

Quantum Ideal Gas

Particle in a Box in QM

Let's start with the Schrodinger Equation $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$

where \hat{H} is given for a 3D box by:

$$\hat{H} = \sum_{i=x,y,z} \frac{\hat{p}_i^2}{2m} + V(x, y, z) \quad \text{where } V(x, y, z) \text{ is a time independent potential.}$$

$$p_x = -i\hbar \frac{\partial}{\partial x}, \quad p_y = -i\hbar \frac{\partial}{\partial y}, \quad p_z = -i\hbar \frac{\partial}{\partial z} \quad \text{so we write SE as:}$$

$$i\hbar \frac{\partial}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x, y, z) \Psi$$

for the box, the potential is:

$$V = 0 \text{ for } 0 < x, y, z < L_x, L_y, L_z$$

$$V = \infty \text{ for } x, y, z > L_x, L_y, L_z \text{ or } x, y, z < 0$$

So on the wall, $\Psi = 0$, and we can solve the time-independent SE, with $u_{\text{standing}}(x, y, z)$, being the spatial part of $\Psi(x, y, z, t)$. Solutions in terms of standing waves are:

$$u_{\text{standing}} = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

with eigenvalues:

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left[\left(\frac{n_x}{L_x} \right)^2 + \left(\frac{n_y}{L_y} \right)^2 + \left(\frac{n_z}{L_z} \right)^2 \right] = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$\text{where } n_x, n_y, n_z = 1, 2, 3, 4, \dots, \infty$$

$E_{n_x, n_y, n_z} \geq E_{1, 1, 1} = E_{\min}$ the ground state of the system.

We want to calculate the number of microstates for the system. For large values of n_x, n_y, n_z , the sum over the microstates (distinct n_x, n_y, n_z) can be approximated by integral on $dn_x dn_y dn_z$.

for each choice of $(\lambda_x, \lambda_y, \lambda_z)$ we have a g_s number of quantum states, g_s is the number of "spin degrees of freedom" or "spin degeneracy":

$$g_s = 2S + 1$$

where S is spin of the particle. The infinitesimal number of 1-particle quantum states (i.e. microstates for this system) are:

$$dW = g_s d\lambda_x d\lambda_y d\lambda_z$$

using $\lambda_i = \frac{L_i p_i}{\hbar \pi}$ from the previous page: $d\lambda_i = \frac{L_i dp_i}{\pi \hbar}$

$$\text{Noting } \frac{1}{(\pi \hbar)^3} = \frac{8}{h^3}: dW = 8g_s \frac{V dp_x dp_y dp_z}{h^3} \quad (*)$$

QM requires a discretised phase space, so we use $(p, p+dp)$ and we integrate over only positive p_i since $\lambda_i > 0$.

Switching to polar coordinates: (p, θ, ϕ)

$$dW(p, p+dp) = \frac{g_s V p^2}{2\pi^2 h^3} dp = g_p(p) dp$$

$$\text{or in terms of wave number } k = p/\hbar: g_k(k) = g_s \frac{V k^2}{2\pi^2}$$

1-Particle Partition Function

The 1-particle partition function is given by: $Z_{1p} = \int e^{-\beta \epsilon} dW$

$$\text{where } \epsilon = \frac{\sum_{i=x,y,z} p_i^2}{2M}$$

Using $(*)$ for dW and noting limits \int can be replaced with $\frac{1}{2} \int_{-\infty}^{\infty}$:

$$Z_{1p} = \frac{g_s V}{\hbar^3} \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\beta \frac{p_i^2}{2m}} dp_i \right)^3 = \frac{g_s V}{\hbar^3} \left(\frac{M k_B T}{2\pi} \right)^{3/2} = g_s \frac{V}{\lambda_{th}^3}$$

Note we used the De Broglie thermal wavelength.

Identical Particles

We will now consider the situation in which the gas has many identical particles. Let's start with $N=2$ and then extend to $N \rightarrow$ huge number.

In QM, identical particles are indistinguishable, so just as in our semiclassical formulation, we will have to include a $\frac{1}{N!}$ factor when counting microstates.

The indistinguishability has other consequences. Let's define an exchange operator \hat{P}_{12} :

$$\hat{P}_{12} \Psi(1,2) = \Psi(2,1) \quad \text{where } 1 \equiv r_1; s_{1z} \quad 2 \equiv r_2; s_{2z}$$

1 and 2 are our labels which are attached to the position (r) and spin (S_z) of the particle in question.

The eigenvalues of \hat{P}_{12} are: $\lambda^2 = 1$ so $\lambda = \pm 1$

The wave functions with $\lambda = 1$ are symmetric under the operation of the exchange operator. The wave functions with $\lambda = -1$ are antisymmetric under the operation of the exchange operator.

The symmetric wave function for a 2 particle system is:

$$\Psi_+(1,2) = \frac{u_a(1)u_b(2) + u_a(2)u_b(1)}{\sqrt{2}}$$

The antisymmetric wave function for a 2 particle system is:

$$\Psi_-(1,2) = \frac{u_a(1)u_b(2) - u_a(2)u_b(1)}{\sqrt{2}}$$

where u_a u_b are single particle wave functions.

Particles with symmetric wave functions are Bosons

Particles with antisymmetric wave functions are Fermions

This is an important difference between Bosons and Fermions.
a and b refer to the choice of quantum numbers n_x, n_y, n_z and s_z .

We see Ψ vanishes if $a=b$. This is a mathematical statement of Pauli's exclusion principle. 2 Fermions cannot share the same quantum numbers.

But Ψ_r does not vanish if $a=b$ so two bosons can share the same quantum numbers.

So we will see differences between a gas of bosons and a gas of fermions

To find allowed energies of an ideal gas, we only need to know allowed energies of a single particle in a box:

$$E_{n_x, n_y, n_z} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

The n_k values give the no. particles in each single particle quantum state k . Each k corresponds to a distinct choice of quantum numbers n_x, n_y, n_z .

$n_k = 0, 1, \dots \infty$ for bosons (since any number of particles can be in a quantum state)

$n_k = 0, 1$ for fermions (since max 1 particle can be in a particular quantum state)

Total number of particles is $N = \sum_k n_k$

The energy of a N particle system is:

$$E = \sum_k E_k = \sum_k n_k E_k$$

$E_k = n_k E_k$ is the energy in the single particle quantum state k^3

Spin Statistics Theorem

Bosons have integer spin $S=0, 1, 2 \dots$ in units of $\frac{1}{2}$

Fermions have half-integer spin: $S=\frac{1}{2}, \frac{3}{2} \dots$ in units of $\frac{1}{2}$

e.g. an electron has $S=\frac{1}{2}$ so it is a fermion.

a photon has $S=1$ so it is a boson.

NB:// although $g_s = 2S+1$, photons are a special case and have $g_s = 2$

The Higgs-Boson is another special case with $S=0$.

Quantum Statistics

The partition function of a quantum ideal gas in the canonical ensemble is:

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}} = \sum_{\{\lambda_1, \lambda_2, \dots\}} e^{-\beta \sum \lambda_k E_k}, \quad \sum_k \lambda_k = N$$

In the canonical ensemble, N is fixed. This makes calculation of Z very difficult so we won't do it here. But it is possible to proceed in 2 ways:

- calculate grand partition function Z_g with no. particles constant N
- calculate Z_g in a specific single particle quantum state k

The 2nd option is simplest, and gives Z_g in specific 1-particle state k as:

$$Z_k = \sum_{\alpha k} e^{\beta N_k (\mu - E_k)}$$

Here, k has a specific value
and sum is over different values of λ_k

The grand potential is: $\Phi_g(E_k = \lambda_k E_k) = -k_B T \ln Z_k$

The mean values of occupation numbers is:

$$\langle \lambda_k \rangle = -\frac{\partial \Phi_g(E_k)}{\partial \mu} = k_B T \frac{\partial \ln Z_k}{\partial \mu}$$

Fermi - Dirac Statistics

For a gas composed entirely of the same species of fermion, we have only 2 possibilities for occupation numbers

$$n_k = 0, 1$$

so grand potential is:

$$\Phi_g = -k_B T \ln \sum_{\substack{n_k \\ = 0, 1}} e^{\beta(\mu - E_k) n_k} = -k_B T \ln [1 + e^{\beta(\mu - E_k)}]$$

We can then calculate Fermi-Dirac distribution:

$$\langle n_k \rangle = -\frac{\partial \Phi_g(E_k)}{\partial \mu} = k_B T \beta \frac{e^{\beta(\mu - E_k)}}{1 + e^{\beta(\mu - E_k)}} = \frac{1}{e^{\beta(E_k - \mu)} + 1}$$

In the continuous limit, we replace discrete energies E_k with a continuous energy E :

$$\langle n_k \rangle = \frac{1}{e^{\beta(E_k - \mu)} + 1} \rightarrow f_{FD}(E) = \frac{1}{e^{\beta(E - \mu)} + 1}$$

This is the Fermi-Dirac Distribution.

Notice $0 \leq \langle n_k \rangle \leq 1$ as required.

Bose-Einstein Statistics

for a gas composed entirely of the same species of boson, we have :

$$n_c = 0, 1, 2, \dots \infty$$

so grand potential is:

$$\Phi_G = -k_B T \sum_{E_k=0,1,2,\dots\infty} e^{\beta(\mu-E_k)} n_k$$

We need this to converge for all E_k and in particular E_{\min}

This is an infinite series of the form:

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r} \quad (r < 1) \quad \text{where for us } r = e^{\beta(\mu-E_k)}$$

For convergence, we require $e^{\beta(\mu-E_k)} < 1$ so $\mu < E_{\min} \approx 0$

$$\Phi_G(E_k) = -k_B T \ln \left[\frac{1}{1-e^{\beta(\mu-E_k)}} \right] = k_B T \ln (1-e^{\beta(\mu-E_k)})$$

We can calculate the Bose-Einstein distribution:

$$\langle n_c \rangle = -\frac{\partial \Phi_G(E_k)}{\partial \mu} = k_B T \beta \frac{e^{\beta(\mu-E_k)}}{1-e^{\beta(\mu-E_k)}} = \frac{1}{e^{\beta(E_k-\mu)}-1}$$

In the continuous limit $E_k \rightarrow \varepsilon$ so:

$$f_{BE}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$

This is the
Bose-Einstein Distribution.

The Classical Limit

Classically, there is no difference between fermions and bosons since spin is a quantum concept.

So we obtain the classical limit when the distribution for fermions and bosons becomes equal:

$$f_{FD} = \frac{1}{e^{\beta(E-\mu)} + 1} \quad f_{BE} = \frac{1}{e^{\beta(E-\mu)} - 1} \quad \begin{matrix} \text{This occurs when} \\ \text{the } -1 \text{ term becomes} \\ \text{negligible} \end{matrix}$$

$$\text{i.e. } e^{\beta(E-\mu)} \gg 1 \quad \text{so} \quad \langle n_k \rangle \approx e^{-\beta(E-\mu)} \ll 1$$

This condition has to be satisfied for all E but $E=0$ in particular.

$$\therefore e^{-\beta\mu} \gg 1 \quad \text{for the classical limit}$$

using $\mu = k_B T \ln(\frac{N}{n} \lambda_{th}^3)$ from an earlier chapter:

$$e^{-\beta\mu} = \frac{V}{N} \frac{1}{\lambda_{th}^3} \gg 1 \quad \therefore \left(\frac{V}{N}\right)^{1/3} = \bar{\lambda} \gg \lambda_{th}$$

where we define $\bar{\lambda} = \left(\frac{V}{N}\right)^{1/3}$ as the mean distance among particles.

We can see $\bar{\lambda} \gg \lambda_{th}$ is not satisfied if T is lowered and $\frac{N}{V}$ is fixed, since $\lambda_{th} \propto T^{-1/2}$ and thus λ_{th} increases as T decreases.

Letting $n = \frac{N}{V}$ and writing explicitly $\lambda_{th} = \frac{\hbar}{\sqrt{2\pi m k}}$

and putting g_s into the definition of λ_{th} , we obtain a

limit on the temperature:

$$T \gg \frac{2\pi\hbar^2 N^{4/3}}{g_s^{2/3} m k_B}$$

so at high temperatures, quantum predictions and classical predictions agree.

At low temperatures, the predictions differ.

Calculation of the Thermodynamic Quantities

We will now study the behaviour of a quantum ideal gas in the limit of low temperature.

The number of particles for a gas of identical particles is given by:

$$N \approx \langle N \rangle = \sum_k \langle n_k \rangle = \sum_k \frac{1}{e^{\beta(E_k - \mu)} + 1}$$

↑ +1 for fermions
 -1 for bosons

In the continuous limit, we approximate the sum with an integral over continuous k :

$$N \approx \langle N \rangle = \sum_k \langle n_k \rangle = g_s V \int \frac{1}{e^{\beta(E - \mu)} + 1} \frac{d^3 p}{h^3}$$

Switching to spherical coordinates and integrating over one octant of Θ and ϕ :

$$n = \frac{N}{V} = \frac{g_s}{2\pi^2 h^3} \int_0^\infty \frac{p^2}{e^{\beta(E(p) - \mu)} + 1} dp \quad \text{where } \mu = \mu(N, T)$$

From this, we can compute as normal and even derive the chemical potential as a function of N and T

In general it is not possible to find an explicit expression for $\mu(N, T)$

Non-Relativistic Regime

So now we have an expression for n . Let's recast it in terms of energy, with $E = p^2/2m$

$$\text{We first write } p^2 dp = \frac{m 2m E dE}{\sqrt{2mE}} = m \sqrt{2mE} dE$$

$$\text{so } n = \frac{2g_s}{\sqrt{\pi} h^3} \left(\frac{m}{2\pi}\right)^{3/2} \int_0^\infty \frac{E^{1/2}}{e^{\beta(E(p) - \mu)} + 1} dE$$

$$so \quad \lambda = \frac{2g_s}{\sqrt{\pi} \hbar^3} \left(\frac{m}{2\pi} \right)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta(\epsilon - \mu)} \pm 1} d\epsilon$$

changing from ϵ to $x = \beta\epsilon$ and using the expression for the de Broglie thermal wavelength (but with a modification to include g_s):

$$\lambda = \frac{2}{\sqrt{\pi}} \frac{1}{\lambda_{th}^3} \int_0^\infty \frac{x^{1/2}}{e^{x - \beta\mu} \pm 1} dx$$

We will later show in the classical limit where $e^{-\beta\mu} \gg 1$:

$$\lambda \lambda_{th}^3 = e^{\beta\mu}$$

We can now derive the other thermodynamic quantities, such as internal energy and grand potential:

$$U = \sum_k \langle n_k \rangle \epsilon_k \rightarrow U = k_B T \frac{2}{\sqrt{\pi}} \frac{V}{\lambda_{th}^3} \int_0^\infty \frac{x^{3/2}}{e^{x - \beta\mu} \pm 1} dx$$

We obtain this from our previous expression for $\lambda (= N)$

In the classical limit, we recover the familiar $U = \frac{3}{2} N k_B T$

We previously found $\Phi_g(E_k) = \mp k_B T \ln [1 \pm e^{\beta(\mu - \epsilon_k)}]$ for a single quantum state k . Summing over all k , one has the grand potential:

$$\Phi_g = \sum_k \Phi_g(E_k) = \mp k_B T \sum_k \ln [1 \pm e^{\beta(\mu - \epsilon_k)}]$$

In the continuous limit, this becomes:

$$\Phi_g = \mp k_B T \frac{2}{\sqrt{\pi}} \frac{V}{\lambda_{th}^3} \int_0^\infty x^{1/2} \ln [1 \pm e^{\beta\mu - x}] dx$$

If we integrate this by parts:

$$\Phi_0 = \pm \frac{2}{3} \int_0^\infty \frac{x^{3/2}}{e^{x-\beta E} \pm 1} dx$$

so $\Phi_0 = -\frac{2}{3}U$ and so in the classical limit $\Phi_0 = -Nk_B T$
 we previously found $\Phi_0 = -PV$ so:

$$PV = Nk_B T$$

The familiar result.

Fermi Degenerate Gas : The Degenerate Limit

A gas is said to be degenerate when it starts to behave differently to a classical gas.

Let's start from the FD distribution function:

$$f_{FD}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$$

In the degenerate limit $T \rightarrow 0$, $\beta = k_B T \rightarrow 0$ so $\beta = \frac{1}{T} \rightarrow \infty$

let's define the Fermi Energy $\varepsilon_F = \mu(T=0)$

Right now the only things we know about ε_F are:

- if $\varepsilon > \varepsilon_F$ then $f_{FD}(\varepsilon) \rightarrow 0$ as $T \rightarrow 0$
- if $\varepsilon < \varepsilon_F$ then $f_{FD}(\varepsilon) \rightarrow 1$ as $T \rightarrow 0$

The mathematically compact way to describe this behaviour is with the Heaviside step function:

$$\Theta(x) = \begin{cases} 0 & \text{if } x < 0 \\ 1 & \text{if } x > 0 \end{cases}$$

so we say:

$$f_{FD}(\varepsilon) \xrightarrow{T \rightarrow 0} \Theta(\varepsilon_F - \varepsilon)$$

$$f_{FD} \xrightarrow{T \rightarrow 0} \Theta(\epsilon_F - \epsilon)$$

so there are no particles with an energy above ϵ_F at $T=0$
and the distribution is continuous up to $\epsilon \leq \epsilon_F$

The physical interpretation of this is as follows:

when the temperature falls, particles want to populate low energy single particle quantum states. But only one particle can be in each of these states (since they are fermions). So each particle populates the next available state up to the last particle populating a state with the fermi energy ϵ_F .

The fermi energy is energy of the most energetic fermion at $T=0$ and can be determined in terms of number density n as follows:

$$N(T=0) = \int_{\epsilon \leq \epsilon_F} \frac{8g_s V d^3 p}{h^3} = 4\pi \int_0^{p_F} \frac{g_s V p^2}{h^3} dp$$

where we used equation for $N \propto \langle N \rangle$ and stated $e^{\beta(\epsilon-\mu)} \rightarrow 0$ for $T \rightarrow 0$
we introduced Fermi momentum defined as $p_F = \sqrt{2M \epsilon_F}$ since $\epsilon \leq \epsilon_F$
and integrated over all octant in spherical coordinates.

Solving the integral, we find:

$$N(T=0) = \frac{g_s}{2\pi^2 h^3} \frac{p_F^3}{3} \Rightarrow p_F = \left(\frac{6\pi^2 n}{g_s} \right)^{1/3}$$

Fermi energy is given by $\epsilon_F = \frac{p_F^2}{2M} = \underline{\underline{\frac{\pi^2}{2M} \left(\frac{6\pi^2 n}{g_s} \right)^{2/3}}}$

So we have found the fermi energy, the
energy of the most energetic fermion at $T=0$

We can also show:

$$U(T=0) = \frac{3}{5} N E_F$$

This is in contrast to a classical gas which would have $U=0$ at $T=0$.

We define Fermi temperature as:

$$T_F = E_F / k_B$$

and it can be shown:

$$U(T) \approx \frac{3}{5} N E_F + N k_B \frac{T^2}{T_F} \quad \text{at any temperature } T$$

we can thus find Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$C_V \approx 2 N k_B \frac{T}{T_F}$$

Clearly $C_V \rightarrow 0$ as $T \rightarrow 0$, respecting 3rd law of TD.

Bose-Einstein Condensation

Let's now consider a gas of identical bosons in the limit $T \rightarrow 0$.

We previously stated the density of particles:

$$n = \frac{2}{\pi^{1/2}} \frac{1}{2\pi^2} \int_0^\infty \frac{x^{1/2}}{e^{x-\beta E} - 1} dx \quad \text{for bosons}$$

If we define "fugacity": $z = e^{\beta \mu}$

then we recast n as:

$$n = \text{Li}_{3/2}(z) \quad \text{where Li}_{3/2}(z) \text{ is a polylogarithm function}$$

$$\text{Li}_{3/2}(z) = \frac{2}{\pi^{1/2}} \int_0^\infty \frac{x^{1/2}}{z^{-1} e^x - 1} dx$$

for Bose-Einstein statistics, we showed $\mu < E_{\text{min}} \sim 0$ so μ is negative so $0 \leq z < 1$.

In the classical limit $e^{-\beta \mu} \gg 1$ so $z \ll 1$ so: $\text{Li}_{3/2}(z) \xrightarrow{z \rightarrow 0} z$

so we get $N\lambda_{\text{th}}^3 = \text{Li}_{3/2}(z) = z$ in the classical limit.

Now consider the opposite. so the high temperature limit where $z \rightarrow 1$ from below.

$$\text{Li}_{3/2}(z=1) = \frac{2}{\pi^2} I_B(\frac{1}{2})$$

$$\text{where } I_B(1/2) \text{ is the Bose integral: } I_B(n) = \int_0^\infty \frac{x^n}{e^{x-1}} dx \\ = \zeta(n+1) \Gamma(n+1)$$

$$\text{Here } \text{Li}_{3/2}(z=1) = \zeta(3/2)$$

↑ The Riemann-zeta function

This tends to a maximum and finite value as $z \rightarrow 1$

However, the LHS ($N\lambda_{\text{th}}^3$) does not have a maximum, since

N can be arbitrarily large, and $\lambda_{\text{th}}^3 \propto T^{-3/2}$ so increased for low T . So for a fixed N , there is a temperature T_c below which $N\lambda_{\text{th}}^3 = \text{Li}_{3/2}(z)$ has no solution.

$$N\lambda_{\text{th}}^3(T=T_c) = \zeta(3/2)$$

$$\therefore T_c = \frac{2\pi\hbar^2}{k_B N} \underbrace{\left(\frac{N}{g_s \zeta(3/2)}\right)^{4/3}}$$

T_c is the condensation temperature

So why does our approach break at $T < T_c$? The reason is because, in order to make it continuous, we replaced a sum over occupation numbers with an integral:

$$NN\langle N \rangle = \sum \frac{1}{e^{\beta(E-\mu)} - 1} \rightarrow \langle N \rangle = g_s V \int \frac{1}{e^{\beta(E-\mu)} - 1} \frac{d^3 p}{h^3}$$

This approximation neglects the contribution of particles with 0 Energy, i.e in the ground state. This is because the integrand vanishes when $E=0$. The approximation is still good for fermi gases since in each quantum state, there is one particle (so max 1 particle with 0 energy). But this is not the case for Bosons. So what do we do?

$$\text{At } T \leq T_c : N = \sum_i \langle n_i \rangle = N_0 + N_1$$

For N_1 and $T \leq T_c$:

$$n_1 \lambda_{\text{th}}^3 = L_{3/2}(z) \quad (*)$$

where N_1 is no. particles in all states except ground states.

N_0 is no. particles in ground states

for $T < T_c$, there is no integral for N_0 . so do $\frac{(*)}{n \lambda_{\text{th}}^3}$:

$$\frac{n_1}{n} = \frac{\lambda_{\text{th}}^3(T_c)}{\lambda_{\text{th}}^3(T)} = \left(\frac{T}{T_c}\right)^{3/2}$$

$$\text{so the number density for ground state is } \frac{n_0}{n} = \frac{n - n_1}{n} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

so as $T \rightarrow 0$ we have $n_0 \rightarrow n$, i.e. The number of particles in ground state increases until they are all in ground state.

This scenario is called Bose-Einstein Condensation.

It is a new form of matter!

Finally, we can calculate heat capacity for $T \leq T_c$.

This is found to be:

$$C_V = \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} N k_B \left(\frac{T}{T_c}\right)^{3/2}$$