$$g(N,s) = \frac{N!}{\left(\frac{1}{2}N+s\right)\left(\frac{1}{2}N-s\right)} = \frac{N!}{N_\uparrow! N_\downarrow!} \qquad g(N,s) \approx \sqrt{\frac{2}{\pi N}}2^N e^{-\frac{2s^2}{N}}$$

$$U(s) = -2smB \qquad 2s = N_\uparrow - N_\downarrow$$

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_{N,V}$$

$$\sigma(N,s) = \ln(g(N,s))$$
$$S = k_B\sigma \qquad \tau = k_B T$$

Accessible States $(s = s_1 + s_2)$:

$$g(s) = \sum_s g_1(s_1)g_2(s-s_1)$$

System/Reservoir State Probability:

$$P(\varepsilon_s) = \frac{1}{z}e^{-\frac{\varepsilon_s}{\tau}}$$

$$z = \sum_s e^{-\frac{\varepsilon_s}{\tau}} \qquad P = -\left(\frac{\partial U}{\partial V}\right)_\sigma = \tau\left(\frac{\partial \sigma}{\partial V}\right)_U = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

$F = U - \tau\sigma$ min. in eq. with const τ, V $\qquad$ $F = -\tau\ln(z)$ to derive P, σ

<u>Ideal Monatomic Gas</u>

Given N atoms: $z_N = \dfrac{(n_Q V)^N}{N!}$ $\qquad$ If $n = \dfrac{N}{V} << n_Q$, $\quad n_Q = \left(\dfrac{M\tau}{2\pi\hbar^2}\right)^{\frac{3}{2}}$

$$PV = N\tau \qquad \sigma = N\left[\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right] \qquad C_V = \frac{3}{2}N$$

A process is reversible if the system remains infinitesimally close to the equilibrium state at all times during the process.

Average in Mode at freq. ω: $\langle s\rangle = \dfrac{1}{e^{\frac{\hbar\omega}{\tau}} - 1}$ $\qquad$ Energy Density at τ: $\langle s\rangle = \dfrac{U}{V} = \dfrac{\pi^2}{15\hbar^3c^3}\tau^4$

Radiant energy per vol: $U_\omega = \dfrac{\hbar}{\pi^2c^3}\dfrac{\omega^3}{e^{\frac{\hbar\omega}{\tau}} - 1}$ $\qquad$ Flux Density: $J_U = \sigma_B T^4$, $\sigma_B = \dfrac{\pi^2 k_B^4}{60\hbar^3c^2}$

Heat Capacity of Dielectric Solid: $C_V = \dfrac{12\pi^4 N k_B}{5}\left(\dfrac{T}{\theta}\right)^3 \to \theta = \left(\dfrac{\hbar\omega}{k_B}\right)\left(\dfrac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V} = -\tau\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$

In diffusive equilibrium if: $\mu_1 = \mu_2$

$$\mu = \mu_{int} + \mu_{ext}$$
$$\mu_{int} = \tau \ln\left(\frac{n}{n_Q}\right)$$
$$\mu_{ext} = \frac{U_{ext}}{N}$$

Gibbs Factor: $P(N, \varepsilon_s) = \dfrac{e^{\frac{N\mu - \varepsilon_s}{\tau}}}{\mathfrak{z}}$

Prob. chem. potential μ and temp τ has N particles in q.s. s of energy ε_s

$$\mathfrak{z} = \sum_N \sum_s e^{\frac{N\mu - \varepsilon_s}{\tau}}$$

$$\lambda = e^{\frac{\mu}{\tau}} \rightarrow \mathfrak{z} = \sum \lambda^N e^{-\frac{\varepsilon_s}{\tau}}$$

Therm. Average: $\langle N \rangle = \lambda \dfrac{\partial}{\partial \lambda} \ln(\mathfrak{z})$

Quant. Particle in Box: $\varepsilon = \dfrac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$

$$U = \tau^2 \left(\frac{\partial \ln(z)}{\partial \tau}\right)_V$$

$$W = PA\Delta x = P\Delta V$$

$$\tau\, d\sigma = dU + P\, dV$$

$$\int_{-\infty}^{\infty} e^{-\alpha^2 n^2}\, dn = \frac{\sqrt{\pi}}{2\alpha}$$

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N}$$

$$\langle N \rangle = \sum_N \sum_s N(N, \varepsilon_s) = \tau \left(\frac{\partial \ln(\mathfrak{z})}{\partial \mu}\right)_{\tau,V}$$

$$\langle \varepsilon_s \rangle = \sum_N \sum_s \varepsilon_s(N, \varepsilon_s) = \tau^2 \left(\frac{\partial \ln(\mathfrak{z})}{\partial \tau}\right)_{\mu,V} + \tau\mu \left(\frac{\partial \ln(\mathfrak{z})}{\partial \mu}\right)_{\tau,V}$$

$f(\varepsilon_n)$ avg. occupancy

Bose-Einstein:

$$f(\varepsilon_n) = \frac{1}{e^{\frac{\varepsilon_n - \mu}{\tau}} - 1}$$

Fermi-Dirac:

$$f(\varepsilon_n) = \frac{1}{e^{\frac{\varepsilon_n - \mu}{\tau}} + 1}$$

Classical Limit:

$$f(\varepsilon_n) = e^{\frac{\mu - \varepsilon_n}{\tau}}$$

	ΔU	$\Delta\sigma$	W	Q
Rev. Isothermal	0	$N \ln\left(\frac{V_2}{V_1}\right)$	$-N\tau \ln\left(\frac{V_2}{V_1}\right)$	$N\tau \ln\left(\frac{V_2}{V_1}\right)$
Rev. Isentropic	$-\frac{3}{2}N\tau_1\left[1 - \left(\frac{V_1}{V_2}\right)^{\frac{2}{3}}\right]$	0	$-\frac{3}{2}N\tau_1\left[1 - \left(\frac{V_1}{V_2}\right)^{\frac{2}{3}}\right]$	0
Irrev. Expansion	0	$N \ln\left(\frac{V_2}{V_1}\right)$	0	0

Constants

$k_B = 1.381 \cdot 10^{-23} \left[\frac{\mathrm{J}}{\mathrm{K}}\right]$ $\sigma_B = 5.67 \cdot 10^{-8} \left[\frac{\mathrm{J}}{\mathrm{m^2 s K^4}}\right]$ $c = 3 \cdot 10^{8} \left[\frac{\mathrm{m}}{\mathrm{s}}\right]$

Energy of Highest-Filled Orbital of Fermi Gas (spin 1/2):

$$\varepsilon_f = \frac{\hbar^2}{2M}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$

Ground State Kinetic Energy:

$$U_o = \frac{3}{5}N\varepsilon_f$$

Density of Orbitals:

$$\mathcal{D}(\varepsilon_f) = 3N/2\varepsilon_f$$

Heat Capacity of Electron Gas ($\tau << \tau_F$):

$$C_{el} = \frac{1}{3}\pi^2\mathcal{D}(\varepsilon_f)\tau \approx N\tau/\tau_F$$

Density of Orbitals (Fermi):

$$\mathcal{D}(\varepsilon_f) = \frac{V}{2\pi^2}\left(\frac{2M}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}$$

Degenerate Gas ($\tau << \tau_o$)

$$\mu = \varepsilon_f\left(1 - \frac{\pi^2\tau^2}{12\varepsilon_f^2}\right) \qquad U = \frac{3}{5}N\varepsilon_f\left(1 + \frac{5\pi^2\tau^2}{12\varepsilon_f^2}\right) \qquad \sigma = C_v = \frac{\pi^2 N\tau}{2\tau_F}$$

Density of Orbitals (Bose):

$$\mathcal{D}(\varepsilon_f) = \frac{V}{4\pi^2}\left(\frac{2M}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}$$

Einstein Condensation Temperature:

$$\tau_E = \frac{2\pi\hbar^2}{M}\left(\frac{N}{2.612V}\right)^{\frac{2}{3}}$$

Carnot Energy Efficiency:

$$\eta_c = \frac{(\tau_h - \tau_l)}{\tau_h} \geq \frac{W_{tot}}{Q_h}$$

Carnot Refrigerator Efficiency:

$$\gamma_c = \frac{\tau_l}{(\tau_h - \tau_l)} \geq \frac{Q_l}{W_{tot}}$$

Gibbs Free Energy:

$$G = U + PV - \tau\sigma = F + PV$$

Gibbs Relations:

$$\left(\frac{\partial G}{\partial \tau}\right)_{N,P} = -\sigma; \ \left(\frac{\partial G}{\partial P}\right)_{N,\tau} = V; \ \left(\frac{\partial G}{\partial N}\right)_{\tau,P} = \mu$$

Law of Mass Action:

$$\prod n_j^{v_j} = K(\tau)$$

Example:

$$2\,\mathrm{A}^+ + \mathrm{B}^- \rightleftharpoons \mathrm{C} \rightarrow \frac{[\mathrm{C}]}{[\mathrm{A}^+]^2[\mathrm{B}^-]} = K_{eq}$$

Ideal Gas:

$$\mu(P,\tau) = \tau \ln\left(\frac{P}{\tau n_Q}\right)$$
$$G(N,P,\tau) = N\tau \ln\left(\frac{P}{\tau n_Q}\right)$$

Clausius-Clapeyron:

$$\frac{dP}{d\tau} = \frac{L}{\tau \Delta v} = \frac{LP}{\tau^2}$$

Van der Waal's Equation:

$$\left(P + \frac{N^2 a}{V^2}\right)(V - bN) = N\tau$$

Free Energy:

$$F_{VdW} = -N\tau\left(\ln\left(\frac{n_Q(V-bN)}{N}\right) + 1\right) - \frac{N^2 a}{V}$$

Van der Waal's Critical Points:

$$\tau_c = \frac{8a}{27b} \qquad P_c = \frac{a}{27b^2} \qquad V_c = 3Nb$$

Van der Waal's Gibbs Energy:

$$G = -N\tau\left(\ln\left(\frac{n_Q(V-bN)}{n}\right) + 1\right) - \frac{2N^2 a}{V}$$

Gibbs Relations:

$$\left(\frac{\partial G}{\partial P}\right)_{\tau,N} = \frac{V}{N};\ \left(\frac{\partial G}{\partial \tau}\right)_{P,N} = -\frac{\sigma}{N} = -S$$

Magnetization:

$$M = \mu n \tanh\left(\frac{\mu\lambda M}{\tau}\right)$$

Conditions:

If $\tau > \tau_c \rightarrow M = 0$; If $\tau < \tau_c \rightarrow M \neq 0$ (stable)

Average Force on Wall:

$$F_{ix} = \frac{2mv_x}{\Delta t}$$

Pressure:

$$P = \frac{Nm}{AL_x}\langle v_x^2 \rangle$$

Gibbs Sum:

$$\mathfrak{z}(\mu,\tau,N) = \sum_{N=0}^{\infty}\sum_{S(N)} \lambda^N e^{-\varepsilon_s(N)}\tau$$

pH:

$$\text{pH} = -\log_{10}\left([\text{H}^+]\right)$$