Advanced Thermodynamics (M2794.007900)

Chapter 18

Bose-Einstein Gases

Min Soo Kim
Seoul National University

Black body

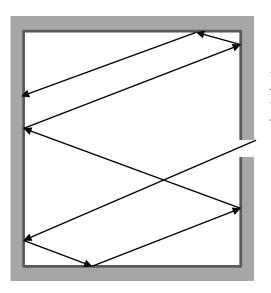
Black body is an idealized physical body that absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence.

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.

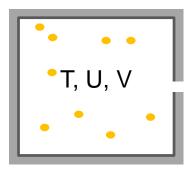


 $\sum N_i \neq N$, because photons continue to be absorbed and emitted. $\sum N_i \epsilon_i = U$, because the wall is isolated.

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

 \rightarrow 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

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

$$N_i = g_i \frac{1}{e^{-\beta \epsilon} - 1} \qquad \left(\beta = -\frac{1}{kT}\right)$$

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

The number of photons per quantum state

$$f_{j} = \frac{N_{j}}{g_{j}} = \frac{1}{e^{\varepsilon_{j}/kT} - 1}$$

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

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

• 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

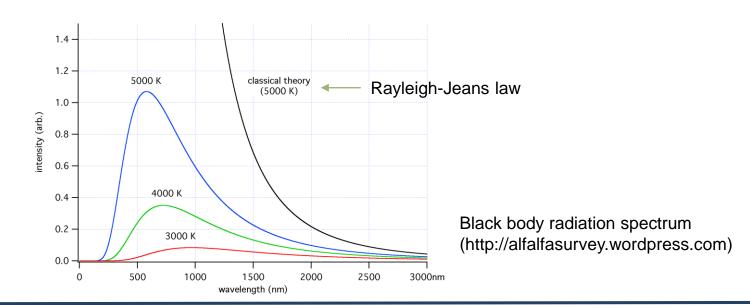
The blackbody spectrum is often expressed in terms of the wavelength.

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

$$v = \frac{c}{\lambda}$$
 $dv = -\frac{c}{\lambda^2}d\lambda$ $|dv| = \frac{c}{\lambda^2}|d\lambda|$

$$\underline{u(\lambda)}d\lambda = \frac{8\pi V \frac{c^2}{\lambda^2} \frac{c}{\lambda^2} d\lambda}{c^3} \frac{\frac{hc}{\lambda}}{e^{hc/\lambda kT} - 1} = 8\pi hcV \frac{d\lambda}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

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



The total energy density

$$U = \int_0^\infty u(\lambda)d\lambda$$

$$\frac{U}{V} = 8\pi hc \int_0^\infty \frac{d\lambda}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

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

$$\frac{U}{V} = \frac{8\pi h}{h^3 c^3} (kT)^4 \underbrace{\int_0^\infty \frac{x^3 dx}{e^x - 1}}_{=\frac{\pi^4}{15}}$$

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

The energy flux

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

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

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

$$x = \frac{hc}{\lambda kT} \qquad \frac{x}{5} = 1 - e^{-x}$$

$$\frac{1}{x^2} \frac{d}{dx} [x^{-5}(e^x - 1)] = \frac{1}{x^2} [x^{-5}e^x - 5x^{-6}(e^x - 1)] = 0$$

$$\therefore x = 4.96$$

$$\frac{hc}{\lambda_{max}kT} = 4.96$$

$$\lambda_{max}T = \frac{hc}{4.96k} = 2.90 \times 10^{-3} \text{mK}$$
Wien's displacement law

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

$$e^{hc/\lambda kT} \approx 1 + \frac{hc}{\lambda kT}$$
 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

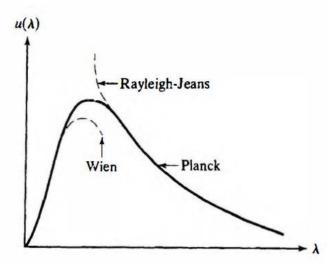


Fig. Sketch of Planck's law, Wien's law and the Rayleigh-Jeans law

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 H = U - TS

$$F = U - TS = aT^4V - \frac{4}{3}aT^4V = -\frac{1}{3}aT^4V$$

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

- 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) $f(\varepsilon) = \frac{1}{\rho(\varepsilon - \mu)/kT}$

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

$$\mu = -kT \ln \frac{Z}{N}$$

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

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

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

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

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

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

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

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

 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 $T = T_B$.

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

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

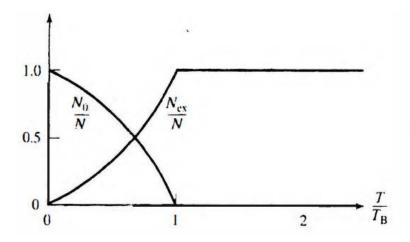
• For $T > T_B$, all the bosons are in excited states.

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

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

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

 \rightarrow 6.02 \times 10²³ ⁴He atoms confined to a volume of 22.4 \times 10⁻³m³, $T_B \sim 0.036$ K



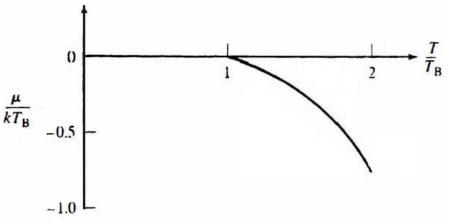


Fig. Variation with temperature of N_0/N and N_{ex}/N for a boson gas

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
$$T > T_R$$
,

$$N_0 = 0$$

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
$$T < T_B$$

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
$$T < T_B$$
,
$$U = \int_0^\varepsilon \varepsilon N(\varepsilon) d\varepsilon$$

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

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

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

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

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

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

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

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 H = U - TS

$$F = U - TS = -0.51NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \qquad T < T_B$$

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

$$P = 1.33kT \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \qquad T < T_B$$

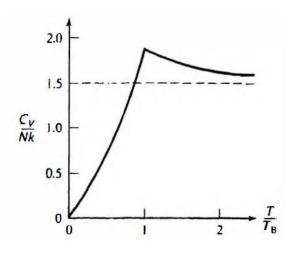


Fig. Variation with temperature of the heat capacity of a boson gas.