Lecture Notes - Week 10 (Lectures 27-29) [1]

Ideal Quantum Gases (continued)

Recall that we have defined the average particle number

$$N_\sigma = \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle_\sigma = \sum_{\mathbf{k}} \frac{1}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} - \sigma} , \tag{4.4.10}$$

and similarly the average energy

$$E_\sigma = \sum_{\mathbf{k}} \mathcal{E}(\mathbf{k}) \langle n_{\mathbf{k}} \rangle_\sigma = \sum_{\mathbf{k}} \frac{\mathcal{E}(\mathbf{k})}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} - \sigma} , \tag{4.4.11}$$

Quantum particles of spin S have $2S+1$ spin states characterised by spin quantum number $m_S = -S, -S+1, \ldots, S-1, S$. In the abscence of magnetic fields all the spin states have the same energy giving rise to a spin degeneracy factor $\gamma = 2S+1$ which we must multiply all our averages by.

4.4.2 Characterising single particle states (particle in a box)

Let us consider a particle which can move freely (i.e. there is no potential) apart from the fact that it is 'confined' to a cubic box of volume $V = L^3$ defined by the periodic boundary conditions [2]

$$\begin{array}{rcl} (x+L, y, z) & \rightarrow & (x, y, z) \\ (x, y+L, z) & \rightarrow & (x, y, z) \\ (x, y, z+L) & \rightarrow & (x, y, z) \end{array} \tag{4.4.12}$$

We can construct energy basis of the single particle as follows :

An energy eigenstate $|\psi_n\rangle$ (unit vector in Hilbert space) will satisfy the time-independent Schrödingier equation :

$$\hat{\mathcal{H}} |\psi_n\rangle = E_n |\psi_n\rangle \quad , \tag{4.4.13}$$

with an associated wave function $\psi_n(\mathbf{r}) = \langle \mathbf{r} | \psi_n \rangle$. In that eigenstate, the probability of finding the particle at position $\mathbf{r}$ is

$$|\psi_n(\mathbf{r})|^2 = |\langle \mathbf{r} | \psi_n \rangle|^2 \tag{4.4.14}$$

Noting that $\hat{\mathcal{H}} = \hat{\mathbf{p}}^2/2m$ and the momentum operator, $\hat{\mathbf{p}} = \frac{\hbar}{i}\nabla$, the Schrödingier equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n(\mathbf{r}) = E_n \psi(\mathbf{r}) \tag{4.4.15}$$

[2] Periodic boundary conditions here (and in most textbooks) have been chosen for calculational convenience. A qualitatively similar but harder calculation can be done for a box with hard reflecting walls. It is expected that in thermodynamic limit of course that the results won't depend on the boundary conditions.

Applying the periodic boundary conditions we obtain the energy eigenstates

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \quad ; \quad \mathbf{k} = \frac{2\pi}{L}(j,l,n) \quad ; \quad E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \quad , \quad k = |\mathbf{k}| \quad , \tag{4.4.16}$$

where $j, l, n \in \mathbb{Z}$ (integers). So we now have a set of energy eigenstates characterised by the quantum numbers j, l, n and with quantised energy levels[3].

Noting that

$$\hat{\mathbf{p}}\, \psi_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\, \psi_{\mathbf{k}}(\mathbf{r}) \quad \Rightarrow \quad \psi_{\mathbf{k}} \rightarrow |\mathbf{k}\rangle \quad , \tag{4.4.17}$$

we can identify our plane-wave states $|\mathbf{k}\rangle$ with $\psi_{\mathbf{k}}$, where $\mathbf{k} = \frac{2\pi}{L}(j,l,n)$ and $\sum_{\mathbf{k}} \equiv \sum_{j,l,n}$

In the limit of large L, the spacing between the energy levels becomes very small and the sum over the integers is well approximated by an integral.

We get the correct measure by noting that in a volume element $d^3k = dk_x dk_y dk_z$, the number of modes is

$$\frac{dk_x}{2\pi/L}\frac{dk_y}{2\pi/L}\frac{dk_y}{2\pi/L} = \frac{L^3}{(2\pi)^3} d^3k = \frac{V}{(2\pi)^3} d^3k \quad . \tag{4.4.18}$$

Hence taking the thermodynamic limit, $L \to \infty$, $\quad \sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k.$

4.4.3 Thermodynamic quantities

We can define particle density $n_\sigma = N_\sigma/V$, energy density $\varepsilon_\sigma = E_\sigma/V$, and pressure $P_\sigma = k_B T \ln \mathcal{Z}_\sigma/V$. Changing variable to $x = \beta\hbar^2 k^2/2m$, we obtain from the definitions for the mean particle number, N_σ, mean energy, E_σ and $\ln \mathcal{Z}_\sigma$, the following expressions (note that we have multiplied by the spin degeneracy factor, γ) :

$$n_\sigma = \frac{\gamma}{\lambda_T^3}\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx\; x^{1/2}}{z^{-1}e^x - \sigma} \tag{4.4.19}$$

$$\beta\varepsilon_\sigma = \frac{\gamma}{\lambda_T^3}\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx\; x^{3/2}}{z^{-1}e^x - \sigma} \tag{4.4.20}$$

$$\beta P_\sigma = -\sigma\frac{\gamma}{\lambda_T^3}\frac{2}{\sqrt{\pi}} \int_0^\infty dx\; x^{1/2} \ln\left(1 - \sigma z e^{-x}\right) = \frac{\gamma}{\lambda_T^3}\frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{dx\; x^{3/2}}{z^{-1}e^x - \sigma} \tag{4.4.21}$$

(last = sign $\Leftrightarrow$ integrate by parts) where $\lambda_T = \hbar\sqrt{\frac{2\pi}{mk_BT}}$ is the thermal wavelength.

In what follows we set $\gamma = 1$ since it is typically a number of order unity which does not qualitatively change most of the results we will be obtaining. Furthermore it will make our formulas simpler!

We can define the **Bose**, $F_m^+(z) \equiv g_m(z)$ and **Fermi**, $F_m^-(z) \equiv f_m(z)$ functions

$$F_m^\sigma(z) = \frac{1}{\Gamma(m)} \int_0^\infty \frac{dx\; x^{m-1}}{z^{-1}e^x - \sigma} \, , \tag{4.4.22}$$

[3] Momentum is also quantised

where $\Gamma(m) = (m-1)!$ with $\Gamma(3/2) = 1/2! = \sqrt{\pi}/2$, $\Gamma(5/2) = 3/2! = 3\sqrt{\pi}/4$.

Then we can express

$$\begin{aligned} n_\sigma(T,\mu) &= \frac{1}{\lambda_T^3} F^\sigma_{3/2}(z) && (4.4.23) \\ \beta P_\sigma(T,\mu) &= \frac{1}{\lambda_T^3} F^\sigma_{5/2}(z) && (4.4.24) \\ \beta \varepsilon_\sigma(T,\mu) &= \frac{3}{2} \beta P_\sigma(T,\mu) && (4.4.25) \end{aligned}$$

All other thermodynamic quantities can similarly be obtained from the functions $F^\sigma_m(z)$

4.4.4 Semiclassical limit

Not examinable

Let us consider the high T, low density (μ large and negative) limit $\Rightarrow z$, small. We can turn the Fermi/Bose functions into power series in z :

$$\begin{aligned} F^\sigma_m(z) &= \frac{1}{\Gamma(m)} \int_0^\infty dx\, x^{m-1} z e^{-x} (1 - \sigma z e^{-x})^{-1} = \sum_{p=1}^\infty \sigma^{p-1} \frac{z^p}{\Gamma(m)} \int_0^\infty dx\, x^{m-1} e^{-px} \\ &= \sum_{p=1}^\infty \sigma^{p-1} \frac{z^p}{p^m} = z + \sigma \frac{z^2}{2^m} + \frac{z^3}{3^m} + \ldots && (4.4.26) \end{aligned}$$

The expression for the particle density then is given by

$$n_\sigma \lambda_T^3 = F^\sigma_{3/2}(z) = z + \sigma \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \ldots \tag{4.4.27}$$

which we can solve perturbatively in n_σ for z ($z(n) = \sum_{p=0} a_p n^p$) as follows :

1. To lowest (i.e. first : $z_{(0)} = a_1 n_\sigma + \ldots$) order

$$z_{(0)} = n_\sigma \lambda_T^3 + O(n_\sigma^2) \tag{4.4.28}$$

2. To next (i.e. second : $z_{(1)} = a_1 n_\sigma + a_2 n_\sigma^2 + \ldots$) order

$$z_{(1)} = n_\sigma \lambda_T^3 - \frac{\sigma}{2^{3/2}} z_{(0)}^2 + O(n_\sigma^3) = n_\sigma \lambda_T^3 - \frac{\sigma}{2^{3/2}} \left(n_\sigma \lambda_T^3\right)^2 + O(n_\sigma^3) \tag{4.4.29}$$

We can now substitute $z \simeq z_{(1)}$ back into the expression for the pressure :

$$\beta P_\sigma \lambda_T^3 = F^\sigma_{5/2}(z) = z + \sigma \frac{z^2}{2^{5/2}} + \ldots$$

to get,

$$\begin{aligned} \beta P_\sigma \lambda_T^3 &= z_{(1)} + \sigma \frac{z_{(0)}^2}{2^{5/2}} + O(n_\sigma^3) \\ &= n_\sigma \lambda_T^3 - \frac{\sigma}{2^{3/2}} \left(n_\sigma \lambda_T^3\right)^2 + \frac{\sigma}{2^{5/2}} \left(n_\sigma \lambda_T^3\right)^2 + O(n_\sigma^3) \\ \Rightarrow\ P_\sigma &= n_\sigma k_B T \left[1 - \frac{\sigma}{2^{5/2}} \left(n_\sigma \lambda_T^3\right) + \ldots\right] && (4.4.30) \end{aligned}$$

We see that fermions, $\sigma = -1$ are repulsive ($P \uparrow$ with $n \uparrow$) while bosons, $\sigma = +1$ are attractive ($P \downarrow$ with $n \uparrow$). It is also evident that QM effects become significant when

$$n_\sigma \geq \frac{1}{\lambda_T^3} ,$$

at **low** temperatures and **high** densities.

Quantum limit of Ideal gases

Now we will apply quantum statistics to the study the low T behaviour of many particle systems. As we will see the inclusion of quantum mechanics will lead to a number of fundamentally new phenomena which are just not present in classical systems.

We now consider separately Bose and Fermi gases in the quantum (low T, high density) limit.

4.5 Ideal Fermi gas

One of the 1st physical applications of Fermi-Dirac statistics was in the clarification of electronic (by electrons) conduction in metals. The classical electron theory of metals was developed by Drude (1900) and Lorentz (1904-5) who modelled the conduction electrons in a metal as a gas, applied Maxwell-Boltzmann statistical mechanics to the **electron gas** and hence were able to make a number of predictions for various metallic properties. There were however a number of problems with matching their theory to experiment.

1. Specific Heat: the specific heat of metals seemed to be almost entirely accounted for by lattice vibrations with no contribution from the electron gas, while their theory predicted a contribution of $\frac{3}{2}k_BT$ per electron of thermal energy (KE) $\Rightarrow$ $\frac{3}{2}k_B$ contribution to C_V.

2. Transport properties: the calculated thermal κ and electical σ conductivity were quite far from experimental data even though their ratios did satisfy the empical Wiedemann-Franz law $\kappa/(\sigma T)$ =constant, implying that whatever the corrections to the classical physics were, they were similar for both conductances.

3. Even more worrrying was the temperature dependence of the mean free path of the electrons implied by experiment could not fit any reasonable theoretical assumption.

All these problems were clarifed when Sommerfeld in a seminal 1928 paper used Fermi-Dirac statistics instead of Maxwell-Boltzmann (classical) statistics to describe the electron gas.

4.5.1 Low Temperature behaviour

We can explain the first point using non-interacting fermions but the other two require analysis of interacting fermions which we are beyond the scope of this course.

Consider a non-interacting fermion gas with fermi occupation number at

$$\langle n_{\mathbf{k}} \rangle_- = \frac{1}{e^{\beta(\mathcal{E}(\mathbf{k})-\mu)}+1}\ , \tag{4.5.1}$$

as $T \to 0 \quad (\beta \to \infty)$ which becomes

$$\langle n_{\mathbf{k}} \rangle_- = \begin{cases} 1\ , \text{ if} & \mathcal{E}(\mathbf{k}) < \mu \\ 0 & \text{otherwise} \end{cases} \tag{4.5.2}$$

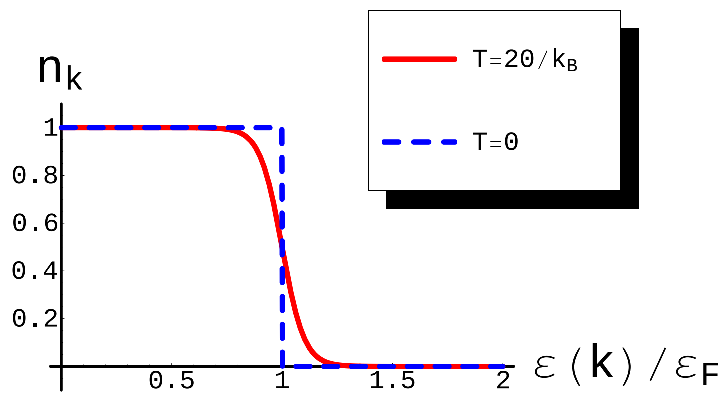

Figure 1: The occupation number of fermi-states.

The value of $\mu(T=0) = \mathcal{E}_F$ is called the **Fermi energy** and all 1-particle states of energy less that $\mathcal{E}_F$ are occupied forming the **Fermi sea**. For the ideal gas this also defines the **Fermi wavevector**, k_F by $\mathcal{E}_F = \hbar^2 k_F^2/2m$.

We can obtain the value of $\mathcal{E}_F$ (k_F) from the fact that the total number of particles

$$\begin{aligned} N &= \sum_{|\mathbf{k}|<k_F} 1 = 1 \times V \int_{k<k_F} \frac{d^3k}{(2\pi)^3} = V \frac{k_F^3}{6\pi^2} \\ \Rightarrow k_F &= \left(6\pi^2 n\right)^{1/3}\ ,\ \mathcal{E}_F = \frac{\hbar^2}{2m}\left(6\pi^2 n\right)^{2/3}\ ,\ \text{where}\ \ n = N/V \end{aligned} \tag{4.5.3}$$

Note that our ideal quantum fermi gas has a unique state at $T=0$, since once the 1-particle momenta are specified (all $\mathbf{k}$ with $k < k_F$) , there is **only** 1 antisymmetrized state: $\Omega = 1 \Rightarrow S(T=0) = k_b \ln \Omega = 0$ and the system satisfies the 3rd Law. This is to be contrasted with the classical ideal gas which has a large number of states $\Omega \propto V^N/N!$ at $T=0$.

4.5.2 Sommerfeld expansion

Not examinable

To see how the fermi gas behaves at low T we "expand" about the ground-state which implies studying $f_m(z)$ for large z. After integration by parts (note $x = \beta\mathcal{E}(k)$),

$$f_m(z) = -\frac{1}{\Gamma(m+1)}\int_0^\infty dx\; x^m \frac{d}{dx}\left(\frac{1}{z^{-1}e^x+1}\right) = -\frac{1}{\Gamma(m+1)}\int_0^\infty dx\; x^m \frac{d}{dx}\langle n_{\mathbf{k}}\rangle_-$$

Since the occupation number changes abruptly from 1 to 0 at $\mathcal{E}_F$, then its derivative will be sharply peaked at that point and we can expand about the peak by setting $x = \ln z + t$

$$f_m(z) = -\frac{1}{\Gamma(m+1)}\int_{-\ln z}^\infty dt\;(\ln z + t)^m \frac{d}{dt}\left(\frac{1}{e^t+1}\right) \simeq -\frac{1}{\Gamma(m+1)}\int_{-\infty}^\infty dt\;(\ln z + t)^m \frac{d}{dt}\left(\frac{1}{e^t+1}\right)$$

where in the last approx. equality we used the fact that the strong peak of the derivative around the fermi energy, implies that most of the contribution from the integral is around $t = 0$ and we can safely set the lower limit of the integral $-\ln z \to -\infty$.

Therefore

$$\begin{aligned} f_m(z) &= -\frac{(\ln z)^m}{\Gamma(m+1)}\int_{-\infty}^\infty dt \sum_{p=0}^\infty {}^mC_p\; t^p\;(\ln z)^{-p}\frac{d}{dt}\left(\frac{1}{e^t+1}\right) \\ &= -\frac{(\ln z)^m}{m!}\sum_{p=0}^\infty \frac{m!}{p!(m-p)!}(\ln z)^{-p}\int_{-\infty}^\infty dt\; t^p \frac{d}{dt}\left(\frac{1}{e^t+1}\right) \end{aligned} \tag{4.5.4}$$

Now from the symmetry of the integrand under $t \to -t$ and integration by parts

$$\frac{1}{p!}\int_{-\infty}^\infty dt\; t^p \frac{d}{dt}\left(\frac{1}{e^t+1}\right) = \begin{cases} 0\;, & p \text{ odd} \\ \dfrac{2}{(p-1)!}\displaystyle\int_0^\infty dt\; t^{p-1}\frac{1}{e^t+1} = 2f_p(1)\;, & p \text{ even} \end{cases} \tag{4.5.5}$$

and

$$\lim_{z\to\infty} f_m(z) = (\ln z)^m \sum_{p=0;\text{even}}^\infty \frac{2f_p(1)}{(m-p)!}(\ln z)^{-p}\;. \tag{4.5.6}$$

This asymptotic expansion is called the **Sommerfeld expansion**.

We can look at the particle density in this high density/low T limit perturbatively :

$$n\lambda_T^3 = f_{3/2}(z) = \frac{(\ln z)^{3/2}}{\Gamma(5/2)}\left[1 + \frac{\pi^2}{6}\cdot\frac{3}{2}\cdot\frac{1}{2}\,(\ln z)^{-2} + \dots\right]\;, \tag{4.5.7}$$

To lowest order :

$$\ln z_{(0)} = \left(\frac{3\sqrt{\pi}}{4}\lambda_T^3 n\right)^{2/3} = \beta\mathcal{E}_F \tag{4.5.8}$$

in agreement with the $T = 0$ fermi sea argument.

Plugging in the lowest order term to obtain the first order correction

$$\begin{aligned} \ln z_{(1)} &= \left[\left(\frac{3\sqrt{\pi}}{4}\lambda_T^3 n\right)\left(1 + \frac{\pi^2}{8}\,(\ln z_{(0)})^{-2} + \dots\right)^{-1}\right]^{2/3} \\ &= \beta\mathcal{E}_F\left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\mathcal{E}_F}\right) + \dots\right) \end{aligned} \tag{4.5.9}$$

There is a dimensionless parameter $k_B T/\mathcal{E}_F$ and we see that as T is varied we go from $\mu = k_B T \ln z > 0$ at low T to $\mu < 0$ (classical) at high T and the sign change occurs at $T \sim T_F \equiv \mathcal{E}_F/k_B$.

The low-T expansion for the energy density is

$$\begin{aligned}
\beta\varepsilon &= \frac{3}{2}\frac{1}{\lambda_T^3} f_{5/2}(z) = \frac{3}{2\lambda_T^3}\frac{(\ln z)^{5/2}}{\Gamma(7/2)}\left[1 + \frac{\pi^2}{6}\cdot\frac{5}{2}\cdot\frac{3}{2}(\ln z)^{-2} + \ldots\right] \\
&= \frac{3}{2\lambda_T^3}\frac{8(\beta\mathcal{E}_F)^{5/2}}{15\sqrt{\pi}}\left(1 - \frac{5}{2}\cdot\frac{\pi^2}{12}(\beta\mathcal{E}_F)^{-2} + \ldots\right)\left(1 + \frac{5\pi^2}{8}(\beta\mathcal{E}_F)^{-2} + \ldots\right) \\
&= \frac{3}{5}\beta\mathcal{E}_F n\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \ldots\right] \qquad (4.5.10)
\end{aligned}$$

Therefore since $\varepsilon = E/V$, $n = N/V$

$$C_V = \frac{dE}{dT} = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F}\right) \qquad (4.5.11)$$

This linear scaling of heat capacity as $T \to 0$ is true for interacting gases as well. It can be explained a simple argument as follows : since the occupation of 1-particle levels is close to a step for $T \ll T_F$, only particles $\sim k_B T$ from the Fermi energy can be excited above it. This is necessarily a small fraction, $T/T_F \ll 1$ of the total number of fermions. Each excited fermion gains energy $\sim k_B T$ leading to internal energy $E \sim N k_B T (T/T_F) \Rightarrow C_V \sim N k_B T/T_F$, a vanishingly small contribution to the specific heat.

We can also calculate the pressure

$$P = P_F\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \ldots\right] \qquad (4.5.12)$$

where $P_F = \frac{2}{5} n\mathcal{E}_F$ is the **fermi pressure** which unlike the classical gas is non-zero at $T = 0$. This repulsion between fermions (due to the exclusion principle) is the fundamental reason for the stability of matter.

4.6 Ideal Bose gas and Bose-Einstein condensation

The average Bose occupation number is $\langle n_{\mathbf{k}}\rangle_+ = \dfrac{1}{e^{\beta(\mathcal{E}(\mathbf{k})-\mu)} - 1}$, which is necessarily positive $\forall$ $\mathbf{k}$ and hence implies

$$\mathcal{E}(\mathbf{k}) - \mu > 0 \;,\; \forall\, \mathbf{k} \quad \Rightarrow \quad \mu < \min\left[\mathcal{E}(\mathbf{k})\right] \quad .$$

Now since $\min\left[\mathcal{E}(\mathbf{k})\right] = \min\left[\frac{\hbar^2 k^2}{2m}\right] = 0$ which occurs at $\mathbf{k} = 0$ this implies that

$$\mu < 0 \quad .$$

At high T (classical limit), μ is large and negative and increases towards zero as T is decreased ($\mu \sim k_B T \ln(n\lambda_T^3)$ at high T while in the (degenerate) quantum limit μ approaches its limiting value $\mu = 0$ as $T \to 0$.

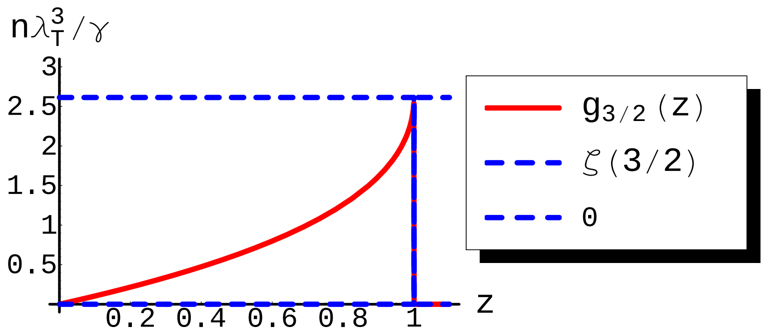

Figure 2: The Bose-Einstein function $g_{3/2}(z)$.

So to understand the 'quantum' behaviour of the Bose gas we must study $g_m(z)$ as $z{\rightarrow}1$ ($z = e^{\beta\mu}$). The functions $g_m(z)$ are monotonically increasing for $0 \leq z \leq 1$ and their maximum values at $z = 1$ are given by

$$\begin{aligned} g_m(1) &= \frac{1}{\Gamma(m)} \int_0^\infty \frac{dx\, x^{m-1}}{e^x - 1} = \frac{1}{\Gamma(m)} \int_0^\infty dx\, x^{m-1} \sum_{p=1}^\infty \left(e^{-x}\right)^p \\ &= \sum_{p=1}^\infty \frac{1}{p^m} = 1 + \frac{1}{2^m} + \frac{1}{3^m} + \cdots = \zeta(m) \quad ; \quad m > 1 \quad , \end{aligned}$$

where $\zeta(x)$ is **Riemann's Zeta function**.

For $m \leq 1$, $\quad g_m(z)$ diverges as $z{\rightarrow}1$.

The density of states (particles) we defined as

$$n = \int \frac{d^3k}{(2\pi)^3} \frac{1}{z^{-1} e^{\beta\mathcal{E}(\mathbf{k})} - 1} = \frac{1}{\lambda_T^3} g_{3/2}(z) \quad \rightarrow \frac{1}{\lambda_T^3}\zeta(3/2) \text{ as } z{\rightarrow}1 \quad .$$

However this sum does not include the (ground) state with $\mathcal{E} = 0$ ($\mathbf{k} = 0$) because the integrand is zero at $\mathbf{k} = 0$. So we have calculated the density of **excited** states (particles) i.e. those with energy $\mathcal{E}(\mathbf{k}) > \mathcal{E}(0)$.

This implies the density of excited particles (in $d = 3$) is bounded by $n_c = \dfrac{1}{\lambda_T^3}\zeta(3/2)$.

$$\boxed{n \leq n_c(T) \qquad (4.6.1)}$$

For $T{\rightarrow}\infty$

$$n\lambda_T^3 = n \left(\hbar \sqrt{\frac{2\pi}{mk_BT}}\right)^3 \ll \zeta(3/2) \simeq 2.612\ldots \quad .$$

But if we continue to lower the temperature , there will be a critical temperature T_c given by (for fixed density n)

$$n = \hbar^{-3} \left(\frac{2\pi}{mk_BT_c}\right)^{-3/2} \zeta(3/2) \quad \Rightarrow \quad T_c = \frac{2\pi\hbar^2}{mk_B} \left(\frac{n}{\zeta(3/2)}\right)^{2/3} \quad .$$

Below $T_c(n)$, z is stuck at unity. This means that the maximum number density of excited particles is then LESS than the TOTAL number density of particles. This means that the remaining gas particles MUST then be in the lowest energy state with $\mathbf{k} = 0$.

This phenomenon of macroscopic occupation of a single 1-particle state is known as **Bose-Einstein condensation**. It is a **phase-transition** due to quantum effects rather than interactions (since we are studying ideal gases) and arises purely from quantum (Bose-Einstein) statistics.

Thus means that for any $T \leq T_c(n)$, $n > n_c(T)$ (the maximum density of excited particles) and as a result,

$$n^* = n_c(T) = \frac{\zeta(3/2)}{\lambda_T^3} \propto T^{3/2}$$

of the particles are in the excited states (called the **normal phase**) and the rest

$$n_0 = n - n^* = n - n_c(T)$$

will be in the ground state (called the **condensed phase**). There is therefore at any temperature T an excited fraction $n^*(T)/n$ and a condensed fraction $n_0(T)/n$ of the Bose gas.

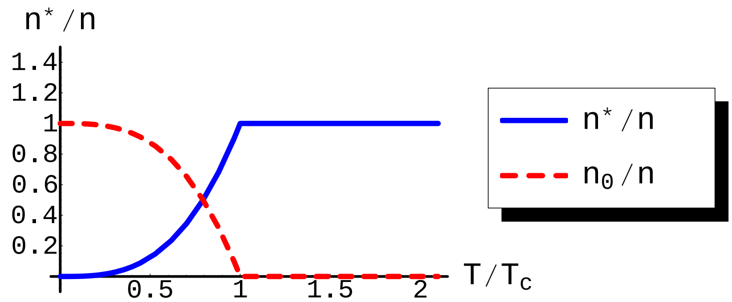

Figure 3: The density of excited state particles n^* and the density of particles in ground state, n_0 as functions of T.

Note that here again that at $T = 0$, there is only one microstate occupied (all the particles are in the ground state) which implies that $\Omega(T = 0) = 1$ and $S(T = 0) = 0$ and hence the 3rd law of thermodynamics is satisfied.

Finally, let us consider the pressure of the Bose gas. For $T < T_c$,

$$\beta P = \frac{1}{\lambda_T^3} g_{5/2}(1) = \frac{1}{\lambda_T^3}\zeta(5/2) \simeq 1.341 \frac{1}{\lambda_T^3} \quad \Rightarrow \quad P \propto T^{5/2} \quad ,$$

and the pressure is **independent** of density. Only the excited fraction has finite momentum and contributes to the pressure.

The phenomenon of Bose-Einstein condensation of a gas has a rather interesting history. It was predicted in 1925 by Albert Einstein (in the proceedings of the Prussian Academy of Sciences, Berlin) based on a model introduced by Satyendra Bose for an ideal gas of bosons. Bose had been describing the statistical mechanics of a gas of massless bosons

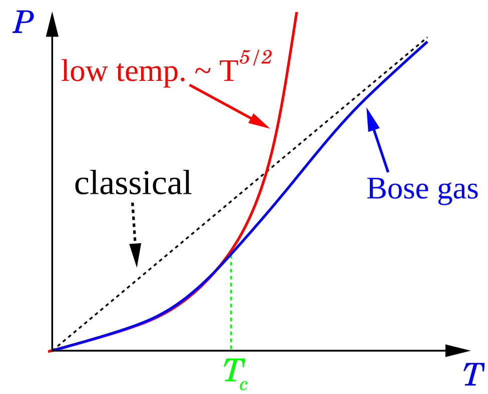

Figure 4: The pressure of a Bose gas as a function of T.

(the photons of EM radiation). Einstein generalised it to massive particles (atoms) and predicted the existence of the transition to the condensed phase.

However it was not until 1995 that Bose-Einstein condensation of a dilute gas was finally observed experimentally by Eric Cornell and Carl Wieman (for which they got the 2001 Nobel prize in physics) at the University of Colorado and Bouldber NIST-JILA lab by cooling a gas of Rubidium atoms to 170 nK (yes that's $\sim 10^{-7}$K - just a hundred billionths of a degree above absolute zero - very cold indeed!).

Soon after Einstein's (typically bold) observation, it was observed that at low T many systems do undergo a related *superfluid* transition which also involves the emergence of coherent quantum state. However the mechanism by which this occurs is somewhat different to our discussion as in this case the interactions between the particles play an important role. A superfluid is characterised by the 'vanishing' of dissipation (viscosity $\rightarrow$0) leading in principle to counterintuitive phenomena like vanishing viscous drag. So it eventually became clear that this wasn't Bose-Einstein condensation and the experimental search for it continued; only reaching it's triumphant conclusion in 1995.

In 2005, a hand-written close to final version (with editorial comments) of Einstein's original manuscript (in German) "Quantum theory of the monatomic ideal gas," dated December 1924 was discovered in Leiden where Einstein was a frequent visitor between 1920 and 1933.

See :

`www.lorentz.leidenuniv.nl/history/Einstein_archive/Einstein_1925_manuscript/`