NVE .v.s NVT ensembles

In an NVE emsemble, the system is isolated from its surroundings. Hence, the total energy (E) of the system is the sum of kinetic (KE) and potential energies (PE). Since there is no energy exchange between the system and its environment, the total energy E should always be conserved in an NVE ensemble.

In contrast, the NVT ensemble allows the system to exchange heat with a reservoir (R). Due to these heat exchanges, the total energy of the system can vary over time. Suppose at time t_1, the total energy is measured as E_1, and at time t_2, it is measured as E_2. How do we calculate the probability of observing E_1 and E_2 in subsequent time frames? For convenience, we denote these probabilities as $p(E_1)$ and $p(E_2)$. We can derive these probabilities with the help of statistical mechanics.

In the context of statistical mechanics, we track each particle (i) in terms of its position ($\mathbf{r}_i$) and momentum ($\mathbf{p}_i$), giving us a total of six numbers for each particle. Each unique snapshot of $\{\mathbf{p}_i, \mathbf{r}_i\}$ is referred to as a microstate. It is possible for a group of microstates to share the same total energy. This group of microstates is called a macrostate, and the number of microstates in a macrostate is referred to as its multiplicity (Ω).

> ### A Toy example of microstate/macrostate/multiplicity.
>
> Image you are flipping three coins multiple times and count the statistics of heads and tails. There are 8 possible combinations: HHH, HHT, HTH, THH, HTT, TTH, THT, TTT. While we are not concerned with the specific sequences, we are interested in the total counts. This means we have 8 microstates in total but only 3 types of macrostates:
>
> - 1 occurrence of 3 heads (HHH), thus $\Omega(3H) = 1$,
>
> - 3 occurrences of 2 heads (HHT, HTH, THH), thus $\Omega(2H) = 3$,
>
> - 3 occurrences of 1 head (HTT, TTH, THT), thus $\Omega(1H) = 3$,
>
> - 1 occurrence of 0 heads (TTT), thus $\Omega(0H) = 1$,

Returning to our original problem, the ratio of $p(E_1)/p(E_2)$ depends on the multiplicities $\Omega(E_1)/\Omega(E_2)$.

$$\frac{P(E_2)}{P(E_1)} = \frac{\Omega(E_2)}{\Omega(E_1)} \approx \frac{\Omega_R(E_2)}{\Omega_R(E_1)} \tag{0.1}$$

> ### Why do we look at the reservoir?
>
> Here we consider an isolated system, consisting of a reservoir and a system, and the reservoir is much bigger than the system. So the actual $\Omega = \Omega_R \Omega_S$, can be approximated by Ω_R. One can intuitively think the majority of mutiplicity should be done by the reseroir.

There is a famous entropy equation, $S = k_B \ln \Omega$,

$$\frac{P(E_2)}{P(E_1)} = \frac{e^{S_R(E_2)/k_B}}{e^{S_R(E_1)/k_B}} = e^{[S_R(E_2) - S_R(E_1)]/k_B} \tag{0.2}$$

> **The relation between S and U under NVT.**
>
> From the **microscopic** view, the system reach an equilibrium when it has the largest entropy. So the change of entropy can be counted as a function of (U, V, N)
>
> $$dS = \frac{1}{T}[dU + PdV - \mu dN] = \frac{dU}{T} \quad \textbf{NVT ensemble}$$
>
> From the **macroscopic** view, you can also think it from the 1st raw.
> Since the change of energy (dU) can be either from Work $(pdV$, omitted at a constant V) or a heat transfer (TdS), so $dU = TdS$ at the NVT ensemble.

For simplicity, we can ignore PdV and μdN terms (since N and V do not change). Thus,

$$dS_R = \frac{1}{T}[U_R(E_2) - U_R(E_1)] \tag{0.3}$$

Note that $U(E_2) + U_R E_2$ should be conserved. Therefore, we have:

$$\frac{P(E_2)}{P(E_1)} = \frac{e^{-E_2/k_B T}}{e^{-E_1/k_B T}} = e^{-(E_2 - E_1)/k_B T} \tag{0.4}$$

In conclusion, the probability of each state in a canonical ensemble (NVT) is proportional to an exponential term:

$$P(s) \propto e^{-E(s)/k_B T} \quad \Rightarrow \quad P(s) = \frac{1}{Z} e^{-E(s)/k_B T} \tag{0.5}$$

where Z is the normalization constant, also known as the **Partition function**.

If we sum over all possible states (e.g., $s_1, s_2, \cdots$), $\sum_{i=1}^{N} p(s_i) = 1$. Thus, $Z = \sum e^{-E(s)/k_B T}$.

In the NVT ensemble, E can take different values, and the probability follows the relation of $e^{-E/k_B T}$, also called Boltzmann distribution.

Next, we will explore the Nose-Hoover thermostat technique to generate an NVT-like distribution by introducing an external variable (e.g., a time-dependent velocity scaling parameter) to the system. **During this propagation, we aim to ensure that the system's total energy follows the NVT distribution with a partition function Z resembling $e^{-E/k_B T}$.**

Partition function of the extended system

So far we have discussed how to perform integration. But we haven't proof why is this formula can ensure an NVT ensemble. Following the definition in eq. 0.9, the corresponding Hamiltonian is

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2ms^2} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gk_B T \ln(s) \tag{0.6}$$

To ensure a canonical ensemble, we want to make the probability of observing the total energy of E is $p(E) \propto \exp(-E/kT)$.

If we proceed to compute the partition function Z for the given H

$$
\begin{aligned}
Z &= \frac{1}{N!} \int dp_s ds d\mathbf{p}^N d\mathbf{r}^N \delta(H - E) \\
&= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N} \delta\left(\sum_{i=1}^N \frac{\mathbf{p}_i'^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gk_B T \ln(s) - E \right) \\
&= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N} \delta\left(\sum_{i=1}^N H^0 + \frac{p_s^2}{2Q} + gk_B T \ln(s) - E \right)
\end{aligned}
\tag{0.7}
$$

Note that here we defined

$$
\mathbf{p}' = \mathbf{p}/s
$$

and

$$
H^0 = \frac{\mathbf{p}_i'^2}{2m} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)
$$

Now let

$$
f(s) = \sum_{i=1}^N H^0 + \frac{p_s^2}{2Q} + gk_B T \ln(s)
$$

and

$$
s_0 = \exp\left[-\frac{H^0 + p_s^2/2Q}{gk_B T} \right] \qquad \leftarrow \quad f(s_0) = 0
$$

$$
f'(s_0) = \frac{gk_B T}{s}
$$

$$
\delta(f(s)) = \delta(s - s_0)/f'(s_0)
$$

Plugin them back to Z (eq. 0.7)

$$
\begin{aligned}
Z &= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N} \frac{s}{gk_B T} \delta\left(s - \exp\left[-\frac{H^0 + p_s^2/2Q - E}{gk_B T} \right] \right) \\
&= \frac{1}{N!} \frac{1}{gk_B T} \int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N+1} \delta\left(s - \exp\left[-\frac{H^0 + p_s^2/2Q - E}{gk_B T} \right] \right) \\
&= \frac{1}{N!} \frac{1}{gk_B T} \int dp_s d\mathbf{p}'^{3N} d\mathbf{r}^{3N} ds s^{3N+1} \delta\left(s - \exp\left[-\frac{H^0 + p_s^2/2Q - E}{gk_B T} \right] \right) \\
&= \frac{1}{N!} \frac{1}{gk_B T} \int dp_s d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left[\left(-\frac{H^0 + p_s^2/2Q - E}{gk_B T} \right) * (3N+1) \right] \\
&= \frac{1}{N!} \frac{1}{gk_B T} \int dp_s \exp\left[\left(-\frac{p_s^2/2Q - E}{gk_B T} \right) * (3N+1) \right] \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left[-\frac{H^0(\mathbf{p}', \mathbf{r}')}{gk_B T} * (3N+1) \right] \\
&= \frac{1}{N!} \frac{1}{gk_B T} \int dp_s \exp\left[\left(-\frac{p_s^2/2Q - E}{gk_B T} \right) * (3N+1) \right] \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left[-\frac{3N+1}{g} \frac{H^0(\mathbf{p}', \mathbf{r}')}{k_B T} \right] \\
&= C \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left(-\frac{3N+1}{g} \frac{H^0(\mathbf{p}', \mathbf{r}')}{k_B T} \right) \\
&= C \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left(\frac{-H^0}{k_B T} \right) \quad \text{(when} \quad g = 3N+1)
\end{aligned}
\tag{0.8}
$$

The p_s part gives a constant dependent on the parameters E, T, Q and g. If we choose $g = 3N + 1$, the partition function Z of the extended system is equivalent to that of the physical system in the canonical ensemble Z_c except for a constant factor, $Z = CZc$. Hence, this approach maintains the system at a desired temperature, allowing it to sample from the canonical ensemble, making the Nose-Hoover thermostat an effective tool for molecular dynamics simulations that require temperature control.

The Nose-Hoover thermostat

The Nose-Hoover thermostat is derived from an extended Lagrangian formalism introduced by Nose, which was later reformulated by Hoover. The idea is to extend the original systems degrees of freedom by introducing an additional variable that acts as a thermal reservoir, allowing the system to exchange energy with this reservoir to maintain the desired temperature. This extended system is then transformed into a form suitable for numerical integration in molecular dynamics.

The Extended Lagrangian by Nose

Nose introduced an extended system by defining a new Lagrangian that includes an additional degree of freedom s , which scales time and allows for the system to fluctuate in a way that mimics the thermal fluctuations in the canonical ensemble. The extended Lagrangian L for a system of N particles is given by:

$$L = \sum_{i=1}^{N} \frac{m_i \dot{\mathbf{r}}_i^2}{2s^2} - U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) + \frac{Q\dot{s}^2}{2} - gk_B T \ln(s) \tag{0.9}$$

where:

- $\mathbf{r}_i$ is the position of the ith particle,

- $\dot{\mathbf{r}}_i$ is the velocity of the ith particle,

- m_i is the mass of the ith particle,

- U is the potential energy,

- s is the time scaling factor,

- $\dot{s}$ is the derivative of s with respect to time,

- Q is a fictitious mass associated with the variable s

- $g = 3N + 1$ (the degrees of freedom plus 1 for the additional s variable),

- T is the desired temperature,

- k_B is the Boltzmann constant.

Using the Euler-Lagrange equations, the equations of motion can be derived from the extended Lagrangian. The generalized coordinates are $\mathbf{r}_i$ and s .

The Euler-Lagrange equation is:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0$$

Applying this to each coordinate:

(a) For $\mathbf{r}_i$:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\right) - \frac{\partial L}{\partial \mathbf{r}_i} = 0$$

This gives:

$$\frac{d}{dt}\left(\frac{m_i \dot{\mathbf{r}}_i}{s^2}\right) = -\frac{\partial U}{\partial \mathbf{r}_i}$$

$$m_i \ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i} - m_i \frac{\dot{s}}{s} \dot{\mathbf{r}}_i$$

(b) For s :

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{s}}\right) - \frac{\partial L}{\partial s} = 0$$

This gives:

$$Q\ddot{s} = \sum_{i=1}^{N} \frac{m_i \dot{\mathbf{r}}_i^2}{s^3} - \frac{gk_B T}{s}$$

$$Q\ddot{s} = \frac{2K}{s} - \frac{gk_B T}{s}$$

where $K = \sum_{i=1}^{N} \frac{m_i \dot{\mathbf{r}}_i^2}{2}$ is the kinetic energy.

Hoovers Reformulation

Hoover simplified Nose's formulation by transforming the equations into the physical time scale, effectively eliminating the explicit dependence on the variable s .

Define a new time variable t' related to s by $dt' = sdt$. In this new time scale, the velocities $\mathbf{v}_i$ are related to the original velocities by $\mathbf{v}_i\prime = \mathbf{v}_i/s$.

The equations of motion become:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i$$

$$\frac{d\mathbf{v}_i}{dt} = \frac{\mathbf{F}_i}{m_i} - \zeta \mathbf{v}_i$$

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$$\frac{d\xi}{dt} = \frac{1}{Q}\left(\frac{2K}{Nk_BT} - 1\right)$$

where $\zeta = \frac{\dot{s}}{s}$ is the friction coefficient, and Q is the thermal inertia parameter.

The variable ζ dynamically adjusts the particle velocities to control the temperature of the system. If the kinetic energy is higher than the target value (indicating a temperature higher than desired), ζ increases, applying a damping force to reduce the velocities. Conversely, if the kinetic energy is too low, ζ decreases, allowing the velocities to increase.