

Chapter 7

IDEAL BOSE SYSTEMS

- * We will examine in further detail systems of non-interacting particles, where Q.M. effects are significant owing to the indistinguishability.
The condition when such effects are significant is

$$\boxed{n\lambda^3 \gtrsim 1} \quad (\text{i.e. not } n\lambda^3 \ll 1)$$

with $\lambda = \frac{h}{(2\pi m T)^{1/2}}$ the thermal wavelength.

- * When $n\lambda^3 \sim 1$ the systems depart from classical behavior, and the departure depends on whether the particles are bosons or fermions.

(7.1) Thermodynamics of an ideal Bose gas

$$\frac{PV}{T} = \ln Q = - \sum_{\varepsilon} \ln (1 - ze^{-\beta\varepsilon}) ; \quad z = e^{P/T}$$

is the starting point. Then

$$N = Z \left(\frac{\partial \ln Q}{\partial z} \right)_{V,T} = \sum_{\varepsilon} \langle n_{\varepsilon} \rangle = \sum_{\varepsilon} \frac{1}{e^{\beta\varepsilon}/z - 1}$$

[Note that $ze^{-\beta\varepsilon} \ll 1$]

In the TD limit $V \rightarrow \infty$ and we can replace the summation by integration

$$\sum_{\varepsilon} \rightarrow \sum_{\kappa} \rightarrow \frac{V}{(2\pi)^3} \int d^3 k = \frac{V}{2\pi^2} \int k^2 dk = \underbrace{\left(\frac{2\pi V}{h^3} \right) (2m)^{3/2} \int \varepsilon^{1/2} d\varepsilon}_{\text{arrow}}$$

$$\frac{\hbar^2 k^2}{2m} = \varepsilon \rightarrow \kappa = \frac{\sqrt{2m\varepsilon}}{\hbar} \rightarrow \kappa^2 dk = \frac{(2m)^{3/2}}{2\hbar^3} \varepsilon^{1/2} d\varepsilon$$

There is one subtle point about this integration:

Note that zero energy state has a weight zero since $\epsilon^{1/2} \rightarrow 0$. This is wrong since in Q.M. treatment all possible states have the same weight of unity.

The solution is to sum separately over the $\epsilon=0$ state.

$$\Rightarrow \frac{P}{T} = -\frac{2\pi}{h^3} (2m)^{3/2} \int \epsilon^{1/2} \ln(1 - ze^{-\beta\epsilon}) d\epsilon - \frac{1}{V} \ln(1-z)$$

and

$$\frac{N}{V} = \frac{2\pi}{h^3} (2m)^{3/2} \int \frac{\epsilon^{1/2} d\epsilon}{e^{\beta\epsilon}/z - 1} + \frac{1}{V} \frac{z}{1-z}$$

(We can still start the integration from $\epsilon=0$ since it contributes zero)

* The singular $\epsilon=0$ terms are negligible in the classical limit.

$$\frac{P}{T} = \underbrace{\text{term of order } \frac{N}{V}}_{\approx 0} + \frac{z}{V} \approx \frac{z}{\lambda^3} + \frac{z}{V} \approx \frac{z}{\lambda^3}$$

$$\int \epsilon^{1/2} \ln(1 - ze^{-\beta\epsilon}) d\epsilon \approx z \int \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon \approx z \frac{1}{\beta^{3/2}} \int x^{1/2} e^{-x} dx \approx \frac{z}{\beta^{3/2}}$$

$$\text{Similarly } \frac{N}{V} \approx \frac{z}{\lambda^3} + \frac{z}{V} = \frac{z}{\lambda^3}$$

* However in the other regime $z \ll 1$ and we can get a large fraction of the system in zero energy states

$$\boxed{\frac{N_0}{V} = \frac{1}{V} \frac{z}{1-z}}$$

This is the famous Bose-Einstein condensation

* As for the pressure of this contribution

$$N_0 = \frac{z}{1-z} \rightarrow \frac{1}{N_0} = \frac{1}{z} - 1 \rightarrow z = \frac{N_0}{N_0+1}$$

and therefore $-\frac{1}{V} \ln(1-z) = \frac{1}{V} \ln(N_0+1) \xrightarrow{\text{scales as}} \frac{\ln N}{N}$

This is negligible in TO limit

We finally get :

$$\frac{P}{T} = - \frac{2}{\pi^{1/2}} \frac{1}{x^3} \int_0^\infty x^{1/2} \ln(1-xe^{-x}) dx = \frac{1}{x^3} g_{5/2}(z)$$

$$\frac{N-N_0}{V} = \frac{2}{\pi^{1/2}} \frac{1}{x^3} \int_0^\infty \frac{x^{1/2}}{e^x/z - 1} dx = \frac{1}{x^3} g_{3/2}(z)$$

- In which the Bose-Einstein functions are defined as

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{e^x/z - 1} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \dots$$

- Integration by parts yields

$g_{5/2}(z)$ in P/T :

$$\int_0^\infty x^{1/2} \ln(1-xe^{-x}) = \frac{x^{3/2}}{3/2} \cdot \frac{ze^{-x}}{1-xe^{-x}} \Big|_0^\infty - \frac{2}{3} \int_0^\infty \frac{x^{3/2}}{e^x/z - 1} dx$$

[Using the definition $z = \frac{\hbar}{(2\pi m T)^{1/2}}$ and $\Gamma(\frac{1}{2}) = \pi^{1/2}$, $\Gamma(\frac{3}{2}) = \frac{\pi^{1/2}}{2}$, $\Gamma(\frac{5}{2}) = \frac{3}{4}\pi^{1/2}$
we obtain the equation for $\frac{P}{T}$]

We can now continue and derive the rest of the T.D.:

- First, if we take $\frac{P}{T} = \frac{1}{x^3} g_{5/2}(z)$ and $\frac{N}{V} = \frac{1}{x^3} g_{3/2}(z) - \frac{1}{V} \ln(1-z)$ and eliminate z (even numerically) then we get equation of state.

- Next, the internal energy of the system is

$$\begin{aligned} U &= - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{z,V} = - \frac{\partial}{\partial \beta} \left(\frac{PV}{T} \right)_{z,V} = - \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} \left(\frac{PV}{T} \right)_{z,V} = T^2 \frac{\partial}{\partial T} \left(\frac{PV}{T} \right)_{z,V} \\ &= T^2 \frac{\partial}{\partial T} \left[\frac{V}{x^3} g_{5/2}(z) \right] = T^2 V g_{5/2}(z) \frac{\partial}{\partial T} \left(\frac{1}{x^3} \right) = \frac{3}{2} T \frac{V}{x^3} g_{5/2}(z) \end{aligned}$$

We find that

$$U = \frac{3}{2} PV$$

High temperature expansion

For $n\lambda^3 \ll 1 \Leftrightarrow z \ll 1$ we can use the series expansion

$$of g_r(z) = z + \frac{z^2}{2} + \frac{z^3}{3} + \dots$$

Then we can get an expansion for z in powers of $n\lambda^3 = \frac{\lambda^3}{V}$
and get

$$\frac{PV}{NT} = \sum_{l=1}^{\infty} \alpha_l \left(\frac{\lambda^3}{V} \right)^{l-1}$$

volume
per particle

with $\alpha_1 = 1$; $\alpha_2 \approx -0.17$; $\alpha_3 = -0.003$ etc.

We get expansion around the ideal gas

$$\frac{PV}{NT} = 1 - 0.17 \left(\frac{\lambda^3}{V} \right) + \dots$$

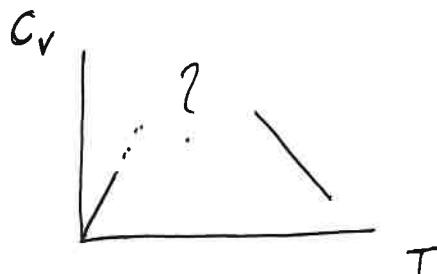
(More details in Pathria's book)

As for the specific heat

$$\frac{C_V}{N} = \frac{3}{2} \left[1 + 0.0084 \left(\frac{\lambda^3}{V} \right) + \text{positive terms} \dots \right]$$

Since $\frac{\lambda^3}{V} \sim \frac{1}{T^{3/2}}$ C_V is decreasing at high T .

But we also know that at $T=0$ $C_V \rightarrow 0$



So it must go through a maximum.

As we will shortly discuss, this maximum is a critical point.

At lower temperatures, the power series expansion fails. 5

We need to use the full equation

$$N_e = N - N_0 = \frac{V}{\pi^3} g_{3/2}(z) = V \frac{(2\pi m T)^{3/2}}{h^3} g_{3/2}(z)$$

* Unless $z \rightarrow 1$, most particles have $E \neq 0$ and $N \approx N_e$.

- When $T \rightarrow 0$, $N_e \sim T^{3/2} \rightarrow 0$ and

$$N \approx N_0 = \frac{z}{1-z} \rightarrow z = \frac{N_0}{N_0 + 1} \rightarrow 1$$

* Another way to see this is to consider the function

$$g_{3/2}(z) = \frac{2}{\pi^{1/2}} \int_0^\infty \frac{x^{1/2}}{e^{x/z} - 1} dx = \frac{z}{1^{3/2}} + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \dots$$

$g_{3/2}(z)$ increases between $0 \leq z \leq 1$ and its

maximum is $g_{3/2}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots = \zeta(\frac{3}{2}) = 2.612$

- As a result,

$$N_e \leq V \frac{(2\pi m T)^{3/2}}{h^3} \zeta(\frac{3}{2}) = N_e^{\max}(T)$$

- This means that if $N \leq N_e^{\max}$, most particles are in the excited state and z is determined from the equation $\frac{N}{V} = \dots$
- But if $N > N_e^{\max}$ then N_e^{\max} will occupy the exciting states, and all the rest will go to the $E=0$ level.

$$\boxed{N_0 = N - V \frac{(2\pi m T)^{3/2}}{h^3} \zeta(\frac{3}{2})}$$

And $z = \frac{N_0}{N_0 + 1} \approx 1 - \frac{1}{N_0} \rightarrow 1$

This unique phenomenon when a macroscopically large number of particles occupies a single quantum state is called the Bose-Einstein Condensation.

We call it "condensation" in analogy to condensation of vapor. ⁶

However: (i) This is a purely QM phenomenon that requires no interaction between molecules.

(ii) The "condensation" is in Energy (or k) space.

* The condition for the condensation is

$$N > N_e^{\max} = \sqrt{\frac{(2\pi m \tau)^{1/2}}{h^3}} \zeta\left(\frac{3}{2}\right)$$

or in terms of temperature,

$$T < T_c = \frac{\hbar^2}{2\pi m} \left[\frac{N}{V \zeta\left(\frac{3}{2}\right)} \right]^{1/3} \quad \left(\text{Note the dependence on density and mass} \right)$$

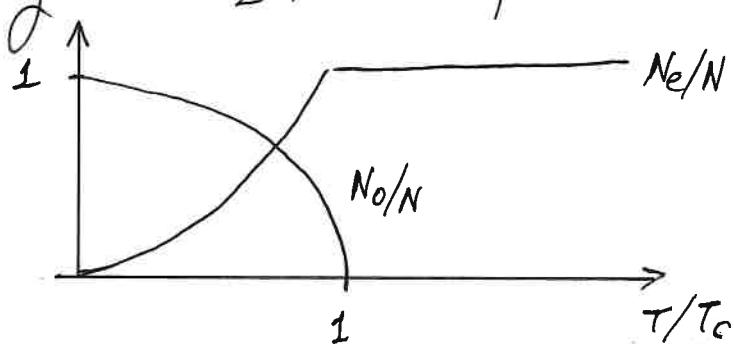
- For $T < T_c$, the system is composed of two phases:

(i) Normal phase of $N_e = N \left(\frac{T}{T_c} \right)^{3/2}$ particles with $\epsilon = 0$

(ii) Condensed phase of $N_0 = N \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right]$ particles

- Above T_c the condensed phase

has only $N_0 \approx \frac{2}{2-1} = 0(1)$ particles (practically zero)



As we learned, the phase diagram is drawn in the PT-plane

For $T < T_c$,

$$P(T) = \frac{T}{\lambda^3} \zeta\left(\frac{5}{2}\right) \sim T^{5/2}$$

* Note that because $z=1$ and does not change, there is no dependence on the density. This means that the system is infinitely compressible (One can change the volume without changing P)

Let's look further into the details :

$$\text{At } T_c, \quad P(T_c) = \frac{T}{\lambda^3} \zeta(\frac{5}{2})$$

and $\frac{N}{V} = \frac{1}{\lambda^3} \zeta(\frac{3}{2})$

$$P(T_c) = \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} \frac{N}{V} T_c$$

$$\approx 0.51 \frac{N}{V} T$$

, that is about half of classical gas pressure.

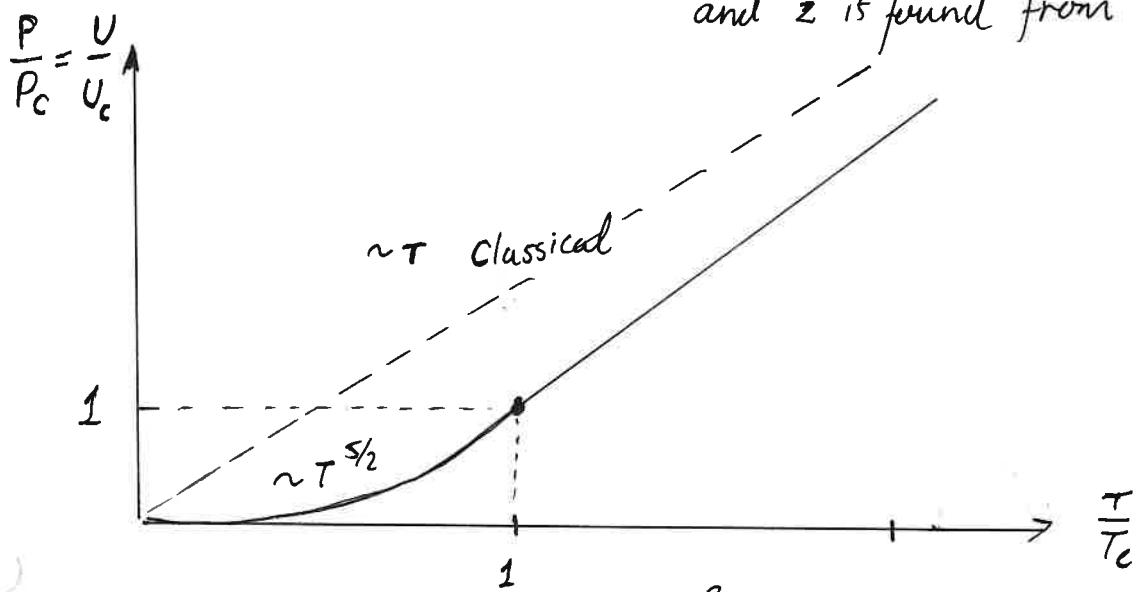
For $T > T_c$, we need to solve the equation of state.

$$\frac{P}{T} = \frac{1}{\lambda^3} g_{5/2}(z)$$

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z)$$

$$\frac{P}{T} = \frac{N}{V} \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

and z is found from $g_{3/2}(z) = \lambda^3 \frac{N}{V}$



Since we saw that $PV = \frac{2}{3}U$ for B.E. gas at any T , the graph also describes also the energy

$$U = \frac{3}{2}PV \quad \text{with} \quad U_c = \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)} N T_c \approx 0.76 N T_c$$

* Thus, we can find the specific heat c_v which is the derivative of U

$$C_v = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \left(\frac{3}{2} PV \right) = \frac{3}{2} V \frac{\partial}{\partial T} \left(\frac{1}{\lambda^3} \zeta(\frac{5}{2}) \right)$$

$$= \frac{3}{2} V \zeta(\frac{5}{2}) \frac{\partial}{\partial T} \left[\frac{T}{\lambda^3} \right] = \frac{15}{4} \zeta(\frac{5}{2}) \frac{V}{\lambda^3} \sim T^{3/2}$$

So the specific heat per particle is

$$\frac{C_V}{N} = \frac{15}{4} \zeta\left(\frac{5}{2}\right) \left(\frac{V}{T^3}\right) \sim T^{3/2} \quad \sigma = \frac{V}{N}$$

At T_c $\frac{N}{V} = \frac{1}{T^3} \zeta\left(\frac{3}{2}\right)$ so $\frac{C_V}{N} = \frac{15}{4} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} = 1.925$

(higher than the classical value $C_V/N = 3/2$)

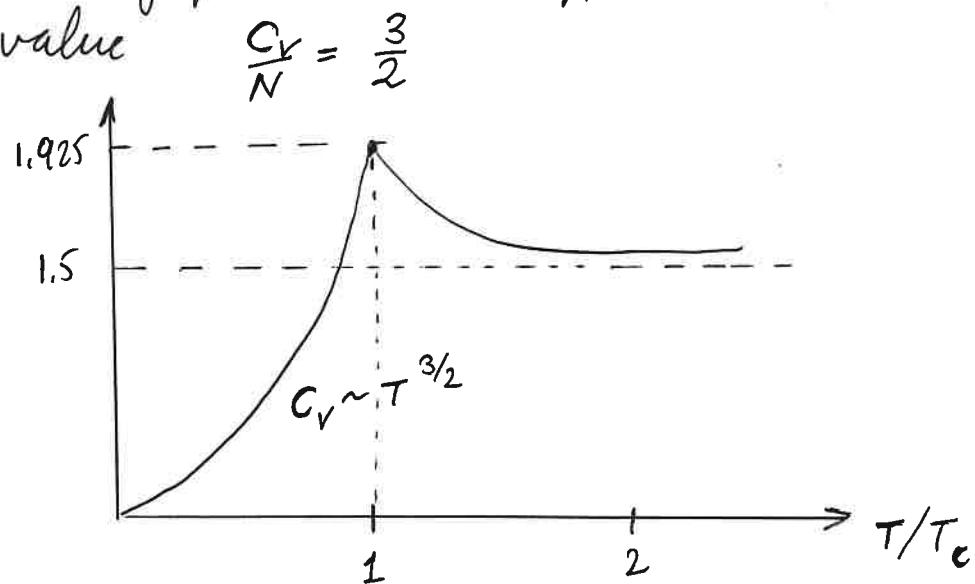
At $T > T_c$ one can calculate the specific heat from

$$\frac{C_V}{N} = \frac{\partial}{\partial T} \left(\frac{U}{N} \right) = \frac{3}{2N} \frac{\partial}{\partial T} (PV) = \frac{\partial}{\partial T} \left[\frac{3}{2} T \frac{g_{3/2}(z)}{g_{5/2}(z)} \right]$$

(Details of the calculation are given in Pathria)

The main features of the specific heat curve are:

- (i) at T_c C_V is continuous (its derivative is not)
- (ii) the asymptotic curve approaches the classical value $\frac{C_V}{N} = \frac{3}{2}$



* This theoretical curve is somewhat similar to the experimental curve measured for liquid He⁴.

The theoretical temperature is $T_c = \frac{\hbar^2}{2\pi m} \cdot \left(\frac{N}{V \zeta(3/2)} \right)^{2/3} \approx 3.1^\circ K$ quite close to the experimental value $2.19^\circ K$

This led to the works of Tisza and London who suggested the two-fluid model.

According to this model the liquid He^4 is composed of a "superfluid" and a "normal" phase.

No particles are in an entropyless ($E=0$) state and the rest are in the normal phase.

The actual experimental curves are quite different, but the concepts of a "superfluid" and a "normal" phase are of value.

The correspondence can be improved by considering interactions, but there are better ways to look at the helium problem.

[The transition was discovered by Keesom in 1928]

Further calculations of isotherms and adiabats are detailed in Pathria's book.

In 1995 BE condensation was first demonstrated in ultracold atomic gases using methods of Doppler cooling and magnetic traps. (section 7.2)

7.3 Thermodynamics of blackbody radiations

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One of the most important applications of Bose-Einstein statistic is to calculate the radiation from a "black body":

A cavity of volume V at a temperature T .

What is the radiation it emits?

Historically, this system was treated in two distinct ways

- (i) Assembly of harmonic oscillators with quantized energy levels $\epsilon = (n + \frac{1}{2})\hbar\omega$ (Planck 1900).
These oscillators are distinguishable.
- (ii) A gas of indistinguishable quanta called photons where energy is $\epsilon = \hbar\omega$ (Bose, Einstein 1924-25)
These photons are indistinguishable.

The energy levels of the oscillator $n = 0, 1, 2, \dots$ are equivalent to the number of photons with frequency ω . While the oscillator picture is historically important, we will follow the second more rigorous view of quantized radiation.

According to the quantum theory of radiation photons are massless bosons of spin 1 (that is \hbar)

Masslessness means that photons move at the speed of light c , and that its spin can have two independent orientations: parallel or anti-parallel to the momentum.

A photon with a definite spin state corresponds to a spin state that either right or left circularly polarised.

However, we can superimpose with definite spins and get linearly polarized photons, which we will consider.

* A photon of frequency ω has:

- Energy = $\hbar\omega$
- Momentum = $\frac{\hbar}{c}\vec{k}$; $|\vec{k}| = \frac{\omega}{c}$
- Polarization = \vec{e} with $|\vec{e}|=1$ and $\vec{e} \cdot \vec{k} = 0$.

Such photon corresponds to a plane-wave of EM radiation whose electric field is

$$\vec{E}(r, t) = \vec{e} e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (\vec{e} \text{ is the direction of } \vec{E})$$

The condition $\vec{e} \cdot \vec{k} = 0$ is a consequence of the transversality of \vec{E} , $\nabla \cdot \vec{E} = 0$ (no charges).

* From all this follows that there are two independent polarization vectors \vec{e} .

* As usual, we assume periodic boundary conditions on a $V = L^3$ cube. This implies that the momenta should be $\vec{k} = \frac{2\pi}{L} \vec{n}$ where $(n_x, n_y, n_z) \in [0, \pm 1, \pm 2, \dots]$

$$\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi)^3} \int 4\pi k^2 dk = \frac{V}{2\pi^2} \int k^2 dk$$

The photons are bosons so there could be many photons with the same \vec{k} and $\vec{e} = n_{\vec{k}, \vec{e}} = \{0, 1, 2, \dots\}$

The total energy of the system will be

$$E\{n_{\vec{k}, \vec{e}}\} = \sum_{\vec{k}, \vec{e}} \hbar\omega n_{\vec{k}, \vec{e}} \quad \text{where } \omega = ck$$

The grand-partition function in this case is

$$Q = \sum_{\{n_{\vec{k}, \vec{e}}\}} e^{-\beta E\{n_{\vec{k}, \vec{e}}\}} = \sum_{\vec{k}, \vec{e}} \exp(-\beta \sum_{\vec{k}, \vec{e}} \hbar\omega n_{\vec{k}, \vec{e}})$$

$$= \prod_{\vec{k}, \vec{e}} \left(\sum_{n_{\vec{k}, \vec{e}}} e^{-\beta \hbar\omega n_{\vec{k}, \vec{e}}} \right) = \prod_{\vec{k}, \vec{e}} \frac{1}{1 - e^{-\beta \hbar\omega}}$$

Thus we get that,

$$\frac{PV}{T} = \ln Q = - \sum_{\vec{k}, \vec{\epsilon}} \log(1 - e^{-\beta \hbar \omega}) = -2 \sum_{\vec{k}} \log(1 - e^{-\beta \hbar \omega})$$

* The average occupation number of photons with momentum \vec{k} (for both $\vec{\epsilon}$) is

$$\langle n_{\vec{k}} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial(\beta \hbar \omega)} \ln Q = \frac{2}{e^{\beta \hbar \omega} - 1}$$

(We found these results in the B.E. statistics
but with $\mu=0$ since there is no constraint on N)

* The energy is

$$U = -\frac{\partial}{\partial \beta} \ln Q = \sum_{\vec{k}} \hbar \omega \langle n_{\vec{k}} \rangle = \sum_{\vec{k}} \frac{2 \hbar \omega}{e^{\beta \hbar \omega} - 1}$$

To calculate the energy we can integrate on \vec{k} ,
or equivalently on ω

$$\sum_{\vec{k}} \rightarrow 2 \cdot \frac{V}{2\pi^2} \int dk \cdot k^2 = \downarrow$$

polarization

$$= \frac{V}{\pi^2 c^3} \int d\omega \cdot \omega^2$$

$$U = \frac{V}{\pi^2 c^3} \cdot \int_0^\infty \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \cdot \omega^2 d\omega$$

By rescaling $x = \beta \hbar \omega$ we get

$$\frac{U}{V} = \frac{1}{\pi^2 c^3 \beta^4 \hbar^3} \int_0^\infty \frac{x^3}{e^{x-1}} dx = \frac{T^4}{\pi^2 (\hbar c)^3} \cdot \frac{\pi^4}{15}$$

and finally

$$U = \frac{V}{V} = \frac{\pi^2 T^4}{15 (\hbar c)^3}$$

This is the Stefan-Boltzmann
law of blackbody radiation

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since there are
two polarizations

* To calculate the pressure we use

$$\frac{PV}{T} = \ln Q = - \sum_{E,\hbar\omega} \ln(1 - e^{-\beta \hbar\omega})$$

integrate by parts $= -\frac{V}{\pi^2 c^3} \int d\omega \cdot \omega^2 \ln(1 - e^{-\beta \hbar\omega})$

$$= -\frac{V}{\pi^2 c^3} \left[\frac{\omega^3}{3} \ln(1 - e^{-\beta \hbar\omega}) \right]_0^\infty - \int_0^\infty d\omega \frac{\omega^3}{3} \cdot \frac{-(-\beta \hbar)}{1 - e^{-\beta \hbar\omega}} e^{-\beta \hbar\omega}$$

$$= \frac{\beta V \hbar}{3 \pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta \hbar\omega} - 1} = \frac{\beta V \hbar}{3 \pi^2 c^3 (\beta \hbar)^4} \int_0^\infty \frac{x^3}{e^x - 1}$$

$$= \frac{V T^3}{3 \pi^2 (\hbar c)^3} \int_0^\infty \frac{x^3}{e^x - 1} = \left(\frac{\pi^2}{45}\right) \frac{V T^3}{(\hbar c)^3}$$

$$\rightarrow P = \frac{T}{V} \cdot \ln Q = \frac{\gamma^2}{45} \frac{T^4}{(\hbar c)^3} \quad \left(= \frac{1}{3} \frac{U}{V} \right)$$

We have seen this general relation for Bosons with energy-momentum relation $E \sim p^5$ ($s=1$)

* The specific heat is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{4 \pi^2}{15} \frac{V T^3}{(\hbar c)^3}$$

* To calculate the rest of the TD we use the fact that the chemical potential vanishes, $\mu=0$ ($z=1=e^{f/T}$)

$$G = \mu N = A + PV = 0 \Rightarrow A = -PV = -\frac{1}{3}U$$

And the entropy is

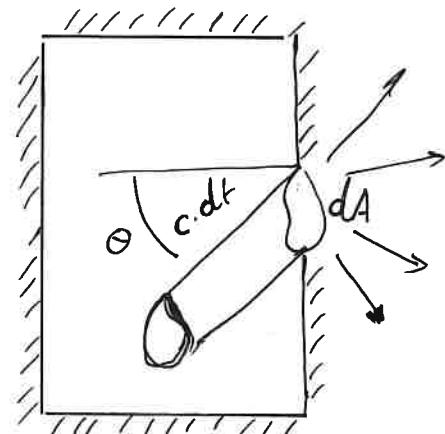
$$S = \frac{U-A}{T} = \frac{4}{3} \frac{U}{T} = 4 \left(\frac{PV}{T} \right)$$

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Experimentally, the theory of black body radiation can be tested by making a small hole and measuring the energy flux through that hole.

All the photons move at the same velocity c . Hence, the energy flux will be

$$I = \frac{u \cdot c dt dA}{dt dA} \langle \cos\theta \rangle$$



$$\begin{aligned} \langle \cos\theta \rangle &= \frac{1}{4\pi} \int d\Omega \cos\theta = \frac{1}{4\pi} \int_0^{\pi} 2\pi d(\cos\theta) \cos\theta \\ &= \frac{1}{2} \left. \frac{\cos^2\theta}{2} \right|_0^1 = \frac{1}{4} \end{aligned}$$

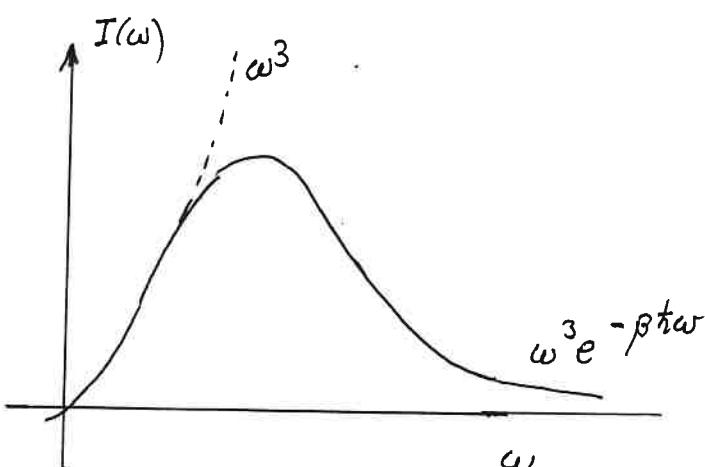
↖ take only those with $\cos\theta > 0$

Finally

$$I = \frac{c}{4} u = \frac{\pi^2}{60 h^3 c^2} T^4$$

The distribution of this flux over the frequencies is

$$I(\omega) = \frac{c}{4} u(\omega) \quad \text{where } u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} e^{-\beta\hbar\omega} \frac{1}{e^{\beta\hbar\omega} - 1}$$



$$(u = \int_0^\infty u(\omega) d\omega)$$

The divergence of the classical curve led Planck to his model.