Quantum Statistical Mechanics

Can we come up with a better way to describe the quantum state of a many-particle system?

In some cases we need to keep track of spatial functions, but often we don't. Let's consider the case when we know the number of particles and their total energy

Example: 3 non-interacting particles in a 1-d harmonic potential. Their total energy is $E_{tot} = \frac{13}{2}\hbar\omega$

- What are possible energies of each particle
- What are the possible combinations?
- Which combination is most likely?
- What is the most probable value of energy ~~ea~~ a randomly selected particle would have?

$$E_{tot} = E_1 + E_2 + E_3 = \hbar\omega(n_1+\tfrac{1}{2}) + \hbar\omega(n_2+\tfrac{1}{2}) + \hbar\omega(n_3+\tfrac{1}{2}) =$$

$$= \hbar\omega(n_1+n_2+n_3) + \frac{3}{2}\hbar\omega = \frac{13}{2}\hbar\omega$$

$$n_1+n_2+n_3 = 5$$

So as long as the sum of n_1, n_2, n_3 ~~is~~ 5 (with each $n_i = 0 \dots 5$) ~~the~~ all these combinations will satisfy the required conditions for total energy and particle number. However, we also must take into account particle statistics.

Distinguishable particles

n_1	n_2	n_3	W, # of permutations	Configuration
5	0	0	3	"0" "1" "2" "3" "4" "5" "6" (2, 0, 0, 0, 0, 1, 0 ...)
0	5	0		* occupation # for each state
0	0	5		
4	1	0		
4	0	1		(1, 1, 0, 0, 1, 0, 0, ...)
1	4	0	6	
0	4	1		
1	0	4		
0	1	4		
3	2	0		
3	0	2		(1, 0, 1, 1, 0, 0, ...)
2	3	0	6	
0	3	2		
2	0	3		
0	2	3		
2	2	1		
2	1	2	3	(0, 1, 2, 0, 0...)
1	2	2		
1	3	1		
1	1	3	3	(0, 2, 01, 0, 0...)
3	1	1		

To describe the various distinguishable configurations of particles it is convenient to use occupation numbers: how many particles occupy each state

Total # of different distinguishable permutations $3+6+6+3+3 = 21$

~~What are the probability to find a particle~~

Possible single particle measurements

State #

$n_i = 0 \quad E_0 = \frac{1}{2}\hbar\omega \quad P_0 = \frac{2}{3}\cdot\frac{3}{21} + \frac{1}{3}\cdot\frac{6}{21} + \frac{1}{3}\cdot\frac{6}{21} = \frac{2}{7}$

$n = 1 \quad E_1 = \frac{3}{2}\hbar\omega \quad P_1 = \frac{1}{3}\frac{6}{21} + \frac{1}{3}\cdot\frac{3}{21} + \frac{2}{3}\cdot\frac{3}{21} = \frac{5}{21}$

$n = 2 \quad E_2 = \frac{5}{2}\hbar\omega \quad P_2 = \frac{1}{3}\cdot\frac{6}{21} + \frac{2}{3}\cdot\frac{3}{21} = \frac{4}{21}$

$n = 3 \quad E_3 = \frac{7}{2}\hbar\omega \quad P_3 = \frac{1}{3}\cdot\frac{6}{21} + \frac{1}{3}\cdot\frac{3}{21} = \frac{1}{7}$

$n = 4 \quad E_4 = \frac{9}{2}\hbar\omega \quad P_4 = \frac{1}{3}\cdot\frac{6}{21} = \frac{2}{21}$

$n = 5 \quad E_5 = \frac{11}{2}\hbar\omega \quad P_5 = \frac{1}{3}\cdot\frac{3}{21} = \frac{1}{21}$

So if choosing randomly we are more likely to find a particle in $n=0$ state with energy $E_0 = \frac{1}{2}\hbar\omega$ (in $2/7 \approx 28\%$ of the times)

However, the most probable configurations

$(1,1,0,0,1,0,0\ldots)$ and $(1,0,1,1,0,0,\ldots)$

Average particle energy $\langle E\rangle = \frac{44}{21}\hbar\omega$

Bosons

All configurations are equally likely

(2, 0, 0, 0, 0, 1, 0 ...), (1, 1, 0, 0, 1, 0, 0 ...), (1, 0, 1, 1, 0, 0, ...)
(0, 1, 2, 0, 0 ...) and (0, 2, 0, 1, 0, 0)

Most probable energies?

$n=0 \quad E_0 = \frac{\hbar\omega}{2} \quad P_0 = \frac{2}{3}\cdot\frac{1}{5} + \frac{1}{3}\cdot\frac{1}{5} + \frac{1}{3}\cdot\frac{1}{5} = \frac{4}{15}$

$n=1 \quad E_1 = \frac{3}{2}\hbar\omega \quad P_1 = \frac{1}{3}\cdot\frac{1}{5} + \frac{1}{3}\cdot\frac{1}{5} + \frac{2}{3}\cdot\frac{1}{5} = \frac{4}{15}$

$n=2 \quad E_2 = \frac{5}{2}\hbar\omega \quad P_2 = \frac{1}{3}\cdot\frac{1}{5} + \frac{2}{3}\cdot\frac{1}{5} = \frac{1}{5}$

$n=3 \quad E_3 = \frac{7}{2}\hbar\omega \quad P_3 = \frac{1}{3}\cdot\frac{1}{5} + \frac{1}{3}\cdot\frac{1}{5} = \frac{2}{15}$

$n=4 \quad E_4 = \frac{9}{2}\hbar\omega \quad P_4 = \frac{1}{3}\cdot\frac{1}{5} = \frac{1}{15}$

$n=5 \quad E_5 = \frac{11}{2}\hbar\omega \quad P_5 = \frac{1}{15}$

Now both E_0 and E_1 are equally likely to be measured with probability 4/15

Average energy $\langle E \rangle = \frac{13}{6}\hbar\omega = \frac{1}{3} E_{total}$

Will this change if we make particle indistinguishable?

<u>Fermions</u> (electrons with identical spins)
Pauli exclusion principle prevents having two particles in the same state.
This eliminates certain combinations

n_1	n_2	n_3	# of permutations W	configuration
4	1	0	1	(1, 1, 0, 0, 1, 0 ...)
3	2	0	1	(0, 0, 1, 1, 0 ...)

Since we cannot distinguish the particles, the permutations within the same configuration does not make sense
Possible energies

$n=0 \quad E_0 = \frac{1}{2}\hbar\omega \qquad P_0 = \frac{1}{3}\cdot\frac{1}{2} + \frac{1}{3}\cdot\frac{1}{2} = \frac{1}{3}$

$n=1 \quad E_1 = \frac{3}{2}\hbar\omega \qquad P_1 = \frac{1}{3}\cdot\frac{1}{2} = \frac{1}{6}$

$n=2 \quad E_2 = \frac{5}{2}\hbar\omega \qquad P_2 = 1/6$

$n=3 \quad E_3 = \frac{7}{2}\hbar\omega \qquad P_3 = 1/6$

$n=4 \quad E_4 = \frac{9}{2}\hbar\omega \qquad P_4 = 1/6$

$n=5 \quad E_5 = \frac{11}{2}\hbar\omega \qquad P_5 = 0$

Still, $E_0 = \frac{1}{2}\hbar\omega$ is most probable single-particle ~~new~~ energy with probability $1/3 \approx 33\%$

~~Averaged particle energy~~

Average energy $\langle E \rangle = \frac{13}{6}\hbar\omega = \frac{1}{3}$ total energy

What if we have many more particles?

Reminder - the number of ways to pick ~~M~~ m items out of M is given by the ~~by~~ binomial coefficient

$$\binom{M}{m} = \frac{M!}{m!(M-m)!}$$

Let's assume we have N particles, ~~with~~ that can occupy $n = 1, 2 \ldots \infty$ quantum states, and each of these states has degeneracy d_i. So if there are N_i particles in ith state, (we assume $N_i < d_i$, when necessary), how many possible permutations ~~there~~ are possible?

Distinguishable particles

state 1 | state 2 | state 3

$$\frac{N!}{N_1!\cancel{(N-N_1)!}} \cdot d_1^{N_1} \quad \frac{\cancel{(N-N_1)!}}{N_2!\cancel{(N-N_1-N_2)!}} d_2^{N_2} \quad \frac{\cancel{(N-N_1-N_2)!}}{N_3!(N-N_1-N_2-N_3)!} d_3^{N_3} \ldots$$

$$W(N_1, N_2, \ldots) = N! \prod_{n=1}^{\infty} \frac{(d_n)^{N_n}}{N_n!}$$

Fermions → only one particle per state

~~state 1~~

$\cancel{\frac{N!}{N_1!(N-N_1)!} \cdot d_1}$

All particles are identical, so there are no permutations b/w them, the only question is what N_n states out of d_n availabe are taken

$$W(N_1, N_2 \ldots) = \prod_{n=1}^{\infty} \binom{d_n}{N_n} = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n-N_n)!}$$

Bosons – particles are indistinguishable, but now several particles can occupy the same state, and we need to count only distinct configurations.

See text book for details

$$W(N_1, N_2 \ldots) = \prod_{n=1}^{\infty} \binom{N_n + d_n - 1}{N_n} = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!\,(d_n - 1)!}$$

In reality, however, we cannot know how many particles are in each state! Usually we know how many particles we have $\sum_{n=1}^{\infty} N_n = N$

and we know the total energy of an ensemble

$$\sum_{n=1}^{\infty} E_n N_n = E$$