

## Physics 112, Review

Multiplicity of a binary system: Suppose that we have  $N$  magnets, each with spin up/down. For

spin excess,  $S = \frac{1}{2}(N_{\uparrow} - N_{\downarrow})$

always even

$$g(N, S) = \binom{N}{N_{\uparrow}} = \frac{N!}{N_{\uparrow}! N_{\downarrow}!} = \frac{N!}{(\frac{N}{2}+S)! (\frac{N}{2}-S)!} \approx g_0 e^{-2S^2/N}$$

Stirling Approximation:

$$\ln(N!) = \frac{1}{2} \ln(2\pi) + (N + 1/2) \ln(N) - N$$

$$\boxed{\ln(N!) \approx N \ln(N) - N}$$

Fundamental Assumption:

A closed system (constant  $U, N, V$ , and all external parameters) is equally likely to be in any of the accessible states.

Ensemble Average:

Consider an ensemble of identical systems, each in one of the accessible states. The average of a property over that group is the ensemble average.

$$\langle X \rangle = \sum_S X(S) P(S) ; \text{ where } S \text{ is a unique state}$$

Thermal Equilibrium:

When 2 systems are put in thermal contact so that they may exchange energy, we tend to find the systems in the state with the largest multiplicity.

For 2 systems in thermal contact,

$$U = U_1 + U_2; \quad \sigma(N, U) = g_1(N_1, U_1) \cdot g_2(N_2, U_2)$$

At thermal equilibrium,  $g$  is maximized. Thus,

$$0 = dg = \left(\frac{\partial g}{\partial U_1}\right) dU_1 + \left(\frac{\partial g}{\partial U_2}\right) dU_2; \quad dU_1 + dU_2 = 0$$

$$\frac{1}{g_1} \left(\frac{\partial g_1}{\partial U_1}\right)_{N_1} = -\frac{1}{g_2} \left(\frac{\partial g_2}{\partial U_2}\right)_{N_2}$$

$$\left(\frac{\partial \log(g_1)}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \log(g_2)}{\partial U_2}\right)_{N_2}$$

We define entropy:  $\boxed{\sigma(N, U) = \log(g(N, U))} ; \quad S = k_B \sigma$

At thermal equilibrium, the temperature of 2 systems are equal,

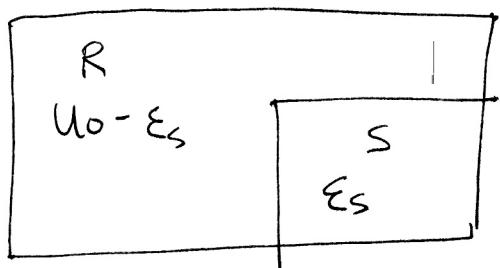
$$\boxed{\frac{1}{T} = \left(\frac{\partial \sigma}{\partial U}\right)_N; \quad T = k_B T}$$

Note:  $\left(\frac{\partial \sigma}{\partial U}\right)_N = \lim_{\Delta U \rightarrow 0} \frac{\sigma(N, U + \Delta U) - \sigma(N, U)}{\Delta U}$

Boltzmann Factor:

Suppose we have a system (total energy  $U_0$ ) composed of a smaller system ( $s$ , energy  $E_s$ ) and a reservoir ( $R$ ).

What is the probability that we will find system  $s$  in the specific state  $s$  with energy  $E_s$ ?



Since we place  $S$  in a specific state, it has multiplicity of 1. The total multiplicity,

$$g = g_R \cdot g_S = g_R$$

Now, for  $U_0 \ll \epsilon_S$ ,

$$\sigma_R(U-\epsilon_S) \approx \sigma_R(U) - \epsilon \left( \frac{\partial \sigma_R}{\partial U} \right)_{U=0} + \dots$$

$$\approx \sigma_R(U) - \epsilon/\tau + \dots$$

Thus,

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g(\epsilon_1)}{g(\epsilon_2)} = \frac{g_R(U_0-\epsilon_1)}{g_R(U_0-\epsilon_2)} \approx \frac{e^{\sigma_R(U-\epsilon_1)}}{e^{\sigma_R(U-\epsilon_2)}} \approx \frac{e^{\sigma_R(U)-\epsilon_1/\tau}}{e^{\sigma_R(U)-\epsilon_2/\tau}}$$

Finally,

$$g(U-\epsilon) = e^{\sigma_R(U)} e^{-\epsilon/\tau}$$

↑                      ↑  
constant            Boltzmann factor

$$\boxed{\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{e^{-\epsilon_1/\tau}}{e^{-\epsilon_2/\tau}}} \quad [\text{Relative probability}]$$

To find the absolute probability, we define the partition function,

$$Z = \sum_S e^{-\epsilon_S/\tau}$$

Now,

$$\boxed{P(\epsilon_S) = \frac{e^{-\epsilon_S/\tau}}{Z}}$$

We can calculate the average energy of the system,

$$U = \langle \epsilon \rangle = \sum_S \epsilon_S P(\epsilon_S) = \frac{1}{Z} \sum_S \epsilon_S e^{-\epsilon_S/\tau}$$

$$\boxed{\langle \epsilon \rangle = \tau^2 \left( \frac{\partial \ln(Z)}{\partial \tau} \right)}$$

## Combining Partition Functions:

$Z \propto g$ . Thus, we expect the total partition function of 2 systems to be the product of the individual partitions.

For example, suppose we have  $N$  atoms in a box, each with partition function  $z_1, z_2, \dots, z_n$

① If the atoms are distinguishable:  $Z = \prod_{j=1}^N z_j$

② If the atoms are indistinguishable:  $Z = \frac{1}{N!} \prod_{j=1}^N z_j = \frac{z_1^N}{N!}$

## Thermodynamic Identity:

For a system at thermal equilibrium with a reservoir and closed such that there is no particle exchange.

$$\cancel{dU = T dS - P dV}$$

$$dU = T dS - P dV$$

Pressure: from the TI, we see

$$P = -\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_U$$

## Helmholtz free Energy:

At constant volume and temperature (and ~~constant  $N$~~  constant  $N$ ), the free energy of a system is minimized when in contact with a thermal reservoir.

~~$$F = U - TS$$~~

$$F = U - TS$$

Now,  $dF = \underbrace{du - \tau d\sigma - \sigma d\tau}_{PdV \text{ from TI}} = -\sigma d\tau - PdV$

Thus,

$$\left[ \left( \frac{\partial F}{\partial \tau} \right)_V = -\sigma ; \left( \frac{\partial F}{\partial V} \right)_{\tau} = -P \right]$$

Determining F from Z:

Given:  $F = U - \tau \sigma ; \sigma = -(\partial F / \partial \tau)_V$

$$F = U + \tau (\partial F / \partial \tau)_V \Rightarrow U = -\tau^2 \frac{\partial}{\partial \tau} (E)$$

Recall also,  $U = \tau^2 \frac{\partial}{\partial \tau} (\ln(Z))$ . Thus,

$$F = -\tau \ln(Z)$$

### Ideal Gas (intro)

One atom in a box:  $\psi(x, y, z) = A \sin(\frac{\pi x}{L} n_x) \sin(\frac{\pi y}{L} n_y) \sin(\frac{\pi z}{L} n_z)$

\* neglect spin!

$$E_n = \frac{\hbar^2}{2m} (n_x^2 + n_y^2 + n_z^2) / \frac{\pi^2}{L^2}$$

$$n_x, n_y, n_z \in \mathbb{N}$$

Thus, the partition function,

$$Z_1 = \sum_{n_x, n_y, n_z} \exp \left[ \left( \frac{\hbar^2 \pi^2}{2m L^2} \right) (n_x^2 + n_y^2 + n_z^2) / \tau \right]$$

$$Z_1 \approx \int_0^\infty dx n_x \int_0^\infty dy n_y \int_0^\infty dz n_z e^{-\alpha^2 (n_x^2 + n_y^2 + n_z^2)} ; \alpha^2 = \frac{\hbar^2 \pi^2}{2m L^2 \tau}$$

$$= \left[ \int_0^\infty dn e^{-\alpha^2 n^2} \right]^3 = \frac{\pi^{3/2}}{8\alpha^3}$$

quantum concentration

$$Z_1 = \frac{V}{(2\pi \hbar^2 / m \tau)^{3/2}} = N_Q V ; N_Q = \left( \frac{m \tau}{2\pi \hbar^2} \right)^{3/2}$$

The  $N$ -particle partition function of an ideal gas becomes,

$$Z_N = \frac{Z_1^N}{N!} = \frac{1}{N!} \left[ \left( \frac{m\tau}{2\pi k} \right)^{3/2} V \right]^N$$

Energy of ideal gas :

$$U = \tau^2 \left( \frac{\partial \ln(Z_N)}{\partial \tau} \right) = \tau^2 \frac{2}{2\tau} \left( -\frac{3}{2} N \ln(1/\tau) \right) = +\frac{3}{2} N \tau$$

$$\boxed{U = \frac{3}{2} N \tau}$$

Free energy of ideal gas :

$$F = -\tau \ln(Z_N) = -\tau \ln(Z_1^N) + \tau \ln(N!)$$

$$\boxed{F = -\tau N \ln(n\alpha V) + \tau \ln(N!)}$$

$$\boxed{F \approx -\tau N \ln(n\alpha V) + \tau N \ln(N) - \tau N}$$

Pressure of ideal gas :

From  $F$ , we can calculate  $P$ ,

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

$$\boxed{PV = N\tau}$$

Entropy of ideal gas :

$$\sigma = -\left( \frac{\partial F}{\partial T} \right)_V = N \ln(n\alpha V) + \frac{3}{2} N - N \ln(N) + N$$

$$\boxed{\sigma = N [\ln(n\alpha/n) + 5/2]}$$

## Equipartition theorem:

If the Hamiltonian of a system is homogeneous of degree 2 in momentum, the classical limit of the average kinetic energy associated with each dof is  $\frac{1}{2}\mathcal{T}$ . Further, a Hamiltonian homogeneous of degree 2 in position will have  $\frac{1}{2}\mathcal{T}$  potential energy in the classical limit per dof.

## Planck Distribution

The spectrum of EM radiation in thermal eq. with a cavity.

Radiation: A mode of oscillation,  $\omega$ , can only be excited in units of  $\hbar\omega$ .

$$E_S = S\hbar\omega \quad [\text{ignoring } \frac{1}{2}\hbar\omega \text{ zero point}]$$

↑ # photons in mode

### # photons per mode:

For a mode  $\omega$ ,

$$Z = \sum_{S=0}^{\infty} e^{-S\hbar\omega/\mathcal{T}} = \frac{1}{1 - e^{-\hbar\omega/\mathcal{T}}}$$

$$\text{Now, } \langle S \rangle = \sum_{S=0}^{\infty} S P(S) = \sum_{S=0}^{\infty} \frac{S e^{-S\hbar\omega/\mathcal{T}}}{1 - e^{-\hbar\omega/\mathcal{T}}}$$

$$\langle S \rangle = \frac{1}{e^{\hbar\omega/\mathcal{T}} - 1}$$

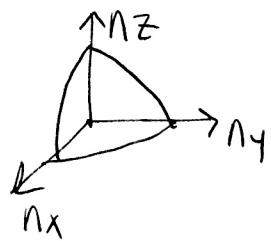
↑ Planck dist. function: average # photons in a single mode of frequency  $\omega$

For radiation in a cavity:

$$n = (n_x^2 + n_y^2 + n_z^2)^{1/2} ; k_n = \frac{\pi}{L} n ; \omega_n = CR_n = \frac{\pi c}{L} n$$

$$E_n = n \hbar \omega$$

Density of states in w:



The number of modes up to n,

$$N(n) = \left(\frac{1}{8}\right)\left(\frac{4}{3}\pi n^3\right) = \frac{\pi}{6} n^3$$

$$N(w) = \frac{\pi}{6} \left(\frac{wL}{\pi c}\right)^3 = \frac{V}{6\pi^2 c^3} w^3$$

$$\rho(w) = \frac{\partial N(w)}{\partial w} = \frac{V}{2\pi^2 c^3} w^2$$

Total energy in a cavity:

$$U = \sum_n \langle E_n \rangle = \sum_n \frac{\hbar \omega_n}{e^{\hbar \omega_n / \tau} - 1}$$

$$\approx \int_0^\infty (2\rho(w)dw) \frac{\hbar w}{e^{\hbar w / \tau} - 1} = \int_0^\infty dw \left( \frac{V w^2}{\pi^2 c^3} \right) \frac{\hbar w}{e^{\hbar w / \tau} - 1}$$

↑ 2 polarizations of radiation

$$U = \frac{\pi^2 V}{15 h^3 c^3} \tau^4 \quad \leftarrow \text{Stefan-Boltzmann law}$$

Spectral density: we see that, from the integral above,

$$U_w = \frac{\hbar}{\pi^2 c^3} \frac{w^2}{e^{\hbar w / \tau} - 1} \quad [dE/dv dw]$$

Intensity: For isotropic radiation,

$$I = \frac{c}{4\pi} U \quad [dE/dA dt d\Omega]$$

Thus, the specific intensity becomes,

$$I_w = \frac{\hbar w^3}{4\pi^3 c^2 (e^{\hbar w / \tau} - 1)} \quad [dE/dA dt d\Omega dw]$$

Note that intensity is a differential quantity. Thus,

$$I_w \neq I_v \neq I_\lambda.$$

Instead,  $I_w dw = I_v dv = I_\lambda d\lambda$ . From this, we find,

$$I_v = \frac{2hv^3}{c^2(e^{hv/c} - 1)}; \quad I_\lambda = \frac{2hc^2}{\lambda^5(e^{hc/\lambda c} - 1)}$$

Stefan-Boltzmann law:



The flux radiating from a hole in a cavity ( $2\pi \text{ sr}$ ) is given by,

$$F = \frac{\pi^2}{60 h^3 c^2} T^4 = \sigma_B T^4$$

↑ Stefan-Boltzmann const.

Photon pressure:  $|\vec{P}| = E/c$

$$\text{Thus, } P = \frac{\partial |\vec{P}|}{\partial t \partial A} = \frac{\partial E \cos \theta}{\partial t \partial A} \cdot \left(\frac{1}{c}\right) = (I \cos \theta d\Omega) \left(\frac{\cos \theta}{c}\right)$$

$$\text{Pressure} = \frac{1}{c} \int I \cos^2 d\Omega$$

### Einstein model

Model a solid as a collection of independent, 3D harmonic oscillators.

$$E = Sh\omega \quad [\text{Ignore zero-point energy}]$$

$$Z_1 = \sum_S e^{-Sh\omega/T} = \frac{1}{1 - e^{-h\omega/T}}$$

The solid is composed of  $3N$  independent HO

$$Z = \left(\frac{1}{1 - e^{-h\omega/T}}\right)^{3N}$$

$$\text{Thus, } U = -\tau^2 \left( \frac{\partial \ln(z)}{\partial \tau} \right) = 3N\hbar\omega \left( \frac{1}{e^{\hbar\omega/\tau} - 1} \right)$$

$$\text{Finally, } C_V = \frac{\partial U}{\partial T} = k_B \frac{\partial U}{\partial \tau} = \frac{3Nk_B (\hbar\omega/\tau)^2 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2}$$

① For  $\tau \gg \hbar\omega$ ,  $e^{\hbar\omega/\tau} \approx 1 + \hbar\omega/\tau$

$$C_V \rightarrow 3Nk_B \quad (\text{classical limit})$$

② For  $\tau \ll \hbar\omega$ ,

$$C_V \rightarrow (\hbar\omega/\tau)^2 e^{-\hbar\omega/\tau}$$

\* But experimentally we find that  $C_V \propto T^3$  as  $T \rightarrow 0$

### Debye Model

There is interaction between atoms in a solid. The state of the system is given by a collection of normal modes (phonons) which are quantized as,

$$\epsilon = S\hbar\omega$$

Number of phonon modes: While there are no limits to the # em modes in a cavity. There can only be  $3N$  modes for a solid composed of  $N$  atoms, each with 3 dof.

We know that the density of states is given by

$$D(\omega) = \frac{\alpha v \overset{\# \text{ dof}}{\swarrow}}{2\pi^2 c^3} \omega^2$$

Thus, we define the Debye frequency such that,

$$D(\omega) = \begin{cases} \frac{\alpha v}{2\pi^2 c^3} \omega^2, & \omega < \omega_D \\ 0, & \omega > \omega_D \end{cases}$$

$$\text{such that } 3N = \int_0^{\omega_D} D(\omega) d\omega$$

$$3N = \int_0^{\omega_D} \frac{\alpha V}{2\pi^2 c^3} \omega^2 d\omega = \frac{\alpha V}{6\pi^2 c^3} \omega_D^3$$

$$\boxed{\omega_D = C \left( \frac{18\pi^2 N}{\alpha V} \right)^{1/3}}$$

Now we can find the energy,

$$U = \sum_n \langle E_n \rangle = \sum_n \langle S_n \rangle \hbar \omega_n = \sum_n \frac{\hbar \omega_n}{e^{\hbar \omega_n / T} - 1}$$

$$U \approx \int_0^{\omega_D} (D(\omega) d\omega) \frac{\hbar \omega}{e^{\hbar \omega / T} - 1} = \frac{\alpha V \hbar}{2\pi^2 c^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\hbar \omega / T} - 1}$$

$$\text{we define, } x = \hbar \omega / T ; x_D = \hbar \omega_D / T = \frac{\hbar C}{T} \left( \frac{18\pi^2 N}{\alpha V} \right)^{1/3}$$

$$U = \frac{\alpha V \hbar}{2\pi^2 c^3} \int_0^{x_D} \frac{(\tau \hbar)^3 x^3}{e^x - 1} (\tau / \hbar) dx$$

$$\boxed{U = \frac{\alpha V T^4}{2\pi^2 c^3 \hbar^3} \int_0^{x_D} \frac{x^3 dx}{e^x - 1} = \frac{\alpha V T^4}{2\pi^2 c^3 \hbar^3} \int_0^{\Theta_D / T} \frac{x^3 dx}{e^x - 1}}$$

$$\text{where } x_D = \Theta_D / T$$

↑ Debye temperature

① At  $T \gg \Theta_D$ ,

$$x_D \ll 1 \Rightarrow e^x \approx 1 + x$$

$$U \approx \frac{\alpha V T^4}{2\pi^2 c^3 \hbar^3} \int_0^{x_D} x^2 dx = \frac{\alpha V T^4}{2\pi^2 c^3 \hbar^3} \frac{1}{3} x_D^3 = 3 N k_B \quad (\text{classical limit})$$

② At  $T \ll \Theta_D$ ,  $x_D \gg 1$ .

$$\int_0^{x_D} \frac{x^3 dx}{e^x - 1} \approx \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

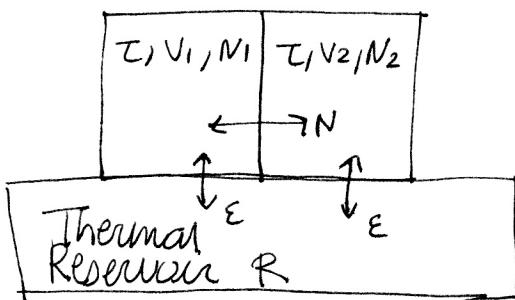
$$\text{Thus, } U(T) \propto T^4$$

$$C_V(T) \propto T^3$$

## Chemical Potential

- ① If 2 systems have the same temperature, there is no net energy flow between them.
- ② If 2 systems have the same chemical potential, there is no net exchange of particle. Particles flow from high potential to low potential.

Suppose systems  $S_1$  and  $S_2$  are in diffusive eq. with each other and the combined system is in thermal eq. with a reservoir.



It still holds that the combined system  $S_1 + S_2$  has minimum free energy at thermal eq. with  $R$ .

$$F = F_1 + F_2 = U_1 + U_2 - T(\sigma_1 + \sigma_2) ; N_1 + N_2 = N$$

At minimum :

$$0 = dF = \left(\frac{\partial F_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial F_2}{\partial N_2}\right) dN_2 ; dN_1 = -dN_2$$

Thus, at equilibrium,

$$\left(\frac{\partial F_1}{\partial N_1}\right)_T = \left(\frac{\partial F_2}{\partial N_2}\right)_T$$

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

$$\mu(T, V, N) \equiv F(T, V, N) - F(T, V, N-1)$$

↑ (strictly, particles are not divisible)

## Chemical potential of an Ideal Gas:

Recall an ideal gas has free energy,

$$F = -\tau \ln(Z) = -\tau [N \ln(n_{QV}) - \ln(N!)]$$

$$\nabla = F(\tau, v, N) - F(\tau, v, N-1)$$

$$= -\tau [N \ln(n_{QV}) - \ln(N!) - (N-1) \ln(n_{QV}) + \ln(N-1)!]$$

$$= -\tau \ln \left[ \frac{(n_{QV})^N}{N!} \frac{(N-1)!}{(n_{QV})^{N-1}} \right] = -\tau \ln \left( \frac{n_{QV}}{N} \right)$$

$$\boxed{\nabla = \tau \ln(N/n_Q)} \quad \leftarrow \text{only depends on the density of particles!}$$

## Summary of Relations

$\tau$ ,  $P$ , and  $\nabla$  in terms of partial derivatives of  $\sigma$ ,  $u$ , and  $F$   
given as functions of their natural independent variables.

	$\sigma(u, v, N)$	$u(\sigma, v, N)$	$F(\tau, v, N)$
$\tau$ :	$\frac{1}{\tau} = \left( \frac{\partial \sigma}{\partial u} \right)_{v, N}$	$\tau = \left( \frac{\partial u}{\partial \sigma} \right)_{v, N}$	-
$P$ :	$\frac{P}{\tau} = \left( \frac{\partial \sigma}{\partial v} \right)_{u, N}$	$-P = \left( \frac{\partial u}{\partial v} \right)_{\sigma, N}$	$-P = \left( \frac{\partial F}{\partial v} \right)_{\tau, N}$
$\nabla$ :	$-\frac{\nabla}{\tau} = \left( \frac{\partial \sigma}{\partial N} \right)_{u, v}$	$\nabla = \left( \frac{\partial u}{\partial N} \right)_{\sigma, v}$	$\nabla = \left( \frac{\partial F}{\partial N} \right)_{\tau, v}$

We can generalize the thermodynamic identity,

$$\boxed{du = \tau d\sigma + \nabla dN - P dv}$$

## Gibbs Factor

We place a system in thermal and diffusive eq with a reservoir R. If we specify the state of system S,

$$g = g_R \cdot g_S = g_R \cdot 1 = g_R$$

Now, the entropy of the reservoir,

$$\begin{aligned} \sigma(N_0 - N, u_0 - \varepsilon) &= \sigma(N_0, u_0) - N \left( \frac{\partial \sigma}{\partial N} \right)_u u - \varepsilon \left( \frac{\partial \sigma}{\partial u} \right)_N + \dots \\ &\approx \sigma(N_0, u_0) + \frac{N\mu}{\tau} - \frac{\varepsilon}{\tau} \end{aligned}$$

Thus,  $\boxed{g(N, \varepsilon) = e^{\sigma(N_0, u_0)} e^{(N\mu - \varepsilon)/\tau}}$

↑  
Gibbs factor

As before,

$$\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{e^{(N_1\mu - \varepsilon_1)/\tau}}{e^{(N_2\mu - \varepsilon_2)/\tau}}$$

This motivates the Gibbs sum, or ground partition function,

$$\boxed{Z = \sum_{n=0}^{\infty} \sum_{S(n)} e^{(N\mu - \varepsilon_S)/\tau}} = \sum_{ASN} e^{(N\mu - \varepsilon)/\tau}$$

(all states and numbers)

Gibbs Free Energy:

- ① Recall  $F$  ~~is~~ is minimized at thermal eq at constant volume
- ②  $\boxed{G = U - T\sigma + PV}$  is minimized at thermal eq. at constant pressure.

G is minimized for a system at eq. with constant P, T:

$$dG = du - Td\sigma - \sigma dT + pdv + vdp$$

Thermo. identity:  $Td\sigma = du - pdN + pdv$ . Thus,

$$dG = N dN = 0$$

\* If  $dN=0$ , G is minimized for a system at eq. with constant P, T

We can also show that

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

Still at eq. with constant P, T:

$$G = u - T\sigma + p\cancel{d}v$$

↑  
intensive (does not change with N)

Extensive and linear in N

$$\text{Thus, } G = N\ell(P, T) = N \left(\frac{\partial G}{\partial N}\right)_{P,T} = N\mu(P, T)$$

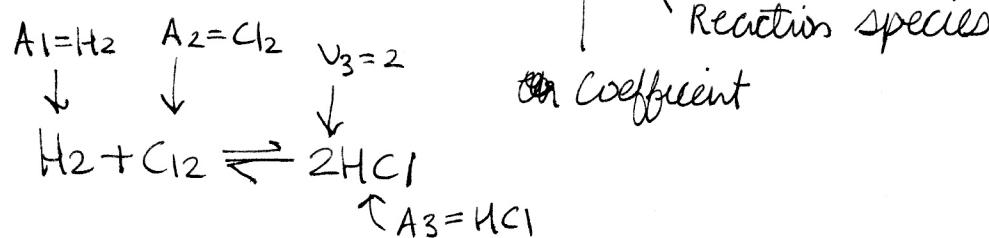
$$\boxed{G(N, P, T) = N\mu(P, T)} \quad [\text{at eq. with P, T}]$$

If more than 1 species is present:  $G = \sum_j N_j \mu_j$

### Equilibrium in Reactions

Chemical reaction:  $v_1 A_1 + \dots + v_n A_n \rightleftharpoons 0$

$$\sum_j v_j A_j = 0$$



At equilibrium) ~~is at~~ (constant  $P, T$ ),  $G$  is a minimum,

$$0 = dG = \sum_j \gamma_j dN_j$$

If we define  $\hat{N} = \#$  times a reaction takes place,

$$dN_j = v_j d\hat{N}$$

$$dG = \left( \sum_j v_j \gamma_j \right) d\hat{N} = 0$$

$$\boxed{\sum_j v_j \gamma_j = 0}$$

[eq. at const  $P, T$ ]

Equilibrium for Ideal Gas:

If we assume each constituent acts as an ideal gas,

$$\gamma_j = T [ \ln(v_j) - \ln(n_{Qj} z_j(\text{int})) ]$$

↑ internal partition function

$$NdG = \sum_j v_j \gamma_j = 0$$

$$\sum_j v_j \ln(n_j) = \sum_j v_j \ln(n_{Qj} z_j(\text{int}))$$

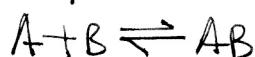
~~law of mass action~~

$$\boxed{T \prod_j n_j^{v_j} = T \prod_j (n_{Qj} z_j(\text{int}))^{v_j} = T \prod_j n_{Qj}^{v_j} e^{-v_j E_j(\text{int})/T}}$$

$$\uparrow z_j(\text{int}) = g_j e^{-E_j/T}$$

↑ For spin-degeneracy

For example :



$$\frac{n_A n_B}{n_{AB}} = \frac{g_A g_B}{g_{AB}} \frac{e^{-E_A/T} e^{-E_B/T}}{e^{-E_{AB}/T}} \frac{n_{QA} n_{QB}}{n_{QAB}}$$

$$= \frac{g_A g_B}{g_{AB}} \left( \frac{m_A m_B}{m_{AB}} \frac{T}{2\pi k^2} \right)^{3/2} e^{-I_{AB}/T} \quad \leftarrow \text{binding energy}$$

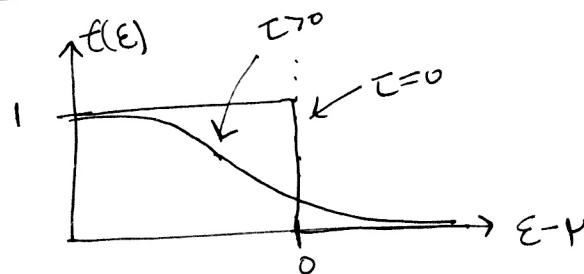
## Fermi - Dirac Distribution:

Define our system to be the orbital of a fermion.  
This orbital, with energy  $\epsilon$ , has a Gibbs sum of

$$\mathcal{Z} = 1 + e^{\frac{\epsilon}{kT}} e^{-\epsilon/kT} = 1 + \gamma e^{-\epsilon/kT}$$

Then,  $\langle N(\epsilon) \rangle = 0 \cdot P(0) + 1 \cdot P(1) = \frac{\gamma e^{-\epsilon/kT}}{1 + \gamma e^{-\epsilon/kT}}$

$$f(\epsilon) = \langle N(\epsilon) \rangle = \frac{1}{e^{[(\epsilon - \epsilon_F)/kT]} + 1} \quad [\text{F-D occupancy}]$$



At  $\tau=0$ , the occupancy changes from  $1 \rightarrow 0$

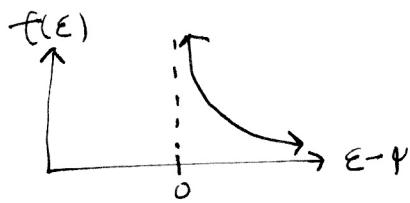
Any orbital with energy less than  $E_F = \nu(\tau=0)$  has occupancy 1 and any orbital with energy greater than  $E_F = \nu(\tau=0)$  has occupancy 0.

## Bose - Einstein Distribution:

Consider now the Gibbs sum of a orbital with energy  $\epsilon$  of a Boson.

$$\mathcal{Z} = \sum_{N=0}^{\infty} \gamma^N e^{-NE/kT} = \frac{1}{1 - \gamma e^{-\epsilon/kT}}$$

$$f(\epsilon) = \langle N(\epsilon) \rangle = \frac{1}{e^{[(\epsilon - \epsilon_F)/kT]} - 1} \quad [\text{B-E occupancy}]$$



## Classical limit of Ideal Gas

An ideal gas is modeled as a system of free, non-interacting particles in a box. The occupancy of an orbital is given by,

$$f(\epsilon) = \frac{1}{e^{[(\epsilon - \mu)/k] \pm i}} = e^{[(N - \epsilon)/k]} \quad \text{in the classical limit where } e^{(\epsilon - \mu)/k} \gg 1$$

Using this, we can recover the relations already found.

$$\cancel{\text{relation}} \quad N = T \ln(n/n_0)$$

$$C_V = 3/2 N$$

$$F = N \tau [\ln(n/n_0) - 1]$$

$$C_P = C_V + N = 5/2 N$$

$$P_V = N \tau$$

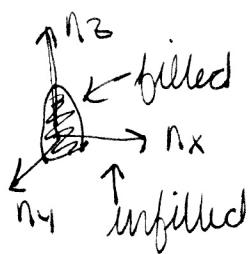
$$U = \frac{3}{2} N \tau$$

$$\sigma = N (\ln(n_0/n) + 5/2)$$

## Fermi Gas

~~Suppose that~~

Fermi Energy: suppose that  $\tau \ll \epsilon_F$ , then we expect all orbitals below  $\epsilon_F$  to be occupied and all above  $\epsilon_F$  to be empty.



$$N = \frac{2}{\text{Spin-1/2}} \left( \frac{1}{8} \right) \left( \frac{4}{3} \pi n_F^3 \right) \implies n_F = \left( \frac{3N}{\pi} \right)^{1/3}$$

$$\text{Thus, } \epsilon_F = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{\pi n_F}{L} \right)^2$$

$$\boxed{\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}}$$

## Density of states :

$$N(N) = \frac{1}{8} \left( \frac{4}{3} \pi n^3 \right) = \frac{\pi}{6} n^3$$

$$N(R) = \frac{\pi}{6} \left( \frac{L}{\pi} R \right)^3 = \frac{L^3}{6\pi^2} R^3$$

$$f(R) = \frac{L^3}{2\pi^2} R^2 = \frac{V}{2\pi^2} R^2$$

$$\begin{aligned} f(R) &= \frac{V}{2\pi^2} R^2 & [3D] \\ &= \frac{A}{2\pi} R & [2D] \\ &= \frac{L}{\pi} & [1D] \end{aligned}$$

## Ground state energy of degenerate $S=1/2, 3D$ Fermi gas :

$$U_0 = 2 \int_0^{R_F} f(R) E(R) dR = 2 \int_0^{R_F} \left( \frac{V}{2\pi^2 R^2} \right) \left( \frac{\hbar^2 R^2}{2m} \right) dR = \frac{V \hbar^2 R_F^5}{N \pi^2 m}$$

$\uparrow$   
 $S=1/2$

$$U_0 = \frac{3}{5} N \epsilon_F$$

## Density of states in energy :

$$P(R) dR = P(E) dE \quad \text{where } E = \frac{\hbar^2 R^2}{2m}$$

$$f(E) = P(R) \left( \frac{dE}{dR} \right)^{-1} = \frac{V}{2\pi^2} R^2 \left( \frac{m}{\hbar^2 R^2} \right) = \frac{V}{2\pi^2} \left( \frac{m}{\hbar^2} \right) \sqrt{\frac{2mE}{\hbar^2}}$$

$$P(E) = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E} \quad \text{for } S=1/2, 3D$$

## Heat capacity :

The energy of a Fermi gas:  $U = \int_0^\infty E P(E) f(E, T, \mu) dE$

If we define  $U_1 = U - \epsilon_F N = \int_0^\infty dE (E - \epsilon_F) f(E) dE$

Then  $C = \frac{\partial U}{\partial T} = \frac{\partial U_1}{\partial T} = \int_0^\infty dE (E - \epsilon_F) f(E) \frac{\partial f}{\partial T} [f(E, T, \mu)]$

①  ~~$f(E)$~~   $\partial f / \partial T$  is only large near  $\epsilon_F$ . Thus

$$C \approx f(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{\partial f}{\partial T} d\epsilon$$

④ When  $T \ll \epsilon_F$ ,  $\mu \approx \mu(0) = \epsilon_F$ . Thus,

$$\frac{df}{d\tau} \approx \frac{(\epsilon - \epsilon_F)}{\tau^2} \frac{e^{(\epsilon - \epsilon_F)/\tau}}{(e^{(\epsilon - \epsilon_F)/\tau} + 1)^2}$$

Thus, for  $x \equiv (\epsilon - \epsilon_F)/\tau$

$$C = \tau P(\epsilon_F) \int_{-\epsilon_F/\tau}^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2}$$

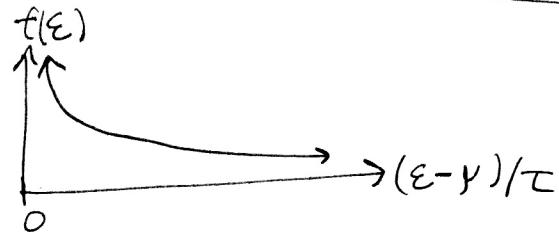
⑤ The factor  $e^x$  is very small at the lower bound  $-\epsilon_F/\tau$ . Thus,

$$C \approx \tau P(\epsilon_F) \int_{-\infty}^{\infty} dx \frac{x^2 e^x}{(e^x + 1)^2}$$

$$C = \frac{1}{3} \pi^2 P(\epsilon_F) \tau$$

Boson Gas

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



Einstein condensation: As  $\tau \rightarrow 0$ , the occupancy of the ground orbital becomes large — equal to the total number of particles.

$$\lim_{\tau \rightarrow 0} f(\epsilon=0, \tau) = N = \lim_{\tau \rightarrow 0} \frac{1}{e^{-\mu/\tau} + 1} \approx \frac{1}{1 - (\mu/\tau) + 1} = \frac{\tau}{\mu}$$

↑  
define ground-state  
energy to be 0

$$N \rightarrow -T_N \quad [\text{as } \tau \rightarrow 0]$$

Orbital occupancy vs. ~~absolute~~ temperature:

$$N = \sum_n f_n = N_0(\tau) + N_e(\tau) = N_0(\tau) + \int_0^{\infty} d\epsilon P(\epsilon) - f(\epsilon, \tau)$$

↑              ↑  
# atoms in    # atoms in all of  
grand state    the excited states

\* We need to separately include  $N_0(\tau)$  because  $P(\epsilon) = 0$  for  $\epsilon = 0$

$$N_e(\tau) = \int_0^\infty \left( \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \right) \epsilon^{1/2} \frac{1}{e^{(\epsilon - \mu)/kT} - 1} d\epsilon$$

For  $\chi = \epsilon/kT$ ,

$$N_e(\tau) = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} T^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^{-\mu/kT} e^x - 1}$$

For low temperatures,

$$e^{-\mu/kT} \approx e^{1/N} \approx 1$$

Thus,

$$N_e(\tau) = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1}$$

$$N_e(\tau) = 2.612 N \alpha V$$

Thus,  $\frac{N_e}{N} = 2.612 \frac{N \alpha V}{n}$

Einstein Condensation Temperature:

$T_E$  = temperature where  $N_e = N$ . Below  $T_E$ , the occupancy of the ground state is macroscopic.

$$N = 2.612 N \alpha V = 2.612 \left( \frac{m T_E}{2\pi \hbar^2} \right)^{3/2} V$$

$$T_E = \frac{2\pi \hbar^2}{m} \left( \frac{N}{2.61} \right)^{2/3}$$

It follows that  $N_e/N = (\tau/\tau_E)^{3/2}$

$$N_e(\tau) = N \left[ 1 - (\tau/\tau_E)^{3/2} \right]$$

Reversible Isothermal expansion

Reversible: The system, at any moment, is infinitesimally close to equilibrium. (Properties are well-defined throughout expansion).

E

$V_1 \rightarrow V_2$  at constant  $T$

① Energy from reservoir moves into system

② Gas does work onto piston :  $w = Q_{in}$

Pressure:  $PV = NT \implies P_1 V_1 = P_2 V_2$

$$P_2 = P_1 (V_1/V_2)$$

Entropy:  $\sigma = N \left[ \ln \left( \frac{V_2}{V_1} \right) + S_2 \right]$

$$\sigma_2 - \sigma_1 = N \ln \left( \frac{V_2}{V_1} \right)$$

Work:  $w = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \left( \frac{NT}{V} \right) dV = NT \ln \left( \frac{V_2}{V_1} \right)$

Reversible expansion at constant  $\sigma$

Isoentropic: Adiabatic with no change in entropy

Temperature:  $\sigma = N \left[ \ln(T^{3/2}) + \ln(V) + \text{const.} \right]$

If entropy is constant  $\implies T^{3/2}V$  is constant

Generalizing,

$$V_1 T_1^{\alpha/2} = V_2 T_2^{\alpha/2} \quad \leftarrow \# \text{dof}$$

$$V_1 T_1^{\gamma-1} = V_2 T_2^{\gamma-1}$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\gamma = \frac{\alpha+2}{2} = C_P/C_V$$

Energy:  $U_2 - U_1 = w(T_2 - T_1) = \frac{\alpha}{2}(T_2 - T_1)$

Work done by gas = - change in  $U$  bc adiabatic

## Sudden Expansion

No work is done during the expansion. If no heat is allowed to flow, then, by energy conservation,  $\Delta U = 0$ .

$$W = Q = \Delta U = 0$$

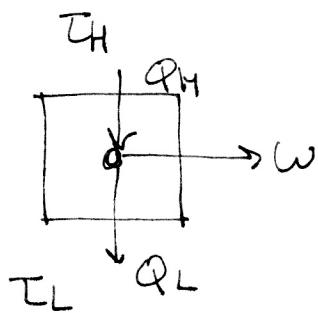
The only change is entropy:  $\sigma_2 - \sigma_1 = N \ln(v_2/v_1)$

## Heat and work

- Heat and work are both forms of energy transfer
- Heat is transfer of energy by thermal contact with a reservoir and is accompanied by a change in entropy
- Work is the transfer of energy by change of external parameters — no change in entropy.

## Heat Engine:

- All types of work are freely convertible (no entropy associated with work).
- ~~Heat~~ can not be completely converted to ~~heat~~ <sup>work</sup>. Entropy enters ~~into~~ the system with heat but does not exit with work.  
~~exists~~  
Entropy can not pile up in the device indefinitely.



Entropy can not pile:

$$\Delta \sigma_L = \Delta \sigma_H$$

$$\frac{Q_L}{T_L} = \frac{Q_H}{T_H}$$

Conservation of energy:

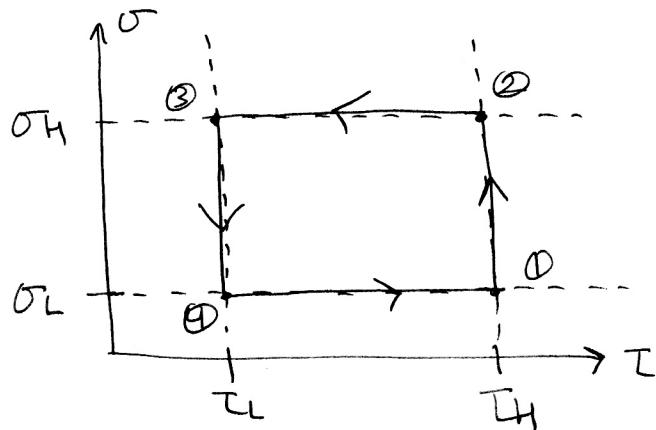
$$W = Q_H - Q_L = Q_H [1 - (\tau_L/\tau_H)]$$

$$\eta_C = \left( \frac{W_{\text{out}}}{Q_{\text{in}}} \right) = \frac{\tau_H - \tau_L}{\tau_H} \quad \leftarrow \text{Carnot efficiency}$$

(best efficiency)

\* Practically,  $\eta < \eta_c$  because entropy enters in the system due to irreversible processes and it must be removed.

### Carnot cycle



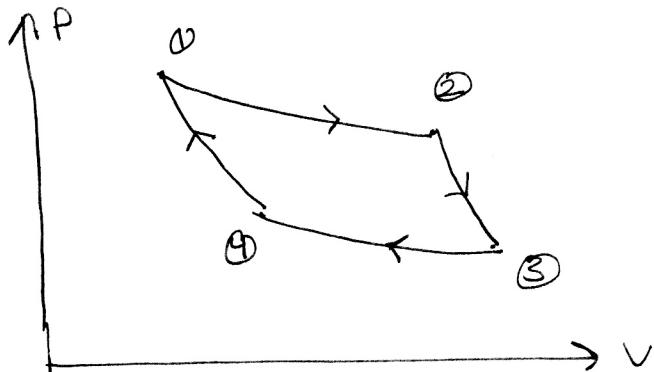
$$\oint du = \int T d\sigma - P dV = 0$$

$$W = \oint T d\sigma = Q_{in} - Q_{out}$$

$$W = (T_H - T_L)(\sigma_H - \sigma_L)$$

↑ area in  $T-\sigma$  plot

Carnot cycle for ideal gas:



1 → 2: Isothermal expansion at  $T_H$

$$Q_H = W_{12} = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \left(\frac{Nk}{V}\right) dV$$

$Q_H = W_{12} = NkH \ln(V_2/V_1) > 0 \implies$  Heat in, equal work out  
Entropy increases

2 → 3: Isentropic expansion as  $T_H \rightarrow T_L$

$$Q = 0$$

$$W_{23} = -\Delta U = CV(T_H - T_L)$$

$$W_{23} = \frac{\alpha}{2} N(T_H - T_L)$$

⇒ gas expands, doing work, lowering temperature  
no heat and no change in entropy

3 → 4: Isothermal compression at  $T_L$

$W_{34} = -Q_E = NT_L \ln(v_4/v_3) \Rightarrow$  ~~heat~~ work is done on the gas. An equal amount of heat is ejected to the reservoir.

4 → 1: Isentropic compression as  $T_L \rightarrow T_H$

$$W_{41} = CV(T_L - T_H) = -CV(T_H - T_L)$$

⇒ gas compresses, environment does work on gas, increasing temperature. ~~No~~ No heat and no change in entropy.

Net work:  $W = W_{12} + W_{23} + W_{34} + W_{41}$ ,

$$= N [T_H \ln(v_2/v_1) + T_L \ln(v_4/v_3)]$$

Now in the isentropic legs:

$$T_2 v_2^{\gamma-1} = T_3 v_3^{\gamma-1}$$

$$T_4 v_4^{\gamma-1} = T_1 v_1^{\gamma-1}$$

$$\frac{v_3}{v_2} = \left(\frac{T_H}{T_L}\right)^{1/\gamma-1}$$

$$\frac{v_4}{v_1} = \left(\frac{T_H}{T_L}\right)^{1/\gamma-1}$$

$$\boxed{\frac{v_3}{v_2} = \frac{v_4}{v_1}}$$

Thus,

$$\boxed{W = N (T_H - T_L) \ln(v_2/v_1)}$$

$$\eta = \frac{W}{Q_H} = \frac{T_H - T_L}{T_H} = \eta_C$$

