$\boxed{\text{NVT-ensemble Monte Carlo}}$ – continuum systems

Metropolis rule : $P_{acc} = \min\{1, \exp(-\beta \Delta u)\}$

Since $P_\nu \propto \exp(-\beta u_\nu)$

Trial moves: (a) microscopically reversible
(b) ergodic
(c) efficient

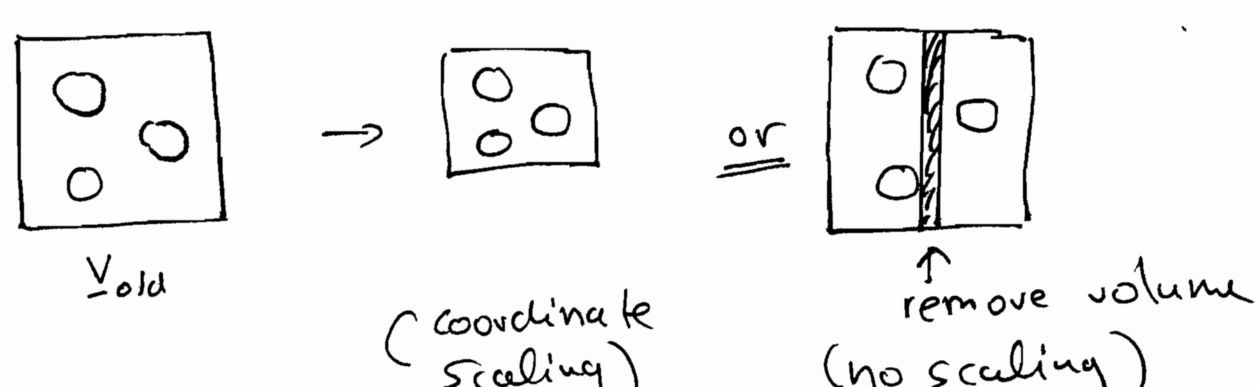
* Particles are picked one at a time at random * Attempt to displace by δr uniformly distributed between 0 and δr_{max}

δr_{max} controls acceptance ratio ; best ~30%

$\boxed{\text{NPT-ensemble Monte Carlo}}$

Recall that $P_\nu \propto \exp(-\beta u_\nu - \beta P V_\nu)$

In addition to particle displacements, need volume fluctuations



Second approach would also work for lattice models.

For <u>coordinate scaling</u>, must have

$$\mathcal{P}_{old} \propto V^N \exp(-\beta U_{old} - \beta P V_{old})$$

↑ "entropic" term to take into account different # of possible positions in different volumes

$$\mathcal{P}_{new} \propto (V+\Delta V)^N \exp(-\beta U_{new} - \beta P V_{new})$$

$$\frac{\mathcal{P}_{new}}{\mathcal{P}_{old}} = \left(\frac{V+\Delta V}{V}\right)^N \exp(-\beta \Delta U - \beta P \Delta V) \quad (A) \qquad \mathcal{P}_{acc} = \min\left(1, \frac{\mathcal{P}_{new}}{\mathcal{P}_{old}}\right)$$

(metropolis)

For <u>volume element creation/annihalation</u>, the particles do not move, so no V^N term is present:

$$\frac{\mathcal{P}_{new}}{\mathcal{P}_{old}} = \exp(-\beta \Delta U - \beta P \Delta V) \quad (B), \quad \mathcal{P}_{acc} = \min\left(1, \frac{\mathcal{P}_{new}}{\mathcal{P}_{old}}\right)$$

Let's determine the equation of state followed by a system of non-interacting particles that undergo a "virtual simulation":

case (A) → must have (for <u>all</u> ΔV)
$$\left(\frac{V+\Delta V}{V}\right)^N \exp(-\beta \cancel{\Delta U} - \beta P_{eq} \Delta V) = 1$$

no interactions

$$\boxed{\mathcal{P}^{+}_{acc} = \mathcal{P}^{-}_{acc} \text{ for } P = P_{eq}}$$

$$\Rightarrow \left(1+\frac{\Delta V}{V}\right)^N = \exp(\beta P_{eq}\Delta V) \Rightarrow$$

Taylor expand

$$\cancel{1} + \frac{N\cancel{\Delta V}}{V} = \cancel{1} + \beta P_{eq}\cancel{\Delta V} \Rightarrow \boxed{P_{eq} = \frac{N k_B T}{V}}$$

Case (B): $\mathcal{P}^{+}_{acc} = \mathcal{P}^{-}_{acc} \Rightarrow$

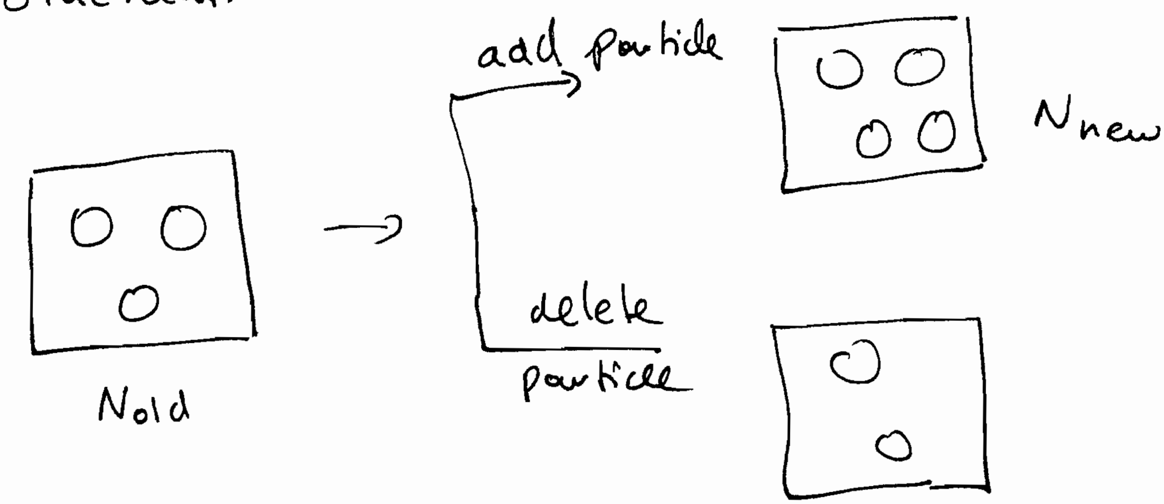
$$\exp(-\beta \underbrace{\cancel{\Delta U}}_{\text{no inter.}} - \beta P_{eq}\Delta V) = \underbrace{\left(1-\frac{\Delta V}{V}\right)^N}_{\text{probability of space being removed \underline{not} containing any particles}}$$

$$\Rightarrow \cancel{1} - \beta P_{eq}\cancel{\Delta V} = \cancel{1} - \frac{N\cancel{\Delta V}}{V} \Rightarrow \boxed{P_{eq} = \frac{N k_B T}{V}}$$

Grand-Canonical (μVT) Monte Carlo

$$\mathcal{P}_\nu \propto \exp(-\beta U_\nu + \beta\mu N_\nu)$$

Particles are created/destroyed to sample fluctuations in N



Since particles have access to complete volume, must take into account "entropic" term:

$$\mathcal{P}_v \propto \frac{V^N}{N!} \exp(-\beta U_v + \beta\mu N_v)$$

$$\frac{P_{new}}{P_{old}} = \begin{cases} \text{add} & \frac{V}{N+1}\exp(-\beta\Delta U + \beta\mu) \\ \text{delete} & \frac{N}{V}\exp(-\beta\Delta U - \beta\mu) \end{cases}$$

$\mathcal{P}_{acc} = \min\left\{1, \frac{P_{new}}{P_{old}}\right\}$ (as usual)

Acceptance of addition/removal step cannot be controlled!

Let's obtain the chemical potential - density relationship for a system of non-interacting particles:

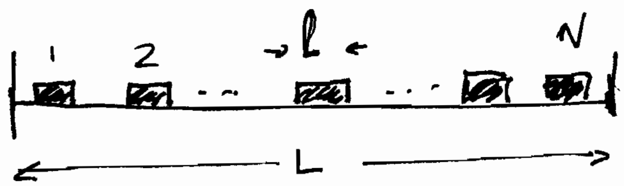
$$\mathcal{P}_{acc}^{+} = \mathcal{P}_{acc}^{-} \Rightarrow \quad 1 = \frac{N_{eq}}{V}\exp(-\beta\cancel{\Delta U} - \beta\mu) \Rightarrow$$

no interactions

$$\Rightarrow \quad \exp(\beta\mu) = \rho_{eq} \Rightarrow \boxed{\beta\mu = \ln \rho_{eq}}$$

A simple application

Calculate the equation of state for a system of N hard rods, each of length ℓ, in a line of length L.



Virtual NPT simulation, volume creation/annihilation

$$P_{acc} = \min\left(1, \exp(-\beta\cancel{\Delta U} - \beta P \Delta L)\right)$$

$\emptyset$ since no interactions

At equilibrium, $P^{+}_{acc} = P^{-}_{acc}$ for any small ΔL

$$P^{+}_{acc} = \exp(-\beta P \Delta L) \underset{\beta P \Delta L \ll 1}{\simeq} 1 - \beta P \Delta L$$

$P^{-}_{acc} = ?$ same as for ideal gases, except now the effective density in free space is higher due to the volume exclusion of the rods

$$P^{-}_{acc} = \left(1 - \frac{\Delta L}{L - \ell N}\right)^N \simeq 1 - \frac{\rho \Delta L}{1 - \rho \ell}, \text{ where } \rho = \frac{N}{L}$$

Setting $P_{acc}^{+} = P_{acc}^{-} \Rightarrow$

$$1 - \beta P \Delta L = 1 - \frac{\rho \Delta L}{1 - \rho \ell} \Rightarrow \boxed{\beta P = \frac{\rho}{1 - \rho \ell}}$$

This is exact in 1-D and is similar to the first (repulsive) term of the van der Waals equation-of state.