Identical Particles in QM

Let us first review what happens in QM with many distinguishable particles. For example, consider one Na and one He atom interacting with each other.

Classically we would have a phase space of $\vec{r}_1, \vec{p}_1$ (Na) $\vec{r}_2, \vec{p}_2$ (He)

In QM, in addition to the position and momentum, each atom has a set of quantum numbers describing its internal state

How do we describe the full space of quantum states?

To do this, let us introduce the notion of a direct product of two vector spaces V_1^l and V_2^l

$$V = V_1^l \otimes V_2^l \qquad \text{①}$$

An element of $v \in V$ ② is an ordered pair

$$v = (v_1, v_2) \qquad \text{③} \quad \text{where} \quad v_1 \in V_1^l \quad v_2 \in V_2^l$$

Clearly, this satisfies all the required properties of a vector space. One can take the direct product of any number of

vector spaces.

It is easy to see that a direct product of the Hilbert spaces of the Na atom and the He atom is sufficient to describe the joint system.

Suppose the Na atom in isolation has Hamiltonian $\mathcal{H}_1$, with eigenstates in the Hilbert space $\mathcal{V}_1$

$$\mathcal{H}_1 \, |\alpha_1\rangle = \mathcal{E}_{\alpha_1}^{(1)} \, |\alpha_1\rangle \qquad \textcircled{4}$$

The states $|\alpha_1\rangle$ have an inner product defined in $\mathcal{V}_1$ and are orthonormal and form a complete basis for $\mathcal{V}_1$

$$\langle \alpha_1 | \beta_1 \rangle = \delta_{\alpha_1 \beta_1} \qquad\qquad \sum_{\alpha_1} |\alpha_1\rangle \langle \alpha_1 | = \mathbb{1}_1 \qquad \textcircled{5}$$

Identity operator of $\mathcal{V}_1$

Similarly, the He atom in isolation has a hamiltonian $\mathcal{H}_2$ and states $|\alpha_2\rangle \in \mathcal{V}_2$

$$\mathcal{H}_2 \, |\alpha_2\rangle = \mathcal{E}_{\alpha_2}^{(2)} \, |\alpha_2\rangle \qquad \textcircled{6}$$

$$\langle \alpha_2 | \beta_2 \rangle = \delta_{\alpha_2 \beta_2} \qquad\qquad \sum_{\alpha_2} |\alpha_2\rangle \langle \alpha_2 | = \mathbb{1}_2 \qquad \textcircled{7}$$

Identity operator of $\mathcal{V}_2$

We can now construct a basis of $\mathcal{V}_1 \otimes \mathcal{V}_2$ as

$$|\alpha_1 \alpha_2\rangle \equiv |\alpha_1\rangle \otimes |\alpha_2\rangle$$

(8)

$$\langle \alpha_1 \alpha_2 | \beta_1 \beta_2 \rangle = \delta_{\alpha_1 \beta_1} \delta_{\alpha_2 \beta_2}$$

$$\sum_{\alpha_1 \alpha_2} |\alpha_1 \alpha_2\rangle \langle \alpha_1 \alpha_2| = \mathbb{1}_{1 \otimes 2} \equiv \mathbb{1}$$

How about operators? Operators acting on V_1 don't do anything to the kets $\wedge$ V_2.

So we can write the action of $\vec{X}_1$ on $|\alpha_1 \alpha_2\rangle$ as

$$\vec{X}_1 |\alpha_1 \alpha_2\rangle = (\vec{X}_1 |\alpha_1\rangle) \otimes |\alpha_2\rangle$$

(9)

So $\vec{X}_1$ acts like the identity operator on V_2. Sometimes, by an abuse of notation we write

$$\vec{X}_1 \equiv \vec{X}_1 \otimes \mathbb{1}_2 \qquad \vec{X}_2 = \mathbb{1}_1 \otimes \vec{X}_2$$

(10)

When the atoms interact the full Hamiltonian will have interaction terms

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12}$$

(11)

Now $|\alpha_1 \alpha_2\rangle$ will in general not be eigenstates of $\mathcal{H}$, but they are still a complete set of orthonormal states in $V = V_1 \otimes V_2$

Now consider wavefunctions. Focus on two distinguishable elementary particles, say an electron and a muon. Ignore their spin and focus on their positions.

$$\mathcal{V}_1 = \text{Hilbert space of electron}$$

(12)

$$\mathcal{V}_2 = \text{Hilbert space of muon}$$

Let the electron be in $|\phi_1\rangle \in \mathcal{V}_1$ and (13)

the muon in $|\phi_2\rangle \in \mathcal{V}_2$ (14)

Now the wavefunction has two position coordinates

$$\langle \bar{x}_e, \bar{x}_\mu | \phi_1, \phi_2 \rangle = \phi_1(\bar{x}_e) \, \phi_2(\bar{x}_\mu)$$

(15)

Of course the e and μ could be in some superposition

$$|\Phi\rangle = a \, |\phi_1\rangle \otimes |\phi_2\rangle + b \, |\psi_1\rangle \otimes |\psi_2\rangle$$

(16)

$$\langle \bar{x}_e, \bar{x}_\mu | \Phi \rangle = \Phi(\bar{x}_e, \vec{x}_\mu) = a \, \phi_1(\bar{x}_e) \, \phi_2(\bar{x}_\mu) + b \, \psi_1(\bar{x}_e) \, \psi_2(\vec{x}_\mu)$$

So the joint wavef^n need not be a simple product of a function of $\bar{x}_e$ times a function of $\bar{x}_\mu$.

We also know the action of momentum operators on these wavefunctions

$$\vec{\mathbb{P}}_e \, \Phi(\bar{x}_e, \bar{x}_\mu) = -i\hbar \, \bar{\nabla}_e \, \Phi(\bar{x}_e, \bar{x}_\mu)$$

$$\vec{\mathbb{P}}_\mu \, \Phi(\bar{x}_e, \bar{x}_\mu) = -i\hbar \, \bar{\nabla}_\mu \, \Phi(\bar{x}_e, \bar{x}_\mu)$$

(17)

We are finally ready to address the issue of identical particles.

Classically, even identical particles are distinguishable. All one has to do is (mentally) label the particles from 1 to N (say) and just watch them as they undergo classical deterministic Hamiltonian evolution.

The point is that in CM one can "watch" the particle without disturbing it.

You may object that in classical Statistical Mechanics we treat all permutations of identical particles as the same micro-state. This is the dividing by N! rule.

However, this rule is just a fudge to avoid the Gibbs paradox, and does not rest on anything fundamental.

True indistinguishability can only occur in QM.

We finally come to the QM of identical particles. The principle is

"Exchanging two identical particles cannot change anything physical"

Recall that when we measure some physical observable Ω on a state $|\psi\rangle$ what we are doing is

1) Finding the eigenstates & eigenvalues of Ω

$$\Omega |\alpha\rangle = \omega_\alpha |\alpha\rangle \quad \text{(18)}$$

2) Then $\quad |\psi\rangle = \sum_\alpha |\alpha\rangle \langle\alpha|\psi\rangle \quad \text{(19)}$

and the probability of measuring the value ω_α for Ω is

$$p(\omega_\alpha) = |\langle\alpha|\psi\rangle|^2 \quad \text{(20)}$$

(21)

So under an exchange of identical particles

$|\langle\alpha|\psi\rangle|$ should remain unchanged for any $|\alpha\rangle$

What exactly do we mean by "exchange"

First consider two Helium atoms in their ground states. The only degrees of freedom are $\bar{x}_1, \bar{p}_1, \bar{x}_2, \bar{p}_2$

The wave function of the state $|\Phi\rangle$ is

$$\langle \bar{x}_1, \bar{x}_2 | \Phi \rangle = \Phi(\bar{x}_1, \bar{x}_2) \quad (22)$$

We will define the exchange operator $\cancel{X}_{12}$ as

$$\langle \bar{x}_1, \bar{x}_2 | \cancel{X}_{12} | \Phi \rangle = \Phi(\bar{x}_2, \bar{x}_1) \quad (23)$$

Therefore one can write

$$\cancel{X}_{12} = \int d^3\bar{x}_1 \, d^3\bar{x}_2 \quad |\bar{x}_1, \bar{x}_2\rangle \langle \bar{x}_2, \bar{x}_1| \quad (24)$$

Now here are two important properties of $\cancel{X}_{12}$.

$$1) \quad \cancel{X}_{12}^\dagger = \cancel{X}_{12} \quad (25)$$

$$2) \quad \cancel{X}_{12}^2 = \mathbb{1}$$

Use the above to convince yourself of 1) & 2).

Because $\cancel{X}_{12}$ is hermitian it has real eigenvalues. Because of property 2) the eigenvalues can only be ± 1. So in $\mathcal{V}_1 \otimes \mathcal{V}_2$

$$|\Psi_+\rangle \in \mathcal{V}_+^2 : \quad \cancel{X}_{12} |\Psi_+\rangle = |\Psi_+\rangle \quad (26)$$ ← Class of states even under exchange

$$|\Psi_-\rangle \in \mathcal{V}_-^2 : \quad \cancel{X}_{12} |\Psi_-\rangle = -|\Psi_-\rangle \quad (27)$$ ← class of states odd under exchange

Every hermitian operator has a complete set of eigenstates, so together, the class $|\Psi_+\rangle$ and the class $|\Psi_-\rangle$ cover $\mathcal{V}_1^2 \otimes \mathcal{V}_2^2$

$$\boxed{\mathcal{V}_+^2 \oplus \mathcal{V}_-^2 = \mathcal{V}_1^2 \otimes \mathcal{V}_2^2} \quad (28)$$

$\uparrow$
the direct sum

Now here is the key point. For a particular kind of identical particle, all states have to belong to either $\mathcal{V}_+$ or $\mathcal{V}_-$

One cannot have linear combinations of states in $\mathcal{V}_+$ and states in $\mathcal{V}_-$ describing a physical state.

To see this, assume that we do have such a linear combination

$$|\widehat{\Phi}\rangle = a|\Psi_{1+}\rangle + b|\Psi_{2-}\rangle$$

$$X_{12}|\widehat{\Phi}\rangle = a|\Psi_{1+}\rangle - b|\Psi_{2-}\rangle \quad (29)$$

$$\langle\alpha|\widehat{\Phi}\rangle = a\langle\alpha|\Psi_{1+}\rangle + b\langle\alpha|\Psi_{2-}\rangle$$

$$\langle\alpha|X_{12}|\widehat{\Phi}\rangle = a\langle\alpha|\Psi_{1+}\rangle - b\langle\alpha|\Psi_{2-}\rangle$$

For all physically observed quantities to be invariant under exchange we want

$$\boxed{|\langle \alpha | \mathcal{\Phi} \rangle| = |\langle \alpha | \cancel{X}_{12} | \mathcal{\Phi} \rangle|} \quad \text{(30)}$$

Thus either $a = 0$ or $b = 0$

Identical particles which have states that are even under exchange are called Bosons (more about S.N. Bose soon) while those with states odd under exchange are called Fermions.

This extends very easily to many-particle states. Say there are N identical particles labelled i, j etc.

$$\boxed{\begin{array}{l} \langle \vec{x}_1, \vec{x}_2, \cdots \vec{x}_N | \mathcal{\Phi} \rangle = \mathcal{\Phi}(\vec{x}_1, \cdots \vec{x}_N) \quad \text{(31)} \quad n^{th}\text{place} \\[4pt] \downarrow \\ \langle \vec{x}_1, \vec{x}_2, \cdots \vec{x}_N | \cancel{X}_{mn} | \mathcal{\Phi} \rangle = \mathcal{\widehat{\Phi}}(\vec{x}_1, \cdots \vec{x}_n, \cdots \vec{x}_m, \cdots \vec{x}_N) \\[4pt] \uparrow \\ m^{th}\text{place} \end{array}}$$

Every pair-exchange operator is hermitian and squares to 1. So its eigenvalues are ± 1.

Bosonic states have

$$\boxed{\cancel{X}_{mn} | \widehat{\mathcal{\Phi}}_B \rangle = | \mathcal{\Phi}_B \rangle} \quad \text{(32)}$$

while Fermionic ones have

$$\boxed{\cancel{X}_{mn} | \mathcal{\Phi}_F \rangle = - | \mathcal{\Phi}_F \rangle} \quad \text{(33)}$$

Let's consider some concrete examples.

Say we have two identical bosons. They happen to be non-interacting. The obvious wave f^n to write down is

$$\Phi(\bar{x}_1, \bar{x}_2) = \phi_1(\bar{x}_1) \phi_2(\bar{x}_2) \quad (34)$$

However, this may not be good enough, because

$$\cancel{X}_{12} \Phi(\bar{x}_1, \bar{x}_2) = \phi_1(\bar{x}_2) \phi_2(\bar{x}_1) \quad (35)$$

If ϕ_1 and ϕ_2 are the same function, then this is an eigenstate $\wedge$ $\cancel{X}_{12}$ with $+1$ eigenvalue, and is thus a good bosonic wave f^n.

If ϕ_1 and ϕ_2 are different functions then

$$\cancel{X}_{12} |\widehat{\Phi}\rangle \neq |\widehat{\Phi}\rangle \quad (36)$$

So we must symmetrize. The correct $|\widehat{\Phi}\rangle$ is

$$\underline{\Phi}_B(\bar{x}_1, \bar{x}_2) = C\left(\phi_1(\bar{x}_1) \phi_2(\bar{x}_2) + \phi_1(\bar{x}_2) \phi_2(\bar{x}_1) \right) \quad (37)$$

Similarly, a good fermionic wave f^n $\wedge$ two identical fermions is

(38)

$$\underline{\widehat{\Phi}}_F(\bar{x}_1, \bar{x}_2) = C\left(\phi_1(\bar{x}_1) \phi_2(\bar{x}_2) - \phi_1(\bar{x}_2) \phi_2(\bar{x}_1) \right)$$

This immediately shows that two identical fermions cannot be in the same quantum state.

This is the famous Pauli exclusion principle and underlies the structure of matter.

So far, we have not considered internal degrees of freedom, such as spin, polarization, etc.

The general rule is that one exchanges all the labels upon the action of $\cancel{\times}_{12}$.

Consider two spin-$\frac{1}{2}$ electrons. If we fix the positions there are 4 possible spin-projections. They are ③⑨

$$\left(\vec{x}_1\uparrow, \vec{x}_2\uparrow\right), \left(\vec{x}_1\uparrow, \vec{x}_2\downarrow\right), \left(\vec{x}_1\downarrow, \vec{x}_2\uparrow\right) \text{ and } \left(\vec{x}_1\downarrow, \vec{x}_2\downarrow\right)$$

So the "wave function" is now a 4-component object. Let us label the spin-projections by s_1, s_2.

Then we have

$$\langle \vec{x}_1, s_1, \vec{x}_2, s_2 | \Phi \rangle = \Phi\left(\vec{x}_1, s_1, \vec{x}_2, s_2\right) \quad ④⓪$$

We define the exchange operator as ④①

$$\cancel{\times}_{12} = \int d^3\vec{x}_1 \, d^3\vec{x}_2 \sum_{s_1, s_2 = \uparrow, \downarrow} |\vec{x}_1, s_1, \vec{x}_2, s_2\rangle \langle \vec{x}_2, s_2, \vec{x}_1, s_1|$$

Suppose we want to construct a two-electron wave f^n, with one electron in an orbital state $\phi_1(\bar{x})$ with spin being an equal superposition of $\uparrow$ and $\downarrow$, while the second electron is in the orbital state $\phi_2(\bar{x})$ with spin $\downarrow$. We start with the product state

$$|\Phi\rangle = \left(\frac{1}{\sqrt{2}}\begin{pmatrix}\phi_1(\bar{x}_1)\\ \phi_1(\bar{x}_1)\end{pmatrix}\right) \otimes \begin{pmatrix}0\\ \phi_2(\bar{x}_2)\end{pmatrix} \quad (42)$$

(43)

$$\Phi(\bar{x}_1,\uparrow,\bar{x}_2,\uparrow) = 0 \qquad \Phi(\bar{x}_1,\uparrow,\bar{x}_2,\downarrow) = \frac{1}{\sqrt{2}}\phi_1(\bar{x}_1)\phi_2(\bar{x}_2)$$

$$\Phi(\bar{x}_1,\downarrow,\bar{x}_2,\uparrow) = 0 \qquad \Phi(\bar{x}_1,\downarrow,\bar{x}_2,\downarrow) = \frac{1}{\sqrt{2}}\phi_1(\bar{x}_1)\phi_2(\bar{x}_2)$$

Now the 4-components of $\quad \cancel{X}_{12}|\Phi\rangle \equiv |\Phi_{ex}\rangle \quad (44)$

$$\Phi_{ex}(\bar{x}_1,\uparrow,\bar{x}_2,\uparrow) = \Phi(\bar{x}_2,\uparrow,\bar{x}_1,\uparrow) = 0$$

$$\Phi_{ex}(\bar{x}_1,\uparrow,\bar{x}_2,\downarrow) = \Phi(\bar{x}_2,\downarrow,\bar{x}_1,\uparrow) = 0 \qquad (45)$$

$$\Phi_{ex}(\bar{x}_1,\downarrow,\bar{x}_2,\uparrow) = \Phi(\bar{x}_2,\uparrow,\bar{x}_1,\downarrow) = \frac{1}{\sqrt{2}}\phi_1(\bar{x}_2)\phi_2(\bar{x}_1)$$

$$\Phi_{ex}(\bar{x}_1,\downarrow,\bar{x}_2,\downarrow) = \Phi(\bar{x}_2,\downarrow,\bar{x}_1,\downarrow) = \frac{1}{\sqrt{2}}\phi_1(\bar{x}_2)\phi_2(\bar{x}_1)$$

So the properly antisymmetrized state is

$$\Phi_F(\bar{x}_1\uparrow,\bar{x}_2,\uparrow) = 0 \qquad \Phi_F(\bar{x}_1\uparrow,\bar{x}_2\downarrow) = \frac{1}{\sqrt{2}}\phi_1(\bar{x}_1)\phi_2(\bar{x}_2)$$

$$\Phi_F(\bar{x}_1\downarrow,\bar{x}_2,\uparrow) = -\frac{1}{\sqrt{2}}\phi_1(\bar{x}_2)\phi_2(\bar{x}_1)$$

(46)

$$\Phi_F(\bar{x}_1\downarrow,\bar{x}_2\downarrow) = \frac{1}{\sqrt{2}}\left(\phi_1(\bar{x}_1)\phi_2(\bar{x}_2) - \phi_1(\bar{x}_2)\phi_2(\bar{x}_1)\right)$$

Bose Statistics & Condensation

In 1924, Einstein received a short manuscript and a very short cover letter from an unknown Indian physicist at Dhaka University. Bose asked Einstein to look at the paper, and if he thought it worthwhile, to translate it into German and have it published.

The paper was a new way of counting states of photons that recovered the Planck distribution from statistical mechanics.

Since 1905, the Planck distribution had been one of Einstein's obsessions, but he had found no satisfactory way to derive it without introducing atoms that would absorb and radiate photons.

So Einstein immediately realized the importance of Bose's way of counting states. He translated the paper and it appeared in Zeitschrift der Physik in 1924.

It is fair to say, from the hindsight of history, that Einstein understood Bose's work much more deeply than Bose himself! He saw the implications for bosonic atoms (now called Bose-Einstein condensation) which is a very big deal indeed.

The "derivation" I have given earlier
of the Planck blackbody distribution is
actually a fudge. You cannot derive it
using "classical indistinguishability". Planck
knew this, which is why he avoided his
own distribution for the rest of his life.

Let us see what the problem is.

Assume that our blackbody cavity is
a cube of L×L×L. Imposing periodic
boundary conditions we get plane waves
with

$$\bar{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad (47)$$

n's are integers.

What we want to do is find the
entropy given the energy. Remember the
number of photons is not fixed.

We will first treat the photons as
particles of a classical identical particle gas.

First let's find the density of one-photon
states.

$$\sum_k f(|\bar{k}|) = \frac{1}{(\Delta k)^3} \sum (\Delta k)^3 f(|\bar{k}|) \approx \frac{1}{(\Delta k)^3} \int d^3k \, f(|\bar{k}|) \qquad (48)$$

$$= \frac{L^3}{(2\pi)^3} \, 4\pi \int_0^\infty k^2 \, dk \, f(k) \qquad\qquad \epsilon = \hbar\omega = \hbar k c$$

$$= \boxed{\frac{L^3}{(2\pi)^3} \frac{4\pi}{(\hbar c)^3} \int_0^\infty \epsilon^2 \, d\epsilon \, f(\epsilon/\hbar c)} \qquad \text{(49)}$$

Accounting for the two polarizations, we see that between ϵ and $\epsilon + \Delta\epsilon$ the number $\mathcal{N}$ 1-photon states is

$$\boxed{g(\epsilon) = \frac{V}{\pi^2 (\hbar c)^3} \, \epsilon^2 \Delta\epsilon} \qquad \text{(50)}$$

Now suppose there are $n(\epsilon)$ photons in this energy interval. The number of different many-photon states is

$$\boxed{\frac{(g(\epsilon))^{n(\epsilon)}}{(n(\epsilon))!}} \qquad \text{(51)}$$

Now the entropy, summing over all energies is

$$\boxed{S = k_B \sum_\epsilon \ln\left[\frac{g(\epsilon)^{n(\epsilon)}}{(n(\epsilon))!} \right]} \qquad \text{(52)}$$

We need to maximize this, subject to the constraint that the total energy is E

$$E = \sum_{\epsilon} \epsilon \, n(\epsilon) \qquad \text{(53)}$$

So let's maximize

$$\tilde{S} = k_B \sum_{\epsilon} \ln\left[\frac{(g(\epsilon))^{n(\epsilon)}}{(n(\epsilon))!}\right] + \lambda\left(E - \sum_{\epsilon} \epsilon \, n(\epsilon)\right) \qquad \text{(54)}$$

with respect to $n(\epsilon)$ and the Lagrange multiplier λ

We will need Stirling's approximation for the factorial

$$\ln(N!) \simeq N \ln N - N + \text{subleading terms} \qquad \text{(55)}$$

$$\tilde{S} = k_B \sum_{\epsilon} \left\{ n(\epsilon) \ln\left[\frac{g(\epsilon)}{n(\epsilon)}\right] + n(\epsilon) \right\} + \lambda\left(E - \sum_{\epsilon} \epsilon \, n(\epsilon)\right) \qquad \text{(56)}$$

$$\frac{dS}{dn(\epsilon)} = k_B \ln\left[\frac{g(\epsilon)}{n(\epsilon)}\right] - \lambda \epsilon = 0 \qquad \text{(57)}$$

$$\Rightarrow \quad n(\epsilon) = g(\epsilon) e^{-\frac{\lambda \epsilon}{k_B}} \qquad \text{(58)}$$

Now the value of λ is fixed by demanding

$$\sum_{\epsilon} n(\epsilon) \, \epsilon = E \qquad \text{(59)}$$

Clearly we can identify $\boxed{\lambda = 1/T} \qquad \text{(60)}$

So this gives the Boltzmann distribution

$$n(\epsilon) = g(\epsilon)\, e^{-\epsilon/k_B T}$$ (61)

$\Rightarrow$ total energy of radiation in the cavity

$$E = \int_0^\infty d\epsilon\; \epsilon\, n(\epsilon) = \frac{V}{\pi^2(\hbar c)^3}\int_0^\infty \epsilon^2 d\epsilon\; \epsilon\, e^{-\epsilon/k_B T}$$ (62)

Does not give the right spectrum at small ϵ. This predicts a spectrum going as ϵ^3 at low energy while the measured spectrum $\sim \epsilon^2$

Scale out $k_B T$ by defining $\xi = \epsilon/k_B T$

$$E = \frac{V}{\pi^2(\hbar c)^3}(k_B T)^4 \int_0^\infty \xi^3 d\xi\, e^{-\xi} \quad\Rightarrow\quad C_v = \left(\frac{\partial E}{\partial T}\right)_V \sim T^3$$ (63)

Correct at low T but not at high T

So treating photons as classical identical particles does not work!

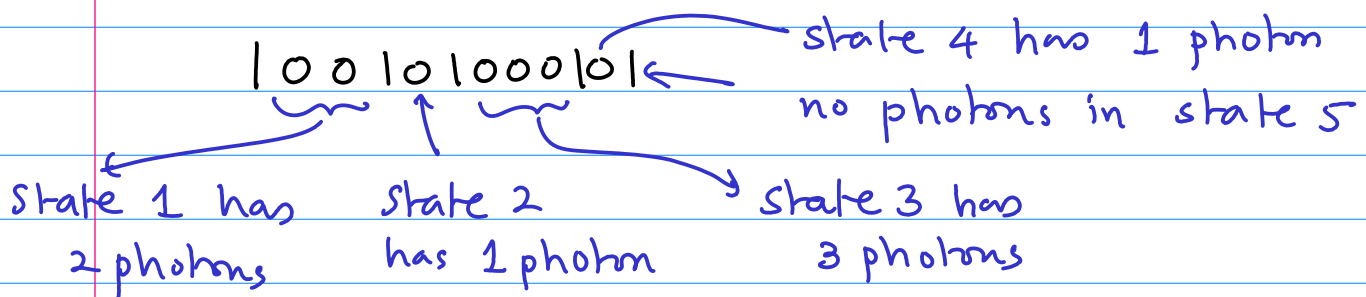Now let's do the counting of states that Bose proposed.

Again consider g states and ask how to count the number of different ways n photons can be arranged in them.

Consider 2 photons and 2 states, say state 1 and state 2

We have the following ways

$$n_1 = 2 \qquad n_2 = 0$$
$$n_1 = 1 \qquad n_2 = 1$$
$$n_1 = 0 \qquad n_2 = 2$$

The key point is that, given how many photons are in a given state there is a unique wave function.

To generalize this to arbitrary g, n lets represent the states by sticks and the photons by balls. For $g = 5 \qquad n = 7$

| o o | o | o | o o o | o | o |

state 4 has 1 photon
no photons in state 5

State 1 has 2 photons
State 2 has 1 photon
State 3 has 3 photons

Any arrangement of sticks and balls that has a stick at the left end is a valid state.

$$\Rightarrow \boxed{\text{number of many-photon states} = \frac{(n+g-1)!}{n! \, (g-1)!}}$$

(64)

$(n+g-1)!$ counts the arrangements of $n+g-1$ distinguishable objects, while the denominator

makes sure that when we permute the balls alone or the sticks alone, we don't generate a different state.

Let us run the entropy argument again, with the new counting of many-photon states.

$$S = k_B \sum_\epsilon \ln \left[\frac{(n(\epsilon) + g(\epsilon) - 1)!}{(n(\epsilon))! \, (g(\epsilon) - 1)!} \right] \quad \text{(65)}$$

Put in the total energy constraint and use Stirling's approximation

$$\tilde{S} = k_B \sum_\epsilon \left\{ (n(\epsilon) + g(\epsilon) - 1) \ln [n(\epsilon) + g(\epsilon) - 1] - (n(\epsilon) + g(\epsilon) - 1) \right.$$
$$- n(\epsilon) \ln n(\epsilon) + n(\epsilon)$$
$$\left. - (g(\epsilon) - 1) \ln (g(\epsilon) - 1) + g(\epsilon) - 1 \right\} \quad \text{(66)}$$
$$+ \lambda \left(E - \sum_\epsilon \epsilon \, n(\epsilon) \right)$$

Use the fact that $g(\epsilon) \gg 1$ to drop the -1 and maximize w.r.t. $n(\epsilon)$ (67)

$$\frac{d\tilde{S}}{dn(\epsilon)} = k_B \left\{ \ln [n(\epsilon) + g(\epsilon)] - \ln [n(\epsilon)] \right\} - \lambda \epsilon = 0$$

$$\Rightarrow \quad \frac{n(\epsilon)}{n(\epsilon) + g(\epsilon)} = e^{-\frac{\lambda \epsilon}{k_B}} \quad \text{(68)} \qquad \lambda \equiv 1/T$$

$$\text{or} \quad n(\epsilon) [1 - e^{-\beta \epsilon}] = g(\epsilon) e^{-\beta \epsilon}$$

$$n(\epsilon) = \frac{g(\epsilon)}{e^{\beta \epsilon} - 1} \qquad (69)$$

$$\Rightarrow \quad E = \int_0^\infty d\epsilon \; \epsilon \, n(\epsilon) = \frac{V}{\pi^2 (\hbar c)^3} \int_0^\infty \frac{\epsilon^3 \, d\epsilon}{e^{\beta \epsilon} - 1} \qquad (70)$$

At small energies $\beta\epsilon \ll 1$ the spectrum is

$$\frac{V}{\pi^2 (\hbar c)^3} \frac{\epsilon^3 \, d\epsilon}{\beta \epsilon} = \frac{V k_B T \; \epsilon^2 \, d\epsilon}{\pi^2 (\hbar c)^3} \qquad (71)$$

This is exactly what is measured.

Einstein took this reasoning a giant step forward when he realized that one can apply similar reasoning to identical particles whose number is conserved, such as atoms $\wedge$ He^4. Moreover, we will assume the gas is ideal, with noninteracting atoms.

Now, to find and maximize the entropy we need to put in two constraints, one for the total energy, and one for the total number $\wedge$ particles. Generalizing (66)

$$\tilde{S} = k_B \sum_\epsilon \Big[(n(\epsilon) + g(\epsilon)) \ln [n(\epsilon) + g(\epsilon)] - n(\epsilon) \ln(n(\epsilon)) \\ - g(\epsilon) \ln g(\epsilon) \Big]$$

$$+ \lambda \Big[E - \sum_\epsilon \epsilon \, n(\epsilon) \Big] + \gamma \Big[N - \sum_\epsilon n(\epsilon) \Big] \qquad (72)$$

γ is a Lagrange multiplier that enforces the total number constraint.

$$\frac{dS}{dn(\epsilon)} = k_B \ln\left[\frac{n(\epsilon) + g(\epsilon)}{n(\epsilon)}\right] - \lambda \epsilon - \gamma = 0 \qquad (73)$$

$$\Rightarrow \quad n(\epsilon) = \frac{g(\epsilon)}{e^{\frac{1}{k_B}(\lambda \epsilon + \gamma)} - 1}$$

$\lambda = \frac{1}{T}$ as usual. $\boxed{\gamma = -\frac{\mu}{T}}$ (74) defines the chemical potential. This tells us the minimum energy needed to add a particle while keeping S and V constant.

$$n(\epsilon) = \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} - 1} \qquad (75)$$

Bose–Einstein distribution

It is clear that if $0 \leq \epsilon < \infty$ then we must have

$$\boxed{\mu \leq 0} \quad (76)$$

to avoid negative occupations.

Let us consider the specific case of a 3D ideal bosonic gas.

$$\epsilon = \frac{p^2}{2M} = \frac{\hbar^2 k^2}{2m} \qquad (77)$$

$$\sum_k f(\epsilon) = \frac{V}{(2\pi)^3} 4\pi \int_0^\infty k^2 dk \, f(\epsilon)$$

change variables to $\epsilon = \frac{\hbar^2 k^2}{2M}$

$$\frac{\hbar^2}{M} k \, dk = d\epsilon$$

$$\Rightarrow k^2 dk = \frac{M}{\hbar^2} d\epsilon \sqrt{\frac{2M\epsilon}{\hbar^2}} = \frac{\sqrt{2M^3}}{\hbar^3} \sqrt{\epsilon} \, d\epsilon$$

$$\Rightarrow \boxed{\sum_k f(\epsilon) = \frac{V}{2\pi^2} \frac{\sqrt{2M^3}}{\hbar^3} \int_0^\infty \sqrt{\epsilon} \, d\epsilon \, f(\epsilon)} \quad \text{(78)}$$

Let us fix the number of particles to N (79)

$$\boxed{N = \sum_\epsilon n(\epsilon) = \sum_\epsilon \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} - 1} = \frac{V}{2\pi^2} \frac{\sqrt{2M^3}}{\hbar^3} \int_0^\infty \frac{\sqrt{\epsilon} \, d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}}$$

The integral certainly converges rapidly as $\epsilon \to \infty$. For $\mu < 0$ there is no singularity as $\epsilon \to 0$.

If we want to increase N at fixed T, we must increase $n(\epsilon)$, which means we must increase μ towards zero from below.

The biggest value of μ we can have is

$$\boxed{\mu_{max} = 0} \quad \text{(80)}$$

$$\Rightarrow \boxed{N_{max}(T) = \frac{V}{2\pi^2} \frac{\sqrt{2M^3}}{\hbar^3} \int_0^\infty \frac{\sqrt{\epsilon}\, d\epsilon}{e^{\beta\epsilon} - 1}} \quad \text{(81)}$$

Now scale out T by defining $\beta\epsilon = \xi$

$$\boxed{N_{max}(T) = \frac{V}{2\pi^2} \frac{\sqrt{2M^3}}{\hbar^3} (k_B T)^{3/2} \int_0^\infty \frac{\sqrt{\xi}\, d\xi}{e^{\xi} - 1}} \quad \text{(82)}$$

The integral is well-defined and finite, but the conclusion we have reached is absurd.

We seem to have found that we cannot increase the density of He^4 beyond a certain maximum density. Moreover, this maximum density goes to zero as $T \to 0$!

The wrong step is (78), (79). We can convert the sum to an integral only if the function $f(\epsilon)$ is smooth enough.

At $\mu_{max} = 0$ the occupation of the $\bar{k} = 0$ state is

$$\frac{1}{e^{\beta \cdot 0} - 1} = ? \qquad \text{Indeterminate.}$$

In fact, this one state can have macroscopic occupation. A finite fraction of all N particles can be in this state.

Let us call the occupation of the $\bar{k}=0$
state N_0. The rest of the states $\bar{k} \neq 0$ have
nonzero energy and their occupations are
smooth.

So at low enough temperature

$$N = N_0 + \frac{V}{2\pi^2} \sqrt{\frac{2M^3}{\hbar^3}} \left(k_B T\right)^{3/2} \int_0^\infty \frac{\sqrt{\xi} \, d\xi}{e^\xi - 1} \qquad \text{(83)}$$

This "condensation" of a macroscopic
number of particles into a single quantum
state is called   Bose-Einstein condensation.

It is related to the phenomenon of superfluidity
but is not identical.

Now let's take a brief look at the
thermodynamics of the other option, fermions.

We already know that two identical fermions
cannot occupy the same quantum state.

We can make further progress if we
assume that the particles are noninteracting

Let $|\alpha\rangle$ be the one-fermion states.

Then $n_\alpha = 0, 1$ are the only choices.

Again, let's assume there are g states at a given energy and n fermions we want to put in them.

(84)

$$\text{Number of many-fermion states} = \binom{g}{n} = \frac{g!}{n! \, (g-n)!}$$

$$\Rightarrow \boxed{S = k_B \sum_\epsilon \ln \left[\frac{(g(\epsilon))!}{(n(\epsilon))! \, (g(\epsilon) - n(\epsilon))!} \right]}$$ (85)

Put in the constraints of total energy E and total number of particles N

$$\tilde{S} = k_B \sum_\epsilon \left\{ g(\epsilon) \ln g(\epsilon) - n(\epsilon) \ln n(\epsilon) - (g(\epsilon) - n(\epsilon)) \ln(g(\epsilon) - n(\epsilon)) \right\}$$

$$+ \lambda \left[E - \sum_\epsilon n(\epsilon) \, \epsilon \right] + \gamma \left[N - \sum_\epsilon n(\epsilon) \right]$$ (86)

Extremize

$$\frac{d\tilde{S}}{dn(\epsilon)} = -\ln n(\epsilon) + \ln(g(\epsilon) - n(\epsilon)) - \frac{\lambda \epsilon + \gamma}{k_B} = 0$$

$$\Rightarrow \quad \frac{n(\epsilon)}{g(\epsilon) - n(\epsilon)} = e^{-\frac{1}{k_B}(\lambda \epsilon + \gamma)}$$

$$\lambda = \frac{1}{T}$$

$$\gamma = -\mu/T$$

$$\Rightarrow \quad \boxed{n(\epsilon) = \frac{g(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1}}$$ (87)

Fermi-Dirac distribution

Because of the +1 in the denominator μ can now be any real number.

As $T \to 0$ we can see that if $\epsilon < \mu$ $n(\epsilon) = g(\epsilon)$ whereas if $\epsilon > \mu$ $n(\epsilon) = 0$

The $T \to 0$ limit of μ is known as the Fermi energy of a system of identical fermions.