Lecture 20 - Quantum statistics

What's Important:
• quantum statistics
Text: Reif

Quantum statistics

The quantum approach to mechanics can be formulated in a statistical form using expectation values or means. For example, the mean energy of a classical gas (without momentum or position-dependent forces) can be cast as

$$\bar{E} = \frac{d^3 q_1 ... \; d^3 q_N E \exp(-\text{ß}E) d^3 p_1 ... d^3 p_N}{d^3 q_1 ... d^3 q_N d^3 p_1 ... d^3 p_N}$$

$$= \frac{E \exp(-\text{ß}E) d^3 p_1 ... d^3 p_N}{d^3 p_1 ... d^3 p_N}$$

(20.1)

For a single particle in contact with a heat bath, this just becomes

$$\bar{E} = \frac{E \exp(-\text{ß}E) d^3 p}{d^3 p} .$$

(20.2)

In other words, take the observable of interest (*E* here), evaluate it using some weight function [$\exp(-\text{ß}E)$], then make sure the weight function is properly normalized (divide by $d^3 p$).

Quantum mechanics can be formulated in the same way. As you know from PHYS 285, Heisenberg's uncertainty principle prevents us from knowing the precise position and momentum of particles. Hence, we take averages or means:

$$\bar{E} = \frac{\rho E \, d^3 p}{\rho \, d^3 p}$$

(20.3)

or

$$\bar{x} = \frac{\rho x \, d^3 x}{\rho \, d^3 x}$$

(20.4)

The quantity ρ is called the density matrix and is analogous to the Boltzmann weight. In terms of the quantum wavefunctions ψ, ρ is defined as

$$\rho \quad \psi^* \psi .$$

(20.5)

Now, all that really counts as far as observables (*e.g. <E>* or *<x>*) are concerned is the density matrix, not the wavefunction. Nevertheless, quantum mechanics was historically formulated in terms of wavefunctions (*e.g.,* Schrödinger's equation).

The fact that we cannot follow the motion of a particle in detail leads to a problem or phenomenon that does not arise in classical mechanics, where particles are individually distinguishable. This means that if we have three particles [even if their characteristics are identical] called Fred, Mary and Joe, we always know in principle which is which, because we can follow their paths with infinite accuracy:
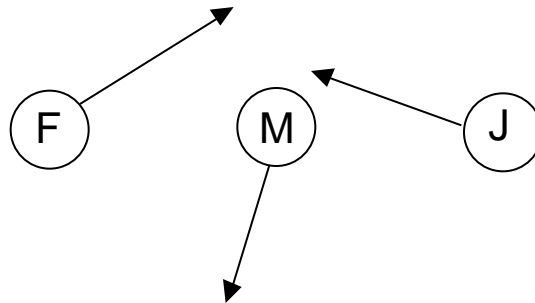
Quantum mechanically, such is not the case, since we only know mean positions, mean energies *etc*. For example, suppose that each particle has $\langle x \rangle$ = constant

$t = 0$

$t = $ later
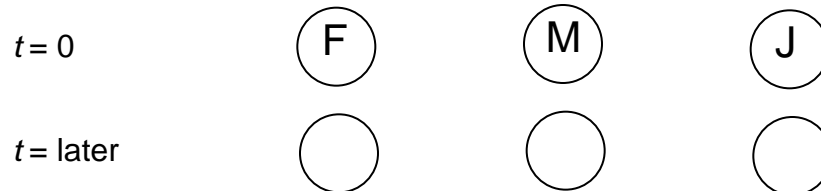
How do we know which particle is which over time?   We don't.   At the quantum mechanical level, all particles of the same type are indistinguishable.

What does this indistinguishable-ness do to the wavefunction ψ? ψ is a function of the coordinates of the particles, and time. Suppose we had a system consisting of three allowed positions and three particles: F J M. The particles can be assigned to the positions in a variety of ways, including

$\psi(x_F, x_M, x_J)$

$\psi(x_J, x_M, x_F)$
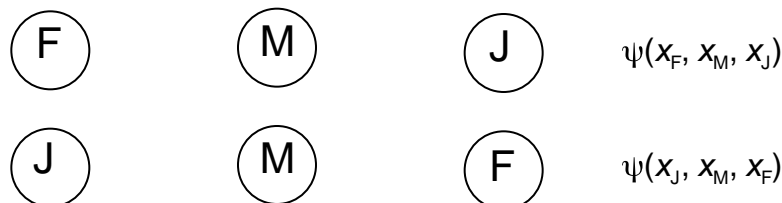
There are a total of 3! = 6 possibilities for the arrangements.   How are all the wavefunctions related?

Since the particles are identical, the density matrix for the arrangements must be the same. Thus, we have two possibilities for the symmetries of $\psi(x_1, x_2, x_3)$:

$\psi(x_1, x_2, x_3) = +\psi(x_2, x_1, x_3)$ symmetric for bosons

$\psi(x_1, x_2, x_3) = -\psi(x_2, x_1, x_3)$ symmetric for fermions.

Bosons   obey Bose-Einstein statistics
                spin = integer • (h / 2)

Fermions   obey Fermi-Dirac statistics
                spin = [odd integer] / 2 • (h / 2)

The symmetry property has a dramatic effect when we consider how many particles can have *all* **x**, **p**, ... the same. Suppose particles 1 and 2 occupy the same state. Then

$$\psi(x, x, x_3) = +\psi(x, x, x_3)$$
$$\psi(x, x, x_3) = -\psi(x, x, x_3)$$

where the first argument is for particle 1, the second for particle 2 etc. The first equation gives us no information, but the second implies that $\psi(x, x, x_3)$ must vanish. In other words:
     No two fermions can have all the same characteristics

The statistics of different particles can be summarized as follows. We consider three states to be occupied by 2 people
          F = Fred   M = Mary   P = person (indistinguishable)

State	Distinguishable (Maxwell-Boltzmann)			Bosons			Fermions		
	1	2	3	1	2	3	1	2	3
	FM	-	-	PP	-	-	P	P	-
	-	FM	-	-	PP	-	P	-	P
	-	-	FM	-	-	PP	-	P	P
	F	M	-	P	P	-			
	F	-	M	P	-	P			
	-	F	M	-	P	P			
	M	F	-						
	M	-	F						
	-	M	F						
	(9 configs)			(6 configs)			(3 configs)		

The ratio of the number of configs with particles in the same state, compared to number in different states is
          3/6 = 1/2   3/3 = 1   0/3=0

Thus:
• *bosons* have **more** particles in the same state than Maxwell-Boltzmann
• *fermions* have **fewer** particles in the same state than Maxwell-Boltzmann.

Implications for partition function

What do the symmetry requirements imply for the partition function? Let's specify a set of states $\varepsilon_1 \varepsilon_2 \varepsilon_3$ ... into which we will place a total of *N* objects. Each state *i* can have

occupancy n_i such that

$$\sum_i n_i = N \qquad \text{(good for MB, BE, FD)}$$

Thus, one configuration of total energy E_R obeys

$$E_R = \sum_i n_i \varepsilon_i = n_1 \varepsilon_1 + n_2 \varepsilon_2 + n_3 \varepsilon_3 \dots$$

For MB and BE, each n_i can have the values 0, 1, 2, 3... The difference between them is that
- MB: each state is distinguishable, and states have degeneracy through permutations (FM-, MF-, ... above)
- BE: states are indistinguishable and have no degeneracy (PP-)

For FD, $n_i = 0$ or 1, because no two particles can occupy the same state.

How do we find the mean values of the occupancy $<n_i>$?   One way is to use the partition function $Z = \sum_R \exp(-\beta E_R)$:

$$\overline{n_i} = \frac{\sum_R n_i \exp(-\beta[n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 +])}{\sum_R \exp(-\beta[n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 +])}$$

$$= \frac{\sum_R -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_i} \exp(-\beta[n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 +])}{\sum_R \exp(-\beta[n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 +])}$$

$$= -\frac{1}{\beta} \cdot \frac{1}{Z} \cdot \frac{\partial}{\partial\varepsilon_i} Z$$

Hence,

$$\overline{n_i} = -\frac{1}{\beta} \cdot \frac{\partial}{\partial\varepsilon_i} \ln Z .$$