Advanced Thermodynamics (M2794.007900)

Chapter 18

Bose-Einstein Gases

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• Black body

Black body is an idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence.

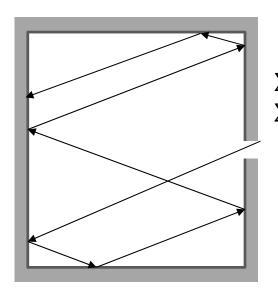
• Black body radiation

A black body in thermal equilibrium emit black body radiation (electromagnetic waves) whose spectrum is only regarded with temperature.



• Black body and Photon gas

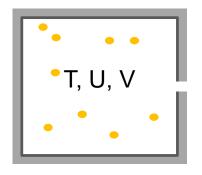
Consider a volume, V enclosed by insulated wall with small hole. Photons injected from the hole nearly re-emitted so that the inner surface of the volume can be regarded as a black body while inner space is treated to be filled with photon gas.



 $\sum N_i \neq N$, because photons continue to be absorbed and emitted. $\sum N_i \epsilon_i = U$, because the wall is isolated.



- Photon gas with Bose Einstein statistics
 - Photon gas enclosed with black body surface follows Boson statistics while having no constraint about particle numbers.
 - Photons are bosons of spin 1 and obey Bose-Einstein statistics.





• The photons emitted by one energy level may be absorbed at another, so the number of photons is not constant

$$\sum N_i \neq N$$

• Bose-Einstein distributions

From Stirling's approximation, $\ln(N!) = N \ln(N) - N$ $\ln(w_{BE}) = \sum [(N_i + g_i - 1) \ln(N_i + g_i - 1) - N_i \ln(N_i) - (g_i - 1) \ln(g_i - 1)]$ N_i for i^{th} energy level is undetermined yet

→ Method of Lagrange multiplier is used to obtain the most probable macro state under two constraints, $\sum N_i \neq N, \sum N_i \epsilon_i = E$

$$\frac{\partial(\ln(w_{BE}))}{\partial N_i} + \alpha \frac{\partial(\sum N_i - N)}{\partial N_i} + \beta \frac{\partial(\sum N_i \epsilon_i - E)}{\partial N_i} = 0$$

the Lagrange multiplier $\alpha = 0$, and $e^{-\alpha} = 1$



• Distribution function

Applying method of Lagrange multipliers to Bose-Einstein distributions,

$$\ln(N_i + g_i - 1) + \frac{g_i + N_i - 1}{g_i + N_i - 1} - \ln(N_i) - \frac{N_i}{N_i} + \beta \epsilon_i = 0$$

Then, the **Bose-Einstein distribution function** becomes as

$$\ln\left(\frac{N_i + g_i - 1}{N_i}\right) = -\beta\epsilon_i$$
$$N_i = g_i \frac{1}{e^{-\beta} - 1} \qquad \left(\beta = -\frac{1}{kT}\right)$$
$$f(\epsilon_i) \equiv \frac{N_i}{g_i} = \frac{1}{e^{-\beta\epsilon_i} - 1} = \frac{1}{e^{\epsilon_i/kT} - 1}$$



• The number of photons per quantum state

$$f_{j} = \frac{N_{j}}{g_{j}} = \frac{1}{e^{\varepsilon_{j}/kT} - 1}$$
$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{\varepsilon/k} - 1}$$
$$f(\nu) = \frac{N(\nu)}{g(\nu)} = \frac{1}{e^{h\nu/kT} - 1}$$

• The number of quantum states with frequencies in the range v to v + dv

$$g(v)dv = 2 \times \frac{4\pi V}{c^3} v^2 dv \qquad c: the speed of light$$
Polarization

• The energy in the range v to v + dv

$$u(v)dv = N(v)dv \times hv$$

= $g(v)f(v)dv \times hv$
= $\frac{8\pi V v^2 dv}{c^3} \cdot \frac{hv}{e^{hv/kT-1}}$ Plank radiation formula

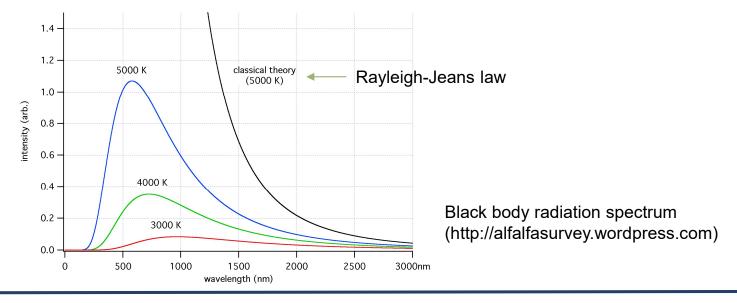


• The blackbody spectrum is often expressed in terms of the wavelength.

Then, $u(v)dv \propto u(\lambda)d\lambda$

$$\begin{aligned} \nu &= \frac{c}{\lambda} \qquad d\nu = -\frac{c}{\lambda^2} d\lambda \qquad |d\nu| = \frac{c}{\lambda^2} |d\lambda| \\ \underline{u(\lambda)}d\lambda &= \frac{8\pi V \frac{c^2}{\lambda^2} \frac{c}{\lambda^2} d\lambda}{c^3} \frac{\frac{hc}{\lambda}}{e^{hc/\lambda kT} - 1} = 8\pi hcV \frac{d\lambda}{\lambda^5 (e^{hc/\lambda k} - 1)} \end{aligned}$$

The energy per unit wavelength in the range λ to $\lambda + d\lambda$ (wavelength spectrum)





• The total energy density

$$U = \int_{0}^{\infty} u(\lambda) d\lambda$$

$$\frac{U}{V} = 8\pi hc \int_{0}^{\infty} \frac{d\lambda}{\lambda^{5}(e^{hc/\lambda kT} - 1)}$$

$$x = \frac{hc}{\lambda kT}$$

$$\frac{U}{V} = \frac{8\pi}{h^{3}c^{3}} (kT)^{4} \frac{\int_{0}^{\infty} \frac{x^{3} dx}{e^{x} - 1}}{=\frac{\pi^{4}}{15}}$$

Thus, $\frac{U}{V} = aT^{4}$ $a = \frac{8\pi^{5}k^{4}}{15h^{3}c^{3}} = 7.55 \times 10^{-16} \,\text{J/(m}^{3}\text{K}^{4})$

• The energy flux

$$e = \frac{c}{4} \left(\frac{U}{V} \right) = \sigma T^4$$
 $\sigma = \frac{ca}{4} = 5.67 \times 10^{-8} \,\mathrm{W/m^2 K^4}$ Stefan – Boltzmann law



The wavelength λ_{max} at which u(λ) is a maximum satisfies a relation known as Wien's displacement law.

$$u(\lambda) = 8\pi hcV \frac{1}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$
$$\frac{d}{d\lambda} [\lambda^5 (e^{hc/\lambda k} - 1)] = 0$$

$$x = \frac{hc}{\lambda kT} \qquad \frac{x}{5} = 1 - e^{-x}$$
$$\frac{1}{x^2} \frac{d}{dx} [x^{-5}(e^x - 1)] = \frac{1}{x^2} [x^{-5}e^x - 5x^{-6}(e^x - 1)] = 0$$
$$\therefore x = 4.96$$

$$\frac{hc}{\lambda_{max}kT} = 4.96$$
$$\lambda_{max}T = \frac{hc}{4.96k} = 2.90 \times 10^{-3} \text{mK}$$

Wien's displacement law



• For long wavelengths, $\frac{hc}{\lambda kT} \ll 1$

$$e^{hc/\lambda k} \approx 1 + \frac{hc}{\lambda kT}$$
 Taylor series
 $u(\lambda)d\lambda = 8\pi hcV \frac{1}{\lambda^5 \left(\frac{hc}{\lambda kT}\right)}$
 $= V \frac{8\pi kT}{\lambda^4} d\lambda$ Rayleigh – Jeans Formula

• For short wavelengths, $e^{\frac{hc}{\lambda kT}} \gg 1$

$$u(\lambda)d\lambda = 8\pi hcV \frac{e^{-hc/\lambda kT}}{\lambda^5} d\lambda$$
 Wien's law

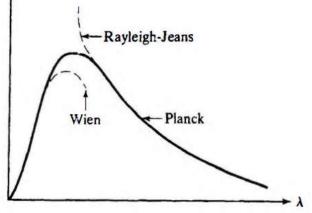


Fig. Sketch of Planck's law, Wien's law and the Rayleigh-Jeans law



18.2 Properties of a Photon Gas

• The heat capacity

$$\frac{U}{V} = aT^{4} = \frac{8\pi^{5}k^{4}}{15h^{3}c^{3}}T^{4} \qquad (a = \frac{8\pi^{5}k^{4}}{15h^{3}c^{3}})$$
$$C_{V} = \frac{\partial U}{\partial T}\Big|_{V} = \frac{32\pi^{5}k^{4}}{15h^{3}c^{3}}T^{3}V$$

• The absolute entropy

$$S = \int_0^T \frac{C_V}{T} dT = \frac{32\pi^5 k^4 V}{15h^3 c^3} \cdot \frac{1}{3}T^3$$

• The Helmholtz function F = U - TS

$$F = U - TS = aT^{4}V - \frac{4}{3}aT^{4}V = -\frac{1}{3}aT^{4}V$$
$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{1}{3}aT^{4} = \frac{1}{3}\left(\frac{U}{V}\right) \qquad cf. \ Ideal \ gas \ P = \frac{2}{3}\frac{U}{V}$$



- The gas of noninteracting particles of large mass such that quantum effects only become important at very low temperatures. → Ideal Bose-Einstein gas
- ⁴He undergoes a remarkable phase transition known as Bose-Einstein condensation.
- The Bose Einstein continuum distribution

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon - \mu)/kT} - 1}$$

Chemical potential $\mu(T) = ?$



• For Maxwell-Boltzmann distribution (Dilute gas)

BE:
$$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT}-1}$$

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/kT}}$$
$$\mu = -kT \ln \frac{Z}{N}$$
$$Z = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$
$$\therefore \frac{\mu}{kT} = -\ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \right]$$

• As an example, for ⁴He at standard temperature and pressure,

$$\frac{\mu}{kT} = -12.43, \frac{\varepsilon}{kT} = 1.5, \frac{\varepsilon - \mu}{kT} = 13.9 \text{ and } f(\varepsilon) = 9 \times 10^{-7}$$

$$g(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi V}{h^3} m^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon \qquad \text{from Chap. 12}$$

$$N = N_0 + N_{ex}$$

$$N_{excited} = \int N(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} \int \frac{\varepsilon^{\frac{1}{2}} d\varepsilon}{e^{(\varepsilon - \mu)/kT} - 1}$$



$$N_{excited} = \int N(\varepsilon)d\varepsilon = \frac{4\sqrt{2}\pi V m^{\frac{3}{2}}}{h^3} \int \frac{\varepsilon^{\frac{1}{2}}d\varepsilon}{e^{(\varepsilon-\mu)/kT} - 1}$$

For the ground state (at very low temperature, this ground state becomes significant as bosons condense into this lowest state), *T* → 0, ε = 0 and N(ε) → N

$$\frac{1}{e^{-\mu/kT} - 1} \cong N$$
$$-\frac{\mu}{kT} = \ln\left(1 + \frac{1}{N}\right) \cong \frac{1}{N} \sim 0$$

• For low temperature,
$$exp\left(-\frac{\mu}{kT}\right) \sim 1$$

$$x = \frac{\varepsilon}{kT}$$

$$N_{ex} = V \frac{2}{\sqrt{\pi}} \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{x^{\frac{1}{2}} dx}{e^x - 1} = 2.612V \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$$

$$= 2.612 \frac{\sqrt{\pi}}{2}$$



• Bose temperature T_B is the temperature above which all the bosons should be in excited states. Thus $N_{ex} = N$ and $T = T_B$.

$$N = 2.612V \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$$
$$T_B = \frac{h^2}{2\pi mk} \left(\frac{N}{2.612V}\right)^{\frac{2}{3}}$$

• For $T > T_B$, all the bosons are in excited states.

For $T < T_B$, increasing number of bosons occupy the ground state until at T = 0.

$$\begin{split} N &= N_0 + N_{ex} \\ \frac{N_{ex}}{N} &= \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \qquad \frac{N_0}{N} = 1 - \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \end{split}$$

 $\rightarrow 6.02 \times 10^{23}$ ⁴He atoms confined to a volume of 22.4×10^{-3} m³, $T_B \sim 0.036$ K



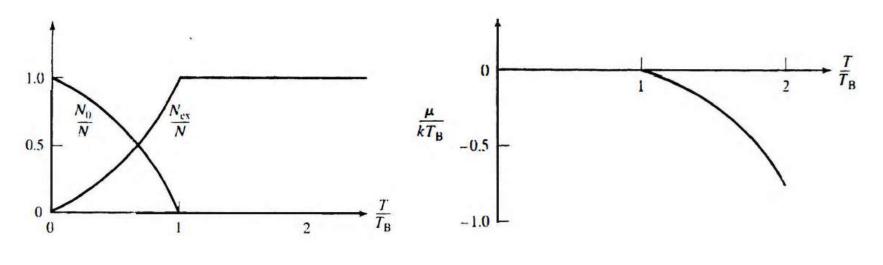


Fig. Variation with temperature of N_0/N and N_{ex}/N for a boson gas

Fig. Variation with temperature of μ/kT_B versus T/T_B .



18.4 Properties of a Boson Gas

• The internal energy

$$U = \sum N_j \varepsilon_j = N_0 \varepsilon_0 + N_{ex} \varepsilon_{ex}$$

For
$$T > T_B$$
, $N_0 = 0$ $U = \frac{3}{2}NkT$

$$T_B = \frac{h^2}{2\pi mk} \left(\frac{N}{2.612V}\right)^{\frac{2}{3}}$$

For
$$T < T_B$$
, $N_0 \gg 1$, $\varepsilon_0 = 0$ $\frac{N_{ex}}{N} = \left(\frac{T}{T_B}\right)^{\frac{3}{2}}$ $U = ?$



18.4 Properties of a Boson Gas

• For
$$T < T_B$$
,

$$U = \int_0^{\varepsilon} \varepsilon N(\varepsilon) d\varepsilon$$

$$= \int_0^{\varepsilon} \varepsilon \cdot \frac{1}{e^{(\varepsilon-\mu)/kT} - 1} \cdot \frac{4\sqrt{2}\pi V}{h^3} m^{\frac{3}{2}} \varepsilon^{\frac{1}{2}} d\varepsilon}{e^{\frac{3}{2}} d\varepsilon}$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^{\infty} \frac{\varepsilon^{\frac{3}{2}} d\varepsilon}{e^{(\varepsilon-\mu)/kT} - 1}$$

$$= -2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^{\infty} \frac{x^{\frac{3}{2}} dx}{e^x - 1} \cdot (kT)^{\frac{5}{2}}$$

$$= \frac{3\sqrt{\pi}}{4} \times 1.34$$

$$= \frac{3}{2} \times 1.33kT \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$

$$= 0.770NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}}$$

$$T_B = \frac{h^2}{2\pi mk} \left(\frac{N}{2.612V}\right)^{\frac{2}{3}}$$



18.4 Properties of a Boson Gas

• The heat capacity

$$C_V = \frac{dU}{dT} = 1.92Nk \left(\frac{T}{T_B}\right)^{\frac{3}{2}}$$

• The absolute entropy

$$S = \int_0^T \frac{C_V dT}{T} = 1.28Nk \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \qquad T \to 0, S \to 0$$

• The Helmholtz function F = U - TS

$$F = U - TS = -0.51NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}} T < T_B$$
$$= -1.33kT \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$
$$P = 1.33kT \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} T < T_B$$

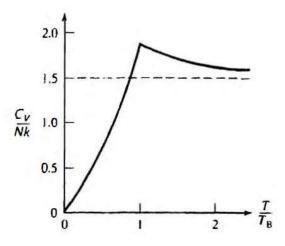


Fig. Variation with temperature of the heat capacity of a boson gas.

