

Energy distribution of the gaseous atoms

What we are after is to find the no. of atoms having K.E. between E & $E + dE$. As they don't have P.E.

$$E = \frac{1}{2} m c^2 \quad \text{or} \quad dE = m c \, dc.$$

$$\text{or} \quad dc = \frac{dE}{m \sqrt{\frac{2E}{m}}} = \frac{dE}{\sqrt{2mE}}.$$

From Maxwell's velocity distribution, we have

$$dn_c = 4\pi n c^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mc^2/2k_B T} dc.$$

$$\therefore dn_E = 4\pi n \frac{2E}{m} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-E/k_B T} \frac{dE}{\sqrt{2mE}}$$

$$dn_E = 2n \sqrt{\frac{E}{\pi}} (k_B T)^{-3/2} e^{-E/k_B T} dE$$

(remember if v is cancelled $dn_E \sim N$)

$$\text{Fraction of atoms} \quad \frac{dn_E}{n} \text{ or } \frac{dN_E}{N} = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \sqrt{E} e^{-E/k_B T} dE = f_E dE$$

$$f_E = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \sqrt{E} e^{-E/k_B T}$$

$$\text{at } E = E_m, \quad \frac{df_E}{dE} = 0.$$

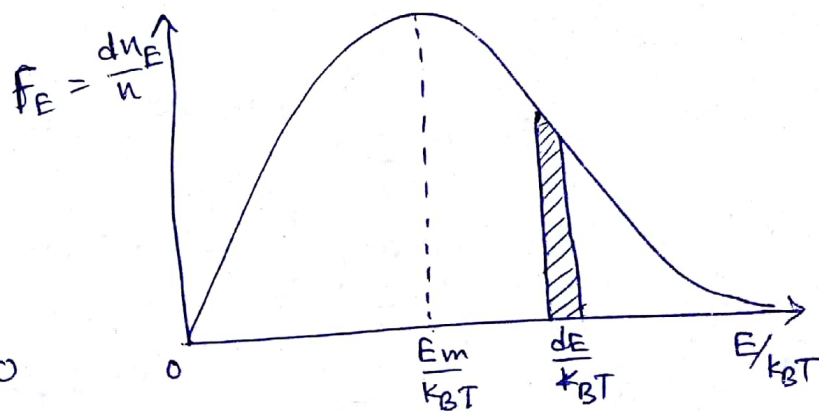
$$\frac{d}{dE} \left\{ \sqrt{E} e^{-E/k_B T} \right\}_{E=E_m} = 0$$

$$\text{or } \frac{1}{2\sqrt{E_m}} e^{-E_m/k_B T} - \frac{\sqrt{E_m}}{k_B T} e^{-E_m/k_B T} = 0.$$

$$\therefore \frac{1}{2\sqrt{E_m}} = \frac{\sqrt{E_m}}{k_B T} \quad \text{or} \quad E_m = \frac{k_B T}{2}.$$

Compare result with $c_m = \sqrt{\frac{2k_B T}{m}}$. Notice that

$$E_m \neq \frac{1}{2} m c_m^2 = \frac{1}{2} m \frac{2k_B T}{m} = k_B T.$$



Momentum distribution of the gaseous atoms

No. of molecules in a range of momentum p to $p+dp$.

$$p = mc \text{ \& } dp = mdc.$$

Again, start from Maxwell's distribution

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} c^2 e^{-\frac{mc^2}{2k_B T}} dc$$

$$\begin{aligned} \therefore dN_p &= 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{p^2}{m^2} e^{-\frac{p^2}{2k_B T m}} \frac{dp}{m} \\ &= N \sqrt{\frac{2}{\pi}} (mk_B T)^{-3/2} p^2 e^{-\frac{p^2}{2mk_B T}} dp = F_p dp. \end{aligned}$$

at $p = p_m$ (most probable momentum), maximum no. of molecules

$$\text{lie } \left. \frac{dF_p}{dp} \right|_{p=p_m} = 0 \quad \propto \quad \left. \frac{d}{dp} (p^2 e^{-\frac{p^2}{2mk_B T}}) \right|_{p=p_m} = 0$$

$$\propto \left. \frac{d}{dp} (p^2 e^{-bp^2}) \right|_{p=p_m} = 0$$

$$\text{put } b = \frac{1}{2mk_B T}$$

$$\propto (2p e^{-bp^2} - p^2 \cdot 2bp e^{-bp^2}) \Big|_{p=p_m} = 0$$

$$\propto [2p e^{-bp^2} (1 - bp^2)] \Big|_{p=p_m} = 0 \quad \Rightarrow \quad p_m = \frac{1}{\sqrt{b}} = \sqrt{2mk_B T}$$

$$\text{Again, } c_m = \sqrt{\frac{2k_B T}{m}}$$

$$\text{So } \underline{mc_m = \sqrt{2mk_B T} = p_m.}$$

So most of the atoms have velocity c_m are also having the momentum mc_m , but ~~to~~ most of them do not have $\frac{1}{2}mc_m^2$ energy, rather most of the atoms have energy half of that.

If P.E. included in gravitational field
Maxwell-Boltzmann distribution.

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times e^{-(mgh + \frac{1}{2}mc^2)/k_B T} c^2 dc$$

Degrees of freedom

1D motion \rightarrow 1 d.o.f.

2D (unconstrained) motion \rightarrow 2 d.o.f.


3D (unconstrained) motion \rightarrow 3 d.o.f.

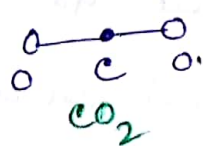
constraint reduce no. of independent variables necessary to designate the configuration of a dynamical system.

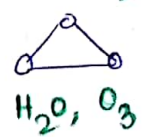
N particles in 3D coordinates $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_N, y_N, z_N)$
with constraint $f_j(x_1, y_1, z_1, \dots, x_N, y_N, z_N) = 0, j = 1, 2, 3, \dots, m.$

$$\therefore \underline{K = 3N - m = \text{d.o.f.}}$$

Example (1) Monoatomic atom : $K = 3$ for one atom.

(2) Diatomic ~~atom~~ molecule :  $K = 2 \times 3 - 1 = 5$ for one molecule.

(3) Triatomic molecule: (a) linear  $K = 3 \times 3 - 2 = 7$

(b) Nonlinear  $K = 3 \times 3 - 3 = 6$

So trivial case, $m = 3N \rightarrow$ only one configuration.

$m > 3N$ not feasible, more constraint equation than unknowns.

$m < 3N$ is only feasible.

Generalized position & velocity coordinates

If a system has N d.o.f. then we can choose a set of N elements $q_1, q_2, q_3, \dots, q_N$ that correspond to configuration & $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_N$ which to velocity vector at that configuration. These are generalized coordinates.

Law of equipartition of energy

Energy of a dynamical system in thermal equilibrium is equally divided amongst its d.o.f. & the value is $\frac{1}{2} k_B T$ for each d.o.f.

Suppose a system of free atoms has f d.o.f.

Every d.o.f. gets $\frac{1}{2} k_B T$ energy, then the energy per gm molecule

$$\therefore U = \frac{1}{2} N f k_B T = \frac{1}{2} R f T \quad [k_B = \frac{R}{N}]$$

$$\therefore C_V = \left(\frac{dU}{dT} \right)_V = R f / 2.$$

From $C_p - C_V = R$, we have $C_p = R + \frac{R f}{2}$.

$$\therefore \frac{C_p}{C_V} = \frac{R + \frac{R f}{2}}{R f / 2} = \frac{2}{f} + 1 \quad \text{or} \quad \boxed{\gamma = 1 + \frac{2}{f}}$$

for monoatomic gas, $k=3$, $\gamma = 1 + \frac{2}{3} = 1.66$.

for diatomic gas, $k=5$, $\gamma = 1 + \frac{2}{5} = 1.4$

for triatomic linear gas, $k=7$, $\gamma = 1 + \frac{2}{7} = 1.28$

for triatomic not colinear gas, $k=6$, $\gamma = 1 + \frac{2}{6} = 1.33$.

Dulong & Petit's law

1819 Experimental investigation \Rightarrow product of atomic weight & specific heat of almost all solid substances are nearly equal to 6 calories.

Consider 1 mole of a solid with each atom/molecule have 3 translational d.o.f. & 2 rotational d.o.f. & 3 vibrational d.o.f. (vibration about mean equilibrium configuration). Rotation isn't allowed in crystal, as they're rigidly fixed.

\therefore Number of d.o.f. of 1 mole solid is $6N$.

Every d.o.f. gets $\frac{1}{2} k_B T$ energy from Equipartition theorem.

$$\therefore \text{Total energy} = U = 6N \frac{1}{2} k_B T = 3N k_B T = 3RT$$

$$\therefore C_V = \left(\frac{dU}{dT} \right)_V = 3R = 3 \times 1.98 \text{ cal} \approx 6 \text{ cal}.$$

Sometimes "atomicity" is also equivalent to d.o.f, $f = \frac{2}{\gamma-1}$.

Variation of γ with temperature

High T, translation + rotation + vibration,

$$f(\text{diatomic molecule}) = 7, \quad \gamma = 1 + \frac{2}{7} = 1.29.$$

like $H_2 > 5000^\circ C$ $C_v = \frac{7}{2}R$

Medium T, translation + rotation

$$f(\text{diatomic molecule}) = 5, \quad \gamma = 1 + \frac{2}{5} = 1.4.$$

like $H_2 \approx 250K$ $C_v = \frac{5}{2}R$

low T, translation

$$f(\text{diatomic molecule}) = 3, \quad \gamma = 1 + \frac{2}{3} = 1.66$$

like $H_2 \approx 70K$ $C_v = \frac{3}{2}R$

CW 1. What is the atomicity of a gas with heat capacity ratio 1.33? Given, $R = 8.31 \text{ J/mol/K}$. Calculate C_p, C_v values also.

$$C_p - C_v = R \quad \text{or} \quad C_v \left(\frac{C_p}{C_v} - 1 \right) = R \quad \text{or} \quad C_v (\gamma - 1) = R.$$

$$\therefore C_v = \frac{R}{\gamma - 1} = \frac{8.31}{1.33 - 1} = 25.18 \text{ J/mol/K}.$$

$$C_p = \gamma C_v = 33.49 \text{ J/mol/K}.$$

$$\therefore \text{Atomicity } f = \frac{2}{\gamma - 1} = \frac{2}{0.33} = 6. \quad (\text{not monoatomic gas}).$$

2. Calculate (a) K.E. of translation of O_2 molecule, (b) total K.E. and (c) total K.E. of a gram molecule at $27^\circ C$. Given $k_B = 1.37 \times 10^{-23} \text{ J/K}$ & $N = 6.02 \times 10^{23}$.

$$O_2 = 3 \text{ translation} + 2 \text{ rotation } (\theta, \phi), \quad f = 5.$$

(x, y, z)

$$(a) \text{ K.E. of translation} = \frac{3}{2} k_B T = \frac{3}{2} \times 1.37 \times 10^{-23} \times 300$$

$$= 6.17 \times 10^{-21} \text{ J}.$$

$$(b) \text{ K.E. of total} = \frac{5}{2} k_B T = 10.275 \times 10^{-21} \text{ J}$$

$$(c) \text{ of 1 gram molecule} = \frac{5}{2} k_B T \times N = 10.275 \times 10^{-21} \times 6.02 \times 10^{23}$$

$$= 6185.55 \text{ J}.$$

γ for a mixture of ideal gases

At temperature T , N_1 moles of ideal gas with f_1 d.o.f.
 N_2 moles of ideal gas with f_2 d.o.f.
 N_3 moles of ideal gas with f_3 d.o.f.
.....
 N_N moles of ideal gas with f_N d.o.f.

$$\text{Total internal energy } U = \frac{1}{2} K_B T N_1 f_1 + \frac{1}{2} K_B T N_2 f_2 + \dots + \frac{1}{2} K_B T N_N f_N$$

$$\therefore C_V = \left(\frac{dU}{dT} \right)_V = \frac{1}{2} K_B (N_1 f_1 + N_2 f_2 + \dots + N_N f_N)$$

$$\text{Also } C_p - C_V = (N_1 + N_2 + \dots + N_N) K_B T \quad [R/N = K_B]$$

$$\begin{aligned} \therefore C_p &= (N_1 + N_2 + \dots + N_N) K_B T + \frac{1}{2} (N_1 f_1 + N_2 f_2 + \dots + N_N f_N) K_B T \\ &= \frac{(2 + f_1) N_1 + (2 + f_2) N_2 + \dots + (2 + f_N) N_N}{2} K_B T \end{aligned}$$

$$\therefore \gamma = \frac{C_p}{C_V} = \frac{(2 + f_1) N_1 + (2 + f_2) N_2 + \dots + (2 + f_N) N_N}{f_1 N_1 + f_2 N_2 + \dots + f_N N_N}$$

Example

1 mole of monoatomic gas ($f=3$) & 1 mole of diatomic gas ($f=5$), $\gamma = \frac{(2 + f_1) N_1 + (2 + f_2) N_2}{f_1 N_1 + f_2 N_2} = \frac{5 + 7}{3 + 5} = 1.5$

$$\boxed{1 \leq \gamma \leq 1.67}$$