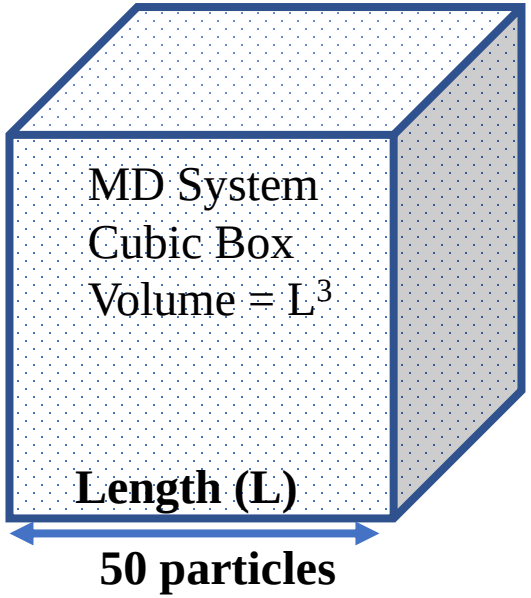
Molecular Dynamics

Boundary Conditions, Cut-off, Temperature and Pressure control

P. SATPATI

Boundary Conditions

- Real system are macroscopic, N ~ 10^{23}
- System considered for MD are small. Thus introduce artifact.

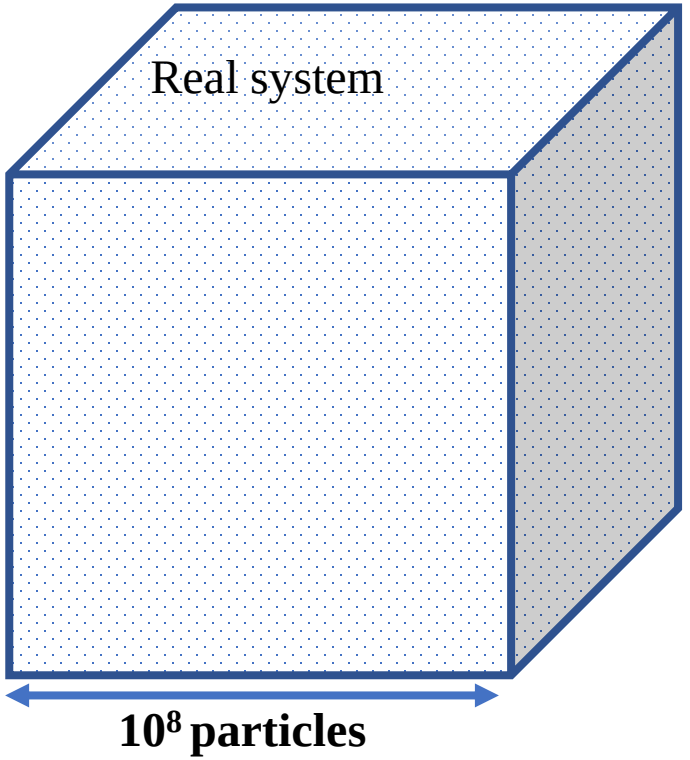


Particles in the MD Box = 50 x 50 x 50 = 125000

Particles on the surface of the MD Box = (50 x 50) x 6 = 15000

Particles facing vacuum in % = (15000/125000)*100 = 12%

MD System ≠ Real System



Total Particles = 10^8 x 10^8 x 10^8 = 10^{24}

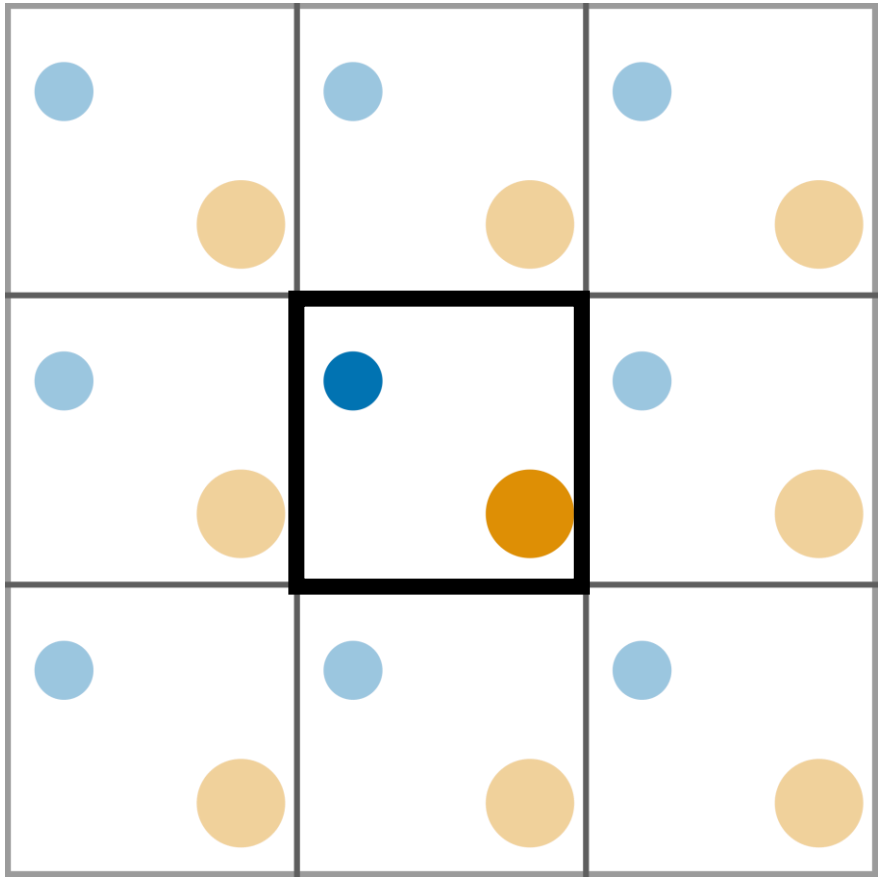
Surface Particles = (10^8 x 10^8) x 6 = 6 x 10^{16}

Particles facing vacuum in % = (6 x 10^{16} / 10^{24})*100 = 0.000006 %

Surface Particle Artifact

Boundary Conditions

Solution to finite size artifact → Periodic Boundary Condition



https://pythoninchemistry.org/sim_and_scat/important_considerations/pbc.html

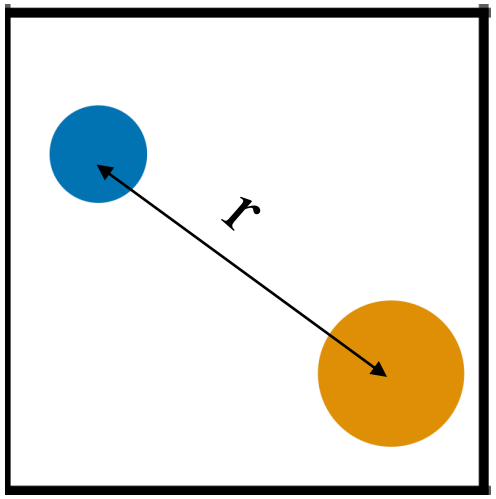
1. **Primary Cell**
2. Replicate in three dimension infinite times (Replica cell).
3. Solve equation of motion for the primary cell (velocity-verlet)
4. What happens in the primary cell. The same happens in every replica cell. Replica cells are exact copy of Primary cell.
   Particle leaves primary cell ⇔ enter from replica cell.
   (TOTAL NUMBER OF PARTICLES CONSERVED)

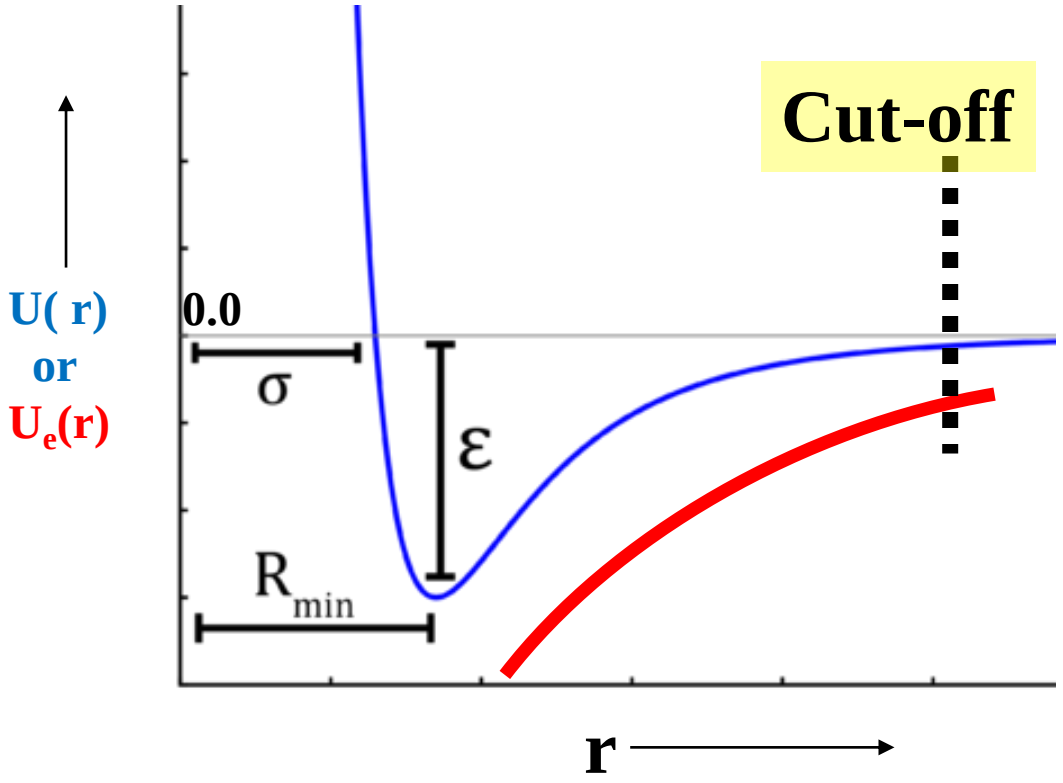
Advantage:

1. No atom feels any surface forces, surface artefact removed.
2. **Electrostatics calculation is easy (EWALD)**

Cut-off

Objective: Reduce the computational cost of non-bonded interaction





Short-Range (LJ)

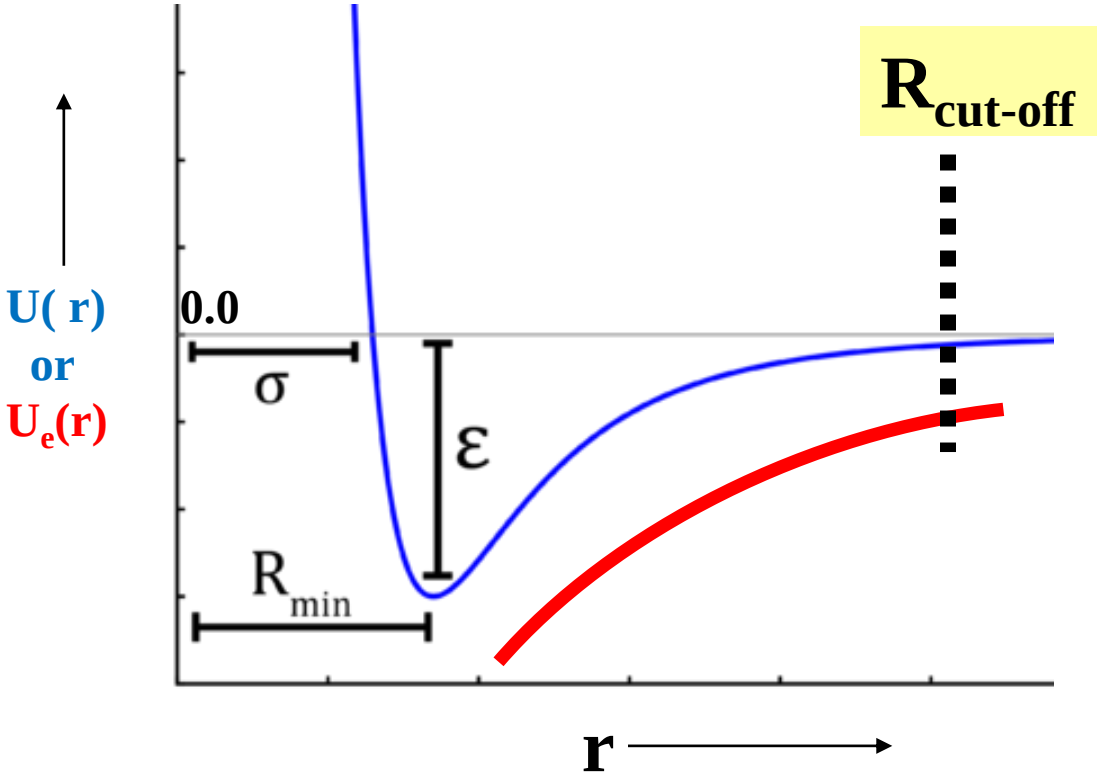
$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Long Range (Coulomb)

$$U_e = k\frac{q_1 q_2}{r}$$

Cut-off

Objective: Reduce the computational cost



Advantage:

> Fast vdw decay to zero
(~ $1/r^6$). GOOD for cut-off.

Problem

> Slow decay of Coulomb.

DISCONTINUIETY IN FORCES (COULOMB).

Short-Range (LJ)

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Long Range (Coulomb)

$$U_e = k\frac{q_1 q_2}{r}$$

Cut-off

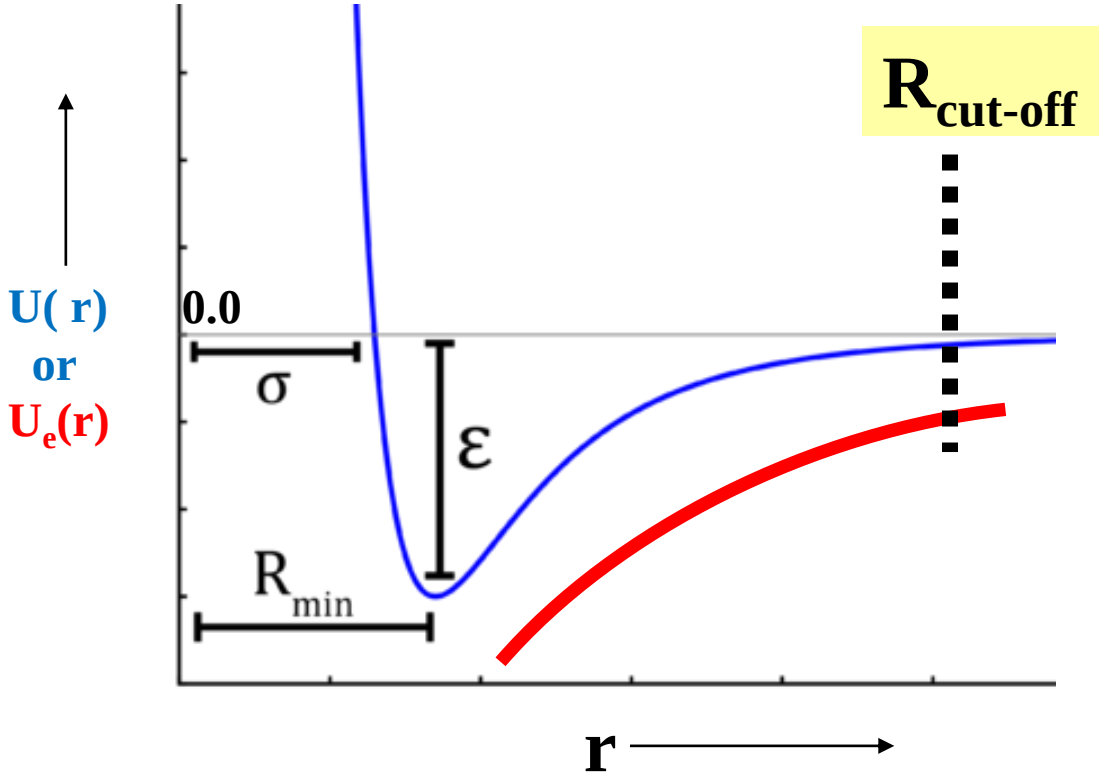
Solution to the Long-Range Coulomb:
Periodic Boundary Condition + EWALD method takes care of Electrostatics

Electrostatics = Direct estimation of short-range electrostatics ($R_{cut\text{-}off}$ used)
+
Long –range electrostatics (Particle Mesh Ewald method)

Remember: Even if you use cut-off for MD simulation. Electrostatics is calculated full.

Cut-off

Objective: Reduce the computational cost



What is the $R_{cut\text{-}off}$ used in simulations ?
Usually ~ 12Å - 14Å

Short-Range (LJ)

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Long Range (Coulomb)

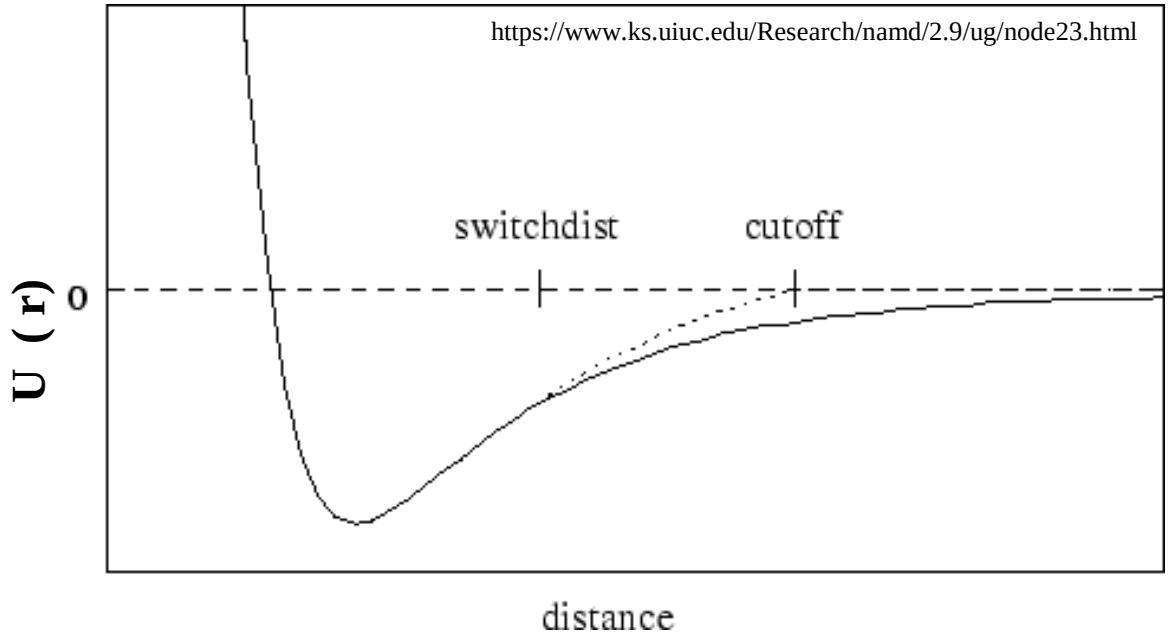
$$U_e = k\frac{q_1 q_2}{r}$$

Van der Waals interactions

van der Waals interactions are always truncated at the cutoff distance, specified by **cutoff.**

The main option that effects van der Waals interactions is the **switching parameter**.
With this option set to on, a smooth switching function will be used to truncate the van der Waals potential energy smoothly at the cutoff distance **(dotted Line).**

If **switching** is set to **off**, the van der Waals energy is just abruptly truncated at the cutoff distance, so that energy may not be conserved.



switchdist must always be less than that of **cutoff**.

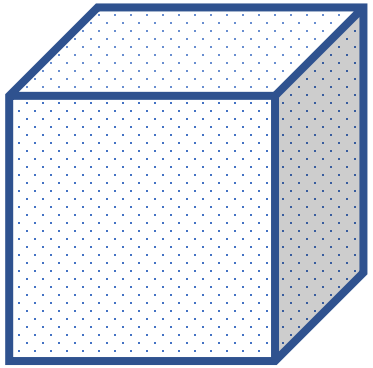
Short-Range (LJ)

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Temperature Control

RECAP…

What is temperature ?



Box of ‘N’ particles

$$\text{Average KE} = (\tfrac{1}{2} m_1 v_1^2 + \tfrac{1}{2} m_2 v_2^2 + \ldots + \tfrac{1}{2} m_N v_N^2)/ \text{N}$$

$$= \frac{\sum_{i=1}^{N} \tfrac{1}{2} mi\ vi^2}{N}$$

$$\text{Average KE} = (3/2)\ K_B\ T \quad \text{(Equipartition Therorem)}$$

$$(3/2)\ K_B\ T = \frac{\sum_{i=1}^{N} \tfrac{1}{2} mi\ vi^2}{N}$$

Temp ⇔ {v_i family}

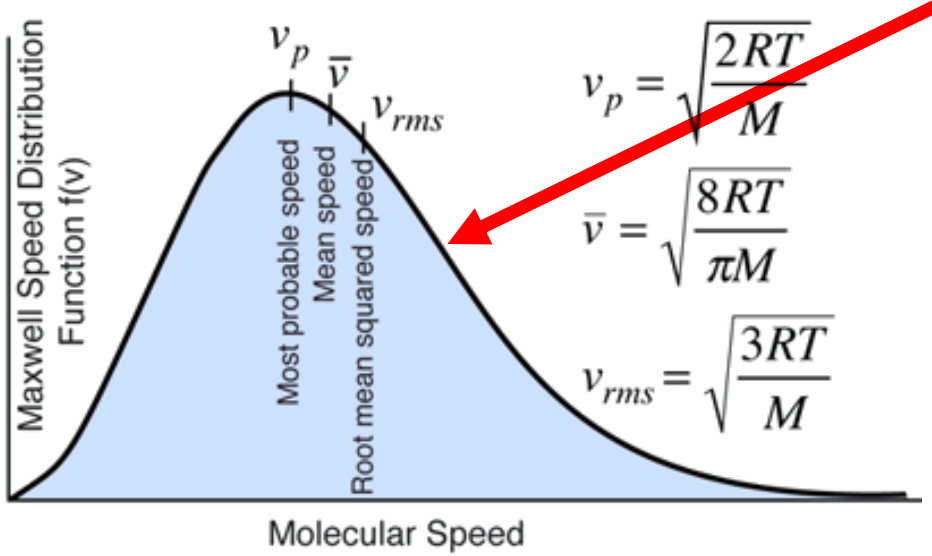
$$=) T = \frac{2 \sum_{i=1}^{N} \tfrac{1}{2} mi\ vi^2}{3\ K_B\ N} = \frac{\sum_{i=1}^{N} mi\ vi^2}{3\ K_B\ N}$$

➢ V_i family at a fixed "T"

Maxwell-Boltzmann distribution at a given temperature (Require THERMAL EQUILIBRIUM)

$\{v_i$ family$\}$ used to assign Initial velocity vi(0) Which is specific to a fixed Temperature "T"

$$f(v) = 4\pi \left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$



$$v_p = \sqrt{\frac{2RT}{M}}$$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Alter $\{v_i\}$ ⇔ Alter Temp

https://socratic.org/questions/5a3da9a0b72cff0f5f5840ed

How to Temperature Control ?

1. Scale velocities and control temperature

Say, at time ‘t’, Temperature = T(t).
If, the velocities are multiplied by a factor “λ”, then the associated difference in Temperature is:

$$\Delta T = T(t, \text{scaled}) - T(t)$$

Simplest way to control Temperature: $\lambda = \sqrt{\frac{T_{new}}{T(t)}}$

Multiply velocities of all atoms by correction factor “λ” to keep the Temperature constant (= T_{new}) at every time-step “Δt”. ***INSTANEOUS HEAT TRANSFER***

$$= \frac{\sum_{i=1}^{N} mi\ (vi\ \lambda)^2}{3\ K_B\ N} - \frac{\sum_{i=1}^{N} mi\ v_i{}^2}{3\ K_B\ N}$$

$$= \lambda^2\ T(t) - T(t)$$

$$= (\lambda^2 - 1)\ T(t)$$

How to Control “Temperature” ?

2. Alternate Way (Berendsen et al 1984)

- Couple system to an external heat bath.
- Bath acts as a source of thermal energy (Supply or remove heat from the system).

The velocities are scaled at each step, such that the rate of change of temperature is proportional to the difference in temperature between the bath and the system.

- Velocities are scaled at each time-step “Δt” by a correction factor “λ” that depends of $\mathbf{\Delta}T = T_{bath} - T(t)$, WHICH TAKES TIME (***NOT*** INSTANTENEOUS)

Rate of change of Temperature

Temperature difference between bath and system

$$\frac{dT(t)}{dt} = \frac{\Delta T}{\tau}$$

Coupling parameter (unit ”time”)
How tightly bath and system is coupled together

$$=) \frac{\Delta T(t)}{\Delta t} = \frac{T_{bath} - T(t)}{\tau}$$

Time-step

$$=) \Delta T(t) = \frac{\Delta t\,(Tbath - T(t))}{\tau}$$

$$=) (\lambda^2 - 1)\,\mathrm{T(t)} = \frac{\Delta t\,(Tbath - T(t))}{\tau}$$

$$=) \lambda^2 = 1 + \frac{\Delta t\,(Tbath - T(t))}{\tau\, T(t)}$$

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

- If $\Delta t = \tau$, Then it is Method (1)
- $\Delta t \neq \tau$ other method:

(Large τ = weak coupling
Small τ = Strong coupling)

[**Berendsen Thermostat**]

Nosé–Hoover thermostat,
Andersen thermostat

Pressure Control

P = Pressure
V = Volume
N = *Number of particles*
T = *temperature*
K_B = *Boltzmann Constant*

Ideal Gas: $PV = N K_B T$

Non-deal (particle interaction present)

$$PV = N K_B T + \frac{1}{3} < \sum_{i=1}^{N} \overline{F}_i \cdot q_i >$$

- ✓ q_i = *Position of particle "i"*
- ✓ $\overline{F}_i = \sum_{i \neq j} \overline{F}_{j \rightarrow i}$ = Force on particle "*i*" by all the other particles

$$P = \frac{1}{V} N K_B T + \frac{1}{3V} < \sum_{i=1}^{N} \overline{F}_i \cdot q_i >$$

P ⇔ V

A macroscopic system (say, MD system) maintains pressure by changing Volume.

How to Control “Pressure” ?

1. Scale “Volume” and control “pressure”

Simplest way to control

Temperature: $\lambda = \sqrt{\frac{P_{new}}{P(t)}}$

Multiply “volume (V)” by correction factor “λ” to keep the Pressure constant (= P_{new}) at every time-step “Δt”.
INSTANEOUS PRESSURE CORRECTION.

How to Control "Pressure" ?

2. Connect system with pressure bath

- Couple system to an external pressure bath.
- Bath acts as a source for fixing the pressure of the system (introduce or remove pressure from the system).

"Volume" scaled at each time-step "Δt" by a correction factor "λ" that depends on [P_{bath} – P(t)]. This takes time "τ_p"

$$\frac{dP(t)}{dt} = \frac{\Delta P}{\tau_p} \Rightarrow \frac{\Delta P(t)}{\Delta t} = \frac{[Pbath - P(t)]}{\tau_p}$$

[**Berendsen Barostat**]

$$\Delta P(t) = \frac{\Delta t}{\tau_p}[Pbath - P(t)]$$

How to Control "Pressure" ?

2. Connect system with pressure bath

$$\Delta P(t) = \frac{\Delta t}{\tau_p}[P_{bath} - P(t)]$$

$$=) (\lambda^2 - 1) P(t) = \frac{\Delta t}{\tau_p}[P_{bath} - P(t)]$$

$$=) \lambda^2 = 1 + \frac{\Delta t}{P(t)\,\tau_p}[P_{bath} - P(t)]$$

$$\lambda^2 = 1 + \frac{\Delta t}{\tau_p}\left[\frac{P_{bath}}{P(t)} - 1\right]$$

- Volume (V) of the simulation box is scaled by a factor "λ" at each time-step "Δt" by a correction that depends of $\Delta P = P_{bath} - P(t)$

WHICH TAKES TIME (***NOT*** INSTANTENEOUS)

Simulation Box scaling by "λ" ≡ Scaling the atomic coordinated by a factor "$\lambda^{\frac{1}{3}}$"

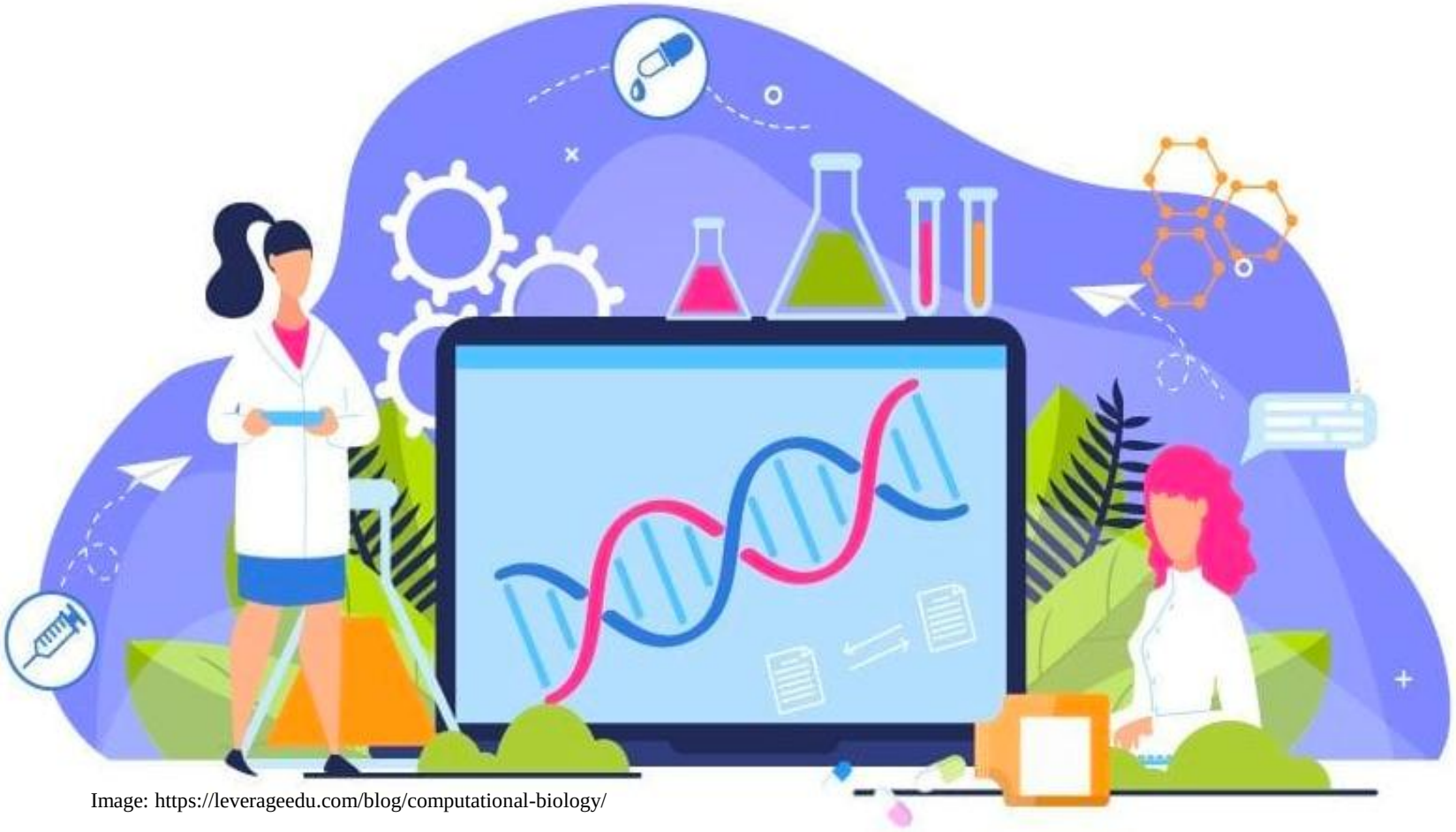


Image: https://leverageedu.com/blog/computational-biology/

Next : Minimization