Statistical Mechanics

Suppose there is a system of N molecules which have the possible states $\xi_1, \xi_2, \xi_3, \ldots$ and we can separate the N molecules into systems such that there are η_1 molecules in system 1, η_2 molecules in system 2, and so on. Now, all possible combinations of the states of each of the N molecules can be listed:

$$\left(\xi_1+\xi_2+\xi_3+\ldots\right)^N=\left(\xi_1+\left(\xi_2+\xi_3+\ldots\right)\right)^N=\sum_{r=0}^{N}\frac{N!}{r!(N-r)!}\xi_1^{N-r}\left(\xi_2+\xi_3+\ldots\right)^r$$

$$\frac{N!}{N!}+\frac{N!}{1!(N-1)!}+\frac{N!}{2!(N-2)!}+\ldots=N!\left(\frac{1}{N!}+\frac{1}{1!(N-1)!}+\frac{1}{2!(N-2)!}+\ldots\right)$$

The sum will reduce to the following:

$$\left(\frac{N!}{\{\eta_1!\}\{\eta_2!\}\{\eta_3!\}\ldots}\right)$$

Define the degeneracy function to be

$$W_N\left(\eta_1,\eta_2,\eta_3,\ldots\right)=\frac{N!}{\eta_1!\eta_2!\eta_3!}$$

which describes the number of possible arrangements of N particles into a set of states.

Book keeping

The most probable distribution should coincide with the average distribution for large numbers. To find the most probably distribution, $\ln W_N\left(\eta_1,\eta_2,\eta_3,\ldots\right)$ must be maximized.

We must first, however, impose the conditions that

$$\sum_{i=1}^{k}\eta_i=N$$

and

$$\sum_{i=1}^{k}\eta_i\varepsilon_i=E$$

Most Probable Distribution

For our problem let

$$F = \ln W - \alpha N - \beta E$$

Finding the slight variations in F:

$$\frac{dF}{d\eta_i} = \frac{d(\ln W)}{d\eta_i} - \alpha\left(\frac{dN}{d\eta_i}\right) - \beta\left(\frac{dE}{d\eta_i}\right)$$

The most probable distribution is the one for which $dF = 0$, so we find when

$$\frac{d(\ln W)}{d\eta_i} - \alpha\left(\frac{dN}{d\eta_i}\right) - \beta\left(\frac{dE}{d\eta_i}\right) = 0$$

Thus, we get

$$\frac{d}{d\eta_i}\left(\ln\left(\frac{N!}{\eta_1!\eta_2!\eta_3!...}\right)\right) - \alpha\frac{d}{d\eta_i}\left(\sum_{i=1}^{k}\eta_i\right) - \beta\frac{d}{d\eta_i}\left(\sum_{i=1}^{k}\varepsilon_i\eta_i\right) = 0$$

or

$$\sum_{i=1}^{k}\left(\frac{d\ln W}{d\eta_i} - \alpha\frac{d(\eta_i)}{d\eta_i} - \beta\frac{d(\varepsilon_i\eta_i)}{d\eta_i}\right) = 0$$

Simplifying,

$$\frac{d(\ln W)}{d\eta_i} - \alpha - \beta\varepsilon_i = 0$$

Using the Stirling Approximation,

$$-\ln(\eta_i) - \alpha - \beta\varepsilon_i = 0$$

thus

$$\eta_i = e^{-\alpha}e^{-\beta\varepsilon_i}$$

Now, we can define the probability of a molecule being in any k state:

$$P(n_i) = \frac{n_i}{N} = \frac{n_i}{\sum_{i=1}^{k} n_i} = \frac{e^{(-\alpha-\beta\varepsilon_i)}}{\sum_{i=1}^{k} e^{(-\alpha-\beta\varepsilon_i)}}$$

The term

$$\sum_{i=1}^{k} e^{(-\alpha-\beta\varepsilon_i)}$$

is called the Gibb's Sum, and it is to be carried out over all states and numbers of particles. In terms of chemical statistics, it is described as

$$Z = \sum_{N}\sum_{\xi} e^{\frac{(N\mu-\varepsilon)}{\tau}}$$

Fermi-Dirac Distribution Function

Suppose we wish to find the thermal average occupancy of a particular orbital. An orbital can be occupied by zero or one fermion. No other occupancy is allowed by the Pauli Exclusion Principle.

The energy of the orbital will be taken as 0 for no occupancy, and ε if it is occupied. Thus, the Gibb's Sum becomes

$$Z = 1 + e^{\frac{(\mu-\phi)}{\tau}}$$

The average occupancy is then just

$$\left\langle N(\varepsilon)\right\rangle = \frac{e^{\frac{(\mu-\varepsilon)}{\tau}}}{1+e^{\frac{(\mu-\varepsilon)}{\tau}}} = \frac{1}{e^{\frac{(\varepsilon-\mu)}{\tau}}+1}$$

Thus, the Fermi-Dirac distribution function is

$$F(\varepsilon) = \frac{1}{e^{\frac{(\varepsilon-\mu)}{\tau}}+1}$$

The Bose-Einstein Distribution

Let ε denote the energy of a single orbital when occupied by a Boson; when there are N Boson's in the orbital, the energy is $N\varepsilon$. Since any number of particles may occupy a given orbital, the Gibbs Sum becomes

$$Z = \sum_{N=0}^{\infty} e^{\frac{(N\mu-N\varepsilon)}{\tau}} = \sum_{N=0}\left(e^{\frac{(\mu-\varepsilon)}{\tau}}\right)^N = \frac{1}{1-e^{\frac{(\mu-\varepsilon)}{\tau}}}$$

Thus, the thermal average occupancy for Bosons becomes

$$\left\langle N\right\rangle = \frac{\left(e^{\frac{(\mu-\varepsilon)}{\tau}}\right)^N}{\sum_{N=0}^{\infty}\left(e^{\frac{(\mu-\varepsilon)}{\tau}}\right)^N} = e^{\frac{\mu}{\tau}}\frac{d\ln Z}{d\left(e^{\frac{\mu}{\tau}}\right)} = \frac{1}{e^{\frac{(\varepsilon-\mu)}{\tau}}-1}$$

Thus, the Bose-Einstein distribution function is

$$F(\varepsilon) = \frac{1}{e^{\frac{(\varepsilon-\mu)}{\tau}}-1}$$

The Fermi Energy

The Fermi energy ε_F is the energy of the highest filled orbital at absolute zero; it is determined by the requirement that the system in the ground state hold N electrons, with each orbital filled with one electron up to the energy

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{\pi n_F}{L}\right)^2$$

For the system to hold N electrons the orbitals must be filled UP TO n_F determined by

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

so

$$n_F = \left(\frac{3N}{\pi}\right)^{\frac{1}{3}}$$

Finally, the Fermi energy can be written as

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{2}{3}}$$