【Chapter 9 Statistical Distributions】

【9.1 Statistical Distributions】

● number of particles of energy ε

$n(\varepsilon) = g(\varepsilon) f(\varepsilon)$

$g(\varepsilon)$ = number of states of energy ε

= statistical weight corresponding to energy ε

$f(\varepsilon)$ = distribution function

= average number of particle in each state of energy ε

= probability of occupancy of each state of energy ε

● Three different kinds of particles

(1) Identical particles, distinguishable, ex：molecules of gas little or negligible overlap for wave functions => Maxwell-Boltzman distribution

(2) Identical particles of 0 or integer spin, indistinguishable wave function overlap. => bosons, not obey exclusion principle. => Bose-Einstein distribution. ex：photons => symmetric wave function.

(3) Identical particles of odd half integer spin ($\frac{1}{2},\frac{3}{2},\frac{5}{2},...$)

indistinguishable => fermions. Obey exclusion principle

=> Fermi-Dirac distribution, ex：e' =>antisymmetric

wave function

【9.2 Maxwell-Boltzman Statistics】

For classical particles

$$f_{MB}(\varepsilon) = Ae^{-\varepsilon/kT}$$ average number of particles $f_{MB}(\varepsilon)$ in a state of energyε

A：depends on number of particles in system analogous to

normalization constant

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$$

$\Rightarrow n(\varepsilon) = Ag(\varepsilon)e^{-\varepsilon/kT}$ total number particles that have energyε

see ex 9.1 & 9.2

【9.3 Molecular Energy in an Ideal Gas】

Consider a continuous distribution of molecular energies instead

of discrete set $\varepsilon_1, \varepsilon_2, \varepsilon_3, ...$

If $n(\varepsilon)d\varepsilon$ is the number of molecules whose energies lie

between ε & $\varepsilon + d\varepsilon$

$$\Rightarrow n(\varepsilon)d\varepsilon = [g(\varepsilon)d\varepsilon][f(\varepsilon)] = Ag(\varepsilon)e^{-\varepsilon/kT}d\varepsilon$$

first find $g(\varepsilon)d\varepsilon$, number of states that have enegy between ε

& $\varepsilon + d\varepsilon$

A molecule of energy ε has a momentum P whose magnitude p

is specified by

$$p = \sqrt{2m\varepsilon} = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

each set of momentum components p_x, p_y, p_z specifies a

different state of motion.

Figure 9.1 (see textbook) The coordinates in momentum space are p_z. The number of momentum states available to a *p* with a momentum whose magnitude is between *p+dp* is proportional to the volume of a spherical *s* momentum space of radius p and thickness *dp*

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

＊ Consider momentum space, see fig 9.1,

Number of states g(p)dp with momentum whose magnitude

are between p & (p+dp)

=> $g(p)dp \propto 4\pi^2 p \cdot dp = Bp^2 dp$ (B：constant)

∵ each p → single energyε

⇨ g(ε)dε   betweenε   & (ε +dε) the same as g(p)dp

⇨ $g(\varepsilon)dp = Bp^2 dp$

∵ $p^2 = 2m\varepsilon$ => $dp = \dfrac{md\varepsilon}{\sqrt{2m\varepsilon}}$

⇨ $g(\varepsilon)d\varepsilon = 2Bm^{\frac{3}{2}}\sqrt{\varepsilon}d\varepsilon$

⇨ $n(\varepsilon)d\varepsilon = C\sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$ ($C = 2m^{3/2}AB = \text{cons}\tan t$)
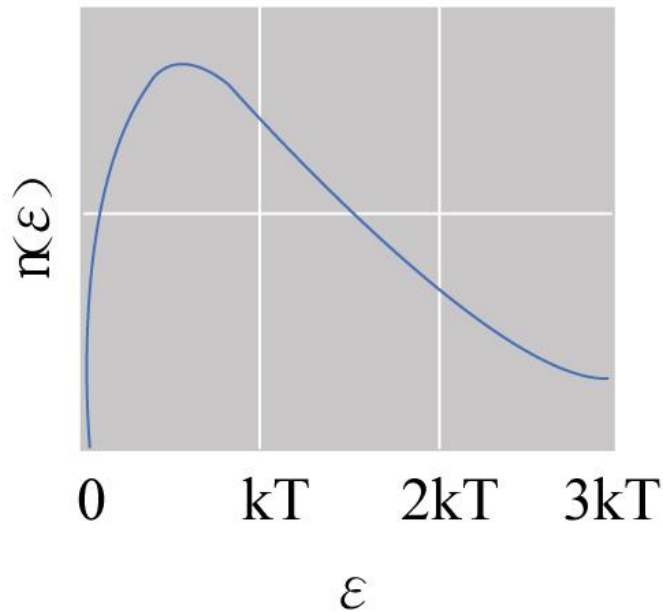

● To find C,

$N = \int_0^\infty n(\varepsilon)d\varepsilon = C\int_0^\infty \sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$

∵ $\int_0^\infty \sqrt{x}e^{-ax}dx = \dfrac{1}{2a}\sqrt{\dfrac{\pi}{a}}$ $a = \dfrac{1}{kT}$

=> $N = \dfrac{C}{2}\sqrt{\pi}(kT)^{\frac{3}{2}}$ => $C = \dfrac{2\pi N}{(\pi kT)^{3/2}}$

⇨ $n(\varepsilon)d\varepsilon = \dfrac{2\pi N}{(\pi kT)^{3/2}}\sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$

see fig 9.2

Figure 9.2 (see textbook) Maxwell-Boltzmann energy distribution for the molecules of an ideal gas.

The average molecular energy is $\bar{\varepsilon} = \dfrac{3}{2}kT$.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum

Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

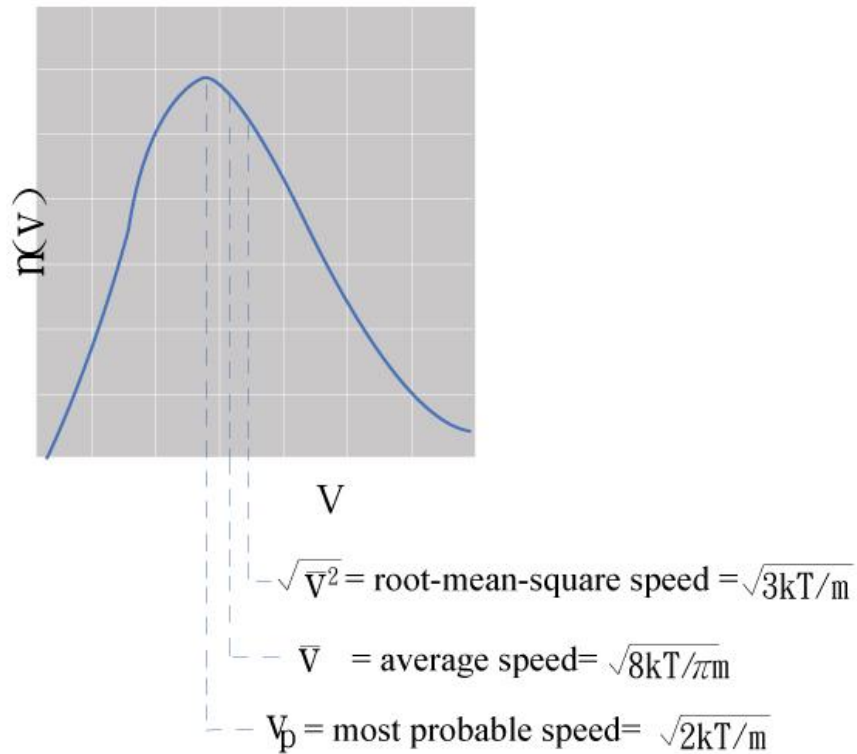Total energy $E = \int_0^\infty \varepsilon^n(\varepsilon)d\varepsilon$

$$= \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^\infty \varepsilon^{3/2} e^{-\varepsilon/kT} d\varepsilon$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}} \left[\frac{3}{4}(kT)^2 \sqrt{\pi kT} \right]$$

$$= \frac{3}{2} NkT$$

⇨ average molecular energy $\varepsilon = \dfrac{3}{2}kT$ independent of

molecule's massε at RT~0.04 eV$= \dfrac{1}{25}$ eV

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Figure 9.3 (see textbook) Maxwell-Boltzmann speed distribution.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics,

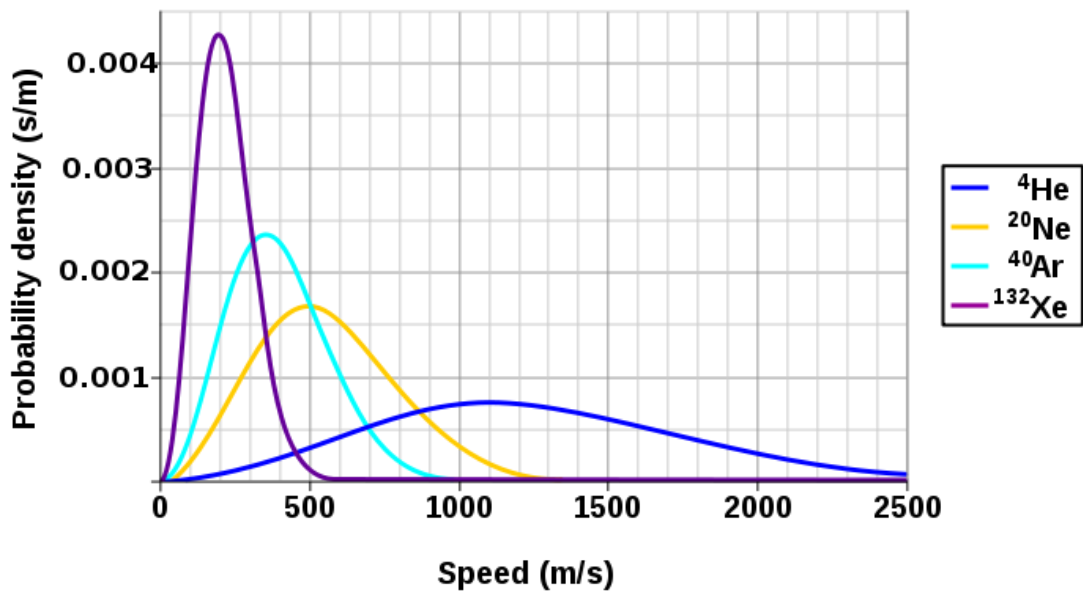RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

*Distribution of Molecular Speeds

$$\varepsilon = \frac{1}{2}mv^2 \qquad d\varepsilon = mvdv$$

$$\Rightarrow n(v)dv = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}dv \quad \text{see fig 9.3}$$

$$\bar{\varepsilon} = \overline{\frac{1}{2}mv^2} = \frac{3}{2}kT \Rightarrow \boxed{v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}}$$

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Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases

Figure 9.4 The distributions of molecular speeds at 298K (from wikipedia)

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum

Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

*Most probable speed $\dfrac{dv(v)}{dv} = 0$

$\Rightarrow \ v_p = \sqrt{\dfrac{2kT}{m}}$ (smaller than $\bar{v}$ & $\sqrt{\overline{v^2}}$)

*Consider two particle 1,2,

two states 1,2,

$\left. \begin{array}{l} \varphi_I = \varphi_a(1)\varphi_b(2) \\[2mm] \varphi_{II} = \varphi_a(2)\varphi_b(1) \end{array} \right\}$ for distinguishable particle

for Bosons $\varphi_B = \dfrac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_b(2) + \varphi_a(2)\varphi_b(1)\right]$ symmetric

for Fermions $\varphi_F = \dfrac{1}{\sigma_2}\left[\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1)\right]$

antisymmetric

*Consider both particles in the same state a

(1) for distinguishable particles, both φ_I & φ_{II} become

$\varphi_M = \varphi_a(1)\varphi_a(2)$

$\Rightarrow \varphi_M^*\varphi_M = \varphi_a^*(1)\varphi_a^*(2)\varphi_a(1)\varphi_a(2)$

(2) for bosons

$$\varphi_B = \frac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_b(2) + \varphi_a(1)\varphi_a(2)\right] = \frac{2}{\sqrt{2}}\varphi_a(1)\varphi_a(2)$$

$$= \sqrt{2}\varphi_a(1)\varphi_a(2)$$

$$\varphi_B^*\varphi_B = 2\varphi_a^*(1)\varphi_a(2)\varphi_a(1)\varphi_a(2) = 2\varphi_M^*\varphi_M$$

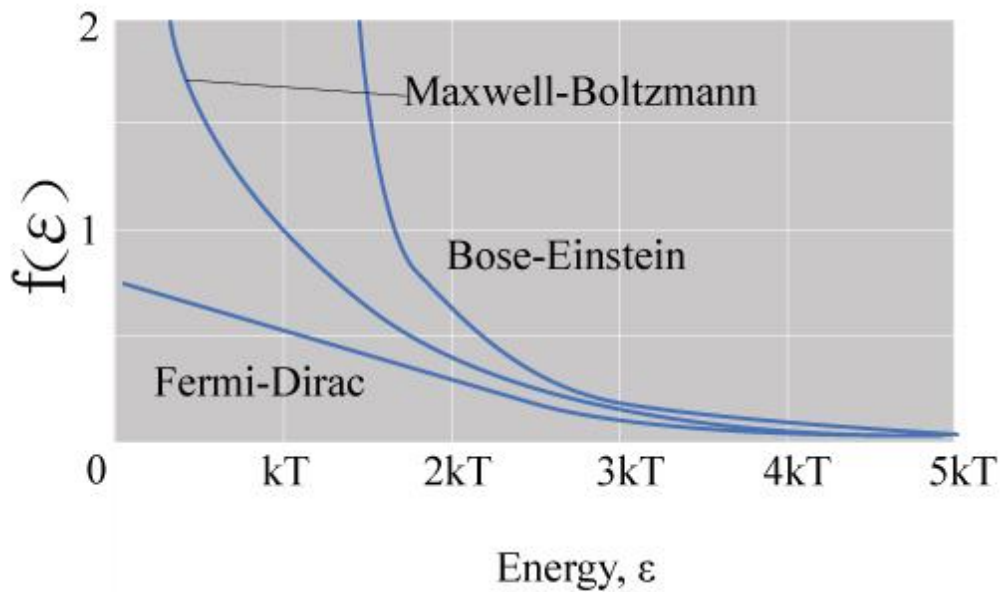$\Rightarrow$ the presence of particle in a certain quantum state increases the probability that other particles are to be found in the same state.

(3) for fermions

$$\varphi_F = \frac{1}{\sqrt{2}}\left[\varphi_a(1)\varphi_a(2) - \varphi_a(1)\varphi_a(2)\right] = 0$$

$\Rightarrow$ the presence of particle in a certain state presents any other particles from being in that state.

Figure 9.5 (see textbook) A comparison of the three distribution functions fir α=-1.   The
Bose-Einstein function is always higher than the Maxwell-Boltzmann one, which is a pure exponential,
and the Fermi-Dirac function is always lower.   The functions give the probability of occupancy of a
state energy ε at the absolute temperature T.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum
Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

*Bose-Einstein distribution

$$f_{BE}(\varepsilon) = \frac{1}{e^{\alpha}e^{\varepsilon/kT} - 1}$$

*Fermi-Dirac distribution

$$f_{FD}(\varepsilon) = \frac{1}{e^{\alpha}e^{\varepsilon/kT} + 1}$$ α ：depends on properties of system and

   may be function of T
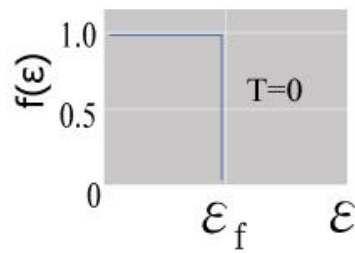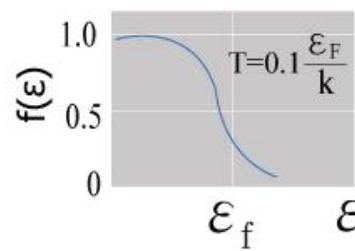
*Whenε >>kT, both case → MB

*When $\varepsilon = -2kT,\ f_{FD}(\varepsilon) = \dfrac{1}{2}$

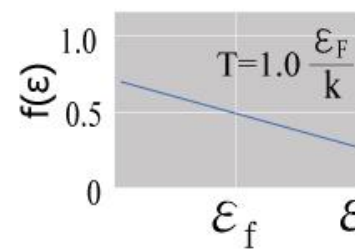This energy is called Fermi energy $\varepsilon_f = -\alpha kT$

$$\Rightarrow f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

(a)

(b)

(c)

Figure 9.6 (see textbook) Distribution function for fermions at three different temperatures.　(a)At T=0, all the energy states up to the Fermi energy ε_F are occupied.　(b) At a low temperature, some fermions will leave states just below ε_F and move into states just above ε_F. (c) At a higher temperature, fermions from any state below ε_F may move into states above ε_F.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

*Consider T = 0

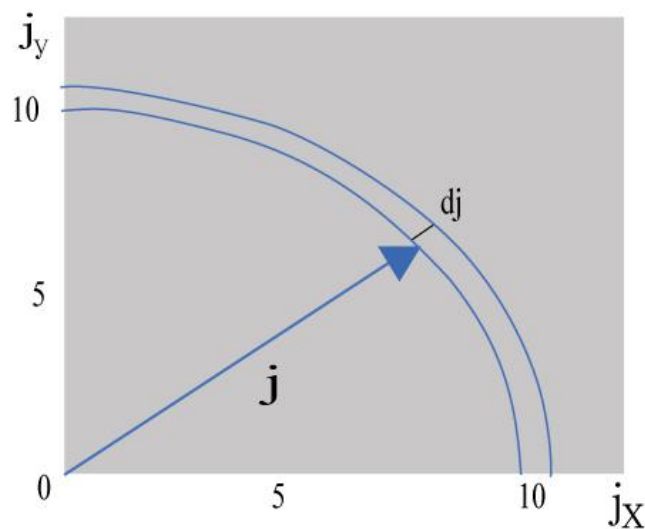$$\text{For } \varepsilon < \varepsilon_F, \quad f_{FD} = \frac{1}{e^{\infty} + 1} = 1$$

$$\text{For } \varepsilon > \varepsilon_F, \quad f_{FD} = \frac{1}{e^{\infty} + 1} = 0$$

*at T = 0, all energy states up to ε_F are occupied, and none above ε_F

The highest state to be occupied have energy $\varepsilon = \varepsilon_F$

See fig 9.6 & table 9.1

Figure 9.7 (see textbook) Each point in j space corresponds to a possible standing wave.

※References:Modern Physics for scysics and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

*Rayleigh-Jeans formula (for black body radiation)
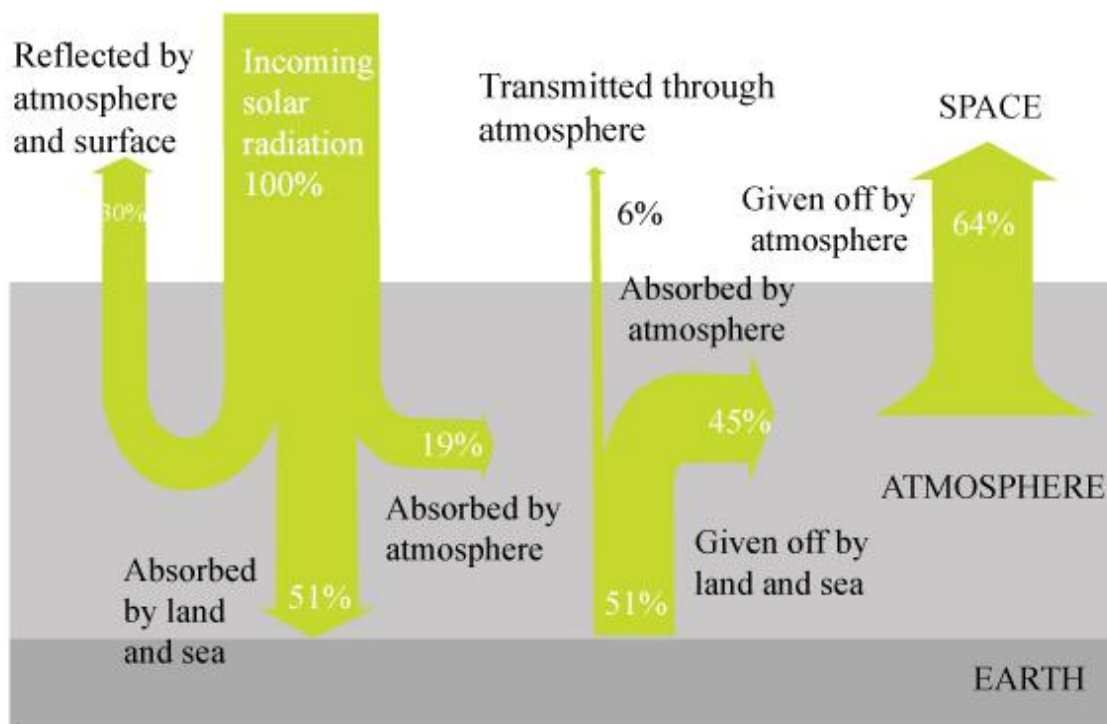
Radiation must consist of standing em waves

⇨ a node needs to occur at each wall in any direction

⇨ the path length from wall to wall = an integer number j of half-wavelengths.

$$j_x = \frac{2L}{\lambda} = 1,2,3,...$$

$$j_y = \frac{2L}{\lambda} = 1,2,3,... \qquad => j_x^2 + j_y^2 + j_z^2 = \left(\frac{2L}{\lambda}\right)^2$$

$$j_z = \frac{2L}{\lambda} = 1,2,3,...$$

Figure 9.8 (see textbook) The greenhouse effect is important in heating the earth's atmosphere. Much of the short-wavelength visible light from the sun that reaches the earth's surface is reradiated as long-wavelength infrared light that readily absorbed by CO_2 and H_2O in the atmosphere.   Some energy also reaches rather than from above by the sun.   The total energy that the earth and its atmosphere radiate into space on the average equals the total energy that they receive from the sun.

※References:Modern Physics for scientists and engineers, Stephen T. Thornton Nonclassical Physics, RandyHarris.Quantum Physics of atoms, molecules,Solids,nuclei and Particles. Eisberg & Resnick

To constant number of standing wave $g(\lambda)d\lambda$ within the cavity whose wavelengths lie between λ & $\lambda + d\lambda$

$\Rightarrow$ constant number of permissible sets of j_x, j_y, j_z values

If j is a vector from the origin to a particular point j_x, j_y, j_z,

its magnitude is $j = \sqrt{j_x^2 + j_y^2 + j_z^2}$

$$g(j)dj = 2\left(\frac{1}{8}\right)(4\pi j^2 dj) = \pi j^2 dj$$

$\quad\quad\quad\quad\downarrow\quad\hookrightarrow$ Only count first Octant

$\quad\quad$ Two perpendicular directions of polarization

$$\because j = \frac{2L}{\lambda} = \frac{2L\nu}{c} \Rightarrow dj = \frac{2L}{c}d\nu$$

$$g(\nu)d\nu = \pi\left(\frac{2L\nu}{c}\right)^2 \frac{2L}{c}d\nu = \frac{8\pi L^3}{c^3}\nu^2 d\nu$$

The cavity volume is L^3

$\Rightarrow$ density of standing waves in a cavity

$$G(\nu)d\nu = \frac{1}{L^3}g(\nu)d\nu = \frac{8\pi\nu^2 d\nu}{c^3}$$

＊ Classical Theory

Use oscillator => average energy $\bar{\varepsilon} = kT$

$\Rightarrow$ $u(v)dv = \bar{\varepsilon}G(v)dv$

$$= \frac{8\pi v^2 kTdv}{c^3} \quad \text{Rayleigh-Jeans formula.}$$

$u(v)\uparrow$ with $v^2\uparrow$ => wrong !!

＊ Planck radiation law

assume oscillators' energy $\varepsilon_n = nkv$

he used Maxwell-Boltzman distribution

number of oscillators with energy $\varepsilon_n \propto e^{-\varepsilon_n/kT}$

$\Rightarrow$ $\bar{\varepsilon} = \dfrac{hv}{e^{hv/kT} - 1}$

$\Rightarrow$ $u(v)dv = \bar{\varepsilon}G(v)dv = \dfrac{8\pi h}{c^3}\dfrac{v^3 dv}{e^{hv/kT} - 1}$

＊ Harmonic oscillator have energy

$\varepsilon_n = \left(n + \dfrac{1}{2}\right)hv$, not nhv

including zero-point energy $\dfrac{1}{2}hv$

$\Rightarrow$ $\bar{\varepsilon}$ is not equal to $\dfrac{hv}{e^{hv/kT} - 1}$

if MB statistics are used.

⇨ Consider em waves in a cavity as a photon gas subject to Bose-Einstein statistics.

The average number of photons $f(v)$ in each state of energy $\varepsilon = hv$ is given by B-E statistics.

Photon distribution function

$$f(v) = \frac{1}{e^{hv/kT} - 1} \quad (\alpha = 0)$$

⇨ $u(v)dv = hvG(v)f(v)dv$

$$= \frac{8\pi h}{c^3} \frac{v^3 dv}{e^{hv/kT} - 1}$$

○ Wien's Displacement Law

Find λ_{max} at given temperature for which the energy density is the greatest.

⇨ solve $du(\lambda)/d\lambda = 0$ for $\lambda = \lambda_{max}$

⇨ $\dfrac{hc}{kT\lambda_{max}} = 4.965$

⇨ $\lambda_{max} \cdot T = \dfrac{hc}{4.965} = 2.898 \times 10^{-3} m \cdot K$

⇨ the peak in the blackbody spectrum shifts to shorter wavelengths (higher frequency) as the temperature is increased.

*Stefan-Boltzman Law

Total energy density u

$$u = \int_0^\infty u(\nu)d\nu = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 = aT^4$$

total energy density $\propto T^4$

$\Rightarrow$ radiated energy R by an object per second per unit area is

$\propto T^4$

$\Rightarrow$ Stefan-Boltzman Law：$R = e\sigma T^4$

$$\sigma = \frac{ac}{4} = 5.67 \times 10^{-8} \text{ W}/\text{m}^2 \cdot \text{K}^4$$

The emissivity e depends on the nature of radiating surface.

【9.7 Specific Heats of Solids】

Molar specific heat of a solid at constant volume C_v

⇨ Energy that must be added to 1 Kmol of the solid, whose volume is held fixed, to raise its temperature by 1 K.

⇨ The internal energy of a solid, resides in the vibrations of its constituent particles. These vibrations may be resolved into components along three perpendicular axes. => use three harmonic oscillators.

⇨ Each atom in a solid should have 3kT of energy.

⇨ Classical internal energy of solid

$$E = 3N_0kT = 3RT$$

⇨ $C_v = \left(\dfrac{\partial E}{\partial T}\right)_v = 3R = 5.97 \, \text{kcal/mol} \cdot \text{K}$ (Dulong-Petit law)

＊ However, for light elements as B, Be, C

$C_v \ll 3R$ at $20°C$

And when $T \to 0$ all solid $C_v \to 0$

See figure at P.320

Einstein's Law

The basic flaw for Dulong-Petit Law → kT for $\bar{\varepsilon}$

Einstein proposed average energy per oscillator $\bar{\varepsilon}$

$$\bar{\varepsilon} = h\nu f(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1} \quad \text{(average phonon energy per one}$$

direction by Debye model)

⇨ internal energy of solid

$$E = 3N_0\bar{\varepsilon} = \frac{3N_0 h\nu}{e^{h\nu/kT} - 1}$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1\right)^2}$$

◯ at high temperature, $h\nu \ll kT$

$$\Rightarrow e^{h\nu/kT} \cong 1 + \frac{h\nu}{kT}$$

$$\Rightarrow \bar{\varepsilon} \approx kT \rightarrow C_v = 3R \qquad \text{(Dulong-Petit values)}$$

at high T, the spacing $h\nu$ between possible energies is

small relative to $kT \Rightarrow \bar{\varepsilon}$ is almost continuous

⇨ classical physics holds.

*at $T \downarrow \downarrow \Rightarrow C_v \downarrow$

∵ when T decreases, spacing between possible energies ↑ ↑

inhibits the possession of energies above zero-point energy

Why the zero-point energy does not enetr this analysis?

∵ $C_v = \left(\frac{\partial E}{\partial T}\right)_v$ zero-point energy $\varepsilon_0 = \frac{1}{2}h\nu \neq$ function of T

【9.8 Free Electron in Metal】

*If e' behave like the molecules of an ideal gas => each would

have $\frac{3}{2}kT$, kinetic energy

$\Rightarrow$ $E_e = \frac{3}{2}N_0kT = \frac{3}{2}RT$

$\Rightarrow$ $C_{ve} = \left(\frac{\partial E_e}{\partial T}\right)_v = \frac{3}{2}R$

$\Rightarrow$ total specific heat $C_v \Rightarrow 3R + \frac{3}{2}R = \frac{9}{2}R$ at high T

But, 3R holds for high T. Why?? e' do not contribute to C_v

*for e', average occupancy per state

$$f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$$

now, we would like to find g(ε)dε ,number of quantum

states available to e' betweenε &ε +dε

same as number of standing waves.

$$g(j)dj = \pi j^2 dj$$

$$j = \frac{2L}{\lambda} \text{ for e' } \lambda = \frac{h}{p} \& p = \sqrt{2mE}$$

$$j = \frac{2L}{\lambda} = \frac{2Lp}{h} = \frac{2L\sqrt{2mE}}{h} \qquad dj = \frac{L}{h}\sqrt{\frac{2m}{\varepsilon}}d\varepsilon$$

$$\Rightarrow \quad g(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi L^3 m^{3/2}}{h^3}\sqrt{\varepsilon}d\varepsilon$$

$$\Rightarrow \quad g(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3}\sqrt{\varepsilon}d\varepsilon$$

*Femi energy

E_f = highest state to be filled

$\because$ each state is limited to one e'

$$\therefore N = \int_0^{\varepsilon_f} g(\varepsilon)d\varepsilon = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3}\varepsilon_f^{3/2}$$

$$\Rightarrow \quad \boxed{\varepsilon_f = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}}$$

(N/V is the density of free e')

【9.9 Electron-Energy Distribution】

$$n(\varepsilon)d\varepsilon = g(\varepsilon)f(\varepsilon)d\varepsilon = \frac{\left(8\sqrt{2}\pi V\, m^{3/2}/h^3\right)\sqrt{\varepsilon}\,d\varepsilon}{e^{(\varepsilon-\varepsilon_f)/kT}+1}$$

$$\Rightarrow n(\varepsilon)d\varepsilon = \frac{(3N/2)\varepsilon_f^{\frac{-3}{2}}\sqrt{\varepsilon}\,d\varepsilon}{e^{(\varepsilon-\varepsilon_f)/kT}+1} \qquad \text{see fig 9.10}$$

*The total energy E_0 at 0 K

$$E_0 = \int_0^{\varepsilon_f} \varepsilon n(\varepsilon)d\varepsilon$$

$$e^{(\varepsilon-\varepsilon_f)/kT} = e^{-\infty} = 0$$

$$\Rightarrow E_0 = \frac{3N}{2}\varepsilon_f^{\frac{-3}{2}}\int_0^{\varepsilon_f}\varepsilon^{\frac{3}{2}}d\varepsilon = \frac{3}{5}N\varepsilon_f$$

$\Rightarrow$ average energy for e' at $T = 0$ $\quad \overline{\varepsilon_0} = \frac{3}{5}\varepsilon_f$

＊ The temperature of an ideal gas whose molecules have an
average kinetic energy of 1 eV is 11,600 K. But $\varepsilon_f \sim$
several eV.

A sample of Cu would have to be at $T > 50,000$ K for its e'
to have the same energy at $T = 0$ K.

＊ The failure of free e' in a metal to contribute appreciably to
C_v is due to the energy distribution.

When a metal is heated, only e' hear the ε_f (ε -$\varepsilon_f \sim$ several
kT) can be excited to higher state.

$$\Rightarrow \quad C_{ve} = \frac{\pi^2}{2}\left(\frac{kT}{\varepsilon_f}\right)R$$

at room temperature, $\dfrac{kT}{\varepsilon_f} \cong 0.016 - 0.0021$ very small

*Ony if T is very low $\Rightarrow C_{ve}$ become significant ($C_v \propto T^3$ but

$C_{ve} \propto T$)

*Or if T is very high $\Rightarrow C_v \rightarrow 3R$ but $C_{ve} \uparrow \uparrow$