Lecture 26 Highlights

We are now going to consider the statistical mechanics of quantum systems. In particular we shall study the macroscopic properties of a collection of many ($N \sim 10^{23}$) identical and indistinguishable Fermions and Bosons with overlapping wavefunctions. We will study a number of systems whose macroscopic thermodynamic behavior is dominated by quantum mechanics, including:

1) Electrons in a solid, and superconductivity
2) Liquid ^{4}He and superfluidity
3) Photons in a box (black body radiation)
4) Ultra-cold atoms in an optical lattice (Bose-Einstein condensation)

The systems we will consider will be at a finite temperature *T*. Temperature is a measure of the average kinetic energy of the particles in the system. Many of the particles will occupy quantum energy states above the ground state. Because the number of particles *N* is so large, there are many microscopic configurations of the particles that are consistent with a fixed particle number (*N*) and total energy (*E*). The fundamental assumption of statistical mechanics is that the system explores all the possible microscopic states that have the same energy, with equal likelihood. This is the concept of 'ergodicity' embodied in the ergodic hypothesis of statistical mechanics.

Consider the example of 3 particles weakly interacting in a one-dimensional infinite square well. The particles have single-particle eigenenergies of $E_n = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$.

If the total energy of the three particles is

$E = E_A + E_B + E_C = (n_A^2 + n_B^2 + n_C^2)\dfrac{\pi^2\hbar^2}{2ma^2} = 243\dfrac{\pi^2\hbar^2}{2ma^2}$, what are the possible microscopic configurations consistent with this total energy? The answer depends on what kind of particles we are talking about. For the case of completely distinguishable Newtonian particles, we live under the fiction that each particle has a unique label, and there are 10 possible states:

Distinguishable: (9,9,9); (3,3,15); (3,15,3); (15,3,3); (5,7,13); (5,13,7); (7,5,13); (7,13,5); (13,5,7); (13,7,5), where the triplet represents the quantum numbers (n_A, n_B, n_C).

For the case of indistinguishable Fermions, we cannot have multiple occupation of the same quantum state. In addition we cannot distinguish the particles once their wavefunctions overlap, so in fact there is only one state possible – that in which the particles occupy 3 distinct states: 5, 7 and 13 (without specifying which particle is in which state!) We need a new notation to describe this situation. We should simply specify the occupation numbers of each state as follows: $n_5 = 1$, $n_7 = 1$, $n_{13} = 1$, $n_i = 0$ for all i not equal to 5, 7 or 13.

The case of indistinguishable Bosons is similar, except that we do not have to satisfy the Pauli exclusion principle. In this case there are three distinct quantum states of the 3 indistinguishable particles:

Configuration 1: $n_9 = 3$, $n_i = 0$ for all i not equal to 9.
Configuration 2: $n_3 = 2$, $n_{15} = 1$, $n_i = 0$ for all i not equal to 3 and 15.
Configuration 3: $n_5 = 1$, $n_7 = 1$, $n_{13} = 1$, $n_i = 0$ for all i not equal to 5, 7 or 13.

To generalize this process to a large number of particles N, consider the following exercise. Consider a general system that has an infinite number of states, with energies labeled as E_i, where i runs from 1 to infinity. Each state has degeneracy g_i. [Recall that in the unperturbed hydrogen atom with no spin the list of quantum numbers is n, ℓ, m, and the degeneracy of the states is equal to n^2. This means for example that for $n = 100$ there are $g_{100} = 10^4$ distinct lists of quantum numbers n, ℓ, m all with the same energy: $\frac{-13.6\,\text{eV}}{100^2}$! The message is that degeneracy in quantum systems generally grows very quickly with increasing eigen-energy.] We have the job of distributing the N particles into these states, subject to two constraints: the total number of particles is fixed at N ($\sum_{i=1}^{\infty} n_i = N$), and the total energy is fixed at E ($\sum_{i=1}^{\infty} n_i E_i = E$).

How can we possibly do this? The approach is to calculate all of the possible microscopic configurations of the particles distributed into the available states (at fixed N and E) and then find the configuration that is most likely to occur, assuming ergodicity. Essentially we must calculate the relative probability of finding every possible microscopic configuration, and seek to maximize that probability. This state, and many others that differ from it only slightly, will dominate the thermodynamic properties of the system.

First we will calculate the number of ways that n_s particles can be distributed into state s of energy E_s and degeneracy g_s. This will be called P_s. Next we will calculate the total number of arrangements for an entire set of occupation numbers $n_1, n_2, n_3, n_4, \ldots n_s, \ldots$ This will be the statistical weight W of the arrangement ($n_1, n_2, n_3, n_4, \ldots n_s, \ldots$):

$$W(n_1, n_2, ..., n_s, ...) = \prod_{s=1}^{\infty} P_s = P_1 P_2 P_3 P_4 \cdots P_s \cdots$$

This weight will be proportional to the probability of finding this particular distribution of occupation numbers. {Note that if $n_s = 0$, there is only one way to make that happen, so the corresponding $P_s = 1$.}

The next step is to maximize W by varying all of the occupation number values subject to the number and total energy constraints. We will then do thermodynamics with the most probable microscopic configuration.