

Fermi and Bose Gases

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- Gibbs Distribution

$$P(N, \varepsilon_S) = \frac{e^{\frac{N\mu - \varepsilon_S}{\tau}}}{3}$$

This is the probability to find S in a quantum state $S(N)$ of N particles and energy ε_S

$$3(\tau, \mu, V) = \sum_N \sum_{\varepsilon_S} e^{\frac{N\mu - \varepsilon_S}{\tau}}$$

- Activity

- We can define the activity as:

$$e^{\frac{\mu}{\tau}} = \lambda$$

- This allows us to rewrite:

$$P(N, \varepsilon_S) = \frac{\lambda^N e^{-\frac{\varepsilon_S}{\tau}}}{3}$$
$$3(\tau, \mu, V) = \sum_N \sum_{\varepsilon_S} \lambda^N e^{-\frac{\varepsilon_S}{\tau}}$$

- Some important averages that follow from this are:

$$\langle N \rangle = \sum_N \sum_{\varepsilon_S} N \cdot P(N, \varepsilon_S) = \tau \left(\frac{\partial \ln(3)}{\partial \mu} \right)_{\tau, V}$$
$$\langle \varepsilon_S \rangle = \sum_N \sum_{\varepsilon_S} \varepsilon_S \cdot P(N, \varepsilon_S) = \tau^2 \left(\frac{\partial \ln(3)}{\partial \tau} \right)_{\mu, V} + \tau \mu \left(\frac{\partial \ln(3)}{\partial \mu} \right)_{\tau, V}$$

- Fermi and Bose Gases

- Such gases are non-interacting (mono-atomic particles of spin = 0)
- Fermions: Half-integer spin particles, like protons, neutrons, electrons, positrons, and hydrogen
- Bosons: Integer spin particles, like photons, phonons
- Pauli Exclusion Principle: An orbital can only be occupied by 0 or 1 fermions of the same species
- Fermi-Dirac Distribution
 - A system, S , inside a reservoir, R , is filled with a gas of non-interacting fermions, and is in thermal and diffusive equilibrium
 - Orbital, ε_n , is in thermal and diffusive equilibrium with other orbitals
- Gibbs Sum for Orbital ε_n

$$\varepsilon_n = \lambda^0 e^{-0/\tau} + \lambda^1 e^{-\frac{\varepsilon_n}{\tau}} = 1 + \lambda e^{-\frac{\varepsilon_n}{\tau}}$$

The average quantity of gas particles, will be written as:

$$\langle N \rangle \equiv f(\varepsilon_n) = \frac{\lambda e^{-\frac{\varepsilon_n}{\tau}}}{3_n} = \frac{1}{\frac{1}{\lambda} e^{\frac{\varepsilon_n}{\tau}} + 1}$$

Inserting λ in, we get the Fermi-Dirac Distribution:

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

This gives us the average occupancy of an orbital ε_n , also known as the average number of particles, or the probability of occupancy. Since it is a probability, we know:

$$0 \leq f(\varepsilon_n) \leq 1$$

• Bose-Einstein Distribution

- For this distribution, we obtain a geometric series for the grand partition function:

$$3_n = 1 + \lambda e^{-\frac{\varepsilon_n}{\tau}} + \left(\lambda e^{-\frac{\varepsilon_n}{\tau}} \right)^2 + \dots = \frac{1}{1 - \lambda e^{-\frac{\varepsilon_n}{\tau}}}$$

- Thus, we assume $\lambda e^{-\frac{\varepsilon_n}{\tau}} < 1 \forall n$
- Finally, we get:

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

- In the classical regime, $e^{\frac{\varepsilon_n - \mu}{\tau}} \gg 1 \forall n$ and there is no difference between a Bose-Einstein and Fermi-Dirac distribution. The classical distribution function is:

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

- Quantum Ideal Gas (Monatomic, $s = 0$, no internal degrees of freedom)

- We can define the occupancy function as:

$$f(\varepsilon_n) = \begin{cases} \frac{1}{e^{\frac{\varepsilon_n - \mu}{\tau}} + 1} & \text{Fermi-Dirac Gas} \\ \frac{1}{e^{\frac{\varepsilon_n - \mu}{\tau}} - 1} & \text{Bose-Einstein Gas} \\ e^{\frac{\mu - \varepsilon_n}{\tau}} & \text{Classical Limit} \end{cases}$$

- Ideal gas in the classical limit

- From above, we can describe the occupancy as:

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

- We can then calculate the chemical potential, μ :

$$N = \sum_n f(\varepsilon_n) = \lambda \sum_n e^{-\frac{\varepsilon_n}{\tau}} = \lambda z_1$$

$$z_1 = n_Q V, \quad n_Q = \underbrace{\left(\frac{M\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}}}_{\text{quantum concentration}}$$

- From here, we can simplify to get:

$$\mu = \tau \ln \left(\frac{n}{n_Q} \right)$$

- We then calculate the Helmholtz free energy, F :

$$F = U - \tau \sigma$$

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

$$F(\tau, V, N) = \int_0^N \mu dN + C(\tau, V)$$

- * We know $C(\tau, V) = 0$ because $F(N = 0) = 0$

- We can split up our expression for the chemical potential to obtain:

$$F(\tau, V, N) = \tau \int_0^N (\ln(N) - \ln(Vn_Q)) dN$$

$$F = \tau (N \ln(N) - N) \Big|_0^N - N \ln(Vn_Q) \Big|_0^N$$

$$F = \tau (N \ln(N) - N - N \ln(Vn_Q))$$

$$F = N\tau \left(\ln\left(\frac{n}{n_Q}\right) - 1 \right)$$

$$F = -N\tau \left(\ln\left(\frac{n_Q}{n}\right) + 1 \right)$$

- Now, we can find the entropy, σ :

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

$$\sigma = N \left(\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2} \right)$$

- And then we find the internal energy:

$$U = F + \tau\sigma$$

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

- Next, we can find pressure, P :

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

- Heat capacity (C) in a reversible process:

- * At constant volume:

$$C = \left(\frac{\partial Q}{\partial \tau} \right)_{V, N}$$

$$\delta Q = \Delta U + W \quad (1^{\text{st}} \text{ law of thermodynamics})$$

$$W = 0 \Rightarrow \delta Q = \Delta U = \frac{3}{2}N\Delta\tau$$

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

* At constant pressure:

$$C_p = \left(\frac{\partial Q}{\partial \tau} \right)_{P,N}$$
$$\delta Q = \frac{3}{2}N\Delta\tau + N\Delta\tau = \frac{5}{2}N\Delta\tau$$
$$C_p = \frac{5}{2}N$$

· This means, in general:

$$C_p = C_v + N$$

* Note: When dealing with a reversible process, we use d when writing a differential; if it is not, δ is generally written

- Reversible Expansion at Constant τ (isothermal)

- Consider again an ideal gas, classical, monatomic, with spin as 0
- Since $N\tau$ is constant, we can find:

$$P_1V_1 = P_2V_2$$

- The change in internal energy:

$$\Delta U = \frac{3}{2}N\tau - \frac{3}{2}N\tau = 0$$

- The change in entropy is:

$$\sigma = N \left(\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right)$$
$$\Delta\sigma = N \ln \left(\frac{V_2}{V_1} \right)$$

- The work done by the system, W , is:

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{N\tau}{V} dV = N\tau \ln \left(\frac{V_2}{V_1} \right)$$

or

$$\delta Q = \Delta U + W \rightarrow W = \delta Q$$

$$\delta Q = \tau \Delta \sigma^1$$

$$\delta Q \leq \tau \Delta \sigma^2$$

$$W = \tau N \ln \left(\frac{V_2}{V_1} \right)$$

- Reversible Expansion at Constant σ (isentropic)

- First and foremost, we know $\Delta \sigma = 0$
- The temperature can be found by:

$$\sigma = N \left(\ln \left(V \tau^{\frac{3}{2}} \right) + C \right)$$

$$\tau_2 = \tau_1 \left(\frac{V_1}{V_2} \right)^{\frac{2}{3}}$$

- From the ideal gas formula, we can find:

$$P_2 = \frac{N \tau_2}{V_2} = \frac{N}{V_2} \tau_1 \left(\frac{V_1}{V_2} \right)^{\frac{2}{3}} = P_1 \left(\frac{V_1}{V_2} \right)^{\frac{5}{3}}$$

- The change in internal energy becomes:

$$\Delta U = \frac{3}{2} N (\tau_2 - \tau_1) < 0$$

- Work done by system:

$$W = -\Delta U$$

- Fast, sudden expansion into vacuum (irreversible)

- The particles have no time to react and do work on each other, so:

$$W = 0$$

- Heat has no time to enter the system:

$$\delta Q = 0$$

¹in a reversible process

²in general

- This means:

$$\Delta U = 0$$

$$\Delta \tau = 0$$

- The change in entropy would be:

$$\Delta \sigma = N \ln \left(\frac{V_2}{V_1} \right)$$

- For an irreversible process, we find:

$$\delta Q \leq \tau \Delta \sigma$$