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, ... with degenerates d_1, d_2, d_3, ... 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

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

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?

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.

Our result from lecture 7:

$$\frac{1}{N_1!}\,\frac{N!}{(N-N_1)!}$$

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 $N_1=3$.

$$\boxed{\psi_1 \, , \, \psi_2}$$

$$\begin{array}{ccc} \psi_1 & \psi_1 & \psi_1 \\ \psi_1 & \psi_1 & \psi_2 \\ \psi_1 & \psi_2 & \psi_1 \\ \psi_1 & \psi_2 & \psi_2 \end{array} \qquad \begin{array}{ccc} \psi_2 & \psi_1 & \psi_1 \\ \psi_2 & \psi_1 & \psi_2 \\ \psi_2 & \psi_2 & \psi_1 \\ \psi_2 & \psi_2 & \psi_2 \end{array} \qquad d_1^{N_1} = 2^3 = 8$$

Each of the 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
$$\boxed{\frac{N!\, d_1^{N_1}}{N_1!\,(N-N_1)!}}$$
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

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

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

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

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

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

Example: three particles

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

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

$$\uparrow \quad \uparrow \quad \uparrow$$

positive integers

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

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

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

$(n_A, n_B, n_C) =$ $(11, 11, 11)$ #1

$(13, 13, 5)$, $(13, 5, 13)$, $(5, 13, 13)$ #2

$(1, 1, 19)$, $(1, 19, 1)$, $(19, 1, 1)$ #3

$(5, 7, 17)$, $(5, 17, 7)$, $(7, 5, 17)$, $(17, 17, 5)$, $(17, 5, 7)$, $(17, 7, 5)$. #4

which belong to four different configurations

	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}	...
#1	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	
#2	0	0	0	0	1	0	0	0	0	0	0	0	2	0	0	0	0	0	0	...
#3	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	...
#4	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	1	0	0	...

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

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

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

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

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

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

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 $\quad Q_3 = 3$

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

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

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_2 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 ; $\dfrac{N!}{N_1!\,(N-N_1)!} \longrightarrow \boxed{\dfrac{d_1!}{N_1!\,(d_1-N_1)!}}$

Let's check for the cases in our example:

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

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

$N_3 = 3 \quad d_1 = 3 \Rightarrow \dfrac{3!}{3!\,(3-3)!} = 1$

$d_1 < N_1 \Rightarrow 0$

The total answer for the case of identical fermions is:

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

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: ψ_1, ψ_2, and ψ_3.

$N_1 = 2$

$$\left.\begin{matrix} \psi_1\psi_1, & \psi_2\psi_2, & \psi_3\psi_3 \\ \psi_1\psi_2, & \psi_1\psi_3, & \psi_2\psi_3 \end{matrix}\right\} \text{6 choices}$$

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: ($N_1 = 3$, $d_1 = 3$)

$\psi_1\psi_1\psi_1$

$\underbrace{\bullet \quad \bullet \quad \bullet}_{\boxed{\text{three in one}}} \quad \times \quad \times$ ← none in 2 or 3

$\psi_1\psi_1\psi_2$

$\underbrace{\bullet \quad \bullet}_{\text{two in one}} \quad \times \quad \underbrace{\bullet}_{\text{one in two}} \quad \times$ ← none in three

$\psi_1 \quad \psi_2 \quad \psi_3$

$\bullet \quad \times \quad \bullet \quad \times \quad \bullet$

(one in each)

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

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

$$\bullet\ \bullet\ \times\ \bullet\ \times\ \bullet\ \bullet\ \bullet\ \times\ \bullet\ \times$$

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

$$\underbrace{\psi_1 \psi_1 \psi_2 \psi_3 \psi_3 \psi_3 \psi_4}_{7\ \text{total}}$$

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

$$\underbrace{a\ \ b\ \ c\ \ d\ \ldots}_{N_1+d_1-1\ \text{total}} \Rightarrow$$

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:

$$\boxed{Q(N_1, N_2, \ldots) = \prod_{i=1}^{\infty} \frac{(N_n+d_n-1)!}{N_n!\,(d_n-1)!}}$$

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, ...) is the one for which Q(N_1, N_2, N_3, ...) 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 constrains:

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

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

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

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

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.

$$G \equiv \ln(Q) + \underset{\lambda_1}{\alpha} \underbrace{\left[N - \sum_{n=1}^{\infty} N_n \right]}_{f_1} + \underset{\lambda_2}{\beta} \underbrace{\left[E - \sum_{n=1}^{\infty} N_n E_n \right]}_{f_2}$$

$$x_n \equiv N_n$$

$\frac{\partial G}{\partial \alpha}$ 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:

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

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

$$\left. - \alpha N_n - \beta E_n N_n \right\} + \alpha N - \beta E .$$

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

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

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

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

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

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

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

Case 3: identical bosons $N_n \gg 1$

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

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: $\beta = \dfrac{1}{k_B T}$

α is generally replaced by a **chemical potential μ(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:

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

$$\boxed{n(\varepsilon) = e^{-(\varepsilon - \mu)/k_B T}}$$ ← Maxwell-Boltzmann distribution (classical result)

Identical fermions:

$$\boxed{n(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}}$$ ← Fermi-Dirac distribution

Identical bosons:

$$\boxed{n(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} - 1}}$$ ← Bose-Einstein distribution