

Lecture 8

Quantum statistical mechanics

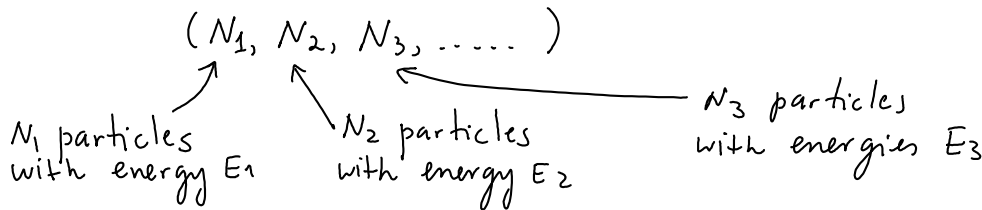
At absolute zero temperature, a physical system occupies the lowest possible energy configuration. When the temperature increases, excited states become populated. The question that we would like to find an answer to is the following:

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 ?

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, \dots with degenerates d_1, d_2, d_3, \dots . This means that there are d_n different states all with energy E_n .

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



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

Case 1: Distinguishable particles

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

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

<p>Our result from lecture 7:</p> $\frac{1}{N_1!} \frac{N!}{(N - N_1)!}$
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So far, we did not account for degeneracy d_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 $N_1 = 3$.

$$\psi_1, \psi_2$$

ψ_1	ψ_1	ψ_1	ψ_2	ψ_1	ψ_1	$d_1^{N_1} = 2^3 = 8$
ψ_1	ψ_1	ψ_2	ψ_2	ψ_1	ψ_2	
ψ_1	ψ_2	ψ_1	ψ_2	ψ_2	ψ_1	
ψ_1	ψ_2	ψ_2	ψ_2	ψ_2	ψ_2	

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

Putting it all together, we get that there are

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

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

$$\left. \begin{array}{l} N \rightarrow N - N_1 \\ N_1 \rightarrow N_2 \\ d_1 \rightarrow d_2 \end{array} \right\} \frac{N! d_1^{N_1}}{N_1! (N - N_1)!} \rightarrow \frac{(N - N_1)! d_2^{N_2}}{N_2! (N - N_1 - N_2)!}$$

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

$$Q(N_1, N_2, N_3, \dots) = \frac{N! d_1^{N_1}}{N_1! (N - N_1)!} \times \frac{(N - N_1)! d_2^{N_2}}{N_2! (N - N_1 - N_2)!} \times \frac{(N - N_1 - N_2)! d_3^{N_3}}{N_3! (N - N_1 - N_2 - N_3)!} \times \dots = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$$

Let's check this result for our example from Lecture 7:

Example: three particles

Three noninteracting particles 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

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

$\uparrow \quad \uparrow \quad \uparrow$
 positive integers

We picked a state with total energy $E = 363 \frac{\pi^2 \hbar^2}{2ma^2}$;

$$n_A^2 + n_B^2 + n_C^2 = 363.$$

In the case of distinguishable particles, there are 13 possible states with this total energy:

$$\begin{aligned}
 (n_A, n_B, n_C) &= (11, 11, 11) && \# 1 \\
 &(13, 13, 5), (13, 5, 13), (5, 13, 13) && \# 2 \\
 &(1, 1, 19), (1, 19, 1), (19, 1, 1) && \# 3 \\
 &(5, 7, 17), (5, 17, 7), (7, 5, 17), (7, 17, 5), (17, 5, 7), (17, 7, 5). && \# 4
 \end{aligned}$$

which belong to four different configurations

$$\begin{aligned}
 &(N_1, N_2, N_3, N_4, N_5, N_6, N_7, N_8, N_9, N_{10}, N_{11}, N_{12}, N_{13}, N_{14}, N_{15}, N_{16}, N_{17}, N_{18}, N_{19}, \dots) \\
 \#1 &(0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 3, 0, 0, 0, 0, 0, 0, 0, \dots) \\
 \#2 &(0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 2, 0, 0, 0, 0, 0, 0, \dots) \\
 \#3 &(2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, \dots) \\
 \#4 &(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \dots)
 \end{aligned}$$

We should get: $Q_1 = 1$, $Q_2 = 3$, $Q_3 = 3$, $Q_4 = 6$.

Our general result is $Q(N_1, N_2, N_3, \dots) = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$

In our example, $N=3$ and $d_n = 1$ for all states (i.e. all states are non-degenerate) \Rightarrow

$$Q(N_1, N_2, \dots) = 6 \prod_{n=1}^{\infty} \frac{1}{N_n!}$$

Configuration 1: $N_{11}=3$, all other $N_i=0$ (remember that $0!=1$)

$$Q_1 = 6 \frac{1}{N_{11}!} = 6 \frac{1}{3!} = 1$$

Configuration 2: $N_5=1$, $N_{13}=2$, all other $N_i=0$

$$Q_2 = 6 \left\{ \frac{1}{N_5!} \times \frac{1}{N_{13}!} \right\} = 6 \cdot 1 \cdot \frac{1}{2} = 3$$

Configuration 3: $N_1=2$, $N_{19}=1$, all other $N_i=0$ $Q_3 = 3$

Configuration 4: $N_5=1$, $N_7=1$, $N_{17}=1$, all other $N_i=0$

$$Q_4 = 6 \left\{ \frac{1}{N_5!} \cdot \frac{1}{N_7!} \cdot \frac{1}{N_{17}!} \right\} = 6 \quad \text{OK.}$$

Case 2: identical fermions

- (1) Our fermions are indistinguishable so it does not matter which particle is in which state.
- (2) There is only one N-particle state with specific set of one-particle states.
- (3) Only one particle can occupy any given state.

Therefore the counting works in the following way (let's pick our N_1 particles again):

We can now only pick particles to put in N_1 "bin" out of d_1 choices since there can be at most d_1 particles with energy E_1 . See the following example:

$d_1 = 3$ so $\psi_1, \psi_2,$ and ψ_3 all have energy E_1 .

$N_1 = 1 \Rightarrow$ We have 3 choices: $\psi_1, \psi_2,$ or ψ_3

$N_1 = 2 \Rightarrow$ We have 3 choices: $\psi_1 \psi_2, \psi_2 \psi_3,$ and $\psi_1 \psi_3$.

$N_1 = 3 \Rightarrow$ We have 1 choice: $\psi_1 \psi_2 \psi_3$.

$N_1 = 4 \Rightarrow$ No combination can be build.

The result is the same as

"how to pick N_1 particle from N particles" only now it is

"how to pick N_1 particles out of d_1 states".

Answer : $\frac{N!}{N_1! (N - N_1)!} \longrightarrow \boxed{\frac{d_1!}{N_1! (d_1 - N_1)!}}$

Let's check for the cases in our example:

$N_1 = 1 \quad d_1 = 3 \Rightarrow \frac{3!}{1! (3-1)!} = 3$

$N_1 = 2 \quad d_1 = 3 \Rightarrow \frac{3!}{2! (3-2)!} = 3$

$N_1 = 3 \quad d_1 = 3 \Rightarrow \frac{3!}{3! (3-3)!} = 1$

$d_1 < N_1 \Rightarrow 0$

The total answer for the case of identical fermions is:

$$Q(N_1, N_2, \dots) = \prod_{i=1}^{\infty} \frac{d_i!}{N_i! (d_i - N_i)!}$$

Case 3: identical bosons

- (1) Our bosons are indistinguishable so it does not matter which particle is in which state.
- (2) There is only one N-particle state with specific set of one-particle states.
- (3) No restrictions on how many particles can occupy the same one-particle state.

So, we can still only pick N_1 particles from d_1 states, but more combinations are allowed. Let's do the same example again ($d_1 = 3$):

$N_1 = 1$ 3 choices: $\psi_1, \psi_2,$ and ψ_3 .
 $N_1 = 2$ $\psi_1\psi_1, \psi_2\psi_2, \psi_3\psi_3$ } 6 choices
 $\psi_1\psi_2, \psi_1\psi_3, \psi_2\psi_3$ }

$N_1=3$ Question for the class: how many choices?

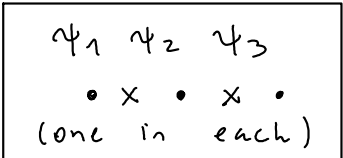
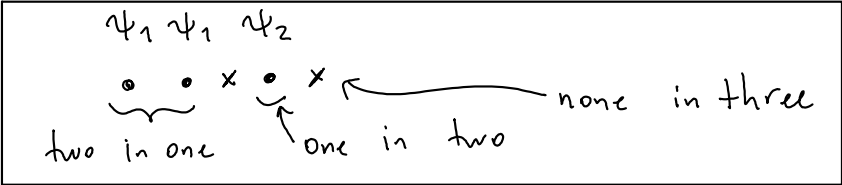
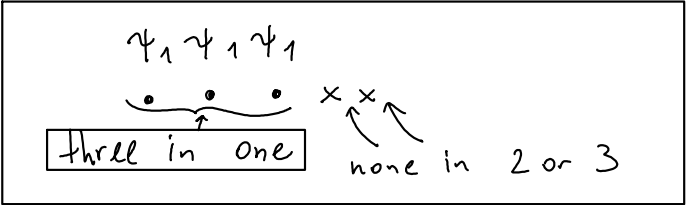
$\psi_1 \psi_1 \psi_1$	$\psi_1 \psi_1 \psi_2$	$\psi_1 \psi_2 \psi_3$
$\psi_2 \psi_2 \psi_2$	$\psi_1 \psi_1 \psi_3$	(all three are different)
$\psi_3 \psi_3 \psi_3$	$\psi_2 \psi_2 \psi_1$	
(all 3 same)	$\psi_2 \psi_2 \psi_3$	
	$\psi_3 \psi_3 \psi_1$	
	$\psi_3 \psi_3 \psi_2$	
	(two the same)	

Total: 10

Question for the class: is $N_1=4$ allowed in this case?

Yes, pick states in the same way: all the same, three the same, two the same, all different.

Let's label our choices like this: ($N_1 = 3, d_1 = 3$)



Note: it is like placing N_1 balls into d_1 baskets.

A bit more complicated example: $N_1=7$ and $d_1=5$:

• • x • x • • • x • x

Question for the class: what state is it? (like $\psi_i \psi_j \psi_k \dots$)

$\psi_1 \psi_1 \psi_2 \psi_3 \psi_3 \psi_3 \psi_4$
 7 total

Now we can write a solution:

(1) There are N_1 dots and (d_1-1) crosses. What we need to know is how many different arrangements of those we can do.

If they all "differently labeled things", like

a b c d ...
 $N_1 + d_1 - 1$ total \Rightarrow

We can arrange N things in $N!$ ways, so the answer is $(N_1+d_1-1)!$

However, all dots are the same, so there are $N_1!$ equivalent ways to permute them that do not change the state. Also, all crosses are equivalent, and permuting them $(d_1-1)!$ ways does not change the state either. Therefore, the answer is:

$$\frac{(N_1 + d_1 - 1)!}{N_1! (d_1 - 1)!}$$

and the total answer for identical bosons is:

$$Q(N_1, N_2, \dots) = \prod_{i=1}^{\infty} \frac{(N_i + d_i - 1)!}{N_i! (d_i - 1)!}$$

The most probable configuration

In thermal equilibrium, every state with energy E and number of particles N is equally likely. Therefore, the most probable configuration (N_1, N_2, N_3, \dots) is the one for which $Q(N_1, N_2, N_3, \dots)$ is the largest, since it can be produced in the largest number of different ways.

Therefore, to find the most probable configuration, we need to find when Q is a maximum, assuming the following constraints:

$$\sum_{n=1}^{\infty} N_n = N$$

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

To maximize function $F(x_1, x_2, x_3, \dots)$ that is subject to constraints $f_1(x_1, x_2, x_3, \dots) = 0$, $f_2(x_1, x_2, x_3, \dots) = 0$, etc., it is convenient to use the method of Lagrange multipliers. We introduce new function

$$G(x_1, x_2, x_3, \dots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \dots$$

and set all derivatives to zero:

$$\frac{\partial G}{\partial x_n} = 0; \quad \frac{\partial G}{\partial \lambda_n} = 0.$$

We will work with $\ln(Q)$ to turn products into sums. The maxima of Q and $\ln(Q)$ occur at the same point since $\ln(Q)$ is a monotonous function.

$$G \equiv \ln(Q) + \alpha \underbrace{\left[N - \sum_{n=1}^{\infty} N_n \right]}_{f_1} + \beta \underbrace{\left[E - \sum_{n=1}^{\infty} N_n E_n \right]}_{f_2}$$

$\uparrow \quad \quad \quad \uparrow$
 $\lambda_1 \quad \quad \quad \lambda_2$

$$x_n \equiv N_n$$

$\frac{\partial G}{\partial \alpha}$ and $\frac{\partial G}{\partial \beta}$ give back the constraints, so we need to get $\frac{\partial G}{\partial N_n} = 0$.

Case 1: distinguishable particles

$$Q = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}$$

$$G = \ln \left(N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!} \right) + \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

$$= \ln(N!) + \sum_{n=1}^{\infty} \left\{ N_n \ln(d_n) - \ln(N_n!) \right\}$$

$$+ \alpha \left[N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[E - \sum_{n=1}^{\infty} N_n E_n \right]$$

We use Stirling's approximation for large occupation numbers N_n :

$$\ln(z!) \approx z \ln z - z \quad \text{for } z \gg 1$$

$$G = \ln(N!) + \sum_{n=1}^{\infty} \left\{ N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n \right\} + \alpha N - \beta E$$

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \cancel{1} + \cancel{1} - \alpha + \beta E_n$$

$$\ln(d_n) - \ln(N_n) - \alpha - \beta E_n = 0$$

$$\ln(N_n) = \ln(d_n) - (\alpha + \beta E_n)$$

$$N_n = d_n e^{-(\alpha + \beta E_n)}$$

Case 2: identical fermions ($N_n \gg 1$)

Doing similar calculation and also assuming $d_n \gg N_n$ we get:

$$N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1}$$

Case 3: identical bosons $N_n \gg 1$

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1}$$

We replace $d_n - 1$ in the numerator by d_n assuming as in the case of fermions that $d_n \gg 1$.

Physical significance of α and β :

β is related to temperature: $\beta = \frac{1}{k_B T}$

α is generally replaced by a **chemical potential $\mu(T)$** :

$$\mu(T) \equiv -\alpha k_B T$$

Now, we can finally write the formulas for the **most probable number of particles n in a particular (one-particle) state with energy ϵ** .

Distinguishable particles:

$$n(\epsilon) = \frac{N_n}{d_n} = e^{-(\alpha + \beta \epsilon)} = e^{-\left(\frac{\mu}{k_B T} + \frac{\epsilon}{k_B T}\right)}$$

$$n(\epsilon) = e^{-(\epsilon - \mu)/k_B T} \leftarrow \text{Maxwell-Boltzmann distribution (classical result)}$$

Identical fermions:

$$n(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1} \leftarrow \text{Fermi-Dirac distribution}$$

Identical bosons:

$$n(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1} \leftarrow \text{Bose-Einstein distribution}$$