NVE .v.s NVT ensembles

In a NVE system, the system is isolated from anywhere else. Hence, the total energy (E) of the system is the sum of kinetic (KE) and potential energies (PE). Since there is no energy transfer between the system and external, *E should be always a conserved value in NVE.*

For the NVT ensemble, the system is set to allow a heat exchange with the reservoir (R). Due to the heat exchanges, the total energy of the system can vary with time. Suppose at time t_1, you measure the total energy found it has a value of E_1, and E_2 at the time t_2. How do we count the probability of seeing E_1 and E_2 in the following time frames? For convenience, we will denote them as $p(E_1)$ and $p(E_2)$. Here we can derive it with a bit help of statistic mechanics.

In the context of statistic mechanics, we keep track of each particle (i) in term of positions ($\mathbf{r}_i$) and momentum ($\mathbf{p}_i$), and hence we will have a total of 6 numbers for each particle. Each individual snapshot of $\{\mathbf{p}_i, \mathbf{r}_i\}$ can be counted as a microstate. It is possible that a group of microstates will have the same total energy. We call this group of microstates as macrostate and the number of microstates as multiplicity (Ω).

An analogical example is that you can flip three coins can count the statistics in terms of the occurrence of heads and tails. In total, there will be 8 combinations, HHH, HHT, HTH, THH, HTT, TTH, THT, TTT. In principle, we are not interested in the details of sequence, but only interested in the total counts. This means we have 8 microstates in total, but only 3 kinds of macrostates, including 1 occurrence of 3 heads (HHH), 3 occurrences of 2 heads (HHT, HTH, THH), 3 occurrences of 1 head (HHT, HTH, THH), 1 occurrences of 0 head. Namely, $\Omega(3H) = \Omega(0H) = 1$ and $\Omega(2H) = \Omega(1H) = 3$.

Back to the problem, the ration of $p(E_1)/p(E_2)$ depends on the measured multiplicity $\Omega(E_1)/\Omega(E_2)$. The corresponding multiplicities of the reservoir are $\Omega_R(s_1)$ and $\Omega_R(s_2)$.

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

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

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

According to the thermodynamic identify (you must learn from the Physics Thermodynamics course),

$$dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R) \tag{0.3}$$

For simplicity, let's ignore PdV and μdN (since N and V don't change).

$$dS_R = \frac{1}{T}(U_R(E_2) - U_R(E_1)) \tag{0.4}$$

Therefore, we have,

$$\frac{P(E_2)}{P(E_1)} = \frac{e^{-E(E_2)/kT}}{e^{-E(E_1)/kT}} = e^{(E_2 - E_1)/kT} \tag{0.5}$$

Now we conclude that the probability of each state under a canonical ensemble (NVT) is proportional to the exponential terms.

$$P(s) \propto e^{-E(s)/kT} \rightarrow P(s) = Z - E(s)/kT \tag{0.6}$$

where Z is the scaling constant, which is also called partition function.

If you count all possible states (e.g., $s_1, s_2, \cdots$), $\sum_i = 1^N p(s_i) = 1$. So $Z = \sum e^{-E(s)/kT}$

In NVT, E can take different values and the probability follows the Boltzmann distribution $e^{-E/kT}$.

In the following, we explore Nose-Hoover thermostat technique to generate a NVT like distribution by adding an external variable (e.g., the time-dependent velocity scaling parameter) to the system. During the propagation, we hope to make the system's total energy follows the NVT distribution. By doing so, we make sure the desired partition function Z will look like $e^{-E/kT}$).

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:

$$L = \sum_{i=1}^{N} \frac{m_i \dot{\mathbf{r}}_i^2}{2s^2} - U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) + \frac{Q\dot{s}^2}{2} - gk_B T \ln(s) \tag{0.7}$$

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:

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

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

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 $\mathbf{v}_i' = \mathbf{v}_i/s$.

The equations of motion become:

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

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

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

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.

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. 0.7, the corresponding Hamiltonian is

$$H = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2ms^2} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gk_BT\ln(s) \tag{0.8}$$

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

$$
\begin{aligned}
Z &= \frac{1}{N!}\int dp_s ds d\mathbf{p}^N d\mathbf{r}^N \delta(H - E) \\
&= \frac{1}{N!}\int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N} \delta\left(\sum_{i=1}^{N}\frac{\mathbf{p}_i'^2}{2ms^2} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) + \frac{p_s^2}{2Q} + gk_BT\ln(s) - E\right) \\
&= \frac{1}{N!}\int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N} \delta\left(\sum_{i=1}^{N} H^0 + \frac{p_s^2}{2Q} + gk_BT\ln(s) - E\right)
\end{aligned}
\tag{0.9}
$$

Note that here we defined

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

and

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

Now let

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

and

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

$$f'(s_0) = \frac{gk_BT}{s}$$

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

Plugin them back to Z (eq. 0.9)

$$
\begin{aligned}
Z &= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N} \frac{s}{gk_BT} \delta\left(s - \exp\left[-\frac{H^0 + p_s^2/2Q - E}{gk_BT}\right]\right) \\
&= \frac{1}{N!} \frac{1}{gk_BT} \int dp_s ds d\mathbf{p}'^{3N} d\mathbf{r}^{3N} s^{3N+1} \delta\left(s - \exp\left[-\frac{H^0 + p_s^2/2Q - E}{gk_BT}\right]\right) \\
&= \frac{1}{N!} \frac{1}{gk_BT} \int dp_s d\mathbf{p}'^{3N} d\mathbf{r}^{3N} ds\, s^{3N+1} \delta\left(s - \exp\left[-\frac{H^0 + p_s^2/2Q - E}{gk_BT}\right]\right) \\
&= \frac{1}{N!} \frac{1}{gk_BT} \int dp_s d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left[\left(-\frac{H^0 + p_s^2/2Q}{gk_BT}\right) * (3N+1)\right] \\
&= \frac{1}{N!} \frac{1}{gk_BT} \int dp_s \exp\left[\left(-\frac{p_s^2/2Q - E}{gk_BT}\right) * (3N+1)\right] \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left[-\frac{H^0(\mathbf{p}',\mathbf{r}')}{gk_BT} * (3N+1)\right] \\
&= \frac{1}{N!} \frac{1}{gk_BT} \int dp_s \exp\left[\left(-\frac{p_s^2/2Q - E}{gk_BT}\right) * (3N+1)\right] \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left[-\frac{3N+1}{g}\frac{H^0(\mathbf{p}',\mathbf{r}')}{k_BT}\right] \\
&= C \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left(-\frac{3N+1}{g}\frac{H^0(\mathbf{p}',\mathbf{r}')}{k_BT}\right) \\
&= C \int d\mathbf{p}'^{3N} d\mathbf{r}^{3N} \exp\left(\frac{-H^0}{k_BT}\right) \quad \text{(when} \quad g = 3N+1\text{)}
\end{aligned}
$$

$$(0.10)$$

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, $Z = CZ_c$. 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.