Lecture 7

Quantum statistical mechanics

At absolute zero temperature, a physical system occupies the lowest possible energy configuration. When the temperature increases, excited states become populated. The question that we would like to find an answer to is the following:

If we have a large number of particles N in thermal equilibrium at temperature T, what is the probability that randomly selected particle has specific energy E_i?

We will use the **fundamental assumption of statistical mechanics: in thermal equilibrium every distinct state with the same total energy E is equally probable**. It means that continuous redistribution of energy does not favor any particular state. Since counting of states obviously depends on the type of particles that we are counting (distinguishable, identical bosons, or identical fermions), these three cases will have to be considered separately.

Example: three particles

To clarity what we are trying to do, we start with the following example: just three noninteracting particle of mass m in the one-dimensional infinite square well.
Our particles are in states A, B, and C, and; therefore, their total energy is

$$E = E_A + E_B + E_C = \frac{\pi^2\hbar^2}{2ma^2}\left(n_A^2 + n_B^2 + n_C^2\right).$$

positive integers

For our example, we are going to pick a state with total energy

$$E = 363\,\frac{\pi^2\hbar^2}{2ma^2}\ ;\ \text{i.e.}$$

$$\boxed{n_A^2 + n_B^2 + n_C^2 = 363.}$$

There are only 4 possible ways we can combine 3 positive integers so their squares sum to 363:

$$11^2 + 11^2 + 11^2 = 363$$
$$13^2 + 13^2 + 5^2 = 363$$
$$19^2 + 1^2 + 1^2 = 363$$
$$5^2 + 7^2 + 17^2 = 363$$

Therefore, there are 13 possible combinations of three particles that will have such total energy:

$$
\begin{array}{l}
(n_A, n_B, n_C) = (11, 11, 11) \\
(13, 13, 5),\ (13, 5, 13),\ (5, 13, 13) \\
(1, 1, 19),\ (1, 19, 1),\ (19, 1, 1) \\
(5,7,17),\ (5,17,7),\ (7,5,17),\ (7,17,5),\ (17,5,7),\ (17, 7, 5).
\end{array}
$$

If particles are distinguishable, each of these 13 combinations represents a different state and in thermal equilibrium they are all equally likely.

However, to develop method to answer our question in a general case, we introduce another way to label states since we don't really care for our purposes which particle is in which state, only what is the total number of particles in each state.

We call this number occupation number N_n for the state ψ_n. For example, occupation number for state ψ_{11} in (11,11,11) combination is $N_{11}=3$ and occupation number for each other state except ψ_{11} (N_1, N_2, N_3, ...) is zero. The collection of all occupation numbers for a three-particle state is called a configuration. Here are the configurations for two combinations above:

For $(n_A, n_B, n_C) = (11, 11, 11)$ the configuration is

$$
\begin{array}{cccccccccccccccccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & \\
(& 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & \boxed{3}, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & \ldots\ )
\end{array}
$$

For $(n_A, n_B, n_C) = (13, 13, 5), (13, 5, 13), (5, 13, 13)$ the configuration is:

just for reference, don't need to write these

$$
\begin{array}{cccccccccccccccccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & \\
(& 0, & 0, & 0, & 0, & \boxed{1}, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & \boxed{2}, & 0, & 0, & 0, & 0, & 0, & 0, & \ldots\ )
\end{array}
$$

One particle is in state ψ_5, two particles are in state ψ_{13}, all other states are unoccupied.

Exercise for class: write configurations for our two remaining cases below

$$(1, 1, 19),\ (1, 19, 1),\ (19, 1, 1)$$

$$
\begin{array}{cccccccccccccccccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & \\
(& \boxed{2}, & 0 & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & \boxed{1}, & \ldots\ )
\end{array}
$$

$$(5,7,17),\ (5,17,7),\ (7,5,17),\ (7,17,5),\ (17,5,7),\ (17, 7, 5).$$

$$
\begin{array}{cccccccccccccccccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & \\
(& 0, & 0, & 0, & 0, & \boxed{1}, & 0, & \boxed{1}, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & 0, & \boxed{1}, & 0, & 0, & \ldots\ )
\end{array}
$$

Since we only care now how many particles are in which state, we only have four possible configurations: we label them 1, 2, 3, 4 in the order that they appear. For distinguishable particles, there is one way to build configuration 1, three ways to build configurations 2 and 3, and 6 ways to build configuration 4. **Therefore, configuration 4 is the most probable one in this example for** distinguishable particles**.**

We are now ready to answer our original question: if we randomly select one of these particles and measure its energy, what is the probability P_n of getting specific energy E_n?

Firstly, we consider the case of distinguishable particles.

1. What is the probability of getting energy E_1?

The only configuration that contains particle in state ψ_1 is configuration #3.

The chance of getting configuration #3 is $3/13$.

If you got configuration #3, the chance of getting particle in state ψ_1 is $\frac{2}{3}$ since only two out three particle will be in that state.

Therefore, the probably of getting energy E_1 as a result of randomly measuring energy of one of the particles is

$$P_1 = \frac{3}{13} \times \frac{2}{3} = \frac{2}{13}.$$

Questions for the class: what are the probabilities of getting energies E_2, E_5, E_7, E_{11}, E_{13}, E_{17}, and E_{19}?

2. $P_2 = 0$ since state ψ_2 does not appear in any configuration. By the postulate of quantum mechanical measurement, we can only get energies E_1, E_5, E_7, E_{11}, E_{13}, E_{17}, and E_{19} in our example.

3. ψ_5 appears in configurations 2 and 4. Probability of getting configurations 2 and 4 are $3/13$ and $6/13$, respectively. Probability of getting E_5 in configurations 2 and 4 are $1/3$ and $1/3$, respectively. Total probability is given by the sum:

$$P_5 = \frac{3}{13} \cdot \frac{1}{3} + \frac{6}{13} \cdot \frac{1}{3} = \frac{3}{13}$$

4. $P_7 = \frac{6}{13} \cdot \frac{1}{3} = \frac{2}{13}$

5. $P_{11} = \frac{1}{13}$

6. $P_{13} = \frac{3}{13} \cdot \frac{2}{3} = \frac{2}{13}$

7. $P_{17} = \frac{6}{13} \cdot \frac{1}{3} = \frac{2}{13}$

8. $P_{19} = \frac{3}{13} \cdot \frac{1}{3} = \frac{1}{13}$

All probabilities, of course, sum to one:

$$P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19} =$$

$$= \frac{2}{13} + \frac{3}{13} + \frac{2}{13} + \frac{1}{13} + \frac{2}{13} + \frac{2}{13} + \frac{1}{13} = 1$$

Next, let us consider the **case of identical fermions**. For simplicity we ignore spin, i.e. assume they are all in the same spin state.

Configurations 1, 2, and 3 are now simply not allowed since we can't have two or three fermions in the same state. There is only one state in configuration 4. Therefore,

$$P_5 = P_7 = P_{17} = \frac{1}{3}$$

and all other probabilities are zero. Again, all probabilities sum to one.
Finally, we consider **identical bosons**.

Symmetrization requirement allows one state in each configuration.

Question for the class: calculate all non-zero probabilities for identical bosons and check that they sum to one.

$$P_1 = \frac{2}{3} \cdot \frac{1}{4} = \frac{1}{6} \qquad P_{13} = \frac{2}{3} \cdot \frac{1}{4} = \frac{1}{6}$$

$$P_5 = \frac{1}{3} \cdot \frac{1}{4} + \frac{1}{3} \cdot \frac{1}{4} = \frac{1}{6} \qquad P_{17} = \frac{1}{4} \cdot \frac{1}{3} = \frac{1}{12}$$

$$P_7 = \frac{1}{3} \cdot \frac{1}{4} = \frac{1}{12} \qquad P_{19} = \frac{1}{4} \cdot \frac{1}{3} = \frac{1}{12}$$

$$P_{11} = \frac{1}{4}$$

$$P_1 + P_5 + P_7 + P_{13} + P_{17} + P_{19} = \frac{2 + 2 + 1 + 3 + 2 + 1 + 1}{12} = 1$$

Summary: result obviously depends on which kind of particles we have!

As number of particles grows, the most probable configuration becomes overwhelmingly more likely than others. As a result, for statistical purposes, we can just ignore other configurations. The distribution of individual particle energies, at equilibrium, is simply their distribution in the most probable configuration. We will now develop more general counting procedure.

The general case

In the general case, we have an arbitrary potential. The one particle energies in this potential are E_1, E_2, E_3, ... with degenerates d_1, d_2, d_3, ... This means that there are d_n different states all with energy E_n. (Remember hydrogen states will n=2,l=0, m=0; n=2, l=1, m=-1, 0, 1. All these four states have the same energy $E_2=-13.6/2^2=-3.4$ eV, so without counting spin, $d_2=4$ for E_2 in this example).

We put N particles with the same mass m in this potential and consider configuration

$$(N_1, N_2, N_3, \ldots\ldots)$$

N_1 particles with energy E_1

N_2 particles with energy E_2

N_3 particles with energies E_3

Question: in how many ways $Q(N_1,N_2,N_3, \ldots)$ can we build such a configuration, i.e. how many distinct states correspond to this configuration?

Example: in our previous example, configuration # 4 in the case of distinguishable particles could be build in 6 different ways: (5, 7, 17), (5, 17, 7), (17, 5, 17), (7, 17, 5), (17, 5, 7), and (17, 7, 5) so $Q=6$.

Why do we want to find the answer to such a question? Because it will tell us which configuration is the most probable one.

Obviously, we need to consider three cases (distinguishable particles, identical fermions, and identical bosons) separately since we demonstrated that we count states differently in these cases.

Case 1: Distinguishable particles

Building $(N_1, N_2, N_3, \ldots)$ from N particles.

first, we find how to pick N_1 particles from N.

Example: in how many ways can you pick 2 particles from 5?

$\boxed{1}$ $\boxed{2}$ $\boxed{3}$ $\boxed{4}$ $\boxed{5}$ $\quad N=5,\ N_1=2$

1. Pick first particle: N=5 choices: 1, 2, 3, 4, 5
2. Pick second particle: 4 choices (N-1) in each case

$$\left.\begin{array}{ccccc} 12 & 21 & 31 & 41 & 51 \\ 13 & 23 & 32 & 42 & 52 \\ 14 & 24 & 34 & 43 & 53 \\ 15 & 25 & 35 & 45 & 54 \end{array}\right\} N(N-1) \text{ choices}$$

In general case: $N(N-1)(N-2)\ldots(N-N_1+1)$ choices

check: $N=5$, $N_1=2$ $\quad N-N_1+1=4$ ok.

However, we don't care in which order the particles were picked so in the list

12	21	31	41	51
13	23	32	42	52
14	24	34	43	53
15	25	35	45	54

the pairs 12, 21 ; 13, 31 , 23, 32; each represent only one state, so we need to divide by $N_1!$ (by 2 in this case).

To convince yourself that it is true in general case, consider $N_1=3$:
The same configurations can be build in $N_1!$ ways:

123	213	312
132	231	321

To say the same thing, we can permute N_1 numbers in $N_1!$ different ways.
Therefore, we need to divide our result above by $N_1!$ to exclude identical cases:

$$\frac{1}{N_1!} N(N-1)(N-2)\dots(N-N_1+1) = \frac{1}{N_1!}\frac{N!}{(N-N_1)!}$$

We can check that it is correct by writing

$$\frac{1}{N_1!}\left(\frac{N(N-1)(N-2)\dots(N-N_1+1)\cancel{(N-N_1)}\cancel{(N-N_1-1)}\dots\cancel{1}}{\cancel{(N-N_1)}\cancel{(N-N_1-1)}\dots\cancel{1}}\right)$$

$$= \frac{1}{N_1!} N(N-1)\dots(N-N_1+1).$$

We now remember that each particle has d_1 choices of states to have energy E_1 (degeneracy of E_1 energy state is d_1). Let's consider example $d_1=2$ and $N_1=3$.

$\boxed{\psi_1, \psi_2}$ have to occupy 3 spaces:

$\psi_1\ \psi_1\ \psi_1$	$\psi_2\ \psi_1\ \psi_1$
$\psi_1\ \psi_1\ \psi_2$	$\psi_2\ \psi_1\ \psi_2$
$\psi_1\ \psi_2\ \psi_1$	$\psi_2\ \psi_2\ \psi_1$
$\psi_1\ \psi_2\ \psi_2$	$\psi_2\ \psi_2\ \psi_2$

$$d_1^{N_1} = 2^3 = 8$$

Each particles 1, 2, 3 has choice of ψ_1 or ψ_2 so number of combinations is $2\times2\times2=2^3$. In the general case, there are $d_1^{N_1}$ choices.

Putting it all together, we get that there are $\boxed{\dfrac{N!\, d_1^{N_1}}{N_1!\,(N-N_1)!}}$

ways to pick N_1 particles from N particles when each of these N_1 particles can be in d_1 different states.

Next step is to pick N_2 particles from remaining ($N-N_1$) particles. The result is the same, only now

$$\left.\begin{aligned} N &\to N-N_1 \\ N_1 &\to N_2 \\ d_1 &\to d_2 \end{aligned}\right\} \quad \frac{N!\, d_1^{N_1}}{N_1!\,(N-N_1)!} \to \boxed{\frac{(N-N_1)!\, d_2^{N_2}}{N_2!\,(N-N_1-N_2)!}}$$

Next we pick N_3 particles from remaining $N-N_1-N_2$ particles, and so on. The total result is:

$$Q(N_1, N_2, N_3, \ldots) = \boxed{\frac{N!\, d_1^{N_1}}{N_1!\,(\cancel{N-N_1})!}} \times \boxed{\frac{(\cancel{N-N_1})!\, d_2^{N_2}}{N_2!\,(\cancel{N-N_1-N_2})!}}$$

$$\times \frac{(\cancel{N-N_1-N_2})!\, d_3^{N_3}}{N_3!\,(N-N_1-N_2-N_3)!} \times \ldots = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$$