Grand Canonical Ensemble

macroscopic system with energy E
number of particles N

# of microstates: $\Omega(E,N)$

much larger system (reservoir) with energy E_{res}
number of particle N_{res}

# of microstates: $\Omega_{res}(E_{res}, N_{res})$

system and reservoir

in thermal contact: can exchange energy
but total energy E_{tot} is fixed
if system has energy E, reservoir has energy $E_{tot} - E$

in chemical contact: can exchange particles
but total number of particle N_{tot} is fixed
if system has N particles, reservoir has $N_{tot} - N$ particle

if system has energy E and particle number N

# of accessible microstates is $\Omega(E,N) \times \Omega_{res}(E_{tot}-E, N_{tot}-N)$

reservoir much larger than system

$$\Longrightarrow \quad E \ll E_{tot}, \quad N \ll N_{tot}$$

expand $\log \Omega_{res}$ to 1^{st} order in E and N

$$\log \Omega_{res}(E_{tot}-E, N_{tot}-N) = S_{res}(E_{tot}-E, N_{tot}-N)$$

$$\simeq S_{res}(E_{tot}, N_{tot}) + \frac{\partial S_{res}}{\partial E_{res}}(E_{tot}, N_{tot})(-E) + \frac{\partial S_{res}}{\partial N_{res}}(E_{tot}, N_{tot})\cdot(-N)$$

$$= S_{res}(E_{tot}, N_{tot}) - \frac{1}{T_{res}}E + \frac{\mu_{res}}{T_{res}}N$$

# of accessible microstates:

$$\Omega(E,N) \times \exp\left(S_{res}(E_{tot}, N_{tot}) - \frac{1}{T_{res}}E + \frac{\mu_{res}}{T_{res}}N\right)$$

$$= \Omega_{res}(E_{tot}, N_{tot}) \times \Omega(E,N)\exp\left(-\frac{1}{T_{res}}E + \frac{\mu_{res}}{T_{res}}N\right)$$

probability distribution for microstates of system

$$P(E_r, N_r) = \frac{1}{Z}\exp(-\beta E_r - \alpha N_r)$$

$$\beta = \frac{1}{T_{res}} \qquad \alpha = -\frac{\mu_{res}}{T_{res}}$$

$$Z = \sum_r \exp(-\beta E_r - \alpha N_r)$$

grand canonical ensemble with temperature T
chemical potential μ

probability distribution of microstates i

$$P_i = \frac{1}{\mathbb{Z}} \exp(-\beta E_r - \alpha N_r) \qquad \beta = \frac{1}{T} \quad \alpha = -\frac{\mu}{T}$$

$$\mathbb{Z} = \sum_r \exp(-\beta E_r - \alpha N_r) \implies \sum_r P_r = 1$$

grand partition function : $\mathbb{Z}(\beta, \alpha)$

average energy: $U = \langle E_r \rangle = \frac{1}{\mathbb{Z}} \sum_r E_r \exp(-\beta E_r - \alpha N_r)$

$$= -\frac{\partial}{\partial \beta} \log \mathbb{Z}(\beta, \alpha)$$

average number: $\overline{N} = \langle N_i \rangle = \frac{1}{\mathbb{Z}} \sum_r E_r \exp(-\beta E_r - \alpha N_r)$

$$= -\frac{\partial}{\partial \alpha} \log \mathbb{Z}(\beta, \alpha)$$

information entropy:

$$S = -\sum_r P_r \log P_r = -\sum_r \left(\frac{1}{\mathbb{Z}} e^{-\beta E_r - \alpha N_r}\right)\left(-\beta E_r - \alpha N_r - \log \mathbb{Z}\right)$$

$$= \beta \frac{1}{\mathbb{Z}} \sum_r E_r e^{-\beta E_r - \alpha N_r} + \alpha \frac{1}{\mathbb{Z}} \sum_r N_r e^{-\alpha E_r - \beta N_r} + \frac{\log \mathbb{Z}}{\mathbb{Z}} \sum_r e^{-\beta E_r - \alpha N_r}$$

$$= \beta U + \alpha \overline{N} + \log \mathbb{Z}$$

$$\log \mathcal{Z} = -\beta U - \alpha \bar{N} + S$$

define grand potential Φ by $\mathcal{Z} = e^{-\beta\Phi}$

$$\log \mathcal{Z} = -\beta \Phi$$

$$\Phi = U - TS - \mu \bar{N}$$

thermodynamic relation

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

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

partial derivative:

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu, V}$$

$$P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T \mu}$$

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

Gibbs free energy: $G = U - TS + PV$

exact extensivity: $G = \bar{N}\mu \implies \Phi = -PV$

grand partition function:

$$\mathcal{Z} = \sum_r e^{-\beta E_r - \alpha N_r}$$

make sum over particle number N explicit

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{r:N_r=N} e^{-\beta E_r - \alpha N_r}$$

$$= \sum_{N=0}^{\infty} e^{-\alpha N} \sum_{r:N_r=N} e^{-\beta E_r}$$

$$= \sum_{N=0}^{\infty} \left(e^{-\alpha}\right)^N Z_N(\beta)$$

$Z_N(\beta)$ = partition function for N particle in canonical ensemble

fugacity: $z = e^{-\alpha} = e^{\beta\mu}$

example: monatomic ideal gas

$$Z_N = \frac{1}{N!}\left(V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{\frac{3}{2}}\right)^N$$

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{1}{N!}\left(V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\right)^N$$

$$= \exp\left(zV\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2}\right) = \exp\left(e^{\mu/T}V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right)$$

$$\log \mathcal{Z} = e^{\mu/T} V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$$

fluctuation in the grand canonical ensemble

mean-square deviations

in energy: $(\Delta E)^2 \equiv \langle (E-U)^2 \rangle = \langle E^2 \rangle - U^2$

$$= -\left(\frac{\partial U}{\partial \beta}\right)_{\alpha,V} = +T^2\left(\frac{\partial U}{\partial T}\right)_{\mu/T,V}$$

in number $(\Delta N)^2 \equiv \langle (N-\bar{N})^2 \rangle = \langle N^2 \rangle - \bar{N}^2$

$$= -\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{\beta,V} = +T\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}$$

U and $\bar{N}$ are extensive, scale as N^1

ΔE and ΔN scale as $N^{1/2}$

relative size of fluctuation $\frac{\Delta E}{U}$, $\frac{\Delta N}{\bar{N}}$ scale as $N^{-1/2}$

go to 0 in thermodynamic limit

fluctuations in number density $n = N/V$

$$\frac{(\Delta n)^2}{\bar{n}^2} = \frac{T}{\bar{N}^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}$$

$\bar{N} = V \cdot \frac{N}{V} = \frac{V}{v}$ where $v = \frac{V}{\bar{N}}$

$$= \frac{T}{\bar{N}^2}\left(-\frac{V}{v^2}\frac{\partial v}{\partial \mu}\right)_{T,V}$$

$d\mu = v\,dP - s\,dT$

$$= -\frac{T}{V}\left(\frac{1}{v}\frac{\partial v}{\partial P}\right)_{T,V} = \frac{T}{V}K_T$$

K_T = isothermal compressibility

$\sim N^{-1}$ unless $K_T = \infty$