Quantum Statistics

7.1 The Gibbs Factor

In Chap 6 we dealt with a system of N particles by treating 1 particle with the Boltzmann factor.

For 2 identical particles we used $Z_{TOT} = \frac{1}{2} Z_1^2$ where $Z_1 = \sum_s e^{-E(s)/k_B T}$.

At low temperatures, this is <u>completely</u>, <u>totally</u> wrong. Low T depends on the system. For gases, low $T \sim 10^{-6}$ K; For electrons in a metal low $T \sim 10^3$ K; For atoms in solid low $T \sim 10-100$ K.

Why a problem? Look at 2 identical particles in 3 states.

$$Z_1 = 1 + e^{-\beta E_2} + e^{-\beta E_3}$$

$$\Rightarrow \frac{1}{2} Z_1^2 = \frac{1}{2}\left(1 + e^{-\beta E_2} + e^{-\beta E_3} + e^{-\beta E_2} + e^{-2\beta E_2} + e^{-\beta(E_2+E_3)} + e^{-\beta E_3} + e^{-\beta(E_2+E_3)} + e^{-2\beta E_3}\right)$$

$$= \underbrace{\frac{1}{2}\left(1 + e^{-2\beta E_2} + e^{-2\beta E_3}\right)}_{\text{wrong}} + \left(1 \cdot e^{-\beta E_2} + 1 \cdot e^{-\beta E_3} + e^{-\beta E_2} e^{-\beta E_3}\right)$$

For Bosons $Z_{TOT} = \left(1 \cdot 1 + e^{-\beta E_2} e^{-\beta E_2} + e^{-\beta E_3} e^{-\beta E_3}\right) + \left(1 \cdot e^{-\beta E_2} + 1 \cdot e^{-\beta E_3} + e^{-\beta E_2} e^{-\beta E_3}\right)$

For Fermions $Z_{TOT} = 0 \qquad + \left(1 \cdot e^{-\beta E_2} + 1 e^{-\beta E_3} + e^{-\beta E_2} e^{-\beta E_3}\right)$

2 Fermions can't be in same state.
2 Bosons can be in same state.

There are two ways for dealing with this situation:

(1) directly sum with correct boson/fermion factor for doubly occupied (theoretical machinery in Q.M. raising/lowering operator a, a^+ for bosons b, b^+ for fermions)

(2) use a short cut based on chemical potential

(1) and (2) give exactly same answer. Since this is a thermo class, will use (2).

See pg 1 of Chap 6 notes for refresher.

Treat quantum state s_a as the system. The state s_a is a single particle state (for example, the 18^{th} state of a particle in a box). We will let particles go into and out of the state s_a.

What is the probability the system is in state s_a?

$$\mathcal{P}(s_a) = \underbrace{C}_{\text{some constant}} \cdot \overset{\text{multiplicity of system}}{1} \cdot \Omega_{Res}(U - E(s_a), V, N - N(s_a)) \qquad U = E_{Res} + \overset{\text{energy of } s_a}{E(s_a)}$$

$$N = N_{Res} + \underbrace{N(s_a)}_{\text{number of objects in } s_a}$$

$$\Rightarrow \frac{\mathcal{P}(s_a)}{\mathcal{P}(s_b)} = \frac{\Omega_{Res}(U - E(s_a), V, N - N(s_a))}{\Omega_{Res}(U - E(s_b), V, N - N(s_b))} =$$

$$= e^{[S_R(U - E(s_a), V, N - N(s_a)) - S_R(U - E(s_b), V, N - N(s_b))]/k_B}$$

As with derivation in Chap 6, this doesn't help much until you realize U, N are extensive quantities $\Rightarrow U >> E(s)$, $N >> N(s)$

$$\Rightarrow S_R(U - E(s_a), V, N - N(s_a)) = S_R(U, V, N) - E(s_a)\left(\frac{\partial S_R}{\partial U}\right)_{V,N} - N(s_a)\left(\frac{\partial S_R}{\partial N}\right)_{U,V}$$

$$= S_R - \frac{E(s_a)}{T} + \frac{\mu N(s_a)}{T}$$

$$\Rightarrow \frac{\mathcal{P}(s_a)}{\mathcal{P}(s_b)} = \frac{e^{-\beta[E(s_a) - \mu N(s_a)]}}{e^{-\beta[E(s_b) - \mu N(s_b)]}}$$

Boltzmann factor $= e^{-\beta E(s)}$

Gibbs factor $= e^{-\beta[E(s) - \mu N(s)]}$

In order for $\sum_s \mathcal{P}(s) = 1 \Rightarrow \mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-\beta[E(s) - \mu N(s)]}$

with $\mathcal{Z} = \sum_s e^{-\beta[E(s) - \mu N(s)]}$ is grand partition function

If there is more than 1 species: Gibbs factor $= e^{-\beta[E(s) - \mu_1 N_1(s) - \mu_2 N_2(s) - \dots]}$

For 1 species $E(s) = \underbrace{\varepsilon(s)}_{\text{energy of 1 particle in state } s} \cdot N(s)$

Textbook example: CO poisoning.

A site on hemoglobin can bind O_2 or CO

Only O_2

$$\overset{\text{no } O_2}{Z = 1} + \overset{1\ O_2}{e^{-(\varepsilon-\mu)/k_BT}} \qquad \varepsilon \simeq -0.7\,eV, \quad \mu = -k_BT\ln\left(\frac{V Z_{int}}{N v_Q}\right) \simeq -0.6\,eV$$

$$= 1 + 40$$

$$\mathcal{P}(\text{occupied}) = \frac{40}{1+40} \simeq 0.98$$

O_2 and CO

$$\overset{\text{no } O_2, CO}{Z = 1} + \overset{1\ O_2}{e^{-(\varepsilon-\mu)/k_BT}} + \overset{1\ CO}{e^{-(\varepsilon'-\mu')/k_BT}} \qquad \varepsilon' \simeq -0.85, \ \mu' \simeq -0.72\,eV$$

CO 100x less abundant

$$= 1 + 40 + 120$$

$$\mathcal{P}(\text{occupied } O_2) = 40/(1+40+120) \cong 0.25$$

Prob 7.6

Show $\bar{N} = \frac{k_BT}{Z}\frac{\partial Z}{\partial \mu}$

$$\partial Z/\partial\mu = \sum_s \beta N(s)\, e^{-\beta[E(s)-\mu N(s)]} \overset{\checkmark}{=} \beta Z \bar{N}$$

Show $\overline{N^2} = \frac{(k_BT)^2}{Z}\frac{\partial^2 Z}{\partial \mu^2}$

$$\partial^2 Z/\partial\mu^2 = \sum_s \beta^2 N^2(s)\, e^{-\beta[E(s)-\mu N(s)]} \overset{\checkmark}{=} \beta^2 Z \overline{N^2}$$

$$\sigma_N^2 = \overline{N^2} - \bar{N}^2 = \frac{(k_BT)^2}{Z}\frac{\partial^2 Z}{\partial\mu^2} - \frac{(k_BT)^2}{Z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2$$

$$\frac{\partial \bar{N}}{\partial \mu} = \frac{k_BT}{Z}\frac{\partial^2 Z}{\partial \mu^2} - \frac{k_BT}{Z^2}\left(\frac{\partial Z}{\partial\mu}\right)^2 = \frac{1}{k_BT}\sigma_N^2$$

$$\Rightarrow \sigma_N = \sqrt{k_BT\, \partial\bar{N}/\partial\mu}$$

Apply to ideal gas $\mu = -k_BT\left[\ln\left[\frac{V Z_{int}}{v_Q}\right] - \ln N\right]$

$$\Rightarrow \frac{\partial \mu}{\partial N} = \frac{k_BT}{N} \Rightarrow \frac{\partial N}{\partial \mu} = \frac{N}{k_BT}$$

$$\sigma_N \overset{\checkmark}{=} \sqrt{\bar{N}}$$