Quantum Statistical Mechanics - II

We now discuss the properties of an ideal gas of identical particles. We have already studied ideal gas in classical microcanonical and canonical ensembles. The indistinguishability of identical particles in quantum mechanics is of a very fundamental nature, and thus has strong bearing on the properties of gases. In particular we will be interested in the case where the system can exchange particles with a heat-bath. Free electron gas in metals and photon gas in a cavity are two examples where number of particles of the system is not fixed. So, the system is described using the grand canonical ensemble.

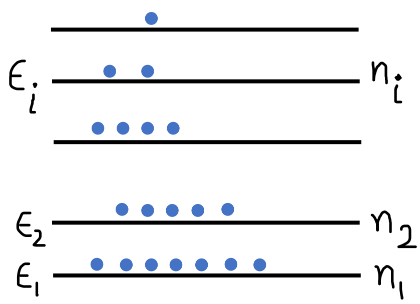
Grand canonical ensemble

The density matrix in the grand canonical ensemble can be written, in general, as

$$\rho_{ii} = \frac{e^{-\beta(E_i - \mu N_i)}}{Z_g} \qquad where\ Z_g = \sum_i e^{-\beta(E_i - \mu N_i)}$$

where μ is the chemical potential, and Z_g the grand partition function. How the microstates of the system are defined, may depend on the specific problem at hand.

For identical particles, it is not important which particle is occupying which energy-level. The only thing important is how many particles are occupying a particular energy level. For example, at an instance, there are n_1 particles in the level 1 with energy ϵ_1, there are $n_2$particles in the level 2 with energy ϵ_2, and so on (see the figure) then, the total energy and number of particles, in a particular microstate, can be calculated as



$$E = \sum_i n_i \epsilon_i \qquad N = \sum_i n_i$$

Note that in the next instance, the arrangement of the particles may change and give a different microstate. As we learned that each configuration corresponds to a particular microstate, and our aim is to estimate the total number of microstates.

The single particle energies ϵ_i depend on the particular problem at hand. For example, for a particle in a box (in 1-dimension), $\epsilon_i = \frac{i^2\, h^2}{8\, m\, L^2}$, where L is the box size. Similarly, for the case of a particle trapped by a harmonic oscillator potential, $\epsilon_i = \frac{h\omega}{2\,\pi}\left(i + \frac{1}{2}\right)$ (in 1-dimension).

The grand canonical partition function can now be written as

$$Z = \sum_{n_1} e^{-\beta\,(n_1\epsilon_1 - \mu\, n_1)} \sum_{n_2} e^{-\beta\,(n_2\epsilon_2 - \mu\, n_2)} \quad \dots \sum_{n_k} e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)} \dots\dots$$

Let us suppose we want to calculate the average occupancy of a particular energy-state ϵ_k. To do that we should multiply ϵ_k by the density matrix, and sum over all the microstates. Resulting,

$$\langle n_k \rangle = \frac{1}{Z} \sum_{n_1} e^{-\beta\,(n_1\epsilon_1 - \mu\, n_1)} \sum_{n_2} e^{-\beta\,(n_2\epsilon_2 - \mu\, n_2)} \quad \dots \sum_{n_k} n_k\, e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)} \dots\dots$$

This implies,

$$\langle n_k \rangle = \frac{\sum_{n_k} n_k\, e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)}}{\sum_{n_k} e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)}}$$

To proceed further, we should know what are the allowed occupancies of the single-particle energy-eigenstates. We know that in quantum mechanics, there are two kinds of particles, Fermions in which occupancy is only 0 or 1, and Bosons in which the occupancy can vary from 0 to ∞.

Bosons (n = 0, 1, 2, …..)

For Bosons, the average occupation of the k'th energy-state is given by

$$\langle n_k \rangle = \frac{\sum_{n_k=0}^{\infty} n_k\, e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)}}{\sum_{n_k=0}^{\infty}\, e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)}}$$

The denominator is geometric progression, and gives $\frac{1}{e^{-\beta\,(\epsilon_k - \mu)}}$

The numerator can be calculated by taking the first derivative of a geometric series,

$$\sum_{n_k=0}^{\infty} \left(\frac{-1}{\beta}\right) \frac{\partial\, e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)}}{\partial \epsilon_k} = \left(\frac{-1}{\beta}\right) \frac{\partial}{\partial \epsilon_k} \left[\sum_{n_k=0}^{\infty} e^{-\beta\,(n_k\epsilon_k - \mu\, n_k)}\right]$$

$$= \left(\frac{-1}{\beta}\right) \frac{\partial}{\partial \epsilon_k} \left[\frac{1}{1 - e^{-\beta\,(\epsilon_k - \mu)}}\right]$$

$$= \frac{e^{-\beta\,(\,\epsilon_k\,-\mu)}}{(1-\ e^{-\beta\,(\,\epsilon_k\,-\mu)})^2}$$

So, the average occupancy of the k'th energy-state is

$$\langle n_k \rangle = \frac{e^{-\beta\,(\,\epsilon_k\,-\mu)}}{1-\ e^{-\beta\,(\,\epsilon_k\,-\mu)}}$$

$$\langle n_k \rangle = \frac{1}{e^{\beta\,(\,\epsilon_k\,-\mu)} - 1}$$

The above formula describes the average occupancy of single-particle energy-states, for particles following Bose-Einstein statistics.

Fermions (n = 0, 1)

For Bosons, the average occupation of the k'th energy-state is given by

$$\langle n_k \rangle = \frac{\sum_{n_k=0}^{1} n_k\ e^{-\beta\,(\,n_k\epsilon_k\,-\mu\,n_k)}}{\sum_{n_k=0}^{1}\ e^{-\beta\,(\,n_k\epsilon_k\,-\mu\,n_k)}} = \frac{e^{-\beta\,(\epsilon_k\,-\mu)}}{1+\ e^{-\beta\,(\epsilon_k\,-\mu)}}$$

$$\langle n_k \rangle = \frac{1}{e^{\beta\,(\epsilon_k\,-\mu)} + 1}$$

The above formula describes the average occupancy of single-particle energy-states, for particles following Fermi-Dirac statistics.

Total number of particles in the system is simply given by

$$\langle N \rangle = \sum_k \langle n_k \rangle$$

which, for the two cases, takes the following form

$$\langle N \rangle = \begin{cases} \sum_k \dfrac{1}{e^{\beta\,(\,\epsilon_k\,-\mu)} - 1} & (\text{Bose} - \text{Einstein}\,) \\ \sum_k \dfrac{1}{e^{\beta\,(\,\epsilon_k\,-\mu)} + 1} & (\text{Fermi} - \text{Dirac}\,) \end{cases}$$

The corresponding partition functions read

$$Z = \begin{cases} \prod_k \dfrac{1}{1 - e^{-\beta(\epsilon_k - \mu)}} & (\text{Bose} - \text{Einstein}) \\ \prod_k \left(1 + e^{-\beta(\epsilon_k - \mu)}\right) & (\text{Fermi} - \text{Dirac}) \end{cases}$$

Using the above relations, we can express the average occupancy of a particular energy-state $\langle n_k \rangle$ as

$$\langle n_k \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_k}$$