Grand Canonical Ensemble : Const. μVT

Corresponds to experimental systems in an open container of fixed volume, in contact with a large reservoir.

→ Important for phase equilibrium calculations ←

Fundamental Equation: $dy^{(0)} = d\ln\Omega = \frac{dS}{k_B} = \beta dU + \beta P dV - \beta\mu dN$

2nd Legendre Transform: $dy^{(2)}$ $d\ln\Xi = -U d\beta + \beta P dV + N d(\beta\mu)$

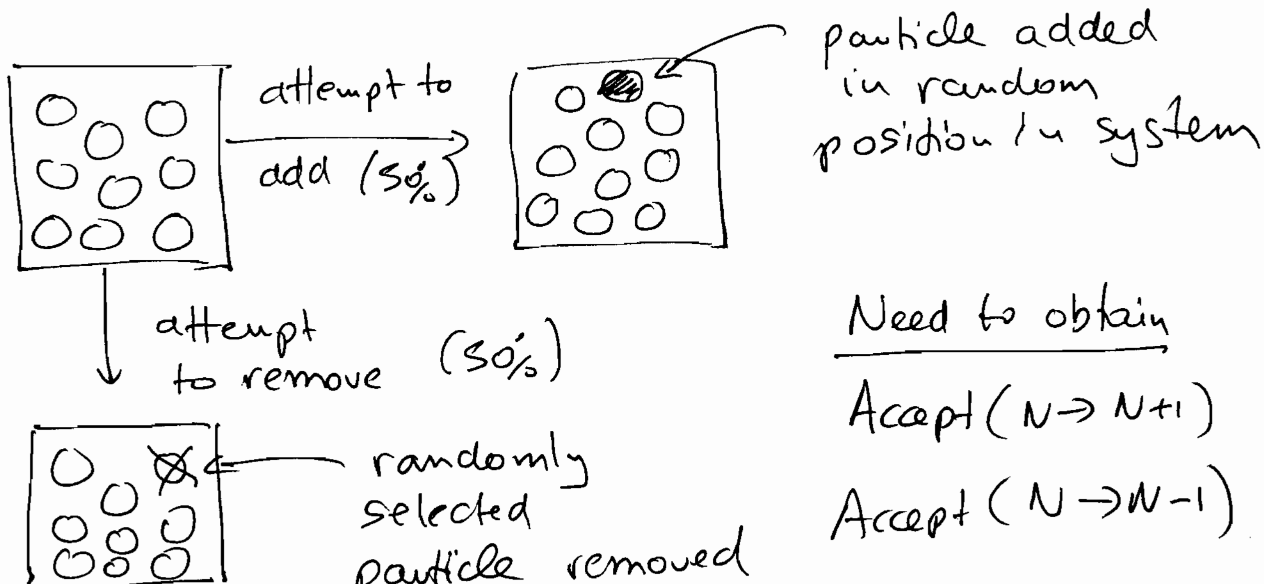
$$y^{(2)} = \ln\Xi = \frac{S}{k_B} - \beta U + \beta\mu N = -\frac{U - TS + \mu N}{k_B T} = \frac{PV}{k_B T}$$

$$\Xi = \sum_{\text{all states}} \exp(-\beta U_\nu + \beta\mu N_\nu) \quad \left\{ \begin{matrix} U_\nu \\ N_\nu \end{matrix} \right\} \text{ fluctuate}$$

$$P_\nu = \frac{\exp(-\beta U_\nu + \beta\mu N_\nu)}{\Xi} \; ; \; \left(\frac{\partial \ln\Xi}{\partial \beta\mu}\right)_{\beta, V} = \langle N \rangle$$

Simulation Implementation (GCMC)

To change the number of particles, we need to have particle addition + removal steps:



Need to obtain

Accept$(N \to N+1)$

Accept$(N \to N-1)$

$$P(N) \propto \frac{V^N}{N!} P_v$$

This takes into account that
1. Particles are indistinguishable
2. There are more microstates as $N \uparrow$

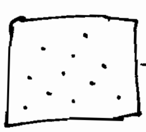
$$\therefore \text{Accept}(N \to N+1) = \frac{P(N+1)}{P(N)} = \frac{V^{N+1}/(N+1)! \exp[-\beta U_{new} + \beta\mu(N+1)]}{V^N/N! \exp(-\beta U_{old} + \beta\mu N)}$$

$$\Rightarrow \boxed{\text{Accept}(N \to N+1) = \frac{V}{N+1} \exp(-\beta \Delta U + \beta\mu)}$$

$$\text{Accept}(N \to N-1) = \frac{P(N-1)}{P(N)} = \frac{V^{N-1}/(N-1)! \exp[-\beta U_{new} + \beta\mu(N-1)]}{V^N/N! \exp(-\beta U_{old} + \beta\mu N)}$$

$$\Rightarrow \boxed{\text{Accept}(N \to N-1) = \frac{N}{V} \exp(-\beta \Delta U - \beta\mu)}$$

To demonstrate the validity of these expressions, let's do a thought experiment of GCMC for an ideal gas.



($\Delta U = 0$)

add $\longrightarrow$ $\text{Accept}(N \to N+1) = \frac{V}{N+1} e^{\beta\mu} \simeq \frac{V}{N} e^{\beta\mu}$ $(N \gg 1)$

remove $\longrightarrow$ $\text{Accept}(N \to N-1) = \frac{N}{V} e^{-\beta\mu}$

These two terms are inverse of each other, so only one is less than one, or both are $= 1$.

At equilibrium, the two probabilities must be equal:

$$\frac{N}{V} e^{-\beta\mu} = 1 \Rightarrow \beta\mu = \ln \frac{N}{V} = \ln \rho$$

chemical potential for ideal gas

Note that box can become empty $(N=0)$ — This is perfectly normal — corresponds to a small box at low ρ in a large reservoir