

Physics 112, Review

multiplicity of a binary system: Suppose that we have N magnets, each with spin up/down. For spin excess, $S = \frac{1}{2}(N_{\uparrow} - N_{\downarrow})$ ~~the~~

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

Stirling Approximation:

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

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

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.

$$\langle X \rangle = \sum_s X(s) P(s) \quad ; \text{ where } s \text{ is a unique state}$$

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,

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

At thermal equilibrium, g is maximized. Thus,

$$0 = dg = \left(\frac{\partial g_1}{\partial U_1}\right) dU_1 + \left(\frac{\partial g_2}{\partial U_2}\right) dU_2; \quad dU_1 + dU_2 = 0$$

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

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

We define entropy: $\sigma(N, U) = \log(\Omega(N, U))$; $S = k_B \sigma$

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

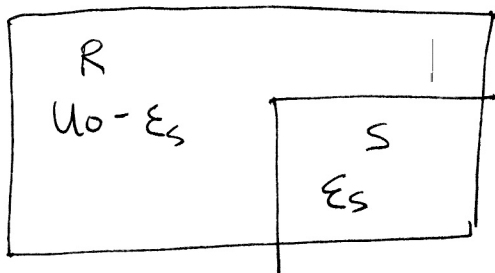
$$\frac{1}{T} = \left(\frac{\partial \sigma}{\partial U}\right)_N; \quad T = k_B T$$

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~~ system (energy ϵ) and a reservoir.

What is the probability that we will find system S in the specific state s with energy ϵ_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 $U_0 \ll \epsilon_S$,

$$\begin{aligned} \sigma_R(U - \epsilon_S) &\approx \sigma_R(U) - \epsilon \left(\frac{\partial \sigma_R}{\partial U} \right)_{U=N} + \dots \\ &\approx \sigma_R(U) - \epsilon/\tau + \dots \end{aligned}$$

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)
$$g(U - \epsilon) = \underbrace{e^{\sigma_R(U)}}_{\text{constant}} \underbrace{e^{-\epsilon/\tau}}_{\text{Boltzmann factor}}$$

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

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

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

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

We can calculate the average energy of the system,

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

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

Combining Partition Functions:

$Z \propto \Omega$. 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.

~~$$du = \tau d\sigma + Pdv$$~~

$$du = \tau d\sigma - Pdv$$

Pressure: from the TI, we see

$$P = - \left(\frac{\partial u}{\partial v} \right)_{\sigma} = \tau \left(\frac{\partial \sigma}{\partial v} \right)_u$$

Helmholtz free Energy:

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

~~$$F \equiv u - \tau \sigma$$~~

$$F \equiv u - \tau \sigma$$

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

Thus, $\boxed{\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma ; \left(\frac{\partial F}{\partial V}\right)_\tau = -p}$

Determining F from Z:

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

$F = u + \tau(\partial F / \partial \tau)_V \implies u = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau} \right)$

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

$\boxed{F = -\tau \ln(Z)}$

Ideal Gas (intro)

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

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

* neglect spin!

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

Thus, the partition function,

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

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

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

Quantum concentration

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

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

$$Z_N = \frac{z_1^N}{N!} = \frac{1}{N!} \left[\left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} V \right]^N$$

Energy of ideal gas:

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

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

Free energy of ideal gas:

$$F = -\tau \ln(Z_N) = -\tau \ln(z_1^N) + \tau \ln(N!)$$

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

Pressure of ideal gas:

From F , we can calculate P ,

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

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

Entropy of ideal gas:

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_v = N \ln(n\alpha v) + \frac{3}{2} N - N \ln(N) + N$$

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

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 $\frac{1}{2}\tau$. Further, a Hamiltonian homogeneous of degree 2 in position will have $\frac{1}{2}\tau$ 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, ω , 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 ω ,

$$Z = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

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

$$\langle s \rangle = \frac{1}{e^{\hbar\omega/\tau} - 1}$$

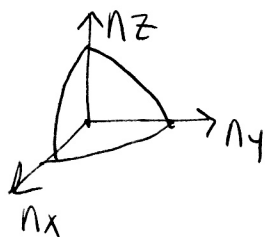
↑ Planck dist. function: average # photons in a single mode of frequency ω

For radiation in a cavity:

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

$$E_n = n \hbar \omega$$

Density of states in ω :



The number of modes up to n ,

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

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

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

Total energy in a cavity:

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

$$\approx \int_0^\infty (2P(\omega) d\omega) \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} = \int_0^\infty d\omega \left(\frac{V \omega^2}{\pi^2 c^3}\right) \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1}$$

↑ 2 polarizations of radiation

$$U = \frac{\pi^2 V}{15 \hbar^3 c^3} T^4$$

← Stefan-Boltzmann law

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

$$U_\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^2}{e^{\hbar \omega / kT} - 1} \quad [dE/dVd\omega]$$

Intensity: For isotropic radiation,

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

Thus, the specific intensity becomes,

$$I_\omega = \frac{\hbar \omega^3}{4\pi^3 c^2 (e^{\hbar \omega / kT} - 1)} \quad [dE/dAdtd\Omega d\omega]$$

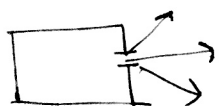
Note that intensity is a differential quantity. Thus,

$$I_\omega \neq I_\nu \neq I_\lambda.$$

Instead, $I_\omega d\omega = I_\nu d\nu = I_\lambda d\lambda$. From this, we find,

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

Stefan-Boltzmann law:



The flux radiating from a hole in a cavity (2π sr) is given by,

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

↑ Stefan-Boltzmann const.

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

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

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

Einstein model

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

$$E = s\hbar\omega \quad [\text{ignore zero-point energy}]$$

$$Z_1 = \sum_s e^{-s\hbar\omega/kT} = \frac{1}{1 - e^{-\hbar\omega/kT}}$$

The solid is composed of $3N$ independent H_0

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

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

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

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,

$$E = \hbar\omega$$

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

$$D(\omega) = \frac{\overset{\leftarrow \# \text{ dof}}{\alpha V}}{2\pi^2(3)} \omega^2$$

Thus, we define the Debye frequency such that,

$$D(\omega) = \begin{cases} \frac{\alpha V}{2\pi^2(3)} \omega^2, & \omega < \omega_D \\ 0, & \omega > \omega_D \end{cases} \quad \text{such that } 3N = \int_0^{\omega_D} D(\omega) d\omega$$

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

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

Now, we can find the energy,

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

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

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

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

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

where $x_D = \Theta_D / T$

↑ Debye temperature

① At $T \gg \Theta_D$,

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

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

② At $T \ll \Theta_D$, $x_D \gg 1$.

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

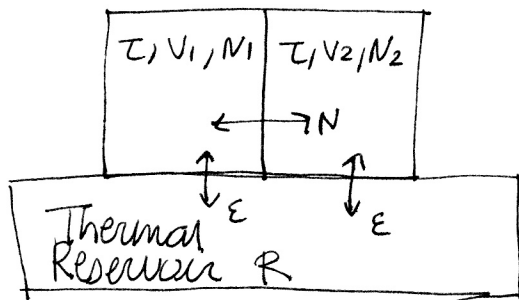
Thus, $U(T) \propto T^4$

$C_V(T) \propto T^3$

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,

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

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

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

↑ (strictly, particles are not divisible)

Chemical potential of an Ideal Gas:

Recall an ideal gas has free energy,

$$F = -\tau \ln(Z) = -\tau [N \ln(n\alpha v) - \ln(N!)]$$

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

$$= -\tau [N \ln(n\alpha v) - \ln(N!) - (N-1) \ln(n\alpha v) + \ln(N-1)!]$$

$$= -\tau \ln \left[\frac{(n\alpha v)^N}{N!} \frac{(N-1)!}{(n\alpha v)^{N-1}} \right] = -\tau \ln \left(\frac{n\alpha v}{N} \right)$$

$$\boxed{\mu = \tau \ln(n/n\alpha)} \quad \leftarrow \text{only depends on the density of particles!}$$

Summary of relations

τ , P , and μ in terms of partial derivatives of σ , u , and F given as functions of their natural independent variables.

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

We can generalize the thermodynamic identity,

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

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,

$$\begin{aligned} \sigma(N_0 - N, U_0 - E) &= \sigma(N_0, U_0) - N \left(\frac{\partial \sigma}{\partial N} \right)_U - E \left(\frac{\partial \sigma}{\partial U} \right)_N + \dots \\ &\approx \sigma(N_0, U_0) + \frac{NP}{T} - \frac{E}{T} \end{aligned}$$

Thus,
$$g(N, E) = e^{\sigma(N_0, U_0)} e^{(NP - E)/T}$$

↑
Gibbs factor

As before,

$$\frac{P(N_1, E_1)}{P(N_2, E_2)} = \frac{e^{(N_1 P - E_1)/T}}{e^{(N_2 P - E_2)/T}}$$

This motivates the Gibbs sum, or grand partition function,

$$Z = \sum_{N=0}^{\infty} \sum_{S(N)} e^{(NP - E_S)/T} = \sum_{ASN} e^{(NP - E)/T}$$

(all states and numbers)

Gibbs Free Energy:

- ① Recall F ~~is~~ is minimized at thermal eq. at constant volume
- ② $G = U - TS + PV$ is minimized at thermal eq. at constant pressure.

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

$$dG = du - Td\sigma - \sigma dT + PdV + VdP$$

Thermo. identities: $Td\sigma = du - \mu dN + PdV$. Thus,

$$dG = \mu dN = 0$$

* 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:

$$G = U - T\sigma + P V$$

Extensive and linear in N

intensive (does not change with N)

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

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

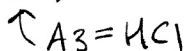
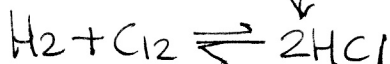
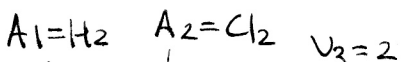
If more than 1 species is present: $G = \sum_j N_j \mu_j$

Equilibria in Reactions

Chemical reaction: $\nu_1 A_1 + \dots + \nu_n A_n = 0$

$$\sum_j \nu_j A_j = 0$$

↑ Reaction species
↑ Coefficient



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

$$0 = dG = \sum_j \mu_j dN_j$$

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

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

$$dG = \left(\sum_j \nu_j \mu_j \right) d\hat{N} = 0$$

$$\boxed{\sum_j \nu_j \mu_j = 0} \quad [\text{eq. at const } P, \tau]$$

Equilibrium for Ideal Gas:

If we assume each constituent acts as an ideal gas,

$$\mu_j = \tau \left[\ln(\nu_j) - \ln(n_{Qj} z_j(\text{int})) \right]$$

↑ internal partition function

$$\text{Now } \sum_j \nu_j \mu_j = 0$$

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

~~$\prod_j n_j^{\nu_j}$~~

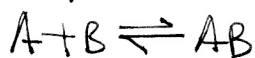
$$\boxed{\prod_j n_j^{\nu_j} = \prod_j (n_{Qj} z_j(\text{int}))^{\nu_j} = \prod_j n_{Qj}^{\nu_j} e^{-\nu_j E_j(\text{int})/\tau}}$$

[law of mass action]

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

↑ For spin-degeneracy

For example:



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

$$= \frac{g_A g_B}{g_{AB}} \left(\frac{m_A m_B}{m_{AB}} \frac{\tau}{2\pi h^2} \right)^{3/2} e^{-I_{AB}/\tau}$$

← binding energy

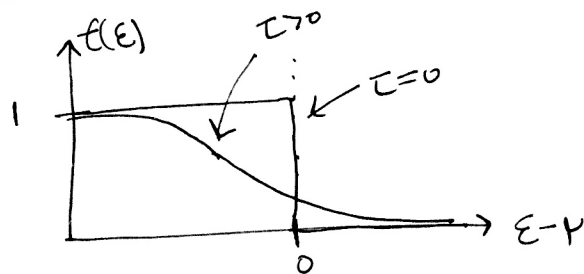
Fermi-Dirac Distribution:

Define ~~our~~ our system to be the orbital of a fermion.
This orbital, with energy ϵ , has a Gibbs sum of

$$Z = 1 + e^{1/\tau} e^{-\epsilon/\tau} = 1 + \lambda e^{-\epsilon/\tau}$$

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

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



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

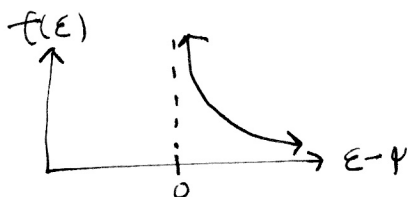
Any orbital with energy less than $E_F = \mu(\tau=0)$ has occupancy 1 and any orbital with energy greater than $E_F = \mu(\tau=0)$ has occupancy 0.

Bose-Einstein Distribution:

Consider now the Gibbs sum of a orbital with energy ϵ of a Boson.

$$Z = \sum_{N=0}^{\infty} \lambda^N e^{-N\epsilon/\tau} = \frac{1}{1 - \lambda e^{-\epsilon/\tau}}$$

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



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,

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

Using this, we can recover the relations already found.

~~Using this~~
~~we can~~

$$N = \tau \ln(n/n_Q)$$

$$C_V = \frac{3}{2}N$$

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

$$C_P = C_V + N = \frac{5}{2}N$$

$$PV = N\tau$$

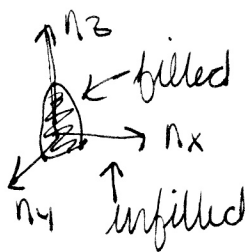
$$U = \frac{3}{2}N\tau$$

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

Fermi Gas

~~Suppose that~~

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



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

↑
spin-1/2

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

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

Density of states:

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

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

$$P(k) = \frac{L^3}{2\pi^2} k^2 = \frac{V}{2\pi^2} k^2$$

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

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

$$U_0 = 2 \int_0^{k_F} P(k) E(k) dk = 2 \int_0^{k_F} \left(\frac{V}{2\pi^2} k^2 \right) \left(\frac{\hbar^2 k^2}{2m} \right) dk = \frac{V \hbar^2 k_F^5}{5\pi^2 m}$$

\uparrow
 $s=1/2$

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

Density of states in energy:

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

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

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

Heat capacity:

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

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

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

$\frac{\partial f}{\partial T}$ is only large near $E = \epsilon_F$. Thus

$$C \approx P(\epsilon_F) \int_0^\infty (E - \epsilon_F) \frac{\partial f}{\partial T} dE$$

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

For $x \equiv \epsilon/k\tau$,

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

For low temperatures,

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

Thus,

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

$$\boxed{N_e(\tau) = 2.612 N_Q V}$$

$$\text{Thus, } \frac{N_e}{N} = 2.612 \frac{N_Q}{N}$$

Einstein Condensation Temperature:

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

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

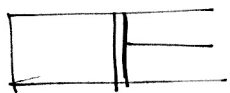
$$\boxed{T_E = \frac{2\pi\hbar^2}{m} \left(\frac{N}{2.612} \right)^{2/3}}$$

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

$$N_0(\tau) = N [1 - (\tau/T_E)^{3/2}]$$

Reversible Isothermal expansion

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



$V_1 \rightarrow V_2$ at constant T

① Energy from reservoir moves into system

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

Pressure: $PV = N\tau \implies P_1 V_1 = P_2 V_2$

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

Entropy: $\sigma = N [\ln(\frac{NqV}{N}) + 5/2]$

$$\sigma_2 - \sigma_1 = N \ln(V_2/V_1)$$

Work: $W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} (\frac{N\tau}{V}) dV = N\tau \ln(V_2/V_1)$

Reversible expansion at constant σ

Isentropic: Adiabatic with no change in entropy

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

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

Generalizing,

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

$$\gamma = \frac{\alpha + 2}{\alpha} = C_p/C_v$$

$$\boxed{\begin{aligned} V_1 T_1^{\gamma-1} &= V_2 T_2^{\gamma-1} \\ P_1 V_1^\gamma &= P_2 V_2^\gamma \end{aligned}}$$

Energy: $u_2 - u_1 = C_V (T_2 - T_1) = \frac{\alpha}{2} (T_2 - T_1)$

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, $\Delta U = 0$.

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

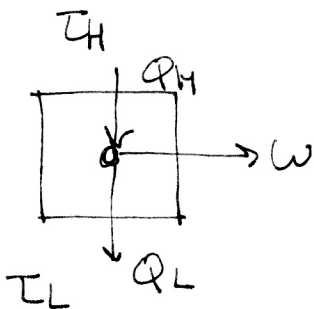
The only change is entropy: $\sigma_2 - \sigma_1 = N \ln(V_2/V_1)$

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~~ ^{work}. Entropy enters ~~into~~ the system with heat but does not exit with work. ~~Exit~~ Entropy can not pile up in the device indefinitely.



Entropy can not pile:

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

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

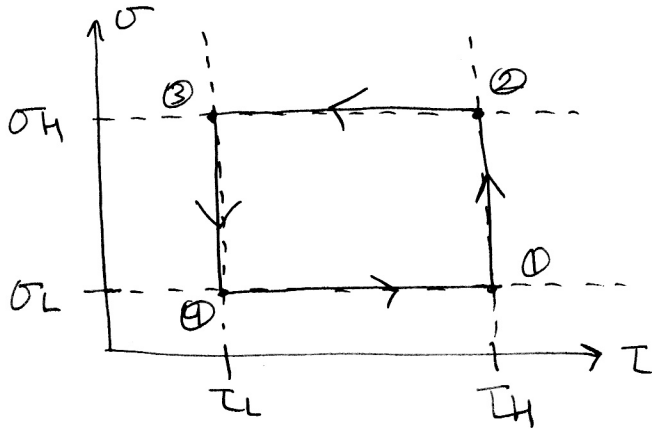
Conservation of energy:

$$W = Q_H - Q_L = Q_H [1 - (T_L/T_H)]$$

$$\eta_c = \left(\frac{W_{out}}{Q_{in}} \right) = \frac{T_H - T_L}{T_H} \leftarrow \text{Carnot efficiency (best efficiency)}$$

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

Carnot cycle



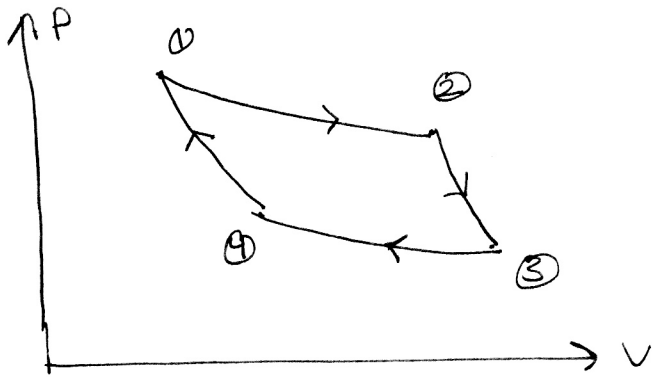
$$\oint du = \int \tau d\sigma - P dV = 0$$

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

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

↑ area in T - σ plot

Carnot cycle for ideal gas:



1 → 2: Isothermal expansion at T_H

$$Q_H = W_{12} = \int_{v_1}^{v_2} P dv = \int_{v_1}^{v_2} \left(\frac{N\tau}{v} \right) dv$$

$$Q_H = W_{12} = N T_H \ln(v_2/v_1) > 0 \implies \text{Heat in, equal work out}$$

Entropy increases

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

$$Q = 0$$

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

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

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

3→4: Isothermal compression at T_L

$$W_{34} = -Q_L = N T_L \ln(V_4/V_3) \implies \text{Gas does work is done on the gas. An equal amount of heat is ejected to the reservoir.}$$

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

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

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

Net work: $W = W_{12} + W_{23} + W_{34} + W_{41}$
 $= N [T_H \ln(V_2/V_1) + T_L \ln(V_4/V_3)]$

Cancel

base 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, $\boxed{W = N (T_H - T_L) \ln(V_2/V_1)}$

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

