

Maximum entropy principle

Equilibrium = state of max σ consistent with constraints (fixed N, V, U)

$$\sigma = \sigma(N, V, U) \quad (\Delta\sigma)_{NVU} < 0$$

First order change in σ from equilibrium: $d\sigma = 0$

First Law

$$dU = \tau d\sigma - p dV + \sum_i \mu_i dN_i = \tilde{Q} + \tilde{W}$$

$$U = \tau\sigma - pV + \sum_i \mu_i N_i$$

$$\left(\frac{\partial U}{\partial \sigma}\right)_{VN} = \tau \quad \left(\frac{\partial U}{\partial V}\right)_{\sigma N} = -p \quad \left(\frac{\partial U}{\partial N_i}\right)_{\sigma V} = \mu_i$$

or

$$\left(\frac{\partial \sigma}{\partial U}\right)_{VN} = \frac{1}{\tau} \quad \left(\frac{\partial \sigma}{\partial V}\right)_{UN} = -\frac{p}{\tau} \quad \left(\frac{\partial \sigma}{\partial N_i}\right)_{UV} = \frac{\mu_i}{\tau}$$

Energy minimum principle

$$U = U(N, V, \sigma) \quad \Delta U > 0$$

U = minimum in equilibrium, consistent with constraints (fixed σ, N, V)

$$F = U - \tau\sigma = -pV + \sum_i \mu_i N_i$$

$$dF = dU - d(\tau\sigma) = -\sigma d\tau - p dV + \sum_i \mu_i dN_i$$

$(\Delta F)_{\tau}$ = total work on system at constant τ

$$H = U + pV = \tau\sigma + \sum_i \mu_i N_i$$

$$dH = dU + d(pV) = \tau d\sigma + V dp + \sum_i \mu_i dN_i$$

$(\Delta H)_p = (\Delta Q)_p$ total heat absorbed at constant p if no chemical work done

$$G = U - \tau\sigma + pV = \sum_i \mu_i N_i$$

$$dG = dU - d(\tau\sigma) + d(pV) = -\sigma d\tau + V dp + \sum_i \mu_i dN_i$$

$(\Delta G)_{\tau p} = \sum_i \mu_i dN_i$ total chemical work done at constant p, τ

$$(dF)_{\tau VN} = 0 \quad (dH)_{\sigma pN} = 0 \quad (dG)_{\tau pN} = 0 \quad \text{all are minimum in equilibrium}$$

first order change with constraints = 0

Stat. Mech - Thermo connection

$$P(s) = \frac{e^{-E_s/\tau}}{Z} \quad Z \equiv \sum_s e^{-E_s/\tau}$$

$$F = -\tau \ln Z = U - \tau \sigma$$

$$P(s, N) = \frac{e^{-(E_s(N) - \mu N)/\tau}}{\mathcal{Z}} \quad \mathcal{Z} \equiv \sum_{N=0}^{\infty} \sum_{s(N)} e^{-(E_s(N) - \mu N)/\tau}$$

$$\Omega = F - \sum_i \mu_i N_i = -\tau \ln \mathcal{Z} = U - \tau \sigma - \sum_i \mu_i N_i = -PV$$

Photons: Planck distribution $E_s = \hbar\omega_1 n_1 + \hbar\omega_2 n_2 + \dots + \hbar\omega_N n_N + \dots = \sum_i \hbar\omega_i n_i$

$$\ln Z = -\ln \prod (1 - e^{-\hbar\omega_i/\tau}) \quad (2 \text{ pol.})$$

$$Z = \sum_{\substack{n_1, n_2, \dots \\ s}} e^{-\sum_i (\hbar\omega_i/\tau) n_i} = \prod_i \left(\sum_{n_i=0}^{\infty} e^{-(\hbar\omega_i/\tau) n_i} \right)$$

$$\ln Z = -\sum_i \ln(1 - e^{-\hbar\omega_i/\tau}) = \prod_i \left(\frac{1}{1 - e^{-\hbar\omega_i/\tau}} \right)$$

$$= -2 \sum_{\vec{n}} \ln(1 - e^{-\hbar\omega_{\vec{n}}/\tau})$$

$$\hbar\omega_{\vec{n}} = \hbar c \frac{\pi}{L} (n_x^2 + n_y^2 + n_z^2)^{1/2} = \hbar c \frac{\pi}{L} n$$

$$\begin{aligned} E_s &= \sum_i \hbar\omega_i n_i \\ \sum_s &= \sum_{n_1, n_2, \dots} \\ \sum_s e^{-E_s/\tau} &= \sum_{n_1} \sum_{n_2} \sum_{n_3=0}^{\infty} \dots e^{-\hbar\omega_1 n_1/\tau} e^{-\hbar\omega_2 n_2/\tau} e^{-\hbar\omega_3 n_3/\tau} \dots \end{aligned}$$

$$= \prod_i \left(\sum_{n_i=0}^{\infty} e^{-(\hbar\omega_i/\tau) n_i} \right)$$

Photons: 3 pol. $E_s = \hbar\omega_1 n_1 + \hbar\omega_2 n_2 + \dots + \hbar\omega_N n_N + \dots$

$$\ln Z = -\sum_i \ln(1 - e^{-\hbar\omega_i/\tau}) = -3 \sum_{\vec{n}} \ln(1 - e^{-\hbar\omega_{\vec{n}}/\tau})$$

$$\hbar\omega_{\vec{n}} = \hbar v \frac{\pi}{L} n \leq \hbar v \frac{\pi}{L} n_D = \hbar\omega_D = \Theta \tau_D$$

$$3N = 3 \cdot \frac{1}{8} \frac{4\pi}{3} n_D^3$$

low τ like photons
high τ different!

Particles

$$\epsilon_s = \frac{\hbar^2}{2m} \left(\frac{\pi}{L} \right)^2 n^2 \quad (n^2 \equiv n_x^2 + n_y^2 + n_z^2)$$

$$\sum_s \epsilon_s = (2S+1) \sum_{\vec{n}}$$

Ideal gases

$$N = \sum_s f(\epsilon_s) \quad \leftarrow \text{equation for } \mu$$

classical limit of μ eqn.

$$N = \left(\sum_s e^{-\epsilon_s/\tau} \right) e^{\mu/\tau} \quad \mu = \tau \ln \left(\frac{N}{\sum_s e^{-\epsilon_s/\tau}} \right)$$

$$U = \sum_s \epsilon_s f(\epsilon_s)$$

$\mu \rightarrow F$:

$$F(N, \tau, V) = \int_0^N \mu(N', \tau, V) dN'$$

if you can find $\mu(N, \tau, V)$, you can find F from: