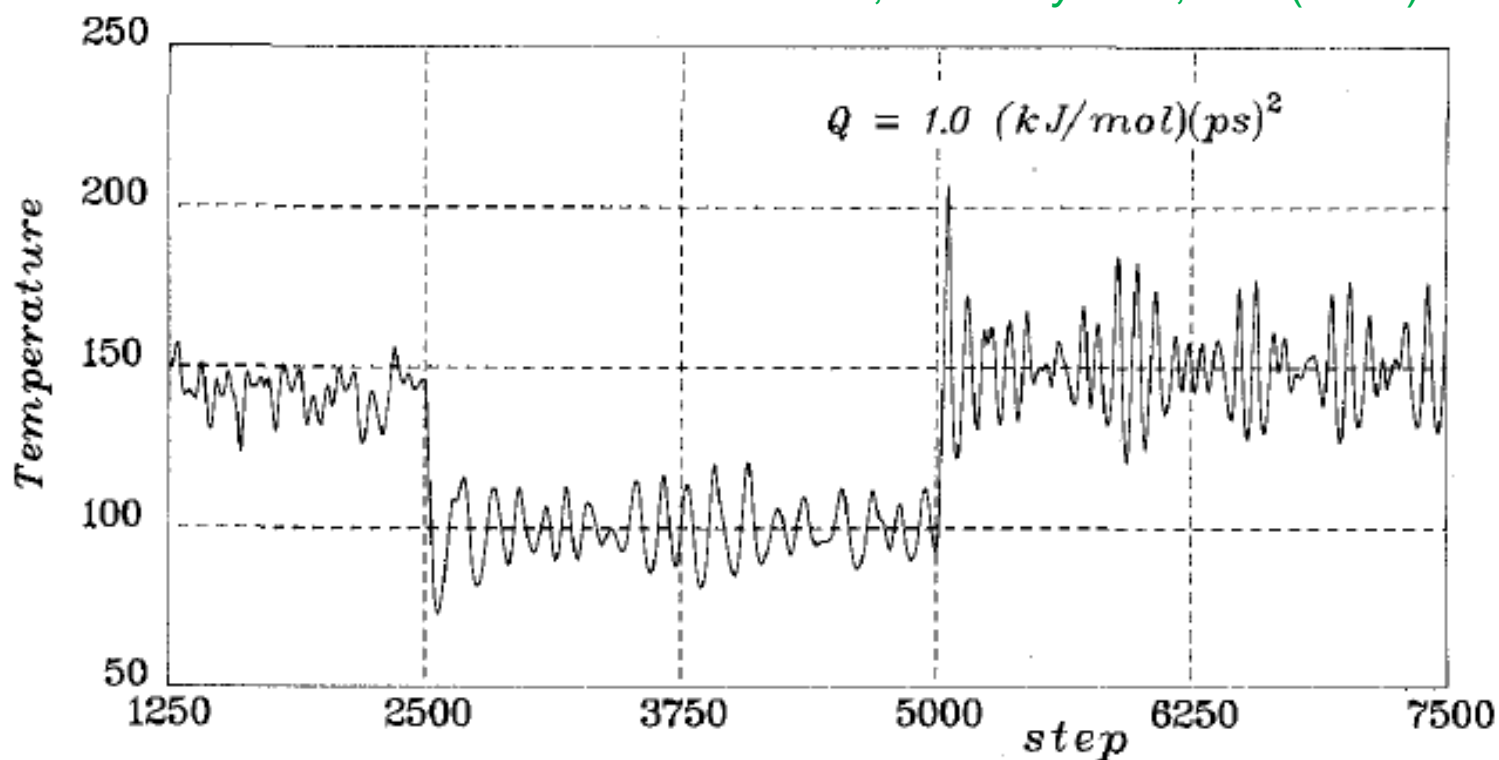


Figure 1. Evolution of the temperature. The first 1250 steps shown (1250–2500 step) are carried out with the standard MD method. At step 2500, the simulation is changed to the constant temperature method with $T_{eq} = 100$ K. At step 5000, T_{eq} is changed to 150 K.

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