LECTURE 13

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 $\overline{n}_s$ of particles in a state s. 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:

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

We can rewrite this as

$$\overline{n}_s = \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\right) e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial \varepsilon_s} \tag{6}$$

or

$$\overline{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} \tag{7}$$

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 $\overline{n}_s$ for Maxwell–Boltzmann, Bose and Fermi statistics.

Maxwell–Boltzmann Statistics

Let us begin by considering the classical case of Maxwell–Boltzmann statistics. In this case the particles are distinguishable but identical, so each particle has the same set of single particle energy levels. As a result we can write the partition function as

$$Z = \zeta^N \tag{8}$$

where the single particle partition function is

$$\zeta = \sum_r e^{-\beta\varepsilon_r} \tag{9}$$

Then

$$\ln Z = N \ln \zeta = N \ln\left(\sum_r e^{-\beta\varepsilon_r}\right) \tag{10}$$

Now we can calculate the mean occupation number

$$\overline{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = -\frac{1}{\beta} N \frac{-\beta e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}} \tag{11}$$

or

$$\overline{n}_s = N \frac{e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}} \tag{12}$$

This is called the "Maxwell–Boltzmann distribution." It is the same as our previous result when we applied the canonical distribution to N independent single particles in a classical system. The sum over r is a sum over single particle states.

Alternative Derivation of Maxwell–Boltzmann Partition Function We can write the partition function of the gas as

$$Z = \sum_R e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} \tag{13}$$

Here we are summing over all possible states R of the gas, i.e., over all values

$$n_r = 0, 1, 2, 3, \ldots \quad \text{for each } r \tag{14}$$

subject to the restriction

$$\sum_r n_r = N \tag{15}$$

Since this is a classical system, the particles have to be considered distinguishable. Thus any permutation of two particles in different states must be counted as a distinct state of the whole gas even though the numbers $n_1, n_2, n_3, \ldots$ are left unchanged. This was the case in our simple example. It is not enough to specify how many particles are in each single–particle state, but it is necessary to specify which particular particle is in which state. For a given set of values $n_1, n_2, n_3, \ldots$, there are

$$\frac{N!}{n_1!n_2!\ldots} \tag{16}$$

possible ways in which the particles can be put into the given single particle states with n_1 particles in state 1, n_2 particles in state 2, etc. This is the number of distinct states since the particles are distinguishable. Hence

$$\begin{aligned} Z &= \sum_{n_1,n_2,\ldots} \frac{N!}{n_1!n_2!\ldots} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} \\ &= \sum_{n_1,n_2,\ldots} \frac{N!}{n_1!n_2!\ldots} \left(e^{-\beta\varepsilon_1}\right)^{n_1} \left(e^{-\beta\varepsilon_2}\right)^{n_2} \ldots \end{aligned} \tag{17}$$

Because of (15), this last expression is just a multinomial expansion. So we can write

$$Z = \left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \ldots\right)^N \tag{18}$$

or

$$\ln Z = N \ln\left(\sum_r e^{-\beta\varepsilon_r}\right) \tag{19}$$

where $\sum_r e^{-\beta\varepsilon_r}$ is just the partition function for a single particle. This is what we got before.

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 $\overline{n}_s$ for the case of photon statistics. The partition function is given by

$$Z = \sum_R e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} \tag{20}$$

where the summation is over all values $n_r = 0, 1, 2, 3, \ldots$ for each r, without any further restriction. We can rewrite (20) as

$$Z = \sum_{n_1,n_2,\ldots} e^{-\beta n_1\varepsilon_1} e^{-\beta n_2\varepsilon_2} e^{-\beta n_3\varepsilon_3} \ldots \tag{21}$$

or

$$Z = \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \varepsilon_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \varepsilon_2}\right)\left(\sum_{n_3=0}^{\infty} e^{-\beta n_3 \varepsilon_3}\right)... \tag{22}$$

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:

$$\sum_{n_s=0}^{\infty} e^{-\beta n_s \varepsilon_s} = 1 + e^{-\beta\varepsilon_s} + e^{-2\beta\varepsilon_s} + ... = \frac{1}{1 - e^{-\beta\varepsilon_s}} \tag{23}$$

Hence eq. (22) becomes

$$Z = \left(\frac{1}{1 - e^{-\beta\varepsilon_1}}\right)\left(\frac{1}{1 - e^{-\beta\varepsilon_2}}\right)\left(\frac{1}{1 - e^{-\beta\varepsilon_3}}\right)... \tag{24}$$

or

$$\ln Z = -\sum_s \ln\left(1 - e^{-\beta\varepsilon_s}\right) \tag{25}$$

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

$$\overline{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = \frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\ln\left(1 - e^{-\beta\varepsilon_s}\right) = \frac{e^{-\beta\varepsilon_s}}{1 - e^{-\beta\varepsilon_s}} \tag{26}$$

or

$$\overline{n}_s = \frac{1}{e^{\beta\varepsilon_s} - 1} \tag{27}$$

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 $\overline{n}_s$ must satisfy the condition

$$\sum_s \overline{n}_s = N \tag{28}$$

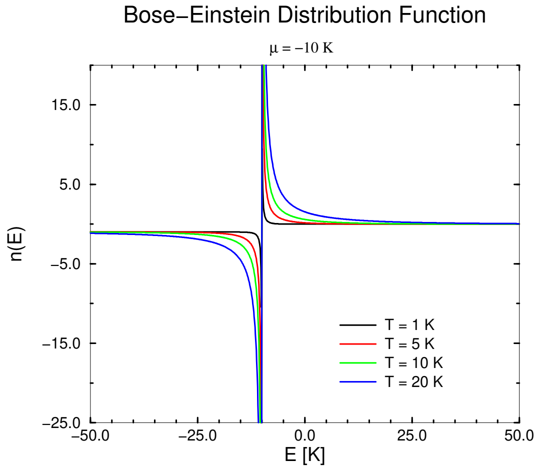
where N is the total number of bosons in the system. In order to satisfy this condition, one slightly modifies the Planck distribution. The result is known as the Bose–Einstein distribution

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1} \tag{29}$$

where μ is the chemical potential. μ is adjusted so that eq. (28) is satisfied. Physically μ is the change in the energy of the system when one particle is added. Eqn. (29) is called the Bose–Einstein distribution function or the Bose distribution function for short. Often one writes this as a function of energy:

$$n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \tag{30}$$

$n(\varepsilon)$ is also called the Bose-Einstein distribution.



Notice that if $\varepsilon < \mu$, then $n(\varepsilon) < 0$ which doesn't make much sense. The Bose distribution only makes sense for $\varepsilon > \mu$.

We can explicitly derive (29). In order to satisfy the condition (28), one multiplies the partition function by a fudge factor $\exp(-\alpha N)$. α is then adjusted to satisfy eqn. (28). α is an example of what is called a Lagrange multiplier.

$$\begin{aligned}
\mathcal{Z} &= \sum_R e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} e^{-\alpha N} \\
&= \sum_R e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} e^{-\alpha(n_1+n_2+\ldots)} \\
&= \sum_{n_1,n_2,\ldots} e^{-(\alpha+\beta\varepsilon_1)n_1-(\alpha+\beta\varepsilon_2)n_2-\ldots} \\
&= \left(\sum_{n_1=0}^{\infty} e^{-(\alpha+\beta\varepsilon_1)n_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-(\alpha+\beta\varepsilon_2)n_2}\right)\ldots \qquad (31)
\end{aligned}$$

$$(32)$$

We use $\mathcal{Z}$ instead of Z because we have an extra factor of $\exp(-\alpha N)$. $\mathcal{Z}$ is the "grand partition function" that we met when we discussed the grand canonical ensemble. This is just a product of simple geometric series. Hence

$$\mathcal{Z} = \left(\frac{1}{1-e^{-(\alpha+\beta\varepsilon_1)}}\right)\left(\frac{1}{1-e^{-(\alpha+\beta\varepsilon_2)}}\right)\ldots \qquad (33)$$

or

$$\ln\mathcal{Z} = -\sum_r \ln\left(1-e^{-(\alpha+\beta\varepsilon_r)}\right) \qquad (34)$$

Recall that when we discussed the grand canonical ensemble and the grand partition function, we set

$$\alpha = -\beta\mu \qquad (35)$$

where μ is the chemical potential. We are basically assuming that we have a system of weakly interacting interacting bosons in contact with both an energy and particle number reservoir, and that the temperature T and the chemical potential μ are fixed by the reservoir. So we can rewrite (34) to obtain the grand partition function:

$$\ln \mathcal{Z} = -\sum_r \ln\left(1 - e^{-\beta(\varepsilon_r - \mu)}\right) \tag{36}$$

We can now calculate the average value of N:

$$\begin{aligned}
\overline{N} &= \frac{1}{\mathcal{Z}} \sum_R N e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)} e^{\beta\mu N} \\
&= \frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\mu} \sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)} e^{\beta\mu N} \\
&= \frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial\mu} \\
&= \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial\mu} \\
&= \frac{1}{\beta}\frac{\partial}{\partial\mu}\left[-\sum_r \ln\left(1 - e^{-\beta(\varepsilon_r - \mu)}\right)\right] \\
&= \frac{1}{\beta}\sum_r \frac{\beta e^{-\beta(\varepsilon_r - \mu)}}{1 - e^{-\beta(\varepsilon_r - \mu)}} \\
&= \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1} \qquad (37)
\end{aligned}$$

μ is fixed by setting $\overline{N} = N$ where N is the total number of bosons in the system.

Finally we will calculate the average number of bosons in state s:

$$\begin{aligned}
\overline{n}_s &= \frac{1}{\mathcal{Z}} \sum_{\text{states}} n_s e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)} e^{\beta\mu(n_1 + n_2 + \ldots)} \\
&= \frac{1}{\mathcal{Z}}\left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\right) \sum_{\text{states}} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)} e^{\beta\mu(n_1 + n_2 + \ldots)} \\
&= -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial\varepsilon_s} \\
&= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\left[-\sum_r \ln\left(1 - e^{-\beta(\varepsilon_r - \mu)}\right)\right] \\
&= -\frac{1}{\beta}\frac{(-\beta) e^{-\beta(\varepsilon_s - \mu)}}{1 - e^{-\beta(\varepsilon_s - \mu)}} \qquad (38)
\end{aligned}$$

or

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1} \tag{39}$$

Note that we can recover the result for photons by setting $\mu = 0$. Also note that

$$\overline{N} = \sum_s \overline{n}_s \tag{40}$$

We will return to the Bose–Einstein distribution when we discuss black body radiation.

Fermi–Dirac Statistics

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

$$\overline{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \varepsilon_s}}{\sum_{n_s} e^{-\beta n_s \varepsilon_s}} \tag{41}$$

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

$$\sum_{n_s=0,1} e^{-\beta n_s \varepsilon_s} = 1 + e^{-\beta \varepsilon_s} \tag{42}$$

The numerator is

$$\sum_{n_s=0,1} n_s e^{-\beta n_s \varepsilon_s} = 0 + e^{-\beta \varepsilon_s} \tag{43}$$

So we have

$$\overline{n}_s = \frac{e^{-\beta \varepsilon_s}}{1 + e^{-\beta \varepsilon_s}} \tag{44}$$

or

$$\overline{n}_s = \frac{1}{e^{\beta \varepsilon_s} + 1} \tag{45}$$

For a real system we have many single particle states and many particles. The expression for $\overline{n}_s$ in this case must satisfy the condition that the number of particles is a constant:

$$\sum_s \overline{n}_s = N \tag{46}$$

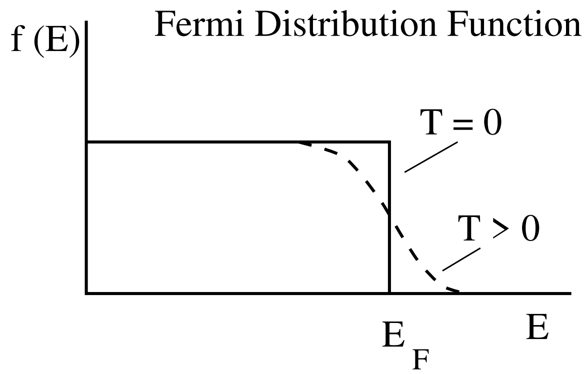
The correct formula which satisfies this condition (46) is

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \tag{47}$$

Often one writes this as a function of energy:

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \tag{48}$$

$f(\varepsilon)$ is called the Fermi distribution function. μ is adjusted to satisfy the constraint (46). As in the Bose–Einstein case, μ is called the chemical potential. This is basically the same as the Fermi energy. Notice that $f(\varepsilon = \mu) = 1/2$. This is always true of the Fermi distribution.



We can formally derive the Fermi distribution in much the same way as we derived the Bose distribution. We once again consider a system of weakly interacting fermions in contact with both an energy and a particle number reservoir. The grand partition function is given by

$$\begin{aligned}
\mathcal{Z} &= \sum_{states} e^{-\beta(E-\mu N)} \\
&= \sum_{n_1,n_2,n_3,\ldots} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)} e^{\beta\mu(n_1+n_2+\ldots)} \\
&= \sum_{n_1,n_2,n_3,\ldots} e^{-\beta(\varepsilon_1-\mu)n_1} e^{-\beta(\varepsilon_2-\mu)n_2} \ldots \\
&= \left(\sum_{n_1=0}^{1} e^{-\beta(\varepsilon_1-\mu)n_1}\right)\left(\sum_{n_2=0}^{1} e^{-\beta(\varepsilon_2-\mu)n_2}\right)\ldots \\
&= \left(1+e^{-\beta(\varepsilon_1-\mu)}\right)\left(1+e^{-\beta(\varepsilon_2-\mu)}\right)\ldots \\
&= \prod_r \left(1+e^{-\beta(\varepsilon_r-\mu)}\right) \qquad (49)
\end{aligned}$$

and

$$\ln\mathcal{Z} = \sum_r \ln\left(1+e^{-\beta(\varepsilon_r-\mu)}\right) \qquad (50)$$

So the mean number of particles in the system is

$$\overline{N} = \frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \frac{1}{\beta}\sum_r \frac{\beta e^{-\beta(\varepsilon_r-\mu)}}{1+e^{-\beta(\varepsilon_r-\mu)}} \qquad (51)$$

or

$$\overline{N} = \sum_r \frac{1}{e^{\beta(\varepsilon_r-\mu)}+1} \qquad (52)$$

The mean number of fermions in state s is

$$\overline{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\ln\mathcal{Z} = -\frac{1}{\beta}\frac{(-\beta)e^{-\beta(\varepsilon_s-\mu)}}{1+e^{-\beta(\varepsilon_s-\mu)}} \qquad (53)$$

or

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \tag{54}$$

Note that

$$\overline{N} = \sum_s \overline{n}_s \tag{55}$$

We will return to this when we discuss metals.

Summary

For future reference the two expressions for the average number of particles in the sth state for bosons and fermions are:

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1} \quad \text{bosons} \tag{56}$$

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \quad \text{fermions} \tag{57}$$

$$\tag{58}$$

A more succinct way to write our results for the quantum statistics of ideal gases is

$$\overline{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} \pm 1} \tag{59}$$

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

$$\sum_s \overline{n}_s = \sum_s \frac{1}{e^{\beta(\varepsilon_s - \mu)} \pm 1} = N \tag{60}$$

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

Classical Limit

Let us consider 2 limiting cases. Consider the low density limit where N is very small. The relation (60) can then only be satisfied if each term in the sum over all states is sufficiently small, i.e., if $\overline{n}_s \ll 1$ 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

$$\sum_s \frac{1}{1 \pm 1} = N \tag{61}$$

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. (60), it is necessary to have

$$\exp[\beta(\varepsilon_s - \mu)] \gg 1 \tag{62}$$

such that

$$\overline{n}_s \ll 1 \tag{63}$$

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 (62) or (63) are satisfied the "classical limit." In this limit $\overline{n}_s$ reduces to

$$\overline{n}_s = e^{-\beta(\varepsilon_s-\mu)} \tag{64}$$

Plugging this into (60), we get

$$\sum_s \overline{n}_s = \sum_s e^{-\beta(\varepsilon_s-\mu)} = e^{\beta\mu}\sum_s e^{-\beta\varepsilon_s} = N \tag{65}$$

or

$$e^{\beta\mu} = \frac{N}{\sum_s e^{-\beta\varepsilon_s}} \tag{66}$$

Thus

$$\overline{n}_s = N\frac{e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}} \tag{67}$$

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.

Relation of Z and $\mathcal{Z}$

In deriving the Bose–Einstein and Fermi–Dirac distributions, we used the grand canonical partition function. We can use $\mathcal{Z}$ to obtain an excellent approximation to the canonical partition function. We can write

$$\begin{aligned}
\mathcal{Z} &= \sum_{\text{all states}} e^{-\beta(E-\mu N)} \\
&= \sum_{\text{all states}} e^{-\beta E} e^{\beta\mu N} \\
&= \sum_{N'=0}^{\infty} e^{\beta\mu N'} \sum_{\text{all states with } N' \text{ particles}} e^{-\beta E} \\
&= \sum_{N'=0}^{\infty} e^{\beta\mu N'} Z(N')
\end{aligned} \tag{68}$$

where $Z(N')$ is the canonical partition function for N' particles. Since $Z(N')$ is a rapidly increasing function of N' and $e^{\beta\mu N'}$ is a rapidly decreasing function of N' (for $\mu < 0$), the grand partition function is sharply peaked at $N' = \overline{N}$. So we can write

$$\begin{aligned}
\mathcal{Z} &= \sum_{N'=0}^{\infty} e^{\beta\mu N'} Z(N') \\
&= Z(\overline{N}) e^{\beta\mu\overline{N}} \,(\Delta^* N')
\end{aligned} \tag{69}$$

where the width of the peak is $\Delta^* N'$. Thus

$$\begin{aligned} \ln \mathcal{Z} &= \ln Z(\overline{N}) + \beta\mu\overline{N} + \ln(\Delta^* N') \\ &\cong \ln Z(\overline{N}) + \beta\mu\overline{N} \end{aligned} \tag{70}$$

since $\ln(\Delta^* N')$ is negligible. Or

$$\ln Z = -\beta\mu N + \ln \mathcal{Z} \tag{71}$$

This is the relation between the partition function Z and the grand partition function $\mathcal{Z}$.

Chemical Potential

Since $e^{\beta\mu N'} Z(N')$ is a sharply peaked function at $N' = \overline{N}$, we can use this to derive an expression for the chemical potential μ. Consider $\ln\left[e^{\beta\mu N'} Z(N')\right]$. By definition the maximum of this is given by

$$\frac{\partial}{\partial N'}\left[\ln Z(N') + \beta\mu N'\right] = \frac{\partial \ln Z(N')}{\partial N'} + \beta\mu = 0 \tag{72}$$

or

$$\mu = -\frac{1}{\beta}\frac{\partial \ln Z(N)}{\partial N} = -k_B T \frac{\partial \ln Z(N)}{\partial N} = \frac{\partial F}{\partial N} \tag{73}$$

This is useful for calculating the chemical potential μ.

Other Conventions for the Grand Canonical Ensemble

In some books, the fugacity y is defined by

$$y = e^{\beta\mu} \tag{74}$$

(Some books use z or λ to denote the fugacity.) The grand partition function is given in terms of the fugacity by

$$\mathcal{Z}(V, T, y) \equiv \sum_{N_r=0}^{\infty} y^{N_r} Z_{N_r}(V, T) \tag{75}$$

with $Z_0 \equiv 1$. In the grand canonical ensemble, pressure is defined by

$$PV = k_B T \ln \mathcal{Z}(V, T, y) \tag{76}$$

where V is volume. Some books define a thermodynamic potential $\Omega(V, T, y)$ by

$$\Omega(V, T, y) = -PV = -k_B T \ln \mathcal{Z}(V, T, y) \tag{77}$$

(Do not confuse the thermodynamic potential with the number of microstates of a system, even though both are sometimes denoted by Ω.) In terms of the grand partition function, the mean number of particles $\overline{N}$ is

$$\overline{N} = y\left[\frac{\partial}{\partial y} \ln \mathcal{Z}(V, T, y)\right]_{V,T} \tag{78}$$

and the mean energy $\overline{E}$ is

$$\overline{E} = -\left[\frac{\partial}{\partial\beta}\ln\mathcal{Z}(V,T,y)\right]_{y,V} \tag{79}$$

(One can compare this to Eq. (70) in Lecture 9

$$\overline{E} = \mu\overline{N} - \frac{\partial}{\partial\beta}\ln\mathcal{Z} \tag{80}$$

to see the importance of noting what is kept constant and what isn't in taking derivatives.)

The first law of thermodynamics then becomes

$$\Delta\overline{E} = Q - W + \mu\Delta\overline{N} \tag{81}$$

or, in differential form,

$$d\overline{E} = TdS - pdV + \mu d\overline{N} \tag{82}$$

Gibbs' Paradox Revisited

Now back to eq. (71). Plugging in $\mathcal{Z}$ for bosons from (34), we have

$$\ln Z = -\beta\mu N - \sum_r \ln\left(1 - e^{-\beta(\varepsilon_r-\mu)}\right) \tag{83}$$

Similarly for fermions eq. (50) yields

$$\ln Z = -\beta\mu N + \sum_r \ln\left(1 + e^{-\beta(\varepsilon_r-\mu)}\right) \tag{84}$$

We can combine these two expressions:

$$\ln Z = -\beta\mu N \pm \sum_r \ln\left(1 \pm e^{-\beta(\varepsilon_r-\mu)}\right) \tag{85}$$

At high temperatures $e^{-\beta(\varepsilon_r-\mu)}$ is small and we can expand the logarithm to obtain

$$\ln Z = -\beta\mu N \pm \sum_r \left(\pm e^{-\beta(\varepsilon_r-\mu)}\right) = -\beta\mu N + N \tag{86}$$

where in the last step we used the high temperature limit of the Bose and Fermi distributions:

$$\begin{aligned}
\sum_r \overline{n}_r &= N \\
\sum_r \frac{1}{e^{\beta(\varepsilon_r-\mu)} \pm 1} &= N \\
\sum_r e^{-\beta(\varepsilon_r-\mu)} &= N \quad \text{at high temperature} \\
e^{\beta\mu}\sum_r e^{-\beta\varepsilon_r} &= N
\end{aligned} \tag{87}$$

Taking the logarithm of both sides of (87) yields

$$\beta\mu + \ln\left(\sum_r e^{-\beta\varepsilon_r}\right) = \ln N \tag{88}$$

or

$$-\beta\mu = -\ln N + \ln\left(\sum_r e^{-\beta\varepsilon_r}\right) \tag{89}$$

Plugging this into (86), we get

$$\begin{aligned} \ln Z &= -\beta\mu N + N \\ &= -N\ln N + N + N\ln\left(\sum_r e^{-\beta\varepsilon_r}\right) \end{aligned} \tag{90}$$

The first two terms are Stirling's approximation to $N!$:

$$\ln N! \cong N\ln N - N \tag{91}$$

The last term in (90) is the Maxwell–Boltzmann partition function.

$$\ln Z_{\mathrm{MB}} = N\ln\left(\sum_r e^{-\beta\varepsilon_r}\right) \tag{92}$$

So (90) becomes

$$\ln Z = -\ln N! + \ln Z_{\mathrm{MB}} \tag{93}$$

or

$$Z = \frac{Z_{\mathrm{MB}}}{N!} \tag{94}$$

This was the resolution to the Gibbs paradox. Without quantum mechanics we had to put in the factor $N!$ by hand. But now we see that the indistinguishability of the particles comes out naturally.