AN INTRODUCTION TO
STATISTICAL PHYSICS AND THERMODYNAMICS

CHAPTER 13
QUANTUM STATISTICS

Introduction

In chapter 11 we developed the “classical” Boltzmann probability function

\[ P_T = C \, e^{-\beta [E_i + pV_i - \mu N_i]} \]  

(13.1)

for a small (microscopic) system in contact with a much larger reservoir. We pointed out there that the temperature, the pressure, and the chemical potential in this expression are the equilibrium values for the reservoir, and the energy, volume, and number of particles, \( E_i, V_i, \) and \( N_i \), are the amounts removed from the reservoir, and, therefore, the values measureable in the microscopic subsystem \( A \).

There are two ways in which we might interpret this equation from a quantum mechanical point of view:
1) we can view the subsystem \( A \) as a set of quantum states in which we can place a certain number of particles, or
2) we can view as the subsystem of interest and determine the number of particles which occupy this particular quantum state. Let us briefly look at each of these cases and differentiate them more clearly.

In the first case, the subsystem \( A \) is viewed as a collection of possible quantum states in which we may “place” the \( N \) particles of the subsystem. The specific way we distribute these particles among the different quantum states will define a particular state \( (s) \) of the system. Any rearrangement of the particles among the quantum states will result in yet another state of the system. The number and spacing of the quantum states of the system, the spectrum of accessible states, depends upon the details of the system under consideration. For example, when we consider the cells in phase space, we are essentially defining the spectrum of accessible states in a semi-classical manner. The number of particles in the system, when the system is in a particular state, is simply designated by \( N_s \). However, up to this point we have not worried about the problem of whether or not more than one particle can be in a single quantum state. Typically, the number of quantum states which are accessible to the \( N \) particles in the subsystem are much greater than the number of particles, so that the probability of finding more than one particle in a single quantum state is very small. When this is true, the methods we have utilized so far are correct. This particular viewpoint can, therefore, be considered as a classical point of view. However, when the number of accessible states is comparable to the number of particles in the system, we must consider the type of particles we are dealing with to obtain the correct results.

![Figure 13.1](image)

**Figure 13.1** In classical statistics, we are dealing with the situation where a single particle has many different possible states that it can occupy (i.e., there are a large number of empty states available for every available particle. When the number of available states is comparable to the number of particles, we must make use of quantum statistics. This is because the Pauli exclusion principle states that no two Fermions can occupy the same quantum state.

This leads us to the second case we mentioned above, in which we view the system of interest as a single quantum state. This quantum state may or may not be occupied. The type of particles that are in the system will determine just how many particles can be placed in a given quantum state.
Thus, when the number of particles in a single quantum state, on average, is much much less than one, so that the type of particle will have little effect, we can use our classical methods. When the number of particles in a system closely correspond to the number of available quantum states, the characteristics of the system depends greatly on the type of particle in the system.

The “Grand Canonical Ensemble” for a Single Quantum State

For the special case where we consider the microscopic system as a single quantum state, \( s \), we can use the general probability function (Equ. 13.1) to write the probability of finding the system in that quantum state as

\[
P_s = C e^{-\beta [E_s - \mu N_s]}
\]

where we ignore the volume removed from the reservoir associated with a single quantum state. If, in addition, we write the energy of the system as the number of particles in state \( s \) times the energy associated with that state, we have \( E_s = N_s \epsilon_s \), giving

\[
P_s = C e^{-\beta [N_s \epsilon_s - \mu N_s]} = C e^{-\beta n [\epsilon_s - \mu]}
\]

where we let \( n = N_s \). Remember that this probability is written as a function of the temperature of the reservoir, the number of particles, \( n \), that are in state \( s \), the energy of the quantum state \( s \), and the chemical potential \( \mu \) of the reservoir, which is related to the change in entropy of the system as additional particles are added to the quantum state.

[Note: This last equation is sometimes written]

\[
P_s = Ce^{-\beta \epsilon_s - \alpha N_s}
\]

where

\[
\alpha = - \beta \mu = - \beta \left[ - T \left( \frac{\partial S}{\partial N} \right)_{E,V} \right] = \frac{1}{k} \left( \frac{\partial S}{\partial N} \right)_{E,V}.
\]

The Occupation Number, \( \langle n \rangle \)

We now want to examine the average number of particles in state \( s \). We will call the average number of particles in state \( s \) the occupation number of that state. We know that the average number of particles in state \( s \) is given by

\[
\langle n \rangle = \frac{\sum_n ne^{-\beta n [\epsilon_s - \mu]}}{\sum_n e^{-\beta n [\epsilon_s - \mu]}}
\]

where the sum is from zero to the maximum number of particles that can be placed in the quantum state \( s \). Now if we let \( x = \beta (\epsilon_s - \mu) \), we can write this as

\[
\langle n \rangle = \frac{\sum_n ne^{-nx}}{\sum_n e^{-nx}} = - \frac{\partial}{\partial x} \ln \left( \sum_n e^{-nx} \right)
\]

We have reduced the problem of determining the occupation number to the evaluation of the sum appearing in this last equation. This sum is from zero to the maximum possible number of particles which can be found in a particular quantum state. In nature we find two types of particles. 1) For some particles, we find that no more than one particle may occupy a given quantum state at one time. These particles are called fermions, and are said to obey “Fermi-Dirac statistics”. Half-integer spin particles, such as electrons, protons, and neutrons are fermions. 2) For other particles, we find that there is no limit on the number of particles which can occupy a given quantum state at the same time. These particles are called bosons, and are said to obey “Bose-Einstein statistics”. Particles with integer spin (such a photons) or zero spin (such as \( \alpha \)-particles) are found to be bosons.
Thus, for fermions, we find that the occupation number is given by

$$\langle n \rangle_f = -\frac{\partial}{\partial x} \ln \left( \sum_{n=0}^{\infty} e^{-nx} \right) = -\frac{\partial}{\partial x} \ln \left( 1 + e^{-x} \right) = \frac{e^{-x}}{1 + e^{-x}} = \frac{1}{e^{x} + 1}$$

(13.8)

or

$$\langle n \rangle_f = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1} \quad \text{fermions}$$

(13.9)

For bosons we must evaluate the geometric sum

$$\sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}} \quad \text{(provided } x > 0)$$

(13.10)

Thus, for bosons, the occupation number is given by

$$\langle n \rangle_b = -\frac{\partial}{\partial x} \ln \left( \sum_{n=0}^{\infty} e^{-nx} \right) = -\frac{\partial}{\partial x} \ln \left[ 1 - e^{-x} \right]^{-1} = \frac{e^{-x}}{1 - e^{-x}} = \frac{1}{e^{x} - 1}$$

(13.11)

or

$$\langle n \rangle_b = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} \quad \text{bosons}$$

(13.12)

where we require $\beta(\epsilon_s - \mu) > 0$. We can, therefore, write the expression for the occupation number for both types of particles in one equation

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} \pm 1} \quad \left\{ \begin{array}{ll} + & \text{for fermions} \\ - & \text{for bosons} \end{array} \right.$$ 

(13.13)

but we must remember the restriction on the argument of the exponential for the case of bosons: it must be positive.

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**Figure 13.2** The occupation number of Fermi particles. When the temperature $T = 0$, we find that all states with energy less than $\mu$ are filled, and all states with energy greater than $\mu$ are empty. Thus, the value of the chemical potential is related to the total energy of the system when $T \to 0$. 

\[ \bar{n}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \]
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Figure 13.3 The occupation number of Bosons. Notice that if $\epsilon = \mu$, the occupation number goes to infinity. Since we require that $\epsilon - \mu$ must be greater than zero, $\mu$ must always be less than the energy of the lowest lying state.

Comparison of the Fermi-Dirac, Bose-Einstein, and Maxwell-Boltzmann (Classical) Occupation Numbers

Now if we compare the energy $(\epsilon - \mu)$ with the “thermal energy” $kT$ in the expression for the occupation number

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

we see that if $(\epsilon - \mu) \gg kT$ the exponential in the denominator is much larger than unity for both bosons and fermions, and the occupation number for both cases approaches

$$\langle n \rangle \approx e^{-\beta(\epsilon - \mu)} \quad \text{when} \quad (\epsilon - \mu) \gg kT \quad (13.14)$$

This is the classical occupation number (i.e., the case where the occupation number is much less than unity and where the likelihood of multiple occupation is very small). In the limit, therefore, where $(\epsilon - \mu) \gg kT$

$$\langle n \rangle_{cl} \approx \langle n \rangle_{bosons} \approx \langle n \rangle_{fermions} \approx e^{-\beta(\epsilon - \mu)} \quad (13.15)$$

and we can use the classical statistical methods developed in the last chapter.

However, for states of low energy, where $(\epsilon - \mu) \approx 0$ we can see that for fermions, $\langle n \rangle_f \rightarrow \frac{1}{2}$; for bosons, $\langle n \rangle_b \rightarrow \infty$; and for the classical systems, $\langle n \rangle_{cl} \rightarrow 1$. Thus, for the case where $(\epsilon - \mu) \lesssim kT$

$$\langle n \rangle_{bosons} > \langle n \rangle_{cl} > \langle n \rangle_{fermions} \quad (13.16)$$

as we can see in Figure 13.4.
Figure 13.4 A plot of the occupation number versus energy for bosons, classical particles, and Fermions at fixed temperature and chemical potential. In the region where $(\epsilon - \mu) \gg kT$, these three occupation numbers become nearly equivalent, allowing us to use classical statistical arguments. However, when $(\epsilon - \mu) \lesssim kT$, $\langle n \rangle_{\text{bosons}} > \langle n \rangle_{\text{cl}} > \langle n \rangle_{\text{fermions}}$.

In the study of dense systems - systems where there is a high probability that more than one particle will occupy a given quantum state at a time - some of the methods we used to calculate probabilities, etc. break down. For example, when we considered indistinguishable, non-interacting particles we found that the partition function was given by

$$Z = \frac{1}{N!} \zeta^N$$

where $\zeta$ is a single particle partition function, and $N$ is the number of particles. We argued that the term in the denominator, $N!$, was required to prevent us from overcounting the number of different ways of distributing the particles among their different states. It turns out that this argument is valid only as long as the particles are in different states. To see the implications of this let's consider two non-interacting particles which can occupy any of five different states. For simplicity, we will imagine that all five states have the same energy and that this energy is zero. For this special case, the Boltzmann factor is unity for all temperatures, and the partition function is identical to the multiplicity (i.e., $Z = \Omega$).

Each particle can be placed in any of the 5 boxes, so that there are 5 different possible arrangements for the first particle. For each of these 5, the other particle can be placed in any of the 5 boxes. Thus, there are $5 \times 5$ different configurations. However, if we consider each of the particles as indistinguishable from the other, there are some states that are really identical to some others. To be even more clear about this, let's enumerate the different states of the system by indicating in which box the particles are found. Let's assume that the first particle is placed in the first box. The second can then be placed in any of the other boxes to give the following possibilities:
These 25 different states would all be distinct if the two particles are somehow distinguishable (like a penny and a nickle). However, if the two particles are indistinguishable, then the states which “look” the same in the table above would actually correspond to the same state of the system. What we did to circumvent this “overcounting” previously was to divide by $N!$ or in this case 2. This would lead to $25/2 = 12.5$ states. But this can’t be, since the number of possible states must be an integer for this system. Notice that the table above is just like a symmetrical matrix. The element above the diagonal are identical to the elements below. Thus there are 10 states above the diagonal and 5 along the diagonal which are distinctly different states, even if the two particles are identical. Thus there are 15 different ways of arranging these two indistinguishable particles - provided that more than one particle can occupy a given state at one time! Notice that if we divide the twenty possible states that arise when the particles are in distinctly different states by 2! we obtain the number 10 - the number of states allowed for indistinguishable particles when only one can occupy a given state. However, the five states containing two identical particles divided by 2! give us the problem.

Thus, when more than one particle can be in a given state the $1/N!$ term does not work properly to reduce the overcounting. It should not be divided into those states with multiple occupancy. This is the case which arises for bosons - where more than one particle can occupy a given state at one time.

If we don’t allow more than one particle per state, then the diagonal terms are not allowed, and we obtain only 10 distinct states. This is the case which arises with fermions. Thus we see that $25/2 = 12.5$ lies halfway between the 10 states allowed for fermions and the 15 states allowed for bosons. The “classical” counting method splits the difference.

The distinction between fermions and bosons is important only when the number of available states is approximately equal to the number of particles present. If, however, the number of states $Z$ is much, much greater than $N$, then the system will act like a classical system, obeying Boltzmann statistics.

**Note on Degeneracy**

Consider the grand partition function for a system composed of two distinct quantum states each with the same energy. This system is in contact with a reservoir of fermi particles at a temperature $T$. The grand partition function for this case is given by

$$Z = \sum e^{-\beta|E-\mu N|}$$

where the sum is to be taken over all possible states of the system. Now there are only four terms in this sum: the first with no particles in the system, the second with one particle in one of the quantum states, the third with one particle in the other quantum state, and the last with one particle in each of the two quantum states, or

$$Z = e^{-\beta|0+0|} + e^{-\beta|e-\mu|} + e^{-\beta|e-\mu|} + e^{-\beta|2e-2\mu|}$$

Notice that this can be written as

$$Z = e^{-\beta|e-\mu|0} + 2e^{-\beta|e-\mu|1} + e^{-\beta|e-\mu|2}$$

The first term is proportional to the probability of there being no particles in the system. The second term is proportional to the probability of there being one particle in the system, and the last is proportional to the probability of there being two particles in the system. The factor of two in the second term is basically the degeneracy of a two state system where the two states have the same energy. The probability of finding a single particle in our system is twice the probability that you might expect based upon the energy of the system alone, because there are two states available to that particle.

In our discussions concerning Bosons and Fermions we have concentrated on single quantum states, not quantum energy levels. The grand partition function for a degenerate quantum energy level is obviously not the same as the grand partition function for a single quantum state. So care must be exercised in working problems where degeneracies occur.