PHYS 425 - w9l2

Last Time: Canonical ensemble

- Boltzmann dist'n
- Partition fcn
- Helmholtz Free Energy

Today: Grand Canonical Ensemble

If we add or remove particles from a system, the we expect their to be an associated change in the internal energy.

$$U = U(S, V, N)$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,N}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,N}}_{-P} dV + \underbrace{\left(\frac{\partial U}{\partial N}\right)_{S,V}}_{\mu} dN$$

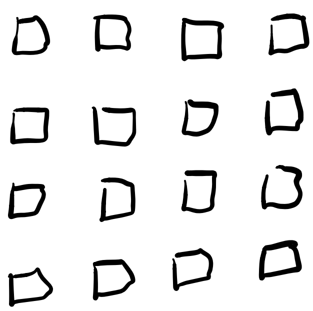
$$dU = \underbrace{TdS}_{\text{heat}} - \underbrace{PdV}_{\text{mech. work}} + \underbrace{\mu dN}_{\text{chemical work}} \quad \textcircled{A}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \quad \text{is chemical potential}$$

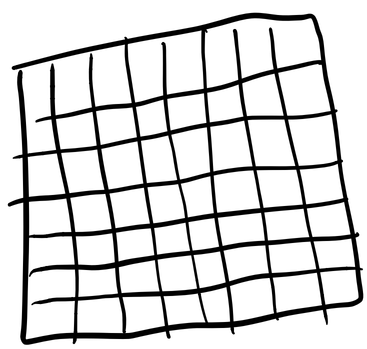
$[\mu] =$ energy

From $\circledast$ $\quad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

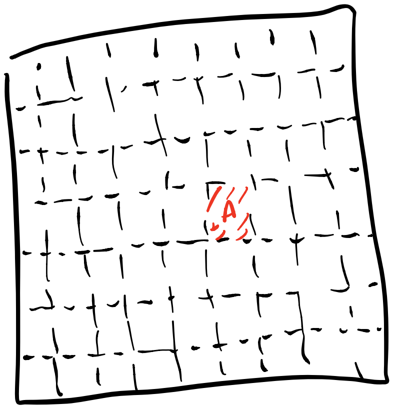
Grand Canonical Ensemble



① microcanonical ensemble
- collection of replica systems all isolated from one another.



② Canonical ensemble
- collection of replica systems in contact w/ thermal reservoir. Energy can flow in & out of systems.



③ Grand Canonical Ensemble

- collection of replica systems in contact w/ thermal reservoir & particle reservoir
Energy & particles can be exchanged among replica systems.

U & N of each replica system can change.

U & N of ensemble as a whole are fixed

$\rightarrow U_T, N_T$

$$dU = TdS - PdV + \mu dN \quad \text{*}$$

For the reservoir $S_R = k_B \ln W_R$

$$\frac{1}{T} = \left(\frac{\partial S_R}{\partial U_R}\right)_{V_R, N_R} = k_B \left(\frac{\partial (\ln W_R)}{\partial U_R}\right)_{V_R, N_R} \quad !$$

$$\mu = -T\left(\frac{\partial S_R}{\partial N_R}\right)_{V_R, U_R} = -k_B T \left(\frac{\partial (\ln W_R)}{\partial N_R}\right)_{V_R, U_R} \quad \#$$

Sol'n of ① & ④ is

$$\ln W_R = k + \frac{U_R - \mu N_R}{k_B T}$$

k: const

$$\therefore W_R = \alpha e^{(U_R - \mu N_R)/k_B T}$$

$\alpha = e^k$ is const.

Suppose system A has energy U_A & N_A particles

⇒ reservoir can add or remove a small amount of energy w/o changing T

$$U_R = U_T - U_A$$

⇒ reservoir can add or remove small no. of particles w/o changing μ

$$N_R = N_T - N_A$$

$$W_R = \alpha \exp\left\{\left[(U_T - U_A) - \mu(N_T - N_A)\right]/k_B T\right\}$$

$$= \underbrace{\alpha \exp\left\{(U_T - \mu N_T)/k_B T\right\}}_{\equiv \alpha' \;\ldots\; \text{const.}} \exp\left\{-\frac{(U_A - \mu N_A)}{k_B T}\right\}$$

$$W_R = \alpha' e^{-(U_A - \mu N_A)/k_B T}$$

no. of possible states for the reservoir when state A has energy U_A & particle no. N_A.

The total no. of states available to the combined system (A & reservoir) is

$$W = W_A W_R$$

If A is restricted to be in one particular state ψ_i w/ $U_A = U_i$ & $N_A = N_i$ then:

$$W_A = 1 \quad \& \quad W_i = 1 \cdot W_R$$

$$\rightarrow \quad W_i = \alpha' e^{-(U_i - \mu N_i)/k_B T}$$

$\therefore$ The total no. of available states to the combined system is:

$$\rightarrow \quad W = \sum_j W_j = \alpha' \sum_j e^{-(U_j - \mu N_j)/k_B T}$$

Sum over all possible states of system A.

Of all possible states W, the prob. p_i of being in state ψ_i is:

$$p_i = \frac{W_i}{W} = \frac{e^{-(U_i - \mu N_i)/k_B T}}{\sum_j e^{-(U_j - \mu N_j)/k_B T}}$$

Grand Canonical dist'n fcn

For canonical ensemble we had

$$p_i = \frac{e^{-U_i/k_B T}}{\sum_j e^{-U_j/k_B T}}$$ Boltzmann dist'n.

Define the grand partition fcn

$$\Xi = \sum_j e^{-(U_j - \mu N_j)/k_B T}$$

Capital greek letter Xi (pronounced "key")

canonical ensemble

$$Z = \sum_j e^{-U_j/k_B T}$$ partition function

$$\rightarrow \quad p_i = \frac{e^{-(U_i - \mu N_i)/k_B T}}{\Xi}$$

Previously showed for canonical ensemble

$$S = -k_B \sum_i p_i \ln p_i$$

This result is also true for the Grand Canonical ensemble by exact same arguments.

$$S = -k_B \sum_i p_i \left\{ -\frac{(u_i - \mu N_i)}{k_B T} - \ln \Xi \right\}$$

$$= \frac{1}{T} \underbrace{\sum_i p_i u_i}_{\bar{u}} - \frac{\mu}{T} \underbrace{\sum_i p_i N_i}_{\bar{N}} + k_B \ln \Xi$$

$$\therefore \quad S = \frac{\bar{u}}{T} - \frac{\mu \bar{N}}{T} + k_B \ln \Xi$$

$$\therefore \quad \boxed{-k_B T \ln \Xi = \bar{u} - \mu \bar{N} - TS}$$

$$\boxed{\Phi_G \equiv -k_B T \ln \Xi = \bar{u} - \mu \bar{N} - TS}$$

Grand Potential

(Analogous to $F = -k_B T \ln Z = u - TS$ for canonical ensemble)

Grand Potential

$$\Phi_G = \underbrace{\bar{U} - TS}_{F} - \mu\bar{N} = -k_B T \ln \Xi$$

$$d\Phi_G = d\bar{U} - TdS - SdT - \mu d\bar{N} - \bar{N}d\mu$$

$$= (\cancel{TdS} - PdV + \cancel{\mu d\bar{N}}) - \cancel{TdS} - SdT$$

$$- \cancel{\mu d\bar{N}} - \bar{N}d\mu$$

$$\therefore\ d\Phi_G = -PdV - SdT - \bar{N}d\mu$$

$$\therefore\ S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$$

$$\boxed{\bar{N} = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{V,T}}$$

Once know Ξ, can calc Φ_G & $\therefore$ thermodynamic properties.