Statistical Mechanics: Lecture 10

Ideal Gas of Quantum Particles

We now come to a very important topic in statistical mechanics, 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

$$\rho_{ii} = \frac{e^{-\beta(E_i-\mu N_i)}}{\mathcal{Z}}, \qquad \mathcal{Z} = \sum_i e^{-\beta(E_i-\mu N_i)} \tag{1}$$

where μ is the chemical potential, and $\mathcal{Z}$ the grand partition function. In the sum, index i denotes the microstates of the system, and E_i and N_i, the energy and number of particles in the i'th microstate. Now, as the particles are assumed to be non-interacting, each particle is governed by an identical Hamiltonian, say $\mathcal{H}_i$, with the eigenvalues denoted by ϵ_n. The energy-levels of each particle are also the same - we will call them single-particle energy levels. For example, many particles can have a particular energy, say, ϵ_k.
One way of summing over the number of microstates of the gas, can be to take each particle one by one, and sum over all its possible energy eigenstates. But, in doing that we will be tacitly giving them identity, because two particles exchanging their state, does not give us a new quantum state, or a new microstate.
Another way of counting could be to realize that if we know the occupancy of each single-particle state, we have specified the particular microstate. For truly 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. Thus, if we denote the occupancy of single particle states $\epsilon_1, \epsilon_2, \epsilon_3, \ldots$ by $n_1, n_2, n_3, \ldots$, a set of values of $n_1, n_2, n_3, \ldots$ specifies a particular microstate. Summing over microstates would mean summing over all possible values of $n_1, n_2, n_3, \ldots$ etc. The energy and number particles of the system, in a particular microstate, can be written as

$$E = \sum_j n_j \epsilon_j, \qquad N = \sum_j n_j \tag{2}$$

The single particle energies ϵ_j depend on the particular problem at hand. For example, for an ideal gas of particles in a box (in 1-dimension), ϵ_j will be $\frac{j^2h^2}{8mL^2}$. Or if all the particles are trapped by a harmonic oscillator potential, ϵ_j will be given by the $(j+1/2)\hbar\omega$ (in 1-dimension).

The grand partition function can now be written as

$$\begin{aligned}
\mathcal{Z} =& \sum_{n_1}\sum_{n_2}\sum_{n_3}\dots\exp\left(-\beta\left[\sum_j n_j\epsilon_j - \mu\sum_j n_j\right]\right)\\
=& \sum_{n_1}\sum_{n_2}\sum_{n_3}\dots\exp\left(-\beta\sum_j n_j(\epsilon_j-\mu)\right)\\
=& \sum_{n_1}\sum_{n_2}\sum_{n_3}\dots\prod_j \exp\left(-\beta n_j(\epsilon_j-\mu)\right)\\
=& \sum_{n_1} e^{-\beta n_1(\epsilon_1-\mu)}\sum_{n_2} e^{-\beta n_2(\epsilon_2-\mu)}\dots\sum_{n_k} e^{-\beta n_k(\epsilon_k-\mu)}\dots
\end{aligned} \tag{3}$$

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. That will yield

$$\begin{aligned}
\langle n_k\rangle =& \sum_{n_1}\sum_{n_2}\sum_{n_3}\dots n_k\exp\left(-\beta\left[\sum_j n_j\epsilon_j - \mu\sum_j n_j\right]\right)\\
=& \frac{1}{\mathcal{Z}}\sum_{n_1}\sum_{n_2}\sum_{n_3}\dots n_k\exp\left(-\beta\sum_j n_j(\epsilon_j-\mu)\right)\\
=& \frac{1}{\mathcal{Z}}\sum_{n_1}\sum_{n_2}\sum_{n_3}\dots n_k\prod_j \exp\left(-\beta n_j(\epsilon_j-\mu)\right)\\
=& \frac{1}{\mathcal{Z}}\sum_{n_1} e^{-\beta n_1(\epsilon_1-\mu)}\sum_{n_2} e^{-\beta n_2(\epsilon_2-\mu)}\dots\sum_{n_k} n_k e^{-\beta n_k(\epsilon_k-\mu)}\dots\sum_{n_i} e^{-\beta n_i(\epsilon_i-\mu)}\dots
\end{aligned} \tag{4}$$

In the above equation, the numerator and the denominator (given by (3)) have most terms common. Each sum in the numerator has a corresponding sum in the denominator, except the sum over n_k, for which the numerator and the denominator terms are different. Consequently all the sums from the numerator and denominator cancel out, except the sum over n_k, giving

$$\langle n_k\rangle = \frac{\sum_{n_k} n_k e^{-\beta n_k(\epsilon_k-\mu)}}{\sum_{n_k} e^{-\beta n_k(\epsilon_k-\mu)}} \tag{5}$$

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=0,1,2,3...)

For fermions, the average occupancy of the k'th energy-state is given by

$$\langle n_k\rangle = \frac{\sum_{n_k=0}^{\infty} n_k e^{-\beta n_k(\epsilon_k-\mu)}}{\sum_{n_k=0}^{\infty} e^{-\beta n_k(\epsilon_k-\mu)}} \tag{6}$$

The denominator is geometric progression, and gives $(1-e^{-\beta(\epsilon_k-\mu)})^{-1}$. The numerator can be calculated by taking the first derivative of a geometric series, and yields $\frac{e^{-\beta(\epsilon_k-\mu)}}{(1-e^{-\beta(\epsilon_k-\mu)})^2}$

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

$$\langle n_k \rangle = \frac{e^{-\beta(\epsilon_k-\mu)}}{1-e^{-\beta(\epsilon_k-\mu)}} \tag{7}$$

or

$$\boxed{\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k-\mu)}-1}} \tag{8}$$

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

Fermions (n=0,1)

For fermions, the average occupancy of the k'th energy-state is given by

$$\langle n_k \rangle = \frac{\sum_{n_k=0}^{1} n_k e^{-\beta n_k(\epsilon_k-\mu)}}{\sum_{n_k=0}^{1} e^{-\beta n_k(\epsilon_k-\mu)}} = \frac{e^{-\beta n_k(\epsilon_k-\mu)}}{1+e^{-\beta n_k(\epsilon_k-\mu)}} \tag{9}$$

or

$$\boxed{\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k-\mu)}+1}} \tag{10}$$

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

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

Finally, we also would like to evaluate the grand partition function $\mathcal{Z}$, given by (3). The sums can now be carried out to yield

$$\mathcal{Z} = \begin{cases} \prod_j \frac{1}{1-e^{-\beta(\epsilon_j-\mu)}} & \text{(Bose-Einstein)} \\ \prod_j \left(1+e^{-\beta(\epsilon_j-\mu)}\right) & \text{(Fermi-Dirac)} \end{cases}$$

From (3) one can see that average occupancy of a energy-state could also have been calculated by the following relation:

$$\langle n_k \rangle = -\frac{1}{\beta}\frac{\partial \log \mathcal{Z}}{\partial \epsilon_k}. \tag{11}$$