QUANTUM STATISTICAL MECHANICS

Let us try building from scratch a general model with which to describe many-particle states. The system we consider will be at some finite temperature T. If our system has many particles (a large N), there will be many microscopic configurations that are consistent with a fixed number of particles N at a total energy E. The fundamental assumption of statistical mechanics is that all these states will be explored with equal likelihood (ergodic hypothesis).

Let us consider a simple case: three weakly interacting particles in a 1-D infinite well. Each of them has energy $\hbar^2\pi^2 n^2/2ma^2$, and the total energy is:

$$E_{TOT} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_a^2 + n_b^2 + n_c^2\right)$$

Let us say that the system's energy is $243\,\frac{\hbar^2\pi^2}{2ma^2}$. How many ways do we have to achieve this result? Here are some: $|9,9,9\rangle$, $|3,3,15\rangle$, $|15,3,3\rangle$, $|3,15,3\rangle$, $|5,7,13\rangle$, $|7,5,13\rangle$, $|5,13,7\rangle$, $|13,5,7\rangle$, $|7,13,5\rangle$, $|13,7,5\rangle$ using Dirac's notation $|n_a, n_b, n_c\rangle$.

We have 10 states, but they are all good only if the particles are distinguishable. If I have identical fermions, there is only one possible state: the antisymmetric combination of the states of the $|5,7,13\rangle$ type: all others have two (or more! $|9,9,9\rangle$!) particles in the same state. If I have identical bosons, I also need to do some work: the states $|3,3,15\rangle$, $|3,15,3\rangle$ and $|15,3,3\rangle$ need to be combined in a symmetric (for particle exchange) state. In a nutshell, we start with 10 acceptable states for a system of indistinguishable particles, out of which we can form only 1 acceptable state for identical fermions, and three states for identical bosons:

fermions: $\frac{1}{\sqrt{6}}\left(|5,7,13\rangle + |13,5,7\rangle + |7,13,5\rangle - |5,13,7\rangle - |7,5,13\rangle - |13,7,5\rangle\right)$

bosons: $|9,9,9\rangle$

$$\frac{1}{\sqrt{3}}\left(|15,3,3\rangle + |3,15,3\rangle + |3,3,15\rangle\right)$$

$$\frac{1}{\sqrt{6}}\left(|5,7,13\rangle + |13,5,7\rangle + |7,13,5\rangle + |5,13,7\rangle + |7,5,13\rangle + |13,7,5\rangle\right)$$

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We need to generalize this to a case of N particles. Let us consider a system with an infinite number of states, with energies E_i $(i = 1 \ldots \infty)$, each state with degeneracy g_i. We need to distribute N particles, with two constraints:

$N = \sum_i n_i$ the total number of particles is fixed (n_i = #particles in state i)

$E = \sum_i E_i n_i$ the total energy is fixed

The idea is to calculate all possible distributions of N particles in the available states such that the total energy is E, and find the configuration that is more likely to occur. We will not demonstrate this, but let it be assumed that, as N increases, the most probable configuration becomes overwhelmingly more likely than any other. How do we find this configuration?

Let us indicate with $(n_1, n_2, \ldots, n_s, \ldots)$ a configuration in which n_1 particles are in the energy state E_1; n_2 have E_2; and so on. Let us indicate with P_s the number of ways I can arrange n_s particles in the energy state s, of energy E_s and degeneracy g_s.

Then, the statistical weight of the configuration $(n_1, n_2, \ldots, n_s \ldots)$ is:

$$W(n_1, n_2, \ldots, n_s, \ldots) = \prod_{s=1}^{\infty} P_s = P_1 \cdot P_2 \cdot P_3 \cdot \ldots \cdot P_s \cdot \ldots$$

W is not a probability, but it is proportional to it. Note that if $n_s = 0$, then $P_s = 1$: there is only one way of realizing that configuration (i.e., having exactly no particles in the state s).

We now need to calculate the W values, and maximise them with the constraints that $\sum n_i = N$ and $\sum n_i E_i = E$.

Let us consider three separate cases:

1) DISTINGUISHABLE PARTICLES:

let us consider the configuration $(n_1, n_2, n_3 \dots)$ and start from state 1. We need to select n_1 particles out of N, and place them in any of the g_1 degenerate states with energy E_1. How many ways are there to accomplish this?

$$P_1 = \underbrace{\binom{N}{n_1}}_{\substack{\text{number of ways I can form a} \\ \text{subset of } n_1 \text{ particles out of } N}} g_1^{n_1}$$

each particle can be put in any one of the g_1 states

Let us now move to n_2. The formula is similar, but now I have to extract n_2 particles out of $N - n_1$:

$$P_2 = \binom{N-n_1}{n_2} g_2^{n_2}$$

Let us write $W(n_1, n_2, \dots)$ explicitely:

$$W(n_1, n_2, n_3 \dots) = \underbrace{\frac{N! \, g_1^{n_1}}{n_1! \, (N-n_1)!}}_{P_1} \cdot \underbrace{\frac{(N-n_1)! \, g_2^{n_2}}{n_2! \, (N-n_1-n_2)!}}_{P_2} \cdot \underbrace{\frac{(N-n_1-n_2)! \, g_3^{n_3}}{n_3! \, (N-n_1-n_2-n_3)!}}_{P_3} \cdot \dots$$

Finally:

$$W(n_1, n_2, n_3 \dots) = N! \prod_i \frac{g_i^{n_i}}{n_i!} \qquad \text{DISTINGUISHABLE PARTICLES}$$

2) IDENTICAL FERMIONS:

this is easy: as soon as $n_i > g_i$, $P_i = 0$: we cannot fit two fermions in the same state. If $n_i = g_i$, then $P_i = 1$: each fermion occupies one of the g_i states, and there is only one way of achieving this configuration, since there fermions are identical. If $n_i < g_i$, instead, we are back to a similar expression we had before:

$$P_i = \binom{g_i}{n_i}$$

i.e., we need to select n_i out of g_i states (and form a wavefunction that respect the symmetry requested of wavefunction for system of identical fermions)

Finally:

$$W(n_1, n_2, n_3 \dots) = \prod_i \binom{g_i}{n_i} \qquad \text{IDENTICAL FERMIONS}$$

3) IDENTICAL BOSONS:

this is tricky. For each energy state s, we have n_s particles to be shared among g_s degenerate states, and more than one particle can go in the same degenerate state. Here is a solution proposed in Griffith's book: let us use • to indicate particles, and × to indicate the border between two degenerate states. Let us say that $n_s = 5$ and $g_s = 3$. Possible configurations can be written as follows:

	# particles in first degenerate state	# particles in second degenerate state	# particles in third degenerate state
× • • × • • •	0	2	3
• × • × • • •	1	1	3
• • × • × • •	2	1	2
• • • × × • •	3	0	2
• • • • • × ×	5	0	0

We transformed our problem into calculating how many ways we have to arrange n_s dots and $g_s - 1$ crosses. This is easy:

$$P_s = \frac{(n_s + g_s - 1)!}{n_s!\,(g_s-1)!}$$

number of ways to arrange a total of $n_s + g_s - 1$ symbols

$g_s - 1$ of those $n_s + g_s - 1$ symbols are undistinguishable crosses

n_s of those $n_s + g_s - 1$ symbols are undistinguishable dots

Finally:

$$W(n_1, n_2, n_3 \dots) = \prod_i \binom{n_s + g_s - 1}{n_s}$$

IDENTICAL BOSONS

The next step consists in maximising $W(n_1, n_2, \dots)$ with the constraints $\sum n_i = N$ and $\sum n_i E_i = E$. We will do so using Lagrange multipliers.

The idea is to create a function $G(n_1, n_2, n_3 \dots \lambda_1, \lambda_2)$, where λ_i are the Lagrange multipliers, and require that G is maximised as a function of all its parameters, including the multipliers λ_i. Here's how it works:

$$G(n_1, n_2, n_3, \dots \lambda_1, \lambda_2) = \ln W(n_1, n_2, \dots) + \lambda_1\left(N - \sum n_i\right) + \lambda_2\left(E - \sum n_i E_i\right)$$

we will ask:

$$\frac{\partial G}{\partial n_i} = 0 \qquad \frac{\partial G}{\partial \lambda_1} = 0 \qquad \frac{\partial G}{\partial \lambda_2} = 0$$

Note that we use $\ln W$ instead of W: since $\ln$ is a monotonic function, the max of $\ln W$ will correspond to the max of W. Since W contains lots of products, which the log transforms into simple additions, this is a convenient transformation.

1) DISTINGUISHABLE PARTICLES :

$$G(n_1, n_2, \dots \lambda_1, \lambda_2) = \ln\left(N! \prod_i \frac{g_i^{n_i}}{n_i!} \right) + \lambda_1\left(N - \sum n_i\right) + \lambda_2\left(E - \sum n_i \varepsilon_i\right)$$

Let us do some math:

$$\ln\left(N! \prod_i \frac{g_i^{n_i}}{n_i!} \right) = \ln(N!) + \sum_i n_i \ln(g_i) - \ln(n_i!)$$

assuming n_s are large, we can use Stirling's approximation:

$$\ln(m!) \simeq m \ln(m) - m$$

We finally find:

$$G(n_1, n_2 \dots, \lambda_1, \lambda_2) \simeq \sum_i \left(n_i \ln(g_i) - n_i \ln(n_i) + n_i - \lambda_1 n_i - \lambda_2 \varepsilon_i n_i \right) +$$

$$+ \ln(N!) + \lambda_1 N + \lambda_2 E$$

$$\frac{\partial G(n_1, n_2 \dots \lambda_1, \lambda_2)}{\partial n_s} = \ln(g_s) - \ln(n_s) - 1 + 1 - \lambda_1 - \lambda_2 \varepsilon_s$$

$$\underset{\substack{\uparrow \\ \text{looking for max}}}{=} 0 \implies \ln(n_s) = \ln(g_s) - \lambda_1 - \lambda_2 \varepsilon_s$$

$$\boxed{n_s = g_s e^{-\lambda_1 - \lambda_2 \varepsilon_s}}$$

2) IDENTICAL FERMIONS:

$$G(n_1, n_2 \dots \lambda_1, \lambda_2) = \ln\left(\prod \frac{g_i!}{n_i!(g_i - n_i)!} \right) + \lambda_1\left(N - \sum n_i\right) + \lambda_2\left(E - \sum_i n_i \varepsilon_i\right)$$

More math:

$$G(n_1, n_2 \dots) = \sum_i \ln(g_i!) - \ln(n_i!) - \ln((g_i - n_i)!) - \lambda_1 n_i - \lambda_2 n_i \varepsilon_i +$$

$$+ \lambda_1 N + \lambda_2 E$$

$$G(m_1, m_2 ..) \underset{\text{Stirling}}{\simeq} \sum_i -m_i \ln(m_i) + m_i - (g_i - m_i)\ln(g_i - m_i) + (g_i - m_i) +$$

$$- \lambda_1 m_i - \lambda_2 m_i E_i + \sum_i \ln(g_i!) + \lambda_1 N + \lambda_2 E$$

$$\frac{\partial G}{\partial m_s} = -\ln(m_s) - 1 + 1 + \ln(g_s - m_s) + 1 - 1 - \lambda_1 - \lambda_2 E_s$$

$$\underset{\text{looking for max}}{=} 0 \implies \ln\left(\frac{g_s - m_s}{m_s}\right) = \lambda_1 + \lambda_2 E_s$$

$$\boxed{m_s = \frac{g_s}{1 + e^{\lambda_1 + \lambda_2 E_s}}}$$

NOTE: we are assuming that $g_s >> m_s$, so that we can use Stirling's approximation on $\ln((g_s - m_s)!)$

3) IDENTICAL BOSONS:

$$G(m_1, m_2 .. \lambda_1, \lambda_2) = \ln\left(\prod_i \frac{(m_i + g_i - 1)!}{m_i!(g_i - 1)!}\right) + \lambda_1\left(N - \sum m_i\right) + \lambda_2\left(E - \sum_i m_i E_i\right)$$

Same tricks:

$$G(m_1, m_2 ...) \underset{\text{Stirling}}{\simeq} \sum (m_i + g_i - 1)\ln(m_1 + g_i - 1) - (m_i + g_i - 1) - m_i \ln(m_i) +$$

$$+ m_i - \lambda_1 m_i - \lambda_2 E_i m_i - \sum_i \ln((g_i - 1)!) + \lambda_1 N + \lambda_2 E$$

$$\frac{\partial G}{\partial m_s} = \ln(m_s + g_s - 1) + \cancel{1} - \cancel{1} - \ln(m_s) - \cancel{1} + \cancel{1} - \lambda_1 - \lambda_2 E_s$$

$$\underset{\text{looking for max}}{=} 0 \implies \ln\left(\frac{m_s + g_s - 1}{m_s}\right) = \lambda_1 + \lambda_2 E_s$$

$$\boxed{m_s = \frac{g_s}{e^{\lambda_1 + E_s \lambda_2} - 1}}$$

NOTE: since g_s is a very large number, as we assumed in the case of fermions, I can drop the 1 on the numerator

What are λ_1 and λ_2? If we consider an ideal gas (large number of non-interacting particles, in a 3D quantum well) and calculate the value of the constraints, we find that:

$$\lambda_2 = 1/k_B T$$

The calculations are in Griffiths 5.4.4. As for λ_1, it is typically defined using the chemical potential $\mu(T)$ as follows:

$$\lambda_1 = -\frac{\mu(T)}{k_B T}$$

$\mu(T)$ is the energy needed to change the number of particles in the system from N to $N+1$

We finally obtain:

$$n(E) = e^{-\frac{E-\mu}{k_B T}} \qquad \text{MAXWELL-BOLTZMANN}$$

$$n(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} \qquad \text{FERMI-DIRAC}$$

$$n(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} - 1} \qquad \text{BOSE-EINSTEIN}$$

where $n(E)$ is the most probable number of particles in a particular one-particle state with energy E (i.e., we take n_s found before at energy E_s and divide by its degeneracy g_s).

Interesting note in Fermi-Dirac case: when $T=0$, at the absolute zero, $n(E)$ can only assume two values: 1 if $E < \mu(0)$, and 0 if $E > \mu(0)$. So, all states are filled up to an energy $\mu(0)$, and none above $\mu(0)$. Hence:

$$\mu(0) = E_F$$

the chemical potential at $T=0$ is equal to the Fermi energy

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Let us use this notation to indicate a system configuration:

$(n_1, n_2, \dots)$

where n_1 indicates the number of particles in a state with energy E_1.

Our system has 3 particles, and a total energy of $243 \cdot \pi^2\hbar^2/2ma^2$.

Here are the possible ways to describe it: → i.e., the possible microscopic configurations the system could be in, when its energy is $243\frac{\pi^2\hbar^2}{2ma^2}$

		#states	dist.	bosons	fermions
$\vert 9,9,9\rangle$:	$(0,0,0,0,0,0,0,0,\underset{n_9}{3},0,\dots)$	1	1	0	
$\vert 3,3,15\rangle$, $\vert 3,15,3\rangle$, $\vert 15,3,3\rangle$:	$(0,0,\underset{n_3}{2},0,0,0,0,0,0,0,0,0,0,0,\underset{n_{15}}{1},0,\dots)$	3	1	0	
$\vert 5,7,13\rangle$ ⋮ $\vert 13,7,5\rangle$:	$(0,0,0,0,1,0,1,0,0,0,0,0,1,0,\dots)$	6	1	1	

small p → P_i

A question we would want to ask is: what is the probability of measuring E_i on a random particle of choice? It is easy to calculate. Let us do a couple of examples:

$P_{30} = 0$: none of the 10 possible states ($|9,9,9\rangle, |3,3,15\rangle \dots, |5,7,13\rangle \dots$) has a particle with energy E_{30}

$P_9 = 1/10$: out of 10 possible states, I need to be in $|9,9,9\rangle$: $1/10$. Once I am in $|9,9,9\rangle$, the probability of measuring E_9 is 1: all three particles return that same value.

$P_3 = \frac{3}{10} \cdot \frac{2}{3}$: I need to be in one of the three states of type 3,3,15; once there, I measure E_3 two times out of three

$P_{15} = \frac{3}{10} \cdot \frac{1}{3}$

$P_5 = \frac{6}{10} \cdot \frac{1}{3} = P_7 = P_{13}$

What if we have three fermions? We saw we are allowed to be in only one state, the anti-symmetric combination of states of the $|5, 7, 13\rangle$ type. Therefore:

$P_5 = P_7 = P_{13} = \frac{1}{3}$: there is only one allowed state, in which particles are in the E_5, E_7, E_{13} states with equal weight

Boson case: we have three possible states: $|9,9,9\rangle$, symmetric combinations of $|15,3,3\rangle$ states, and symmetric combinations of $|5,7,13\rangle$ states. Hence:

$P_9 = 1/3 \cdot 1$

$P_{15} = 1/3 \cdot 1/3$

$P_3 = 1/3 \cdot 2/3$

$P_5 = P_7 = P_{13} = 1/3 \cdot 1/3$

Note that, in any case (distinguishable particles, identical fermions, identical bosons), we have:

$$\sum_i P_i = 1$$

NOTE: when we generalize this to a many-particle system, we will define $\mathcal{P}_s$ as the number of ways to achieve a certain configuration (n_s particles among g_s degenerate energy levels with energy E_s): that $\mathcal{P}_s$ is <u>not</u> a probability

capital $\mathcal{P}$