

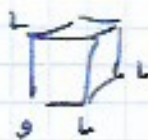
## §7. IDEAL GAS IN CANONICAL ENSEMBLE

A simple particle in a box

$$\Psi_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(n_x \frac{\pi x}{L}\right) \sin\left(n_y \frac{\pi y}{L}\right) \sin\left(n_z \frac{\pi z}{L}\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

$$n_i = 1, 2, 3, \dots$$



Partition function for a single atom  $Z_1$

$$Z_1 = \sum_{n_x, n_y, n_z} e^{-\beta E_{n_x n_y n_z}} =$$

$$= \int_0^L dx \int_0^L dy \int_0^L dz e^{-\beta \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)}$$

$$= \left\{ x = \frac{\sqrt{\frac{\beta \hbar^2}{2m} \left(\frac{\pi}{L}\right)^2} n_x}{\text{etc.}} \right\} = \quad V = L^3$$

when  $L \rightarrow \infty \quad \sum \rightarrow \int dn_x$   
 $\Delta \epsilon \ll k_B T$

$$= \left( \frac{1}{\sqrt{\frac{\beta \hbar^2}{2m} \left(\frac{\pi}{L}\right)^2}} \right)^3 \left( \int_0^\infty dx e^{-x^2} \right)^3 = \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} V$$

Let  $n_Q = \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2}$        $[n_Q] = \left[ \frac{k_B \cdot T \cdot m}{\hbar^2 \cdot s^2} \right]^{3/2} =$

quantum concentration       $= \left[ \frac{k_B}{k_B \cdot m^2 \cdot s^2} \right]^{3/2} = \left[ \frac{1}{m^3} \right]$

$$\lambda_{dB} = \left( \frac{1}{n_Q} \right)^{1/3} = \sqrt[3]{\frac{2\pi \hbar^2}{m k_B T}} \quad [\lambda_{dB}] = [m]$$

de Broglie thermal wavelength

hence,

$$Z_1 = n_Q V = \left( \frac{L}{\lambda_{dB}} \right)^3$$



Alternative definition of thermal wave length

kinetic energy:  $E_{kin} = \frac{mv^2}{2} = k_B T$

$k = \frac{2\pi}{\lambda}$

$\lambda_{dB} = \frac{2\pi}{k} = \frac{2\pi}{\sqrt{\frac{2mE_{kin}}{h^2}}} = \sqrt{\frac{h^2}{m k_B T}}$



classical



$\lambda_{dB}$  - characteristic wave length of a quantum particle at given T. Large T, classical limit,  $\lambda_{dB} \rightarrow 0$

Example He gas at normal conditions (T=300K, p=1atm)

$n = 2.5 \cdot 10^{19} \frac{1}{cm^3}$

$n_Q = 0.8 \cdot 10^{25} \frac{1}{cm^3}$

$Z_1 = \frac{n_Q}{n} = 0.3 \cdot 10^6$

$n = \frac{1}{v}$  concentration

v - volume per particle

$v = \frac{V}{N}$

Classical gas if

$\frac{n}{n_Q} \ll 1$

or  $n \ll n_Q$

in other words

$\lambda_{dB} \ll \sqrt[3]{v}$

wave length

typical distance between point particles

Ideal gas is a non-interacting gas in classical limit



Internal energy of a simple atom

$$U_1 = \frac{1}{Z_1} \sum_n \epsilon_n e^{-\beta \epsilon_n} = k_B T^2 \frac{\partial \ln Z_1}{\partial T}$$

$$\ln Z_1 = \ln \left[ \left( \frac{2\pi m k_B T}{2\pi \hbar^2} \right)^{3/2} V \right] = \frac{3}{2} \ln k_B T + \dots$$

high  
T - indep.

$$U_1 = k_B T^2 \frac{\partial}{\partial T} \left( \frac{3}{2} \ln k_B T \right) = \frac{3}{2} k_B T$$

Energy per particle  $U_1 = \frac{3}{2} k_B T$

N - non-interacting particles

$$Z = \frac{1}{N!} (Z_1)^N$$

N! - particles identical

$$Z = \frac{1}{N!} (n \lambda^3)^N = \frac{1}{N!} \left( \frac{V}{\lambda_{dB}^3} \right)^N$$

$$\lambda_{dB} = \sqrt{\frac{2\pi \hbar^2}{m k_B T}}$$

Internal energy

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = \frac{3}{2} N k_B T = n R T$$

$$U = n R T$$

R - gas constant

$$R = k_B N_A$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = n R = \text{const.}$$

$$n = \frac{N}{N_A} - \text{mole number}$$



## Free (Helmholtz) energy

$$\ln N! = N \ln N - N$$

$$\begin{aligned} F &= -k_B T \ln Z = -k_B T \ln Z_1 + k_B T \ln N! = \\ &= -k_B T N \ln \left( \frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} - k_B T \ln V + k_B T N \ln N - k_B T N = \\ &= -k_B T N \left[ \ln \left( \frac{n_Q V}{N} \right) - 1 \right] = -k_B T N \left[ \ln \left( \frac{n_Q}{n} \right) - 1 \right] \end{aligned}$$

## Pressure

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{k_B T N}{V} = \frac{1}{V} n R$$

$\Rightarrow$

$$PV = nRT$$

equation of states for an ideal gas (Clausius)

## Entropy

$$S = - \left( \frac{\partial F}{\partial T} \right)_V =$$

$$S = \frac{k_B N}{nR} \left[ \ln \left( \frac{n_Q}{n} \right) + \frac{5}{2} \right]$$

Sackur-Tetrode formula

of course,  $U = F + TS = \frac{3}{2} N k_B T$

if we "forget"  $N!$  factor

$$Z = (n_Q V)^N$$

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = \frac{3}{2} N k_B T \quad \underline{OK}$$

$$F = -k_B T \ln Z = -k_B T N \ln(n_Q V)$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{k_B T N}{V} \quad \underline{OK}$$

no  $N$  in denominator!

$$S = - \left( \frac{\partial F}{\partial T} \right)_V = k_B N \left[ \ln \left( \frac{n_Q}{n} \right) + \frac{3}{2} \right]$$

no !!!



## Gibbs paradox



The system is increased twice

$$N \rightarrow 2N$$

$$V \rightarrow 2V$$

$$F \rightarrow 2F$$

$$S \rightarrow 2S$$

Extensive variables

Distinguishable particles (no  $N!$  factor)

$$F \rightarrow F' = -k_B T (2N) \ln(2N \theta V) = 2F - \underline{2N k_B T \ln 2}$$

$$\begin{aligned} S \rightarrow S' &= 2 k_B N \left[ \ln(2N \theta V) + \frac{3}{2} \right] = \\ &= 2 k_B N \left[ \ln(N \theta V) + \frac{3}{2} \right] + 2 k_B N \ln 2 = \\ &= 2S + \underline{2 k_B N \ln 2} = - \left( \frac{\partial F'}{\partial T} \right)_V \end{aligned}$$

Indistinguishable particles (with  $N!$  factor)

$$F \rightarrow F' = -2 k_B T N \left[ \ln \left( \frac{n \theta}{N} \right) - 1 \right] = 2F$$

$$S \rightarrow S' = 2 k_B N \left[ \ln \left( \frac{n \theta}{N} \right) + \frac{5}{2} \right] = 2S$$

T	T
V	V
N	N

We remove the partition.

If particles identical, the process is reversible (!) and  $S + S = S' = 2S$

If particles are indistinguishable, the process is irreversible and the entropy increases

$$S + S \rightarrow S' = 2S + \Delta S$$

$$\boxed{\Delta S = 2 k_B N \ln 2} \quad - \quad \underline{\text{missing entropy}}$$



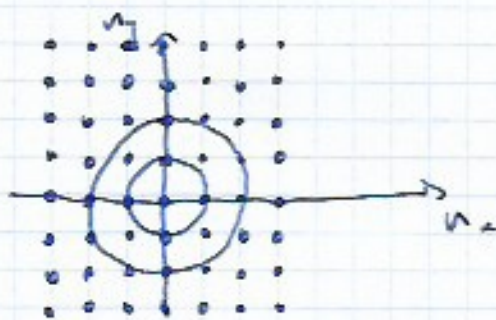
# § 8. MAXWELL DISTRIBUTION

For an ideal gas  $Z_1 = \frac{V \Omega}{\lambda^3} = \frac{V}{\lambda^3} \rightarrow \infty$

$$P_1(\epsilon_n) = \frac{1}{Z_1} e^{-\beta \epsilon_n}, \quad \epsilon_n = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} n \right)^2, \quad n^2 = n_x^2 + n_y^2 + n_z^2$$

A probability density that an atom has quantum numbers  $n$  in  $[n, n+dn]$  is given by

$$P_1(n) = (\text{number of orbitals in } [n, n+dn]) \times (\text{probability of occupying this orbital})$$



Note  $n_x, n_y, n_z > 0$ , we take  $\frac{1}{8}$  of a sphere of radius  $n$  at  $n \rightarrow \infty$ .

$$\frac{1}{8} (4\pi n^2) dn$$

$$P_1(n) = \frac{1}{2} \pi n^2 \frac{1}{Z_1} e^{-\beta \epsilon_n} = \frac{1}{2} \pi n^2 \frac{\Omega \lambda^3}{L^3} e^{-\beta \epsilon_n}$$

In Maxwell distribution we need a probability distribution for a classical speed  $v$

$$\frac{1}{2} m v^2 = \frac{\hbar^2}{2m} \left( \frac{\pi}{L} n \right)^2 \Rightarrow v = \frac{\hbar \pi}{m L} n \Rightarrow n = \frac{m L}{\hbar \pi} v$$

$$dn = \frac{dn}{dv} dv = \frac{m L}{\hbar \pi} dv$$

For  $N$ -atoms, a probability to find particles with  $[v, v+dv]$

$$N P_1(v) dv = ?$$



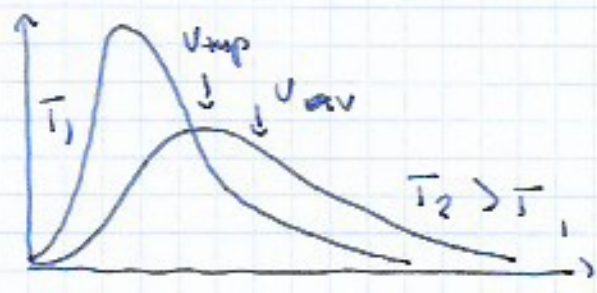
$$N \frac{1}{2} \frac{d^3 v}{L^3} n^2 e^{-\beta \epsilon_n} dv =$$

$$= N \frac{1}{2} \frac{d^3 v}{L^3} \left(\frac{mL}{2\pi\hbar}\right)^3 v^2 e^{-\beta \frac{mv^2}{2}} \frac{dv}{dv} = \dots$$

$$\dots = 4\pi \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} v^2 e^{-\beta \frac{mv^2}{2}} dv$$

Finally, the relative  $P(v) = \frac{N P_i(v)}{N}$  number of particles with the velocity  $v$  is

$$P(v) = 4\pi \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} v^2 e^{-\beta \frac{mv^2}{2}} \quad \text{Maxwell distribution}$$



$$\int_0^{\infty} dv P(v) = 1$$

$$v_{av} = \sqrt{\frac{8\ln 2 T}{\pi m}}$$

$$v_{rms} = \sqrt{\frac{2\ln 2 T}{m}}$$

gas	$v_{av}$ [ $10^4 \frac{cm}{s}$ ]
H <sub>2</sub>	16.9
He	12.1
Ar	5.7
O <sub>2</sub>	4.2
free electrons	10.3

( $10^4 \text{ cm} = 0,1 \text{ km}$ )



# Other forms of Maxwell distribution

velocity components ( $v_x, v_y, v_z$ )

$$4\pi v^2 dv = dv_x dv_y dv_z$$

$$P(v) dv = \left( \sqrt{\frac{m}{2\pi k_B T}} \right)^3 dv_x dv_y dv_z e^{-\beta \frac{m}{2} (v_x^2 + v_y^2 + v_z^2)}$$

hence

$$P(v) dv = \prod_{i=1}^3 P(v_i) dv_i$$

$$P(v_i) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\beta \frac{m v_i^2}{2}}$$

Gauss functions

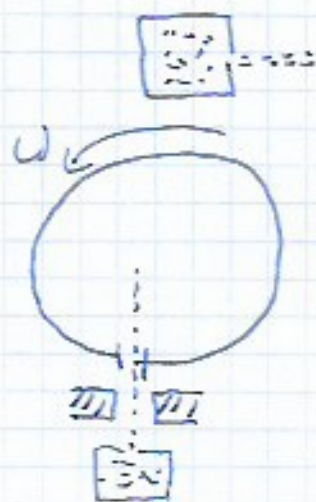
energy

$$E = \frac{1}{2} m v^2 \rightarrow v = \sqrt{\frac{2E}{m}}$$

$$dE = m v dv = \sqrt{2mE} dv, \quad \frac{dv}{dE} dE = \frac{1}{\sqrt{2mE}} dE$$

$$P(E) dE = \frac{2}{\sqrt{\pi}} \left( \frac{1}{k_B T} \right)^{3/2} \sqrt{E} e^{-\frac{E}{k_B T}} dE$$

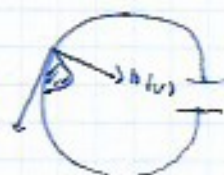
How Maxwell distribution is experimentally seen?



flux of particles  $j = v n(v)$

$$dj = v dn(v) \sim N \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^3 e^{-\frac{mv^2}{2k_B T}} dv$$

$\uparrow$  # of particles emitted in  $(v, v+dv)$



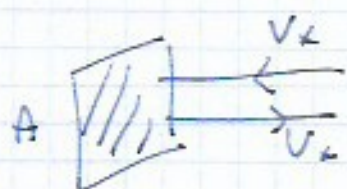
silver sediment

on cylinder has different thickness

The fastest particles arrive firstly.



# Ideal gas - application of Maxwell distribution



change of momentum  $\Delta p = 2mv_x$

$$\Delta p = F \Delta t \rightarrow F = \frac{2mv_x}{\Delta t}$$

1) pressure from one particle  $p_1 = \frac{F}{A}$

2)  $n$  particles hit in  $\Delta t$

3) total pressure  $p = p_1 n$



ratio of volumes

$$n = \left( \frac{l \cdot A}{V} \right) N = \frac{v_x \Delta t A}{V} N = v_x \Delta t A \frac{N}{V}$$

# of particles in a box of length  $l = v_x \Delta t$

total number of particles

$$p_{tot} = p_1 \cdot n = \frac{F}{A} \cdot v_x \Delta t \cdot A \cdot \frac{N}{V} = 2m v_x^2 \frac{N}{V}$$

## Average pressure

$$p = \langle p_{tot} \rangle = \frac{N}{V} 2m \int_0^{\infty} v_x^2 p(v_x) dv_x = \frac{N}{V} \frac{2}{3} m \langle v^2 \rangle$$

"  $\frac{3}{2} \frac{k_B T}{m}$  "

$$\Rightarrow \boxed{pV = N k_B T}$$

Clapeyron's equation of state for an ideal gas

## Internal energy

$$\boxed{U = N \langle E \rangle = N \frac{m}{2} \langle v^2 \rangle = N \frac{3}{2} k_B T}$$

$$\boxed{pV = \frac{2}{3} U}$$

"average of momentum change"

"average of kinetic energy"



# IV PLANCK DISTRIBUTION APPLICATIONS

## § 1. PLANCK DISTRIBUTION

A Universal Planck distribution describes a radiation of electromagnetic field from a resonant cavity, thermal fluctuations of <sup>electric</sup>  $\sqrt{C_{\nu}}$   $\nu$ , spectrum of ion oscillations in crystals.

Consider a single mode of vibration of frequency  $f = \frac{1}{T}$  [Hz = 1/s] (mechanical). We also use  $\omega = 2\pi f$  [ $\frac{rad}{s}$ ] (radiosc). vibrations can be mechanical or electrical.

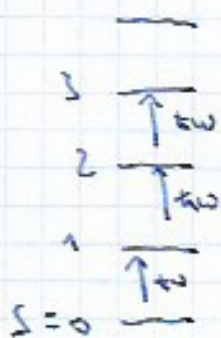
Planck, 1900 - a single mode of vibration with frequency  $\omega$  is created in discrete portion of energies, such that energy of system is

$$E_s = \hbar \omega (s + \frac{1}{2}) = hf (s + \frac{1}{2})$$

$$s = 0, 1, 2, 3, \dots$$

↑ zero point energy

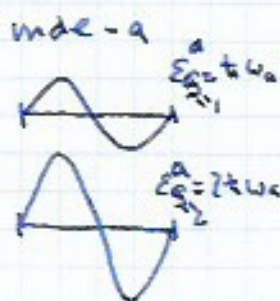
↑ spectrum of harmonic oscillator



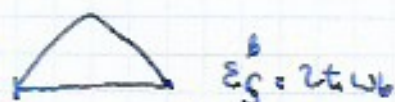
- harmonic oscillator was realized

- electromagnetic oscillations or

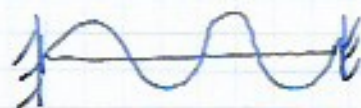
mechanical oscillations are



extended in space



mode-b





$s$  → quantum number of an oscillator of frequency  $\omega$   
 → number of quanta of frequency  $\omega$

### Canonical ensemble

$$P(s) = \frac{1}{Z} e^{-\beta \epsilon_s} = \frac{1}{Z} e^{-\beta \hbar \omega (s + \frac{1}{2})}$$

### Partition function

$$Z = \sum_{s=0}^{\infty} (e^{-\beta \hbar \omega})^s e^{-\beta \hbar \omega \frac{1}{2}} = \frac{e^{-\beta \hbar \omega \frac{1}{2}}}{1 - e^{-\beta \hbar \omega}}$$

$$\sum_{s=0}^{\infty} x^s = \frac{1}{1-x}, \quad |x| < 1 \quad \text{geometric progress, } e^{-\beta \hbar \omega} < 1$$

$\omega > 0, \beta > 0$

### Average number of quanta

$$\langle s \rangle = \sum_{s=0}^{\infty} s P(s) = \frac{1}{Z} \sum_{s=0}^{\infty} s e^{-\beta \hbar \omega s} e^{-\beta \hbar \omega \frac{1}{2}}$$

note:  $\sum_{s=0}^{\infty} s e^{-y s} = -\frac{d}{dy} \sum_{s=0}^{\infty} e^{-y s} = -\frac{d}{dy} \left( \frac{1}{1-e^{-y}} \right) = \frac{e^{-y}}{(1-e^{-y})^2}$

$y = \beta \hbar \omega$

$$\langle s \rangle = \frac{1}{\frac{e^{-\beta \hbar \omega \frac{1}{2}}}{1 - e^{-\beta \hbar \omega}}} \cdot \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} e^{-\beta \hbar \omega \frac{1}{2}} = \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$\langle s \rangle = \bar{s} = \frac{1}{e^{\beta \hbar \omega} - 1}$$



Planck distribution for a simple mode of vibration in thermal equilibrium with environment.



## Internal energy of a single mode

$$u = \langle \varepsilon \rangle = \hbar \omega \left( \langle n \rangle + \frac{1}{2} \right) = \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} + \frac{\hbar \omega}{2}$$

- ) low temperature limit  $k_B T \ll \hbar \omega$  (quantum)

$$Z \approx e^{-\beta \frac{\hbar \omega}{2}}$$

$$u \approx \hbar \omega e^{-\frac{\hbar \omega}{k_B T}} + \frac{\hbar \omega}{2}$$

- ) high temperature limit  $k_B T \gg \hbar \omega$  (classical)

$$Z \approx \frac{k_B T}{\hbar \omega}$$

$$u \approx \frac{\hbar \omega}{1 + \frac{\hbar \omega}{k_B T} + \dots} \approx k_B T + \text{const.}$$

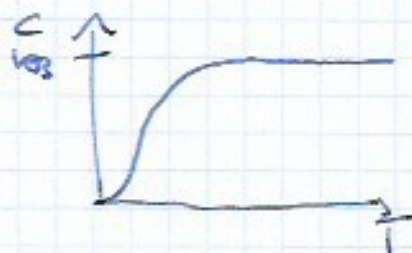
- ) Specific heat

$$C = \frac{du}{dT} = \frac{(\hbar \omega)^2}{4(k_B T)^2 \sinh^2 \left( \frac{\hbar \omega}{2k_B T} \right)}$$

-no zero modes

Warning: popular formulation of equipartition theorem: "on each degree of freedom there is  $\frac{1}{2} k_B T$  energy" is not correct

$$C = \begin{cases} k_B & T \rightarrow \infty \\ \frac{(\hbar \omega)^2}{(k_B T)^2} e^{-\frac{\hbar \omega}{k_B T}} & T \rightarrow 0 \end{cases}$$



- ) Free energy

$$F = -k_B T \ln Z = \frac{\hbar \omega}{2} + k_B T \ln(1 - e^{-\beta \hbar \omega})$$

- ) Entropy

$$F = U - TS \rightarrow S = \frac{U - F}{T}$$

$$S = \frac{1}{T} \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} - k_B T \ln(1 - e^{-\beta \hbar \omega}) \right)$$