Chapter 2. Molecular Dynamics in Various Ensembles

**Microcanonical Ensemble:** when the simulated system is isolated from the rest of universe or it forms its own universe, samples taken from all the phase space \((p, q)\) form a microcanonical ensemble.

Constraints: 1. Total energy is conserved; \((E)\)
2. The number of basic particles is conserved; \((N)\)
3. There is a boundary limit. \((V)\)

also called \((NVE)\) ensemble.
Basic Thermodynamics

Equilibrium: when samples can be meaningfully used for state-function (thermodynamic property) measurements, system is in equilibrium.

1. It is a relative concept, dependent on overall sampling length.
2. It is a concept conditioned by ergodic requirements.
Basic Thermodynamics

Second law of thermodynamics: maximum entropy theorem

During the course of system’s approaching the equilibrium state, entropy is maximized when the total energy is conserved. (NVE)

Alternative: **minimum energy theorem**
During the course of system’s approaching the equilibrium state, energy is minimized when the entropy is conserved (NVS).

Entropy: a measure of system diversity (disorder).

\[
dS = \left(\frac{dQ}{T}\right)_{resversible}
\]
\[
dE = dQ + dW
\]
\[
dV = 0, dW = 0
\]
\[
1/T = \left(\frac{dS}{dE}\right)_{N,V}
\]
Molecular Dynamics

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Basic Thermodynamics – Statistical Mechanics

For a large subset of a huge system, in the equilibrium state,

Total $E = E_1 + E_2$ under mean field condition

If $\Omega(E,V,N)$ represents the occurrence probability (or degeneracy)

$$\Omega(E,V,N) = \sum_{\Gamma} \delta(H(\Gamma) - E)$$

$$S = k \ln \Omega$$
For a large subset of a huge system, in the equilibrium state,

\[ \text{Total } E = E_1 + E_2 \text{ under mean field condition} \]

\[ S = k \ln \Omega \]

\[ \left( \frac{\partial k \ln \Omega(E_1, E - E_1)}{\partial E_1} \right)_{N,V,E} = 0 \]

\[ \left( \frac{\partial k \ln \Omega(E_1, V, N)}{\partial E_1} \right)_{N,V,E} = \beta \]

\[ \beta = 1/(kT) \]
Basic Statistical Mechanics

Simple example: (NVE)

Two state potential energy function: $E = (E_0, E_1)$ for two recognizable particles
Total energy $E_0 + E_1$

$$\Omega = 2$$

$$s = k \ln 2$$

$$k = 1.38E - 23$$
Basic Statistical Mechanics

Simple example: (NVE)

Two state potential energy function: \( E = (0, E_0, E_1, E_0 + E_1) \) for two recognizable particles. Total energy \( E_0 + E_1 \)

\[
\Omega = 4
\]

\[
s = k \ln 4
\]

\[
k = 1.38E - 23
\]
Microcanonical Ensemble in MD simulation:

1. The occurrence probability is independent of subset of energies.
2. Ensemble property is dependent on the maximum entropy.
3. Easy to implement.
4. Difficult to control macroscopic condition.
5. It can be used as thermo reservoir for canonical ensemble simulations.
Canonical Ensemble: when the simulated system is embedded in an infinite heat bath, but does not have particle exchange with this bath, it forms a canonical ensemble.

Constraints: 1. System temperature is conserved (not absolutely constant); (T)
   2. The number of basic particles is conserved; (N)
   3. There is a boundary limit (V); or there is a constant pressure (P)

also called (NVT) ensemble or (NPT) ensemble.
Canonical Ensemble

Canonical ensemble can be considered as a sub-microcanonical ensemble, where particle collisions occur on the “boundary”.

In practice, the temperature buffer region can be flexibly designed and its boundary with the simulated region can also be flexibly designed.

Centers of canonical ensemble algorithm developments
Canonical Ensemble

Canonical ensemble can be derived from microcanonical ensemble, too.

\[ E = E_A + E_B \]

For a given system energy \( E_A \), reservoir probability determines its probability.

\[ \Omega(E - E_A) \]

In micro-canonical ensemble, higher energy has larger probability. Why?

So lower system energy should have larger probability. Why?
Canonical Ensemble

\[ E = E_A + E_B \]

For a given system energy \( E_A \), reservoir probability determines its probability.

Because simulated system is much smaller than the buffer portion, Taylor expansion:

\[ \ln \Omega(E - E_A) = \ln \Omega(E) - E_A \frac{\partial \ln \Omega(E)}{\partial E} = \ln \Omega(E) - \frac{E_A}{kT} \]

Probability for the system with energy \( E_A \):

\[ P(E_A) = \frac{\exp(-E_A / kT)}{\sum_i \exp(-E_i / kT)} \]
We should learn from this derivation on canonical ensemble algorithm design:

1. The thermal reservoir is essential, because it governs the Boltzmann distribution.

2. The thermal volume of the thermal reservoir should be large enough to reflect the Taylor expansion.

Canonical Ensemble

\[ P(E_A) = \frac{\exp(-E_A / kT)}{\sum_i \exp(-E_i / kT)} \]
Temperature in Canonical Ensemble

\[ \langle E_K \rangle = \frac{3}{2} NkT \]

Canonical ensemble is not absolutely constant-temperature or isokinetic ensemble.

Maxwell-Boltzmann distribution:

\[ \rho(|p|) = \left( \frac{\beta}{2\pi m} \right)^{3/2} \exp \left[ -\beta \frac{|p|^2}{2m} \right] \]
Thermal Reservoir Algorithm Design

- Reservoir can be flexible, represented by other natures of particle, force, or interactions.

2. Coupling boundary can also be flexible, not restrained by the spatial boundary.

3. Computation overhead should be small.

The Simplest Algorithm: Velocity Re-scaling

\[ \Delta T = \frac{1}{2} \sum_{i=1}^{N} \frac{2}{3} m_i (\lambda v_i)^2 - \frac{1}{2} \sum_{i=1}^{N} \frac{2}{3} m_i v_i^2 \]

\[ \Delta T = (\lambda^2 - 1)T(t) \]

\[ \lambda = \sqrt{T_{new}/T(t)} \]

\[ T_{new} = T_{target} \]
Molecular Dynamics

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The Simplest Algorithm: Velocity Re-scaling

1. Not real canonical ensemble, although it is close.

2. Maxwell-Boltzmann distribution can not be guaranteed. Scaling frequency is not robust (ad hoc).

3. Propagation stability can be destroyed.

4. How to make judgments during the simulations?

   kinetic energy and potential energy exchange.
Velocity Re-scaling scheme has absolute target temperature every time-step.

To generate a temperature fluctuation, the difference between the target temperature and the instantaneous temperature can be used to drive the temperature change

\[
\frac{dT(t)}{dt} = \frac{1}{\tau} (T_{bath} - T(t))
\]

The temperature change between successive time steps is:

\[
\Delta T = \frac{\delta t}{\tau} (T_{bath} - T(t))
\]
In practice, we need to perform a temperature dependent velocity rescaling:

\[ \lambda^2 = 1 + \frac{\delta t}{\tau} \left( \frac{T_{\text{bath}}}{T(t)} - 1 \right) \]

When the coupling parameter is equal to the time step, Berendsen thermostat is equivalent to the velocity rescaling method.

For large uniform systems, scaling ratio \( \delta t / \tau = 0.0025 \) can produce a pseudo Maxwell-Boltzmann Distribution.
Local Temperature Trapping

The temperature fluctuation is important for the trapped kinetic energy to be released.

When a large scaling ratio is applied, the temperature fluctuation will be prohibited.

When a small scaling ratio is applied, the temperature averaging can not be easily guaranteed.

Intrinsic problem: thermo-diffusivity is low.
Stochastic Collision method:
Anderson Thermostat

The velocities of randomly selected particles are randomly reset, based on Maxwell-Boltzmann distribution.

**Random selection:** if random number $[0, 1] > \nu dt$,
\[ \nu \] is stochastic collision frequency.
\[ dt \] is the time step.
the corresponding particle is selected.

**Random Reset:** Gaussian(velocity) based on Maxwell-Boltzmann distribution.
**Integration: Velocity Verlet Algorithm**

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<th>t-Δt</th>
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<tr>
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Given current position, velocity, and force
Molecular Dynamics

Integration: Velocity Verlet Algorithm

Compute new position
Integration: Velocity Verlet Algorithm

Compute velocity at half step
Integration: Velocity Verlet Algorithm

Compute force at new position
Integration: Velocity Verlet Algorithm

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<th>t-$\Delta t$</th>
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<tr>
<td>r</td>
<td></td>
<td>Compute velocity at full step</td>
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<tr>
<td>v</td>
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At this step, some particles’ velocities will be reset based on the Anderson formulation.
Molecular Dynamics

Integration: Velocity Verlet Algorithm

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<th>t-2(\Delta t)</th>
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Advance to next time step, repeat
The Anderson process is equivalent to the Monte Carlo move.

This process becomes a Markov process (no memory). And the canonical distribution (Boltzmann distribution) can be guaranteed.

**Question:** Can we provide random input from Force rather than Velocity? If so, which integrator is ideal? What is the advantage and What is the disadvantage?
Stochastic Collision method: 
Anderson Thermostat

Frequency influence on the phase space exploration:

If frequency is too high, collision will dominate and inhibit an efficient exploration of the phase space to meet the ergodic requirement.

If frequency is too low, the canonical distribution will be formed slowly to meet the canonical requirement.

Suggested collision rate:

\[
\frac{C\lambda_T}{\rho^{1/3} N^{2/3}}
\]
Any targeted property: temperature, pressure, energy difference, geometry, ... can be coupled to the original Hamiltonian to achieve the desired distributions.

It is equivalent to the biased Monte Carlo.
Nose-Hoover Thermostat

\[ H_{\text{extended}} = U_o + \sum_{i=1}^{N} \frac{p_i^2}{2m_i s_r^2} + \frac{1}{2} M_r \left| \frac{ds_r}{dt} \right|^2 + L \frac{\ln s_r}{\beta} \]

1. \( s_r \) has to be greater than 1. (Lagrangian multiplier)

2. \( s_r \) plays a role in rescaling the time-step.

3. So, the real time step fluctuates.

4. The Q is equivalent to the Q of the canonical ensemble.
Grand Canonical Ensemble

Grand Canonical Ensemble: when the simulated system is embedded in an infinite heat bath, and can exchange particle with the infinite particle reservoir, it forms a grand canonical ensemble.

Constraints: 1. System temperature is conserved (not absolutely constant); \( T \)
   2. The chemical potential of the particle reservoir is constant \( \mu \)
   3. There is a boundary limit \( V \); or there is a constant pressure \( P \)

also called (GVT) ensemble or (GPT) ensemble.
Grand Canonical Ensemble

Canonical ensemble can be considered as a sub-microcanonical ensemble, where particle collisions and exchanges occur on the “boundary”.

In practice, the reservoir buffer region can be flexibly designed and its boundary with the simulated region can also be flexibly designed.

Centers of grand canonical ensemble algorithm developments
Canonical Ensemble

\[ P(E_A) = \frac{\exp(-E_A / kT)}{\sum_i \exp(-E_i / kT)} \]

How to write **Grand Canonical Ensemble** partition function:

\[ P = \frac{\sum_{N=0}^{\infty} (N!)^{-1} V^N z^N \int dr \exp(-\beta E)}{Q_{\mu VT}} \]

\[ z = \frac{\exp(\beta\mu)}{(h^2 / 2\pi mk_B T)^{3/2}} \]
How to Realize Grand Canonical Ensemble in Monte Carlo?

1. Internal Displacements
\[ \rho_{accp} = \min(1, \exp(-\beta E)) \]

2. Insertion and removal
\[ \rho_{accp} = \min(1, \exp(-\beta (E_{n-1} + u - E_n))) \]
\[ \rho_{accp} = \min(1, \exp(-\beta (E_{n+1} - u - E_n))) \]
Hybrid Monte Carlo for Grand Canonical Ensemble?

1. **Internal Displacements**  Canonical ensemble Molecular Dynamics

2. **Insertion and removal**

\[
\rho_{accp} = \min(1, \exp(-\beta(E_{n-1} + u - E_{n})))
\]

\[
\rho_{accp} = \min(1, \exp(-\beta(E_{n+1} - u - E_{n})))
\]
Extended Hamiltonian to Realize Grand Canonical Ensemble
Extended Hamiltonian to Realize Grand Canonical Ensemble

One particle scheme:

\[ H_{\text{extended}} = H_o (n - 1) + \frac{1}{2} M_r \left| \frac{ds_r}{dt} \right|^2 + s_r (U_o - \mu) + \mu \]

\[ 0 \leq S_r \leq 1 \]
**Molecular Dynamics**

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Extended Hamiltonian to Realize Grand Canonical Ensemble

One particle scheme: \[ H_{extended} = H_o (n - 1) + \frac{1}{2} M_r \left| \frac{ds_r}{dt} \right|^2 + s_r (U_o - \mu) + \mu \]

\[ 0 \leq S_r \leq 1 \]

Drawbacks: 1. Particle number fluctuation magnitude can be larger than 1.

2. When \( S_r = 0 \), it can take long simulation time for the ghost particle to locate a position again. Why?
   Interaction Singularity.
Extended Hamiltonian to Realize Grand Canonical Ensemble

One particle scheme: \[ H_{\text{extended}} = H_o(n-1) + \frac{1}{2} M_r \left| \frac{dS_r}{dt} \right|^2 + s_r(U_o - \mu) + \mu \]

\(0 \leq S_r \leq 1\)

How to solve the interaction singularity, when \(S_r = 0\) ?

Two General Strategies: 1. Make the switching \(S_r(U_o - \mu)\) nonlinear.

2. Adiabatic switching method
Extended Hamiltonian to Realize Grand Canonical Ensemble

One particle scheme:

$$H_{\text{extended}} = H_0(n-1) + \frac{1}{2} M_r \left( \frac{ds_r}{dt} \right)^2 + s_r U_o - s_r \mu + \mu$$

$$0 \leq S_r \leq 1$$

Nonlinear switching $S_r U_o$

Original Lennard-Jones interaction:

$$\varepsilon \left[ \frac{A}{r^{12}} - \frac{B}{r^6} \right]$$

Nonlinear Switching (Softcore potential):

$$s_r \left\{ \varepsilon \left[ \frac{A}{(r^2 + \sigma(1-s_r))^6} - \frac{B}{(r^2 + \sigma(1-s_r))^3} \right] \right\}$$
Extended Hamiltonian to Realize Grand Canonical Ensemble

\[
\left\{ \epsilon \left[ \frac{A}{(r^2 + \sigma(1-s_r))^6} - \frac{B}{(r^2 + \sigma(1-s_r))^3} \right] \right\}
\]

Another Advantage:
Extended Hamiltonian to Realize Grand Canonical Ensemble

Adiabatic switching method: Extended Hamiltonian Hybrid Monte Carlo

\[ H_{\text{extended}} = H_o(n-1) + \frac{1}{2} M_r \left( \frac{ds_r}{dt} \right)^2 + s_r(U_o - \mu) + \mu \]

1. When Sr = 0 or 1, at a pre-set time interval \( N^* \tau \), fixing the position of the ghost particle.
2. Adiabatically switch Sr from 0 to 1 or switch Sr from 1 to 0, the energy change will be \( E_{n-1} - E_n \) or \( E_{n+1} - E_n \)

\[ \rho_{\text{accp}} = \min(1, \exp(-\beta(E_{n-1} + u - E_n))) \]
\[ \rho_{\text{accp}} = \min(1, \exp(-\beta(E_{n+1} - u - E_n))) \]