

Useful Equations

First Law of Thermo $Q = W + \Delta E$. **Ideal Gas** $PV = NkT$, $k_B = 1.381 \times 10^{-23} J/K$

Equipartition $E = (f/2)NkT$, $f \equiv$ active degrees of freedom. **Heat capacity of ideal gas**

$C_V = \frac{f}{2}Nk$, $C_p = \frac{f}{2}Nk + Nk$. **Entropy of Monatomic ideal gas, Sackur-Tetrode**

$$\text{Equation } S = k_B \ln \Omega_N = Nk_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$

Canonical Ensemble: partition function $Z = \sum_j \exp(-E_j/kT)$; probability of occupying

$$\text{state } j, P_j = \frac{\exp(-\beta E_j)}{Z}; \langle E \rangle = kT^2 \left(\frac{\partial(\ln Z)}{\partial T} \right); S = \frac{\langle E \rangle}{T} + k \ln Z.$$

In the above Z can be **N-particle or one-particle** partition function. For **one-particle partition function** Z_1 , the following relations are valid:

N **distinguishable** non-interacting particles, $Z_N = Z_1^N$; N **indistinguishable** non-interacting particles, $Z_N = Z_1^N / N!$

Semi-classical one-particle partition $Z_1 = \int_0^\infty D(\varepsilon) \exp(-\beta \varepsilon)$.

Gibb's Method for finding **density of state**, which in three dimensions (3D) is

$$\frac{(\text{Position Volume})(\text{Momentum Volume})}{h^3} = \frac{V}{h^3} 4\pi p^2 dp. \text{ Then uses the free particle}$$

dispersion relation $\varepsilon = p^2/2m \rightarrow d\varepsilon = 2pdः/m$ to give $D(\varepsilon) = \frac{2\pi(2m)^{3/2} V \varepsilon^{1/2}}{h^3}$. Number of

particle state with energy $\varepsilon = \varepsilon_1$ to $\varepsilon = \varepsilon_2$, $N_{\varepsilon_1, \varepsilon_2} = \int_{\varepsilon_1}^{\varepsilon_2} d\varepsilon D(\varepsilon)$. **Integrals:**

$$\int_0^\infty \exp(-ax^2) = \sqrt{\pi}/2a^{1/2}, \int_0^\infty x^2 \exp(-ax^2) = \sqrt{\pi}/4a^{3/2}, \int_0^\infty x^4 \exp(-ax^2) = 3\sqrt{\pi}/(8a^{5/2}),$$

$$\int_0^\infty \exp(-ax) = (1/a); \int_0^\infty x \exp(-ax) = (1/a^2); \int_0^\infty x^n \exp(-ax) = (n!/(a^{n+1}))$$

Stirling's Approximation: $\ln N! = N \ln N - N$

Chemical Potential: Energy needed to put one particle into a system.

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}, G = N\mu, \mu = k_B T \ln \left(\frac{V}{N\lambda^3} \right)$$

Grand-canonical Ensemble

Grand partition function, $\Xi = \sum_i z^{N_i} \exp(-\beta E_i)$, $z = \exp(\beta\mu)$.

Probability of state i with energy E_i and particle number N_i , $P_i = \frac{z^{N_i} \exp(-\beta E_i)}{\Xi}$.

Average Energy $\langle E \rangle = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)$ and **average particle number** $\langle N_i \rangle = N = z \frac{\partial \ln \Xi}{\partial z}$.

Grand Potential $\Omega_g = -k_B T \ln \Xi = -PV$

Fermi-Dirac (FD) Degenerate gas

Average number of particle in state of energy ϵ , $\langle n \rangle_{FD} = \frac{1}{z^{-1} \exp(\beta\epsilon) + 1}$, $z = \exp(\beta\mu)$.

$$N = \sum_{\epsilon} \frac{1}{z^{-1} \exp(\beta\epsilon) + 1} = \int_0^{\infty} d\epsilon \frac{1}{z^{-1} \exp(\beta\epsilon) + 1} D(\epsilon), \quad \frac{PV}{k_B T} = \ln \Xi = \sum_{\epsilon} \ln(1 + z \exp(-\beta\epsilon)).$$

$$\frac{PV}{k_B T} = \int_0^{\infty} d\epsilon D(\epsilon) \ln(1 + z \exp(-\beta\epsilon)).$$

Fermi-Dirac Functions $f_v(z) = \frac{1}{\Gamma(v)} \int_0^{\infty} \frac{x^{v-1} dx}{z^{-1} \exp(x) + 1}$, $\Gamma(v) = (v-1)!$

$$\Gamma(m+1) = m!, \quad m=0,1,2..,0! = 1; \quad \Gamma\left(m + \frac{1}{2}\right) = \frac{1 \cdot 3 \cdot 5 \cdots (2m-1)}{2^m} \sqrt{\pi}, \quad m=1,2,3.., \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

Useful for **classical limit, low z**, $f_v(z) = z - \frac{z^2}{2^v} + \frac{z^3}{3^v} - \frac{z^4}{4^v} + \dots$.

Low temperature limit, $z = \exp(\beta\mu)$, $\xi = \beta\mu = \ln z$:

$$f_v(z) = \frac{\xi^v}{\Gamma(v+1)} \left[1 + v(v-1) \frac{\pi^2}{6} \frac{1}{\xi^2} + v(v-1)(v-2)(v-3) \frac{7\pi^4}{360} \frac{1}{\xi^4} + \dots \right]. \quad \text{Using } \xi^v = (\ln z)^v,$$

$$f_{5/2}(z) = \frac{8}{15\pi^{1/2}} (\ln z)^{5/2} \left[1 + \frac{5\pi^2}{8} \frac{1}{(\ln z)^2} + \dots \right], \quad f_{3/2}(z) = \frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} + \dots \right].$$

$$T \sim 0, \quad \text{3D with dispersion } \epsilon = p^2/2m, \quad N = \int_0^{\epsilon_F} D(\epsilon) d\epsilon = \int_0^{\epsilon_F} 2 \times \frac{2\pi(2m)^{3/2} V \epsilon^{1/2}}{h^3} d\epsilon \rightarrow$$

$$\text{Fermi Energy } \epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}; \quad \text{Fermi temperature } T_F = \frac{\epsilon_F}{k_B}; \quad \text{Energy}$$

$$\langle E \rangle = \int_0^{\epsilon_F} \epsilon D(\epsilon) d\epsilon = \frac{3}{5} N \epsilon_F, \quad \text{Chemical Potential } \mu = \epsilon_F.$$

Finite but sufficiently low temperature, equations valid for all Fermion system

$$\mu = \epsilon_F - \frac{\pi^2}{6} \frac{D'(\epsilon_F)}{D(\epsilon)} (k_B T)^2. \quad \langle E \rangle = E_{gs} + \frac{\pi^2}{6} D(\epsilon_F) (k_B T)^2, \quad E_{gs} = \int_0^{\epsilon_F} d\epsilon \epsilon D(\epsilon). \quad (\text{FD1ABC})$$

$$\text{EXAMPLE: 3D Fermi Gas with } D(\epsilon) = 2 \times \frac{2\pi(2m)^{3/2} V \epsilon^{1/2}}{h^3},$$

$$N = \sum_{\varepsilon} \frac{1}{z^{-1} \exp(\beta\varepsilon) + 1} = \int_0^{\infty} d\varepsilon \frac{1}{z^{-1} \exp(\beta\varepsilon) + 1} D(\varepsilon) = \frac{4\pi(2m)^{3/2}V}{h^3} \int_0^{\infty} d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1} \exp(\beta\varepsilon) + 1},$$

$$N = \frac{2V}{(h^2/(2m))^{3/2}} \frac{\pi^{3/2}}{\Gamma(3/2)} \int_0^{\infty} d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1} \exp(\beta\varepsilon) + 1}, \text{ where } \Gamma\left(\frac{3}{2}\right) = \frac{\pi^{1/2}}{2}. \text{ Use } x = \beta\varepsilon = \frac{\varepsilon}{k_B T},$$

$$\frac{2V}{(h^2/(2mk_B T))^{3/2}} \frac{\pi^{3/2}}{\Gamma(3/2)} \int_0^{\infty} d\varepsilon \frac{x^{(3/2)-1}}{z^{-1} \exp(x) + 1}, N = \frac{2V}{\lambda^3} f_{3/2}(z), \lambda = \frac{h}{(2\pi m k_B T)^{1/2}}.$$

Also can show $\frac{PV}{k_B T} = \int_0^{\infty} d\varepsilon D(\varepsilon) \ln(1 + z \exp(-\beta\varepsilon)) = \frac{2V}{\lambda^3} f_{5/2}(z).$

$$\langle E \rangle = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{z,V}, \frac{PV}{k_B T} = \ln \Xi, \langle E \rangle = \frac{3}{2} \frac{k_B T}{\lambda^3} V f_{5/2} = \frac{3}{2} N k_B T \frac{f_{5/2}}{f_{3/2}}.$$

Chemical potential at Low T: $f_{3/2}(z) = \frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} + .. \right], z = \exp \beta \mu.$

$$N = \frac{2V}{\lambda^3} f_{3/2}(z) \rightarrow f_{3/2}(z) = \frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} + .. \right] = \left(\frac{N}{2V} \right) \lambda^3, \text{ with } \ln z = \frac{\mu}{k_B T},$$

$$\lambda = \frac{h}{(2\pi m k_B T)^{1/2}} \rightarrow \left(\frac{\mu}{k_B T} \right)^{3/2} = \left(\frac{3\pi^{1/2} N}{8V} \right) \frac{h^3}{(2\pi m k_B T)^{3/2}} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + .. \right]^{-1}. \text{ Some terms}$$

$$\text{cancel leading to } \mu = \frac{h^2}{2m} \left(\frac{3}{8\pi} \frac{N}{V} \right)^{2/3} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + .. \right]^{-2/3} = \varepsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + .. \right]^{-2/3}$$

Zeroth order solution keeps the first term on right hand side (RHS) to give $\mu = \varepsilon_F$. **First**

order approximation keeps up to T^2 order in RHS $\mu = \varepsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + .. \right]^{-2/3}$, and use

$$\mu = \varepsilon_F \text{ on that term, then } \textbf{Taylor expand } \mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + .. \right].$$

For the energy, $\langle E \rangle = \frac{3}{2} N k_B T \frac{f_{5/2}}{f_{3/2}}$, which can be combined with

$$f_{5/2}(z) = \frac{8}{15\pi^{1/2}} (\ln z)^{5/2} \left[1 + \frac{5\pi^2}{8} \frac{1}{(\ln z)^2} + .. \right], f_{3/2}(z) = \frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} + .. \right],$$

$$\langle E \rangle = \frac{3}{2} N k_B T \times \frac{8}{15\pi^{1/2}} (\ln z)^{5/2} \left[1 + \frac{5\pi^2}{8} \frac{1}{(\ln z)^2} + \dots \right] \div \left[\frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} + \dots \right] \right],$$

$$\langle E \rangle = \frac{3}{2} N k_B T \times \frac{2}{5} (\ln z) \left[1 + \frac{5\pi^2}{8} \frac{1}{(\ln z)^2} + \dots \right] \left[1 + \frac{\pi^2}{8} \frac{1}{(\ln z)^2} + \dots \right]^{-1} \text{ We use } \ln z = \frac{\mu}{k_B T},$$

$$\langle E \rangle = \frac{3}{2} N k_B T \times \frac{2}{5} \left(\frac{\mu}{k_B T} \right) \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right]^{-1} \text{ To obtain term up to } T^2$$

Use $\mu = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right]$ for 1st term, and $\mu = \varepsilon_F$ for other 2 terms, and Taylor

$$\text{expand last term } \langle E \rangle = \frac{3}{5} \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right] \left[1 - \frac{\pi^2}{8} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right]$$

$$\langle E \rangle \approx \frac{3}{5} \varepsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right].$$

NOTE: 1) For different dimension or dispersion relation, we will obtain different $D(\varepsilon)$, and the same method can be used to obtain this result, or simply use (**FD1ABC**); 2) For classical results (High T, or dilute low N/V) use low z expansion of $f_v(z)$, and you should recover the **classical ideal gas results**.

Bose-Einstein (BE) gas

$$\text{Bose-Einstein(BE) function: } g_v = \frac{1}{\Gamma(v)} \int_0^\infty \frac{x^{v-1}}{z^{-1} \exp(x) - 1}.$$

Expansion form, $g_v = z + \frac{z^2}{2^v} + \frac{z^3}{3^v} + \frac{z^4}{4^v} + \dots, 1 < z < 0$. High T (classical), $g_v \approx z$, small z.

Low temperature, $z \rightarrow 1, g_v(1) = \zeta(v)$ the Riemann-Zeta function.

$$\text{3D BE gas with dispersion relation } \varepsilon = \frac{p^2}{2m}, D(\varepsilon) = \frac{2\pi V (2m)^{3/2}}{h^3} \varepsilon^{1/2},$$

$$N = \int_0^\infty \frac{D(\varepsilon) d\varepsilon}{z^{-1} \exp(\beta\varepsilon) - 1} = \frac{V g_{3/2}(z)}{\lambda^3}, \text{ and } \frac{PV}{k_B T} = - \int_0^\infty d\varepsilon D(\varepsilon) \ln(1 - z \exp(-\beta\varepsilon)) = \frac{V g_{5/2}(z)}{\lambda^3},$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \langle E \rangle = - \left(\frac{\partial q}{\partial \beta} \right)_{z,V}, q = \frac{PV}{k_B T}. \text{ Heat capacity, constant volume,}$$

$C_v = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V}$, **constant pressure**, $C_p = \left(\frac{\partial H}{\partial T} \right)_{N,P}$, Enthalpy $H = \langle E \rangle + PV$. Using

above we can show $\langle E \rangle = \frac{3}{2} k_B T \frac{V}{\lambda^3} g_{5/2}(z) = \frac{3}{2} N k_B T \frac{g_{5/2}(z)}{g_{3/2}(z)}$, also $PV = \frac{2}{3} \langle E \rangle$.

Heat Capacity C_v : $\langle E \rangle$ is a function of T and z (or V), with **fugacity** $z = \exp(\beta\mu)$:

$$C_v = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B \left[\frac{g_{5/2}(z)}{g_{3/2}(z)} + T \frac{1}{g_{3/2}(z)} \left(\frac{\partial g_{5/2}}{\partial T} \right)_{N,V} - T \frac{g_{5/2}(z)}{g_{3/2}^2(z)} \left(\frac{\partial g_{3/2}}{\partial T} \right)_{N,V} \right].$$

We must find $\left(\frac{\partial g_{3/2}}{\partial T} \right)_{N,V}$ and $\left(\frac{\partial g_{5/2}}{\partial T} \right)_{N,V}$. Start with $N = \frac{V g_{3/2}(z)}{\lambda^3} \rightarrow g_{3/2}(z) = \frac{N}{V} \lambda^3$, and

$$\lambda^3 \propto T^{-3/2} \rightarrow \left(\frac{\partial g_{3/2}}{\partial T} \right)_{N,V} = -\frac{3}{2T} g_{3/2}(z). \text{ But using, } g_v(z) = z + \frac{z^2}{2^v} + \dots \rightarrow z \frac{dg_v}{dz} = g_{v-1},$$

$$\text{which gives } \left(\frac{\partial g_{3/2}}{\partial T} \right)_{N,V} = \frac{dg_{3/2}}{dz} \left(\frac{\partial z}{\partial T} \right)_{N,V} = -\frac{3}{2T} g_{3/2}(z) \rightarrow \left(\frac{\partial z}{\partial T} \right)_{N,V} = -z \frac{3}{2T} \frac{g_{3/2}}{g_{1/2}}.$$

$$\left(\frac{\partial g_{5/2}}{\partial T} \right)_{N,V} = \frac{dg_{5/2}}{dz} \left(\frac{\partial z}{\partial T} \right)_{N,V} = -\frac{3}{2T} \frac{g_{3/2}^2}{g_{1/2}}, \text{ and } \left(\frac{\partial g_{1/2}}{\partial T} \right)_{N,V} = -\frac{3}{2T} \frac{g_{3/2} g_{-1/2}}{g_{1/2}}.$$

$$\text{Using the above relations, } \frac{C_v}{N k_B} = \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)}, T > T_B.$$

Special Behavior of BE gas at Low Temperature

At Low temperature, $z \rightarrow 1$, $g_v(z=1) = \zeta(v)$. Some values are $\zeta(2) = \frac{\pi^2}{6}$; $\zeta(4) = \frac{\pi^4}{90}$;

$$\zeta(6) = \frac{\pi^6}{945}; \zeta\left(\frac{3}{2}\right) = 2.61238; \zeta\left(\frac{5}{2}\right) = 1.34349; \zeta\left(\frac{7}{2}\right) = 1.12673; \zeta(3) = 1.20206;$$

$$\zeta(5) = 1.03693; \zeta(7) = 1.00835.$$

Some values of v have special behavior as $z \rightarrow 1$, or $\alpha \rightarrow 0$ $z = \exp(\beta\mu) = \exp-\alpha$.

$$g_v(\exp-\alpha) = \frac{\Gamma(1-v)}{\alpha^{1-v}} + \sum_{i=0}^{\infty} \frac{(-1)^i}{i!} \zeta(v-i) \alpha^i, \lim_{\alpha \rightarrow 0} g_v(\exp \alpha) \approx \frac{\Gamma(1-v)}{\alpha^{1-v}}.$$

$$\text{EXAMPLE: 3D Bose-Einstein Gas with } D(\epsilon) = \frac{2\pi(2m)^{3/2} V \epsilon^{1/2}}{h^3},$$

$$N = \int_0^{\infty} \frac{D(\epsilon) d\epsilon}{z^{-1} \exp(\beta\epsilon) - 1} = \frac{2\pi(2m)^{3/2} V}{h^3} \int_0^{\infty} d\epsilon \frac{\epsilon^{1/2}}{z^{-1} \exp(\beta\epsilon) - 1}. \text{ Use } x = \beta\epsilon = \frac{\epsilon}{k_B T},$$

$$N = \frac{V}{\lambda^3} \frac{1}{\Gamma(3/2)} \int_0^\infty dx \frac{x^{(3/2)-1}}{z^{-1} \exp(x) - 1} = \frac{V}{\lambda^3} g_{3/2}(z), \quad \lambda = \frac{h}{(2\pi m k_B T)^{1/2}}.$$

The integral neglect the number of particles in the ground state, N_0 , also called $\langle n_1 \rangle$, so that the relation above is really for particle in the excited states, $N_e = \frac{V}{\lambda^3} g_{3/2}(z)$. The total number of particles is $N = N_0 + N_e$, and above the transition temperature, $T > T_B$, the number of particle in the ground state is zero, $N_0 = 0, N_e = N$. For $T \gg T_B$, z is a small positive number, but as $T \rightarrow T_B, z \rightarrow 1$, and $g_{3/2}(z) \rightarrow g_{3/2}(1) = \zeta(3/2)$. For $T \leq T_B, z = 1$, and $N_0 > 0$, and $N_e = \frac{V}{\lambda^3} g_{3/2}(1) = \frac{V}{\lambda^3} \zeta(3/2)$. To find the transition temperature T_B , note

$$\text{that at this temperature } T = T_B, N = N_e, \text{ so } N = \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) = \frac{V}{\left(h^3 / (2\pi m k_B T_B)^{3/2}\right)} \zeta\left(\frac{3}{2}\right),$$

$$\text{which gives } T_B^{3/2} = \left(\frac{h^2}{2\pi m k_B}\right)^{3/2} \left(\frac{N}{V \zeta(3/2)}\right). \text{ For } T < T_B, N_e = \frac{V}{\left(h^3 / (2\pi m k_B T)^{3/2}\right)} \zeta\left(\frac{3}{2}\right),$$

$$N_e = NT^{3/2} \left(\left(\frac{h^2}{2\pi m k_B}\right)^{3/2} \left(\frac{N}{V \zeta(3/2)}\right) \right)^{-1} = N \left(\frac{T}{T_B}\right)^{3/2}, N_0 = N - N_e = N \left(1 - \left(\frac{T}{T_B}\right)^{3/2}\right).$$

EXAMPLE: 2D BE system, with dispersion $\varepsilon = p^2 / 2m$.

Start with quantum counting $\sum(\dots) \rightarrow \frac{A}{h^2} 2\pi pdp$ in 2D, where A is the total area, accessible to the gas. Use dispersion relation $\varepsilon = p^2 / 2m \rightarrow pdp = md\varepsilon$,

$$\sum(\dots) \rightarrow \frac{A}{h^2} 2\pi pdp = \frac{A}{h^2} 2\pi m d\varepsilon, \text{ and } D(\varepsilon) = \frac{A}{h^2} 2\pi m.$$

$$N = \int_0^\infty \frac{D(\varepsilon) d\varepsilon}{z^{-1} \exp(\beta\varepsilon) - 1} = \frac{2\pi mA}{h^2} \int_0^\infty d\varepsilon \frac{1}{z^{-1} \exp(\beta\varepsilon) - 1}, \text{ with } x = \beta\varepsilon,$$

$$N = \frac{A}{\lambda^2} \int_0^\infty dx \frac{1}{z^{-1} \exp(x) - 1} = \frac{A}{\lambda^2} \left[\ln(1 - z \exp(-x)) \right]_0^\infty \rightarrow N = -\frac{A}{\lambda^2} \ln(1 - z).$$

Since $N > 0, 0 < z < 1$, so as $z \rightarrow 1, N = N_e \rightarrow \infty$, so unlike in **3D** there is **no limit** on the **number of particles** can occupy the **excited states**. Hence it appears that there BE condensation do not occur in 2D for **ideal BE gas**.

EXAMPLE: Size of White Dwarfs

Gravitational pressure $P_{\text{gravity}} = \left(\frac{M}{(4\pi R^3 / 3)} \right) R \left(\frac{1}{2} \frac{GM}{R^2} \right)$ that tending to **collapse** star.

Fermi gas pressure $P_0 = \frac{2}{5} \left(\frac{3}{8\pi} \right)^{2/3} \frac{\hbar^2}{2m} \left(\frac{N}{(4\pi R^3 / 3)} \right)^{5/3}$ **opposing collapse of star**.

Here m is the mass of an electron. If we assume that the star is made up of He4 (2 protons + 2 neutrons), then the number of nucleons (protons or neutrons) in the star is about

$N_n = \frac{M}{m_p}$, where M is the “effective” mass of the star, and $m_p = 1.67 \times 10^{-27} \text{ kg}$ is mass of

a nucleon. There are 2 electrons per He4, the number of electrons $N = \frac{N_n}{2} = \frac{M}{2m_p}$, which

gives $P_0 = \frac{2}{5} \left(\frac{3}{8\pi} \right)^{2/3} \frac{\hbar^2}{2m} \left(\frac{1}{2m_p (4\pi R^3 / 3)} \right)^{5/3} M^{5/3}$. At equilibrium the two pressures must

be equal: $P_0 = P_{\text{gravity}} \rightarrow \frac{R}{R_\odot} = C \left(\frac{M_\odot}{M} \right)^{1/3}$, where $M_\odot = 1.9891 \times 10^{30} \text{ kg}$ is the mass of the

sun, and $R_\odot = 6.957 \times 10^8 \text{ m}$ is the sun’s radius, and C is the constant to be determined.

EXAMPLE: Photon Gas Density of state of EM modes in the frequency range v to $v+dv$,

$D_{\text{EM}} dv = \left(\frac{8\pi}{c^3} \right) V v^2 dv$. **Helmholtz Free Energy** is $F = \langle E \rangle - TS$, and equation 7.10, it is

$F = -k_B T \ln Z_N$, where Z_N is the N-particle **partition function**. For **identical non-interacting distinguishable particles** $Z_N = Z_1^N$, where Z_1 is the **one-particle partition function**. Hence, the **N-particle Helmholtz free energy** is essentially **additive**:

$F(N) = -k_B T \ln Z_1^N = \sum_{i=1}^N -k_B T \ln Z_1 + \text{constant}$, where $Z_1 = Z_2 = Z_3 = \dots = Z_N$.

Using $Z = \sum_{\epsilon} \exp(-\beta\epsilon)$, where it is possible for two or more states to have the same energy. For **indistinguishable** and **identical** photons of a **single mode** with frequency, v , and energy $\epsilon_n = nhv$, where n is the number of photons of **that mode**, and

$$Z = \sum_{n=0}^{\infty} \exp(-\beta nhv), \sum_{n=0}^k r^n = \frac{1-r^{k+1}}{1-r}, Z_v = \sum_{n=0}^{\infty} \left[\exp(-\beta hv) \right]^n = \frac{1}{1-\exp(-\beta hv)}.$$

$F_{\text{photon}} = \sum_i -k_B T \ln Z_i = -k_B T \int_0^{\infty} dv D_{\text{EM}}(v) \ln \left(\frac{1}{1-\exp(-\beta hv)} \right)$. Integrate by parts,

$$F_{\text{photon}} = -k_B T \left(\frac{8\pi}{c^3} \right) V \beta h \int_0^\infty dv \frac{v^3}{3} \frac{\exp(-\beta hv)}{1 - \exp(-\beta hv)} = -k_B T \left(\frac{8\pi}{c^3} \right) V \left(\frac{k_B T}{h} \right)^3 \frac{\pi^4}{45}.$$

In above we used the substitution $x = \beta v$, and the Riemann-Zeta Function $\zeta(4)$.

Free Energy 1st Law of Thermo, **Change in Energy** $\Delta E = T\Delta S - P\Delta V$, but with inclusion of chemical potential, μ , $\Delta E = T\Delta S - P\Delta V + \mu\Delta N$, so we say that energy, $E(S, V, N)$, is **naturally** a function of **thermo**-variables S, V and N, we can use this to determine the partial differentiation identity of 10.8, 10.9, and also $(\partial E / \partial N)_{S,V} = \mu$. But

we can also write $\Delta S = \frac{1}{T}\Delta E + \frac{P}{T}\Delta V - \frac{\mu}{T}\Delta N$, which means that Entropy $S(E, V, N)$ is **naturally** a function of **thermo**-variables E, V and N, and consequently we can use this to find, $(\partial S / \partial E)_{V,N} = 1/T$, $(\partial S / \partial V)_{E,N} = P/T$, $(\partial S / \partial N)_{E,V} = -\mu/T$.

Helmholtz Free Energy: Suppose we want a **free energy**, that is naturally a function of T, V and N, we can see that we must eliminate ΔS from $\Delta E = T\Delta S - P\Delta V + \mu\Delta N$. If you think about this, it is easy to see that this is Helmholtz Free Energy $F = E - TS$. Take the differential we get $\Delta F = \Delta E - T\Delta S - S\Delta T$, which combine with $\Delta E = T\Delta S - P\Delta V + \mu\Delta N$ gives $\Delta F = -S\Delta T - P\Delta V + \mu\Delta N$, which means that $F(T, V, N)$ is naturally a function of T, V, N. Take the differential $F(T, V, N) \rightarrow \Delta F = \left(\frac{\partial F}{\partial T} \right)_{V,N} \Delta T + \left(\frac{\partial F}{\partial V} \right)_{T,N} \Delta V + \left(\frac{\partial F}{\partial N} \right)_{T,V} \Delta N$,

and compare with the original ΔF , to obtain $\left(\frac{\partial F}{\partial T} \right)_{V,N} = -S$; $\left(\frac{\partial F}{\partial V} \right)_{T,N} = -P$; $\left(\frac{\partial F}{\partial N} \right)_{T,V} = \mu$.

Helmholtz Free Energy is associated with the **canonical ensemble**, where $F = -k_B T \ln Z$, where $Z = \sum \exp(-\beta \epsilon)$ is the **partition function**.

Important: In the **microcanonical ensemble** the **second law** states that a system will evolve to an **equilibrium** state that **maximizes** the entropy $S(E, V, N)$. In the **canonical ensemble** it will evolve to a state that **minimizes** the **Helmholtz Free energy** $F(T, V, N)$.

Other free energies are Enthalpy $H(S, P, N)$ and Gibb's Free energy $G(T, P, N)$.

CONSTANT: Boltzman $k_B = 1.381 \times 10^{-23} J/K$; Planck's $h = 6.626 \times 10^{-34} J \cdot s$;

Nucleon's mass (proton or neutron) $m_n = 1.67 \times 10^{-27} kg$; electron's mass

$m = 9.11 \times 10^{-31} kg$; Avogrado number $N_A = 6.023 \times 10^{23} mole^{-1}$;

$$G = 6.67 \times 10^{-11} m^3 \cdot kg^{-1} \cdot s^{-2} \quad \text{Taylor Series: } \ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} \dots;$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots; (1+x)^a \sim 1 + ax \text{ small } x; \exp(x) = 1 + x + \frac{x^2}{2!} + \dots$$