LECTURE 3

Maxwell–Boltzmann, Fermi, and Bose Statistics

Suppose we have a gas of N identical point particles in a box of volume V. When we say "gas", we mean that the particles are not interacting with one another. Suppose we know the single particle states in this gas. We would like to know what are the possible states of the system as a whole. There are 3 possible cases. Which one is appropriate depends on whether we use Maxwell–Boltzmann, Fermi or Bose statistics. Let's consider a very simple case in which we have 2 particles in the box and the box has 2 single particle states. How many distinct ways can we put the particles into the 2 states?

Maxwell–Boltzmann Statistics: This is sometimes called the classical case. In this case the particles are distinguishable so let's label them A and B. Let's call the 2 single particle states 1 and 2. For Maxwell–Boltzmann statistics any number of particles can be in any state. So let's enumerate the states of the system:

```
Single Particle State          1               2
--------------------------------------------------------------------------
                              AB
                                              AB
                              A               B
                              B               A
```

We get a total of 4 states of the system as a whole. Half of the states have the particles bunched in the same state and half have them in separate states.

Bose–Einstein Statistics: This is a quantum mechanical case. This means that the particles are indistinguishable. Both particles are labelled A. Recall that bosons have integer spin: 0, 1, 2, etc. For Bose statistics any number of particles can be in one state. So let's again enumerate the states of the system:

```
Single Particle State          1               2
--------------------------------------------------------------------------
                               AA
                                               AA
                               A               A
```

We get a total of 3 states of the system as a whole. 2/3 of the states have the particles bunched in the same state and 1/3 of the states have them in separate states.

Fermi Statistics: This is another quantum mechanical case. Again the particles are indistinguishable. Both particles are labelled A. Recall that fermions have half–integer spin: 1/2, 3/2, etc. According to the Pauli exclusion principle, no more than one particle can be in any one single particle state. So let's again enumerate the states of the system:

```
Single Particle State          1               2
--------------------------------------------------------------------------
                              A               A
```

We get a total of 1 state of the system as a whole. None of the states have the particles bunched up; the Pauli exclusion principle forbids that. 100% of the states have the particles in separate states.

This simple example shows how the type of statistics influences the possible states of the system.

Distribution Functions

We can formalize this somewhat. We consider a gas of N identical particles in a volume V in equilibrium at the temperature T. We shall use the following notation:

- Label the possible quantum states of a single particle by r or s.
- Denote the energy of a particle in state r by ε_r.
- Denote the number of particles in state r by n_r.
- Label the possible quantum states of the whole gas by R.

Since the particles in the gas are not interacting or are interacting weakly, we can describe the state R of the system as having n_1 particles in state $r = 1$, n_2 particles in state $r = 2$, etc. The total energy of the state is

$$E_R = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 ... = \sum_r n_r\varepsilon_r \tag{1}$$

Since the total number of particles is N, then we must have

$$\sum_r n_r = N \tag{2}$$

The partition function is given by

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + ...)} \tag{3}$$

Here the sum is over all the possible states R of the whole gas, i.e., essentially over all the various possible values of the numbers n_1, n_2, n_3, ...

Now we want to find the mean number $< n_s >$ of particles in a state s. The $< ... >$ refer to a thermal average. Since

$$P_R = \frac{e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + ...)}}{Z} \tag{4}$$

is the probability of finding the gas in a particular state where there are n_1 particles in state 1, n_2 particles in state 2, etc., one can write for the mean number of particles in a state s:

$$< n_s > = \sum_R n_s P_R = \frac{\sum_R n_s e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + ...)}}{Z} \tag{5}$$

We can rewrite this as

$$< n_s >= \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\right) e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+...)} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial\varepsilon_s} \tag{6}$$

or

$$< n_s >= -\frac{1}{\beta}\frac{\partial \ln Z}{\partial\varepsilon_s} \tag{7}$$

So to calculate the mean number of particles in a given single–particle state s, we just have to calculate the partition function Z and take the appropriate derivative. We want to calculate $< n_s >$ for both Bose and Fermi statistics.

Bose–Einstein and Photon Statistics

Here the particles are to be considered as indistinguishable, so that the state of the gas can be specified by merely listing the number of particles in each single particle state: n_1, n_2, n_3, ... Since there is no limit to the number of particles that can occupy a state, n_s can equal 0,1,2,3,... for each state s. For photons the total number of particles is not fixed since photons can readily be emitted or absorbed by the walls of the container. Let's calculate $< n_s >$ for the case of photon statistics. The partition function is given by

$$Z = \sum_R e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+...)} \tag{8}$$

where the summation is over all values $n_r = 0, 1, 2, 3, ...$ for each r, without any further restriction. We can rewrite (8) as

$$Z = \sum_{n_1,n_2,...} e^{-\beta n_1\varepsilon_1} e^{-\beta n_2\varepsilon_2} e^{-\beta n_3\varepsilon_3} ... \tag{9}$$

or

$$Z = \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1\varepsilon_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta n_2\varepsilon_2}\right)\left(\sum_{n_3=0}^{\infty} e^{-\beta n_3\varepsilon_3}\right) ... \tag{10}$$

But each sum is a geometric series whose first term is 1 and where the ratio between successive terms is $\exp(-\beta\varepsilon_r)$. Thus it can be easily summed:

$$\sum_{n_s=0}^{\infty} e^{-\beta n_s\varepsilon_s} = 1 + e^{-\beta\varepsilon_s} + e^{-2\beta\varepsilon_s} + ... = \frac{1}{1-e^{-\beta\varepsilon_s}} \tag{11}$$

Hence eq. (10) becomes

$$Z = \left(\frac{1}{1-e^{-\beta\varepsilon_1}}\right)\left(\frac{1}{1-e^{-\beta\varepsilon_2}}\right)\left(\frac{1}{1-e^{-\beta\varepsilon_3}}\right) ... \tag{12}$$

or

$$\ln Z = -\sum_s \ln\left(1-e^{-\beta\varepsilon_s}\right) \tag{13}$$

So if we plug this into eqn. (7), we get

$$< n_s >= -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = \frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\ln\left(1-e^{-\beta\varepsilon_s}\right) = \frac{e^{-\beta\varepsilon_s}}{1-e^{-\beta\varepsilon_s}} \tag{14}$$

or

$$< n_s >= \frac{1}{e^{\beta\varepsilon_s}-1} \tag{15}$$

This is called the "Planck distribution." We'll come back to this a bit later when we talk about black body radiation.

Photons are bosons, but their total number is not conserved because they can be absorbed and emitted. Other types of bosons, however, do have their total number conserved. One example is ^{4}He atoms. A ^{4}He atom is a boson because if you add the spin of the proton, neutron, and 2 electrons, you always will get an integer. If the number of bosons is conserved, then $< n_s >$ must satisfy the condition

$$\sum_s < n_s >= N \tag{16}$$

where N is the total number of bosons in the system. In order to satisfy this condition, one slightly modifies the Planck distribution. The result is known as the Bose–Einstein distribution

$$< n_s >= \frac{1}{e^{\beta(\varepsilon_s-\mu)}-1} \tag{17}$$

where μ is the chemical potential. μ is adjusted so that eq. (16) is satisfied. Physically μ is the change in the energy of the system when one particle is added. Eqn. (17) is called the Bose–Einstein distribution function or the Bose distribution function for short. We will return to the Bose–Einstein distribution when we discuss Bose–Einstein condensation.

Fermi–Dirac Statistics

Recall that fermions have half–integer spin statistics and that at most one fermion could occupy a each single particle state. This means that $n_s = 0$ or 1. We can easily get some idea of what $< n_s >$ by considering the very simple case of a system with just one single particle state. In this case

$$< n_s >= \frac{\sum_{n_s} n_s e^{-\beta n_s\varepsilon_s}}{\sum_{n_s} e^{-\beta n_s\varepsilon_s}} \tag{18}$$

In this case the sums just have 2 terms. The denominator is

$$\sum_{n_s=0,1} e^{-\beta n_s\varepsilon_s} = 1 + e^{-\beta\varepsilon_s} \tag{19}$$

The numerator is

$$\sum_{n_s=0,1} n_s e^{-\beta n_s\varepsilon_s} = 0 + e^{-\beta\varepsilon_s} \tag{20}$$

So we have

$$< n_s >= \frac{e^{-\beta\varepsilon_s}}{1 + e^{-\beta\varepsilon_s}} \tag{21}$$

or

$$< n_s >= \frac{1}{e^{\beta\varepsilon_s} + 1} \tag{22}$$

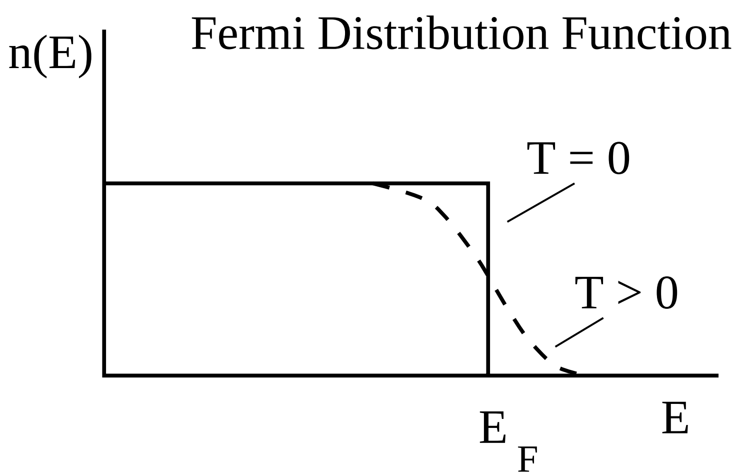
For a real system we have many single particle states and many particles. The expression for $< n_s >$ in this case must satisfy the condition that the number of particles is a constant:

$$\sum_s < n_s >= N \tag{23}$$

The correct formula which satisfies this condition (23) is

$$< n_s >= \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \tag{24}$$

This is called the Fermi distribution function. μ is adjusted to satisfy the constraint (23). As in the Bose–Einstein case, μ is called the chemical potential. This is basically the same as the Fermi energy. We will return to this when we discuss metals and superconductors.



Classical Limit

We can summarize our results for the quantum statistics of ideal gases with

$$< n_s >= \frac{1}{e^{\beta(\varepsilon_s - \mu)} \pm 1} \tag{25}$$

where the upper sign refers to Fermi statistics and the lower sign refers to Bose statistics. If the gas consists of a fixed number of particles, μ is determined by

$$\sum_s < n_s >= \sum_s \frac{1}{e^{\beta(\varepsilon_s - \mu)} \pm 1} = N \tag{26}$$

In general the number N of particles is much smaller than the total number of single particle states s.

Let us consider 2 limiting cases. Consider the low density limit where N is very small. The relation (26) can then only be satisfied if each term in the sum over all states is sufficiently small, i.e., if $< n_s >\ll 1$ or $\exp[\beta(\varepsilon_s - \mu)] \gg 1$ for all states s.

The other case to consider is the high temperature limit. Since $\beta = 1/k_B T$, the high temperature limit corresponds to small β. Now if β were 0, we would have

$$\sum_s \frac{1}{1 \pm 1} = N \tag{27}$$

which is a disaster for both the Fermi–Dirac and Bose–Einstein cases. But $\beta = 0$ means that $T = \infty$. Let's assume that the temperature is high but not infinite, so that β is small but not 0. At high temperatures, lots of high energy states are occupied. By "high energy," I mean that $\varepsilon_s \gg \mu$. In order to satisfy the fixed N constraint of eqn. (26), it is necessary to have

$$\exp[\beta(\varepsilon_s - \mu)] \gg 1 \tag{28}$$

such that

$$< n_s >\ll 1 \tag{29}$$

for all states s. (Remember that there are many more states s than particles N.) This is the same condition that came up in the low density case. We call the limit of sufficiently low concentration or sufficiently high temperature where (28) or (29) are satisfied the "classical limit." In this limit $< n_s >$ reduces to

$$< n_s >= e^{-\beta(\varepsilon_s - \mu)} \tag{30}$$

Plugging this into (26), we get

$$\sum_s < n_s >= \sum_s e^{-\beta(\varepsilon_s - \mu)} = e^{\beta\mu} \sum_s e^{-\beta\varepsilon_s} = N \tag{31}$$

or

$$e^{\beta\mu} = \frac{N}{\sum_s e^{-\beta\varepsilon_s}} \tag{32}$$

Thus

$$< n_s >= N \frac{e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}} \tag{33}$$

Hence we see that in the classical limit of sufficiently low density or sufficiently high temperature, the Fermi–Dirac and Bose–Einstein distribution laws reduce to the Maxwell–Boltzmann distribution. One can also show that the classical limit corresponds to the case where the average distance between the particles is much larger than the size of the mean de Broglie wavelength $< \lambda >$ associated with each particle

$$< \lambda >= 2\pi \frac{\hbar}{< p >} \tag{34}$$

where $< p >$ is the mean momentum of a particle. Associating a wavelength with a particle is part of wave–particle duality.