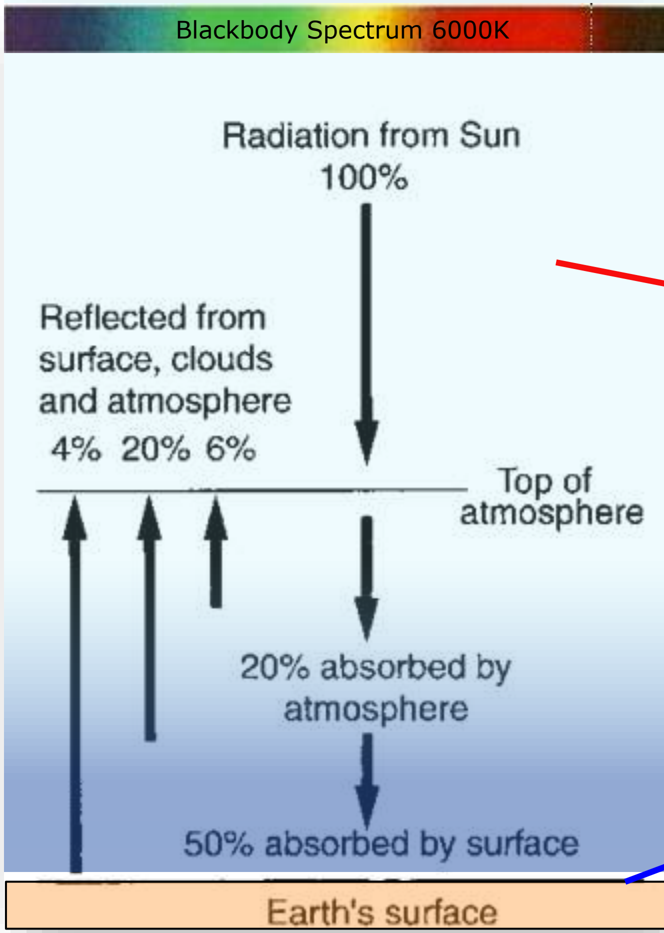
Agenda: Quantum Statistics

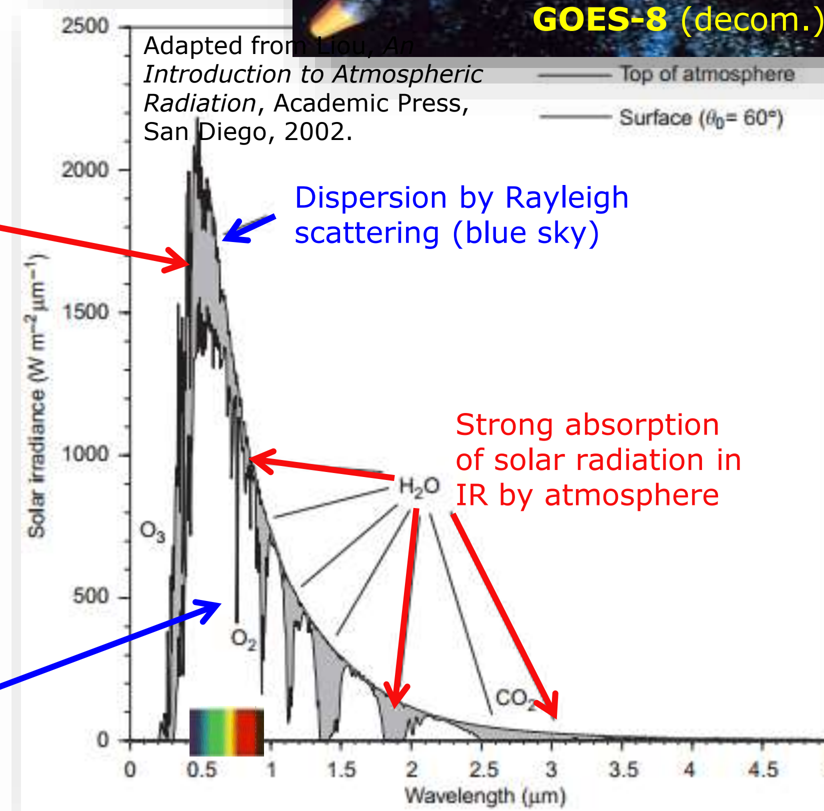
- Concepts in quantum mechanics
  - Quantal traveling waves and translational motion
  - Quantum model for vibrations (also Bosons)
  - Quantum model for vibrations
- Quantum partition functions for Fermions
- Quantum Fermi gas
- Bosons, Bose radiation gas

Planetary Electromagnetic Photon Flux

Absorption of solar radiation by the atmosphere is determined using spectroscopic satellite, aircraft, and surface data. See recent Atmospheric Radiation Measurement Enhanced Shortwave Experiment (ARESE)

See, e.g., F. P. J. Valero et al., J. GEOPHYS. RES., 105, 4743 (2000)



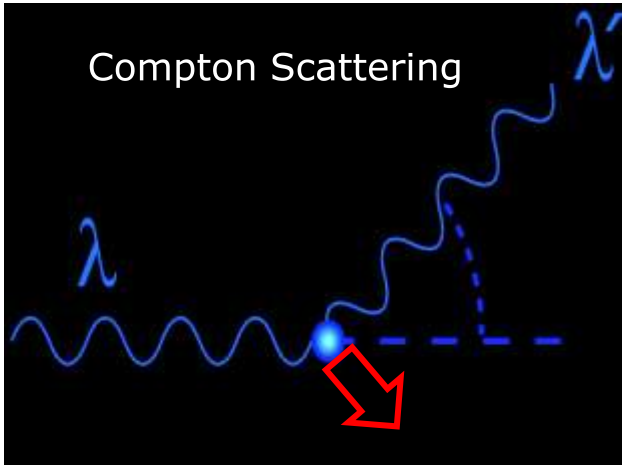


Scattered or absorbed radiation not available for warming Earth surface. → T_E < 255K !!???

Photons of Electromagnetic Radiation

Electromagnetic radiation 3D waves materialize as photons = energy packets

Radiation frequency ν, *circular frequency* $\varpi = 2\pi\cdot\nu$, *wave length* λ
speed of light $c = \lambda\cdot\nu$



Energy quantum $\varepsilon = h\cdot\nu = \hbar\cdot\varpi$,
linear momentum $p = \varepsilon/c$
Angular momentum $(spin = 1\hbar) \rightarrow$ *Boson*
2 polarizations degeneracy $= 2$, *mass* $m_{ph} = 0$,
relativistic $\varepsilon = \sqrt{(p\cdot c)^2 + (m_{ph}c)^2} = p\cdot c$

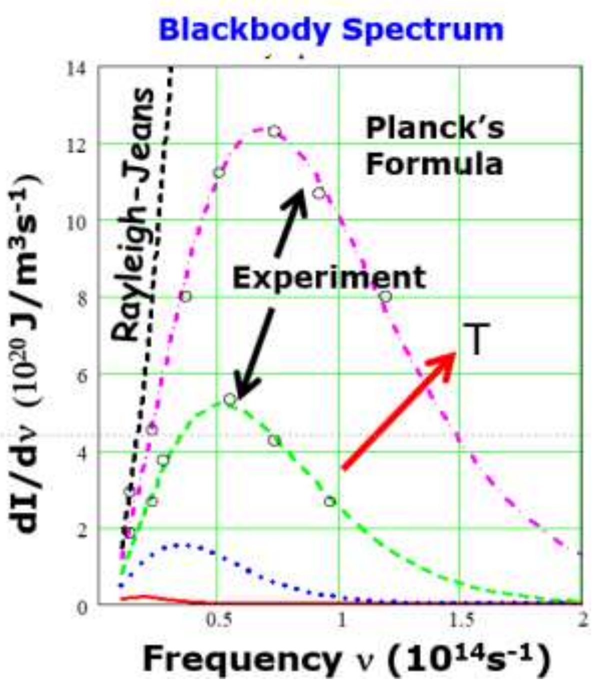
Occupation of ε : $f(\varepsilon) = \dfrac{1}{e^{\beta\cdot(\varepsilon-\mu)} - 1}$

Phase space density (waves in a box)

$$dn(\nu) = 2\frac{1}{h^3}d^3\vec{p}\cdot d^3\vec{r} = 2\frac{dV}{h^3}4\pi p^2 dp = 2\frac{dV}{c^3}4\pi\cdot\nu^2 d\nu$$

Planck's Radiation Law

$$\frac{d^2 n(\nu)}{dV\,d\nu} = \frac{8\pi}{c^3}\nu^2 \rightarrow Energy\ "radiance"$$



$Planck's\ constant$

$h = 6.626 \cdot 10^{-34}\,Js$

$$\frac{dI(\nu,T)}{d\nu} = \frac{d^2 n(\nu)}{dV\,d\nu} \cdot f(\nu,T) \cdot (h\nu)$$

#states occupancy energy

$$\frac{dI(\nu,T)}{d\nu} =: u(\nu,T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_B T} - 1}$$

Energy density

$Stefan - Boltzmann\ Law:\ Rad\,energy/time \cdot area$

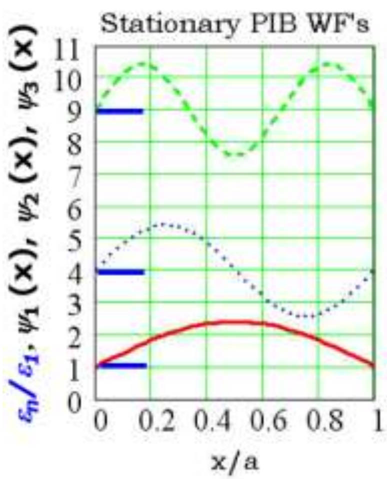
$$R = \frac{c}{4} I(T) = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} T^4 = \sigma_{SB} \cdot T^4$$

$Stefan - Boltzmann\ constant$

$$\sigma_{SB} = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} = 5.67 \cdot 10^{-8}\,Jm^{-2}s^{-1}K^{-4}$$

Radiation Pressure

Radiation field enclosed in a container (box, cube side length a)



$$Generally: \langle p\rangle = -\left(\frac{\partial}{\partial V}\langle E\rangle\right)_S ; \langle E\rangle = \sum_i \langle n_i\rangle \cdot \varepsilon_i$$

$$\langle p\rangle = -\sum_i \langle n_i\rangle \cdot \left(\frac{\partial}{\partial V}\varepsilon_i\right)_S \qquad \varepsilon_i = i\cdot h\cdot \nu = i\cdot h\cdot c/\lambda = 2i\cdot h\cdot c/a$$

$$\varepsilon_i = 2i\cdot h\cdot c\cdot V^{-1/3} \rightarrow \left(\frac{\partial}{\partial V}\varepsilon_i\right)_S = -\frac{2}{3} i\cdot h\cdot c\cdot V^{-4/3} = -\frac{1}{3}\frac{\varepsilon_i}{V}$$

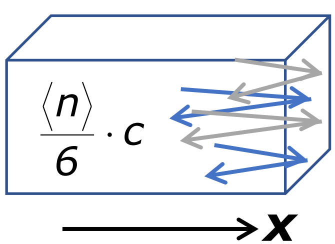
Boson pressure

$$\langle p\rangle = \frac{1}{3}\frac{\langle E\rangle}{V} = \frac{1}{3}\cdot u(T)$$

Classical gas pressure

$$\langle p\rangle_{cl} = \frac{2}{3}\frac{\langle E\rangle}{V}$$

Pressure (momentum transfer to wall)

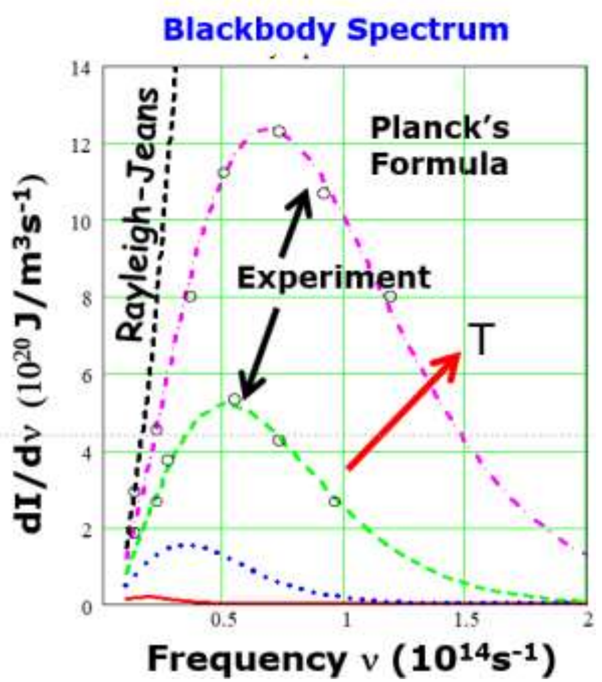


$$p(\nu,T) = \left(\frac{1}{6}c\right)\cdot\left[\frac{d^2n(\nu)}{dV\,d\nu}\cdot f(\nu,T)\right]\cdot\left(2\frac{h\nu}{c}\right)$$

$$= \frac{1}{3}\frac{dI(\nu,T)}{d\nu} \rightarrow p(T) = \frac{1}{3}I(T)$$

Planck's Radiation Law

$$\frac{d^2 n(\nu)}{dV\,d\nu} = \frac{8\pi}{c^3}\nu^2 \rightarrow Energy\ "radiance"$$



$$\frac{dI(\nu,T)}{d\nu} = \frac{d^2 n(\nu)}{dV\,d\nu} \cdot f(\nu,T) \cdot (h\nu)$$

#states occupancy energy

$$\frac{dI(\nu,T)}{d\nu} =: u(\nu,T) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1}$$

Energy density

Stefan – Boltzmann Law : Rad energy / time · area

$$R = \frac{c}{4} I(T) = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} T^4 = \sigma_{SB} \cdot T^4$$

Planck's constant

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Stefan – Boltzmann constant

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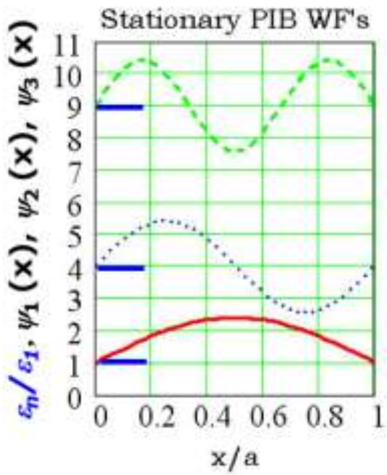
Partition Function and Radiation Pressure

Radiation field enclosed in a container (box, volume ***V***) → phase space !



$$\text{Photon number } dN = 2\cdot\frac{V}{h^3}d^3\vec{p}\ (2\ \text{polarizations})$$

$$\rightarrow d^3\vec{p} = 4\pi\left|\vec{p}\right|^2\cdot d\left|\vec{p}\right| = \frac{4\pi}{c^3}h^3\nu^2 d\nu$$

$$Ln\,\Xi = -2\cdot\frac{V}{h^3}\int d^3\vec{p}\cdot Ln\left(1-e^{-\beta\cdot\left|\vec{p}\right|\cdot c}\right)$$

$$= \frac{-8\pi}{\beta^3h^3c^3}V\cdot\int_0^\infty(\beta h\nu)^2\cdot Ln\left(1-e^{-\beta\cdot h\nu}\right)d(\beta h\nu)$$

$$Ln\,\Xi = \left(\frac{\pi^4}{45}\frac{8\pi k_B^3}{(hc)^3}\right)\cdot V\cdot T^3 = \left(\frac{4}{3}\frac{\sigma_{SB}}{k_B\cdot c}\right)\cdot V\cdot T^3$$

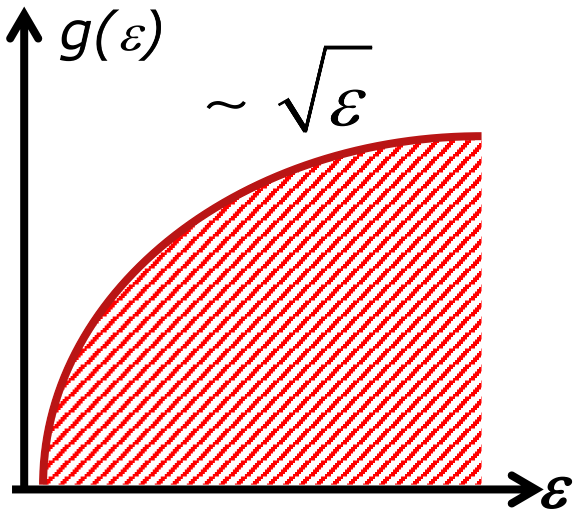
⇨ Can calculate all thermodynamic quantities

Examples:

$$E(T,V) = V\cdot u(T) = \langle E\rangle = -\frac{\partial}{\partial\beta}Ln\,\Xi = \left(\frac{4\cdot\sigma_{SB}}{c}\right)\cdot V\cdot T^4$$

$$\text{Pressure } p = \left(\frac{4\cdot\sigma_{SB}}{3\cdot c}\right)\cdot T^4$$

Massive Bosons (Noble Gas Atoms)



Based on phase space :

$$g(\varepsilon) = \frac{dn}{d\varepsilon} = \frac{2\pi}{h^3} V (2m)^{3/2} \sqrt{\varepsilon} = C \cdot \sqrt{\varepsilon}$$

$\Rightarrow$ $g(0) = 0$ (*OK for Fermions*) $\rightarrow$

ground state for Bosons not included

at *T=0* → Boson ground state $\varepsilon = 0$,

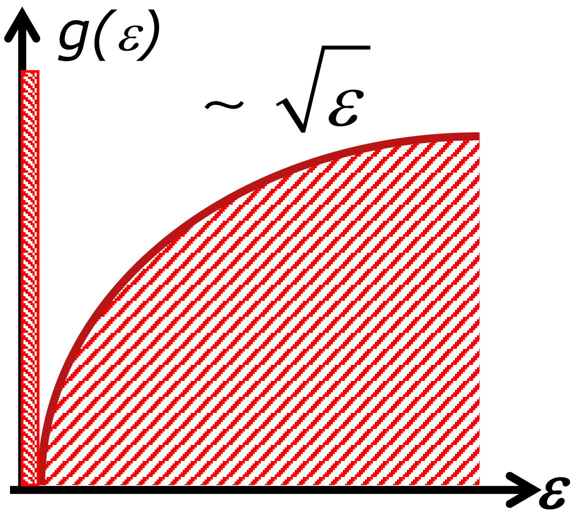
all $\boldsymbol{A_0}$ *Bosons are in ground state*

$$\langle n(\varepsilon) \rangle = f(\varepsilon) = \frac{1}{e^{\beta \cdot (\varepsilon - \mu)} - 1} \quad \xrightarrow{T \to 0} \quad f(0) = \boxed{A_0 = \frac{1}{e^{-\beta \cdot \mu} - 1}} = \frac{e^{\beta \cdot \mu}}{1 - e^{\beta \cdot \mu}}$$

$$A = A_0 + A_{exc} \rightarrow \boxed{A_{exc} = \int_0^\infty f(\varepsilon) \cdot g(\varepsilon) d\varepsilon}$$

Large # Bosons : $A_0 \gg 1 \rightarrow e^{-\beta \cdot \mu} \sim 1$

Massive Bosons



T≈0 → many (=$\boldsymbol{A_0}$) Bosons are in ground state

$$A_{exc} = \int_0^\infty f(\varepsilon)\cdot g(\varepsilon) =$$

$$= \frac{2\pi}{h^3} V (2m)^{3/2} \int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\beta\cdot\varepsilon}-1} d\varepsilon$$

$$= \frac{2\pi}{h^3} V (2mk_B)^{3/2} \left(\int_0^\infty \frac{\sqrt{x}}{e^{x}-1} dx \right)$$

definite integral

$1.306\sqrt{\pi}$

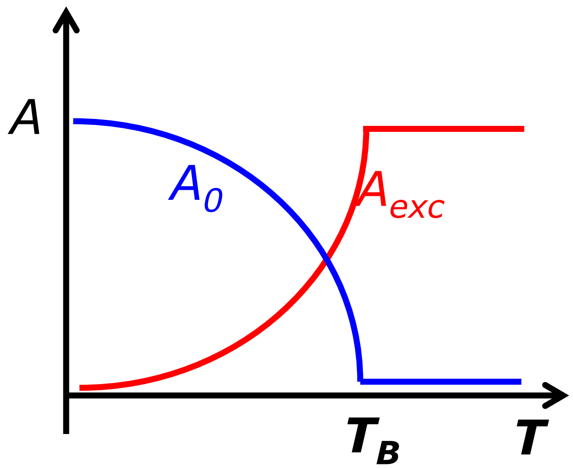
$$A_{exc} = 2.612 \cdot V \cdot \left(\frac{2\pi m k_B}{h^2} T \right)^{3/2}$$

At $T = T_B =$ "*Bose temperature*" $A_{exc} \approx A$:

$$T_B = \frac{h^2}{2\pi m k_B} \left(\frac{A}{2.612 \cdot V} \right)^{2/3}$$

Bose Condensate

Boson Populations A_0, A_{exc}



Critical Bose Temperature

$$T_B = \frac{h^2}{2\pi m k_B}\left(\frac{A}{2.612 \cdot V}\right)^{2/3}$$

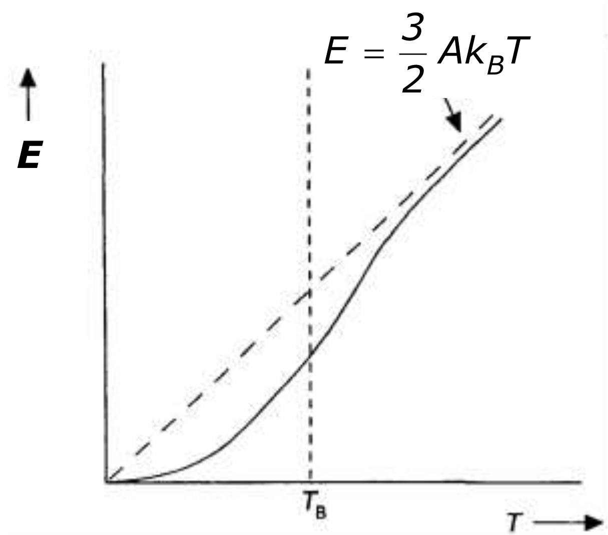
$$\frac{A_{exc}(T)}{A} = \begin{cases} (T/T_B)^{3/2} & for \;\; T \le T_B \\ 1 & for \; T > T_B \end{cases}$$

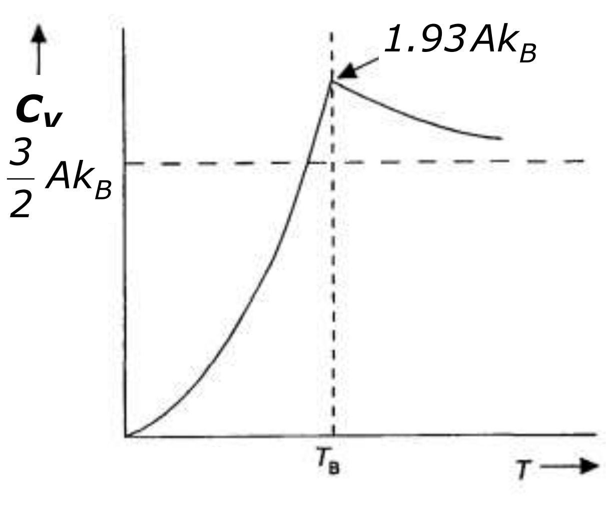
In g.s. $\varepsilon = 0$ *at finite* $T \le T_B$:

$$A_0(T) = A - A_{ex}(T) = A \cdot \left\{1 - \left(\frac{T}{T_B}\right)^{3/2}\right\}$$

$$T > T_B \rightarrow A_0(T) \approx 0$$

Bose Gas Properties





T<T_B → estimate Boson energy

$$\langle \varepsilon(T) \rangle \sim k_B T \quad A_{exc}(T) \approx A \cdot (T/T_B)^{3/2}$$

$$\langle E \rangle \sim A \cdot k_B T \cdot (T/T_B)^{3/2} \propto T^{5/2}$$

$$C_V \approx \frac{d}{dT} \langle E \rangle \sim \frac{5}{2} A \cdot k_B \cdot (T/T_B)^{3/2}$$

More accurate :

$$\langle E \rangle = 0.771 \cdot A \cdot k_B T \cdot (T/T_B)^{3/2}$$

$$C_V = 1.93 \cdot A \cdot k_B \cdot (T/T_B)^{3/2} \leq 1.93 \cdot A \cdot k_B$$

T>T_B → Boson energy <E> & C_V approach classical values

Experimental check: heat capacity of liquid ^{4}He = bosons (***J*** = 0), λ-point

End of
Fermi-Bose Statistics