$TdS = dU + PdV - \mu dN$

Boltzmann

$\omega_j = \frac{N! g_j^{N_j}}{N_j!(N-N_j)!}$

$\omega_B = N! \prod \frac{g_j^{N_j}}{N_j!}$

$f_j = \frac{N_j}{g_j} = \frac{N}{Z} e^{-\epsilon_j/kT}$

Maxwell-Boltzmann

$\omega_j = \frac{g_j^{N_j}}{N_j!}$

$\omega_{MB} = \prod \frac{g_j^{N_j}}{N_j!}$

$f_j = \frac{N}{Z} e^{-\epsilon_j/kT} = (e^{(\epsilon_j-\mu)/kT})^{-1}$

Fermi-Dirac

$\omega_j = \frac{g_j!}{N_j!(g_j-N_j)!}$

$\omega_{FD} = \prod \frac{g_j!}{N_j!(g_j-N_j)!}$

$f_j = (e^{(\epsilon_j-\mu)/kT} + 1)^{-1}$

Bose-Einstein

$\omega_j = \frac{(N_j+g_j-1)!}{N_j!(g_j-1)!}$

$\omega_{BE} = \prod \frac{(N_j+g_j-1)!}{N_j!(g_j-1)!}$

$f_j = (e^{(\epsilon_j-\mu)/kT} - 1)^{-1}$

Derive Distribution

$\ln(N!) \approx N\ln(N) - N$

$0 = \frac{\partial}{\partial N_j}(\ln(\omega) + \alpha(\sum N_j - N) + \beta(\sum \epsilon_j N_j - U))$

$\alpha, \beta : TdS = dU + PdV - \mu dN$

Derive Density of States

$n^2 = \left(\frac{8mV^{-2/3}}{h^2}\right)\epsilon \equiv R^2$

$n = \frac{1}{8}\frac{4\pi R^3}{3}$

$g(\epsilon)d\epsilon = \gamma_s \frac{dn}{d\epsilon} d\epsilon$

$g(\epsilon)d\epsilon = \gamma_s \frac{4\sqrt{2}\pi V}{h^3} m^{3/2}\epsilon^{1/2} d\epsilon$

Mash / Definitions

$\Delta \ln(\omega) = \ln(\omega_f/\omega_i)$

$\Delta \ln(\omega) = -\frac{\mu}{kT}\Delta N$

B: $U = \sum N_j \epsilon_j = \frac{N}{Z}\sum g_j \epsilon_j e^{-\epsilon_j/kT}$

$\omega_B = N!\, \omega_{MB}$

$\frac{1}{y}\frac{dy}{dx} = \frac{d\ln(y)}{dx}$

$\epsilon_j = n_j^2 \frac{\pi^2\hbar^2}{2mV^{2/3}}$

$P = -\left(\frac{\partial F}{\partial V}\right)_T$

$F \equiv U - TS$

$F =^? -NkT \ \ln Z$

$H \equiv U + PV = G + TS$

$G \equiv U - TS + PV = H - TS$

Single Comp Sys: $G = \mu N$

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

B: $p_j = \frac{N_j}{N} = \frac{g_j}{Z} e^{\beta \epsilon_j}$

$\bar{E} = \sum p_j E_j$

$C_V = \frac{\partial U}{\partial T}$

gas: $U = d_{free} NkT/2$

$S = \int_0^T \frac{C_V dT'}{T'}$

$U = \int \epsilon N(\epsilon) d\epsilon$

$f, N, g \implies U \implies S \implies F \implies P, Cv$

Ideal Gas

$\omega_{BE} > \omega_{MB} > \omega_{FD}$

$FD, BE \to MB$

$[N, T, Z, \ln(Z)]$

$MB \implies S, F, \mu$

$S = \frac{U}{T} + Nk(1 - \ln(\frac{N}{Z}))$

$F = NkT(\ln(\frac{N}{Z}) - 1)$

$\mu = kT\ln(\frac{N}{Z})$

Z: $\gamma_s = 1$

$Z = V(2\pi mkT/h^2)^{3/2} = V n_Q$

$\ln(Z) = \frac{3}{2}\ln(T) + \ln(V) + \frac{3}{2}\ln\left(\frac{2\pi mk}{h^2}\right)$

$PV = NkT$

$U = \frac{3}{2}NkT$

lim: $\lambda_{dB}^3 << \frac{V}{N}, \lambda_{dB} \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$, $(\frac{V}{N})^{1/3} = l \equiv d_{avg}$

MSD: $g(\epsilon)d\epsilon, Z, \epsilon \to \frac{1}{2}mv^2$

$\implies N(\epsilon)d\epsilon = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT} dv$

$\Delta\omega_{mix} = \frac{\omega_2}{\omega_1} = \frac{N!}{N_1!N_2!}$,

$\Delta S = ... = -Nk(x_1\ln(x_1) + x_2\ln(x_2))$

$Z_{mono} = Z_{trans}$

$Z_{dia} = Z_{trans} Z_{vib} Z_{rot}$

$Z_{vib} = \frac{exp(-\theta^{vib}/2T)}{1-exp(-\theta^{vib}/2T)}$

$Z_{rot} = \frac{T}{\theta^{rot}}$

Oscillations

$\epsilon_j = (j + \frac{1}{2})h\nu$

$\theta_{vib} = \frac{h\nu}{k}$

$\theta_{vib,H2} = 6000\text{K}$

$\implies Z_{vib}$

$U_{vib} = NkT^2 \frac{\partial \ln(Z)}{\partial T} = Nk\theta(\frac{1}{2} + \frac{1}{exp(\theta/T)-1})$

$\approx NkT, \frac{T}{\theta} >> 1$

$T >> 1 \implies C_V = Nk$

$T << 1 \implies C_V = Nk(\frac{\theta}{T})^2 e^{-\theta/T}$

localized, dist $\implies$ Boltzmann, $g_j = 1$

Rotations

$\epsilon_j = j(j+1)\frac{\hbar^2}{2I}$

$\theta_{rot} = \frac{\hbar^2}{2Ik}$

$\theta_{rot,H2} = 80\text{K}$

$g_j = 2j + 1$

$T >> \theta_{rot}$

$\implies Z = \frac{T}{\theta_{rot}}$

$\implies U_{rot} = NkT$

$\implies C_{V,rot} = Nk$

$T << \theta_{rot}$

$\implies \ln(Z) \approx \ln(1 + 3e^{-2\theta_{rot}/T}) \approx 3e^{-2\theta_{rot}/T}$

$\implies U = 6Nk\theta_{rot} e^{-2\theta_{rot}/T}$

$\implies C_{V,rot} = 3Nk(\frac{2\theta_{rot}}{T})^2 e^{-2\theta_{rot}/T}$

Einstein Solids

$F = -NkT \ \ln Z$

$S = \frac{U}{T} + 3Nk \ \ln Z$

$\theta_E = h\nu/k, \ \nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}$

$U = 3Nk\theta_E(\frac{1}{2} + \frac{1}{e^{\theta_E/T}-1})$

$T >> \theta_E \implies C_V \approx 3Nk$

$T << \theta_E \implies C_V \approx 3Nk(\theta_E/T)^2 e^{-\theta_E/T}$

Debye

$g(\nu)d\nu = 4\pi V\left[\frac{1}{c_l^3} + \frac{2}{c_t^3}\right]\nu^2 d\nu$

$N(\nu)d\nu = \left(\frac{9N}{\nu_m^3}\right)\frac{\nu^2 d\nu}{e^{h\nu/kT}-1}$ for $\nu \leq \nu_m$

$\theta_D = \frac{h\nu_m}{k}$

Fermi Energy

$\mu(0) = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$

$\epsilon_F = kT_F$

$T << T_F$

$\implies \mu \approx \mu(0)\left(1 - \frac{\pi^2}{12}\left[\frac{T}{T_F}\right]^2\right)$

High T $\implies$ Ideal Gas

spatial wavefn $N = (num) \times \frac{1}{8} \times \frac{4}{3}\pi n_{max}^3$

$\epsilon_F = \frac{h^2}{8m} V^{-2/3} n_{max}^2$

Blackbody

$f_j = \frac{1}{e^{\epsilon_j/kT}-1}$

Two polarization states $\implies$ $g(\nu)d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu$

Planck Radiation $u(\nu)d\nu = g(\nu)f(h\nu)h\nu d\nu$

$\implies u(\nu)d\nu = \frac{8\pi hV}{c^3}\left(\frac{\nu^3 d\nu}{e^{h\nu/kT}-1}\right)$

$\implies u(\lambda)d\lambda = 8\pi hcV\left(\frac{d\lambda}{\lambda^5(e^{h\nu/kT}-1)}\right)$

$\nu = c/\lambda \implies d\nu = (-c/\lambda^2)d\lambda$

λ_{max} defined by $0 = \frac{d}{d\lambda}[\lambda^5(e^{hc/\lambda kT} - 1)]$

$\implies \lambda_{max}T = 2.90 \times 10^{-3}$

$P_{rad} =$(Area)$\sigma T^4, \sigma = 5.67 \times 10^{-8}$

$hc/\lambda kT >> 1$

$\implies u(\lambda)d\lambda = V\frac{8\pi kT}{\lambda^4}d\lambda$

$hc/\lambda kT << 1$

$\implies u(\lambda)d\lambda = V\frac{8\pi hc}{\lambda^5}e^{-hc/\lambda kT}d\lambda$

$Flux = (1-A)F_S/4 = \sigma T_S^4, \sigma = 5.67 \times 10^{-8}$

Photon Gas

$N = 2.02 \times 10^7 T^3 V$

$U = 7.55 \times 10^{-16} T^4 V$

$S = \frac{32\pi^5 kV}{45}\left(\frac{kT}{hc}\right)^3$

Single Osc, no restriction on N

$\implies \ln(z) = -\ln(1 - e^{-h\nu/kT})$

So using $g(\nu)d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu$ get

$\ln(Z) = \frac{8\pi^5}{45}\left(\frac{kT}{hc}\right)^3 V$

$U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} = \frac{8\pi^5 k}{15}\left(\frac{k}{hc}\right)^3 T^4 V$

$\mu = -kT\left(\frac{\partial \ln Z}{\partial N}\right)_{V,T} = 0$

$S = U/T + k\ln Z = \frac{32\pi^5 k}{45}\left(\frac{k}{hc}\right)^3 T^3 V$

$P = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} = U/3V$

BE Condensation

$N = \int_0^\infty N(\epsilon)d\epsilon = \int_0^\infty f(\epsilon)g(\epsilon)d\epsilon$

$\implies N_{ex} = 2.612V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$, this also gives T_B when $N_{ex} = N$

$U = 0.77NkT\left(\frac{T}{T_B}\right)^{3/2}$

$\epsilon_0 = \frac{3h^2}{8mV^{2/3}}$

$N_0 = N(1 - [T/T_C]^{3/2})$

$S = 1.28Nk[T/T_C]^{3/2}$