We go back to the problem of an ideal gas. Consider the solutions to the Schrödinger equation for a single particle in a box, as we did before (Lecture 9). We call these solutions ‘orbitals’. There are an infinite number of such solutions. We make the leap and assume that if there are \( N \) identical particles in the box, and they do not interact, we can describe the system as being occupied by \( N \) particles occupying \( N \) single-particle orbitals. This is a big assumption that will be revisited later.

The spin-statistics theorem of quantum mechanics states that there are two types of elementary particles: Fermions (of half-integer spin) and Bosons (of integer spin). A list of elementary particles and their spins is posted on the class web site.

If many identical Fermions are placed in a box and there is strong overlap of the wavefunctions, the Pauli exclusion principle says that no two of these Fermions can occupy the same exact quantum state. This places a strong constraint on the Gibbs sum for the Fermion case. These considerations do not apply to many identical Boson systems. In the Fermion case, a particular orbital can either be unoccupied or occupied by exactly 1 particle. In the Boson case, any number of particles can occupy a particular orbital, including 0.

First we will calculate the Gibbs sum for the Fermion case. We consider the system to be a single orbital, arbitrarily chosen from the infinite number of single-particle orbitals available to a particle in a box. The reservoir is the set of all other orbitals. We assume that the system and reservoir are in both thermal and diffusive equilibrium. The Gibbs sum is

\[
Z = \sum_{N=0}^{\infty} \sum e^{(N\mu - \varepsilon_s(N))/\tau} = \sum_{N=0}^1 \sum e^{(N\mu - \varepsilon_s(N))/\tau} = e^{(0\mu - \varepsilon_s(0))/\tau} + e^{(1\mu - \varepsilon_s(1))/\tau}.
\]

We adopt the convention that the zero particle state is the zero of energy \( \varepsilon_s(0) = 0 \). The single particle state has an energy we call \( \varepsilon_s(1) = \varepsilon \). The Gibbs sum becomes

\[
Z = 1 + e^{(\mu - \varepsilon)/\tau} = 1 + \lambda e^{-\varepsilon/\tau}, \text{ where } \lambda \text{ is the activity.}
\]

The thermal average occupancy of the state can be calculated simply as

\[
\langle N \rangle = 0 \times \frac{1}{1 + e^{(\mu - \varepsilon)/\tau}} + 1 \times \frac{\lambda e^{-\varepsilon/\tau}}{1 + e^{(\mu - \varepsilon)/\tau}} = \frac{\lambda e^{-\varepsilon/\tau}}{1 + e^{(\mu - \varepsilon)/\tau}}.
\]

Dividing top and bottom by \( \lambda e^{-\epsilon/\tau} \) gives \( f(\varepsilon) = \langle N \rangle = \frac{\lambda e^{-\varepsilon - \mu + \mu}{/\tau + 1}}{1 + e^{(\mu - \varepsilon)/\tau}} \) which is known as the Fermi-Dirac distribution. We will make a further leap by saying that this distribution applies for any orbital of any energy \( \varepsilon \), because the original choice of orbital was arbitrary. At zero temperature this distribution is \( f(\varepsilon) = 1 \), for \( \varepsilon - \mu < 0 \), and \( f(\varepsilon) = 0 \), for \( \varepsilon - \mu > 0 \). In other words all the states of energy below \( \mu \) are filled, and all states above \( \mu \) are empty. The filled states are sometimes called the ‘Fermi sea’. At finite temperature, the discontinuous distribution softens with \( f(\varepsilon = \mu) = 1/2 \). Only Fermions within energies a few \( \tau \) below \( \mu \) will be ‘promoted’ to the unoccupied higher energy states above \( \mu \).

Next we derive the Gibbs sum for the Boson case. Once again we consider the system to be a single orbital, arbitrarily chosen from the infinite number of single-particle orbitals available to a particle in a box. The reservoir is the set of all other orbitals. We assume that the system and reservoir are in both thermal and diffusive equilibrium. The Gibbs sum is \( Z = \sum_{N=0}^{\infty} \sum e^{(N\mu - \varepsilon_s(N))/\tau} \), and any number of particles can go into the orbital, hence the first sum could go up to \( N \). For a large system, \( N \) is effectively infinite. The orbital has a single-particle energy of \( \varepsilon \), and we assume that when it is occupied by \( N \) particles the energy of the system is simply \( \varepsilon_s(N) = N\varepsilon \). The Gibbs sum now becomes

\[
Z = \sum_{N=0}^{\infty} \sum e^{(N\mu - \varepsilon_s(N))/\tau} = \sum_{N=0}^{\infty} \sum e^{(N\mu - \varepsilon_s(N))/\tau} = e^{(0\mu - \varepsilon_s(0))/\tau} + e^{(1\mu - \varepsilon_s(1))/\tau}.
\]
\[ Z = \sum_{N=0}^{\infty} e^{(N\mu - N\varepsilon)/\tau} = \sum_{N=0}^{\infty} (\lambda e^{-\varepsilon/\tau})^N. \]

If we assume that \( \lambda e^{-\varepsilon/\tau} < 1 \), then this sum will converge to
\[ Z = \frac{1}{1-\lambda e^{-\varepsilon/\tau}}. \]

We can evaluate the thermal average occupation number as \( \langle N \rangle = \frac{\lambda}{\partial \log Z / \partial \lambda} \), which gives
\[ f(\varepsilon) = \langle N \rangle = \frac{1}{\lambda e^{\varepsilon/\tau} - 1} = \frac{1}{e^{(\varepsilon-\mu)/\tau} - 1}, \]
which is known as the Bose-Einstein distribution. Note that it differs from the Fermi-Dirac distribution only in the minus sign in the denominator!

Taking the logarithm of both sides of the convergence condition \( \lambda e^{-\varepsilon/\tau} < 1 \) for Bosons results in the constraint \( \frac{\varepsilon - \mu}{\tau} > 0 \), which says that the chemical potential is bounded above by the lowest energy orbital in the system.

Note that in the limit \( \frac{\varepsilon - \mu}{\tau} \gg 1 \), both distributions go to the same functional form, \( f(\varepsilon) \approx e^{-(\varepsilon-\mu)/\tau} \), which is the classical limit \( f(\varepsilon) \ll 1 \), which is equivalent to the dilute limit \( \frac{n}{n_0} \ll 1 \).