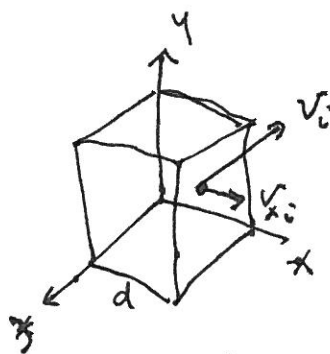


21.1 Molecular Model of an ideal gas

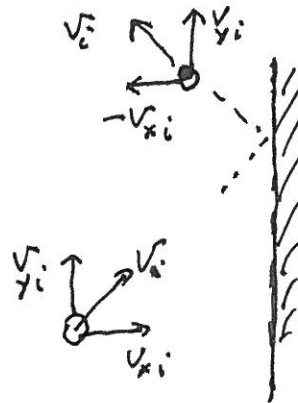
Assumptions

1. The number is big. The separation between gases is very large compared to their dimensions
2. Each individual molecules obey Newton's law. But as a whole, they move randomly
3. Molecules interact by short-range force during elastic collisions
4. Molecules make elastic collision with the container walls
5. All molecules are identical

Pressure of N molecules in volume V .



$i \equiv i^{\text{th}}$ molecules



x-momentum change

$$\Delta p_{xi} = -m v_{xi} - m v_{xi} = -2m v_{xi}$$

$$F_i \Delta t = \Delta p_{xi} = -2m v_{xi}$$

$$\Delta t = \frac{2d}{v_{xi}} = \text{time interval between two collisions with the same wall.}$$

$\therefore \overline{F}_i \Delta t = -2mV_{xi}$, $\overline{F} \equiv$ Average force component P21-2
 for molecule to move across the
 cube and back

\Rightarrow long time average force on the molecule

$$\overline{F}_i = \frac{-2mV_{xi}}{\Delta t} = \frac{-2mV_{xi}}{2d} = \frac{-mV_{xi}^2}{d}$$

$$\overline{F}_{i, \text{on wall}} = -\overline{F}_i = \frac{mV_{xi}^2}{d}$$

$$\text{Total average force } \overline{F} = \sum_{i=1}^N \frac{mV_{xi}^2}{d} = \frac{m}{d} \sum_{i=1}^N V_{xi}^2$$

$$\overline{V_x^2} = \frac{\sum_{i=1}^N V_{xi}^2}{N} = \text{Average } V_x^2$$

$$\therefore F = \frac{m}{d} N \overline{V_x^2}$$

$$V_i^2 = V_{xi}^2 + V_{yi}^2 + V_{zi}^2 \rightarrow \overline{V^2} = \overline{V_x^2} + \overline{V_y^2} + \overline{V_z^2}$$

$$\therefore \overline{V^2} = 3 \overline{V_x^2}$$

$$\text{Thus } F = \frac{N}{3} \left(\frac{m \overline{V^2}}{d} \right)$$

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3} \frac{N}{d^3} m \overline{V^2} = \frac{1}{3} \left(\frac{N}{V} \right) m \overline{V^2}$$

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \overline{V^2} \right) \sim \left(\frac{N}{V} \right) \left(\frac{1}{2} m \overline{V^2} \right)$$

kinetic energy

$P \rightarrow$ Macroscopic quantity

$\frac{1}{2} m \overline{V^2} \rightarrow$ Microscopic quantity

$$\left\{ \begin{array}{l} PV = \frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2 \right) \\ PV = N k_B T \end{array} \right. \rightarrow T = \frac{2}{3 k_B} \left(\frac{1}{2} m \bar{v}^2 \right)$$

$$PV = N k_B T$$

ideal gas law

= temperature is a measurement of average kinetic energy.

$$\text{or } \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$$

k_B = Boltzmann's constant

$$\frac{1}{2} m \bar{v}_x^2 = \frac{1}{2} k_B T$$

$$\frac{1}{2} m \bar{v}_y^2 = \frac{1}{2} k_B T$$

$$\frac{1}{2} m \bar{v}_z^2 = \frac{1}{2} k_B T$$

}

Equal partition theorem

Each degree of freedom contribute $\frac{1}{2} k_B T$ to the energy of a system

$$K_{\text{total}} = N \left(\frac{1}{2} m \bar{v}^2 \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

$$k_B = \frac{R}{N_A}$$

— The internal energy of an ideal gas depends only on the temperature

$\sqrt{\bar{v}^2}$ = root-mean-square (rms) speed

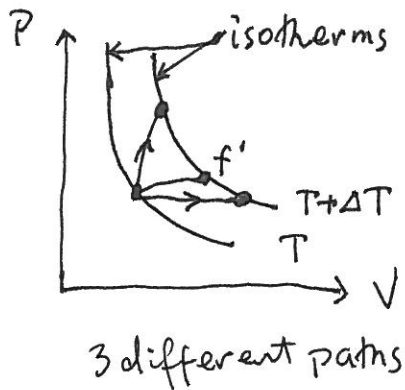
$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 R T}{M}}$$

$$\text{He @ } 20^\circ\text{C} \quad v_{\text{rms}} = 1352 \text{ m/s}$$

$$\text{H}_2 \quad v_{\text{rms}} = 1902 \text{ m/s}$$

21.2 Molar specific heat of an ideal gas

P21-4



$$\Delta T = T_f - T_i$$

for three different paths, ΔT is the same, so ΔE_{int} is the same

$$\text{But } Q = \Delta E_{int} - W$$

$W \equiv$ work done on the gas

$$Q = n C_v \Delta T \quad (\text{constant volume})$$

$$Q = n C_p \Delta T \quad (\text{constant pressure})$$

① constant volume $W = -\int p dV = 0$, $Q = \Delta E_{int}$

$$Q = \Delta E_{int} = n C_v \Delta T$$

$$C_v = \frac{1}{n} \frac{dE_{int}}{dT}, \quad E_{int} = E_{tot. transl.} = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

$$= \frac{1}{n} \frac{d}{dT} \left(\frac{3}{2} n R T \right)$$

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

② constant pressure

$$\Delta E_{int} = Q - W = n C_p \Delta T + (-P \Delta V)$$

$$n C_v \Delta T = n C_p \Delta T - n R \Delta T$$

$$\therefore C_p - C_v = R$$

$$C_p = \frac{3}{2} R + R = \frac{5}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2} R}{\frac{3}{2} R} = \frac{5}{3}$$

at constant pressure.
work need to be done to expand the volume

21.3 Adiabatic process for an ideal gas

$$Q = 0.$$

$$\Delta E_{\text{int}} = Q + W = \overset{W}{Q} = n C_V dT = -P dV$$

$$\text{But } PV = nRT$$

$$P dV + V dp = nR dT$$

$$= -\frac{R}{C_V} P dV$$

$$\frac{dV}{V} + \frac{dP}{P} = -\left(\frac{C_p - C_V}{C_V}\right) \frac{dV}{V}$$

$$= (1 - \gamma) \frac{dV}{V}$$

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

$$\ln P + \gamma \ln V = \text{constant}$$

$$PV^\gamma = \text{constant}$$

21.4 The equipartition of Energy

C_v and C_p discussed before are for monoatomic gases.
for molecules with more than 2 atoms.

Internal energy has translational, vibrational and rotational

Consider a diatomic molecule,

there are total 5 degree of freedoms

3 translational (x, y, z)

2 rotational

for N atom molecules

$$\begin{aligned} \bar{E}_{int} &= 3N \left(\frac{1}{2} k_B T \right) + 2N \left(\frac{1}{2} k_B T \right) \\ &= \frac{5}{2} N k_B T = \frac{5}{2} n R T \quad (\text{neglecting vibrational}) \end{aligned}$$

$$C_v = \frac{1}{n} \frac{d\bar{E}_{int}}{dT} = \frac{1}{n} \frac{d}{dT} \left(\frac{5}{2} n R T \right) = \frac{5}{2} R$$

$$C_p = C_v + R = \frac{7}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = \frac{7}{5} = 1.40$$

Including vibration



$\bar{E}_{int} = \text{kinetic} + \text{potential}$
2 degrees of freedoms

$$\begin{aligned} \bar{E}_{int} &= 3N \left(\frac{1}{2} k_B T \right) + 2N \left(\frac{1}{2} k_B T \right) + 2N \left(\frac{1}{2} k_B T \right) \\ &= \frac{7}{2} n R T \end{aligned}$$

$$C_v = \frac{1}{n} \frac{d(\bar{E}_{int})}{dT} = \frac{1}{n} \frac{d}{dT} \left(\frac{7}{2} n R T \right) = \frac{7}{2} R$$

~ This does not agree with
table 21.2.

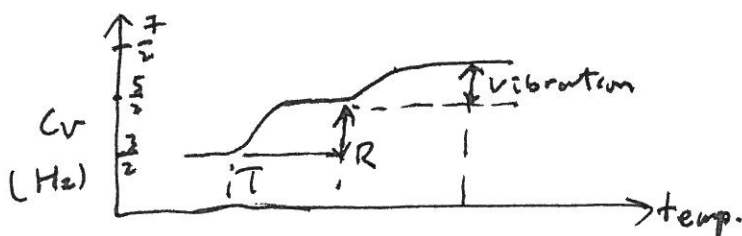


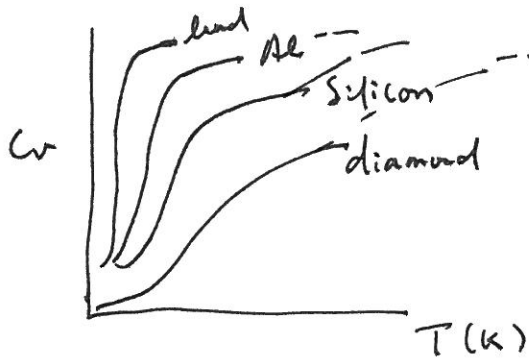
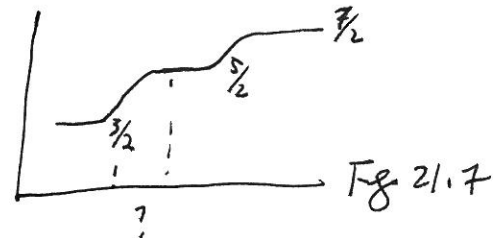
Fig 21-7

Suggests a break down
of this simple classical model.
at lower temperature. H_2
behave like monoatomic
molecules.

for polyatomic molecules. More degrees of freedom for both rotational and vibrational, so the specific heat is higher.
 → In general this is true.

To explain Fig 21.7, Quantum physics (Quantization of energy) is needed to explain the behavior of molecules' specific heat.

Molar specific heat of solids



As temperature approach zero.

$$C_v \rightarrow 0$$

At higher temperature

$$C_v \rightarrow 3R = 25 \text{ J/mole} \cdot \text{K}$$

→ Dulong-Petit law

Dulong-Petit law. (can be explained using Equipartition Energy theorem)

in x-direction

$$\bar{E}_{int} = \frac{1}{2} m v_x^2 + \frac{1}{2} k x^2 \quad (2 \text{ degrees of freedom})$$

in \hat{y} and \hat{z} direction $(2 \times 2 = 4 \text{ degrees of freedom})$

Total 6 degrees of freedom

$$E_{int} = N \left(6 \times \frac{1}{2} k_B T \right) = 3N k_B T = 3nRT$$

$$C_v = \frac{1}{n} \frac{d}{dT} (E_{int}) = \frac{1}{n} \frac{d}{dT} (3nRT) = 3R$$

→ this is OK in high temperature

But not low temperature

21.5 Boltzmann distribution law

What is the distribution of energy of molecules?

→ Chaotic

number density $n_v(E)$

$n_v(E) dE$ ≡ number of molecules per unit volume with energy between E and $E+dE$

≡ distribution function

$$n_v(E) = n_0 e^{-E/k_B T}$$

, n_0 is defined that $n_0 dE$

has the number of molecules per

≡ Boltzmann distribution law

unit volume having energy between $E=0$ and $E=dE$

21.6 Distribution of molecular speeds

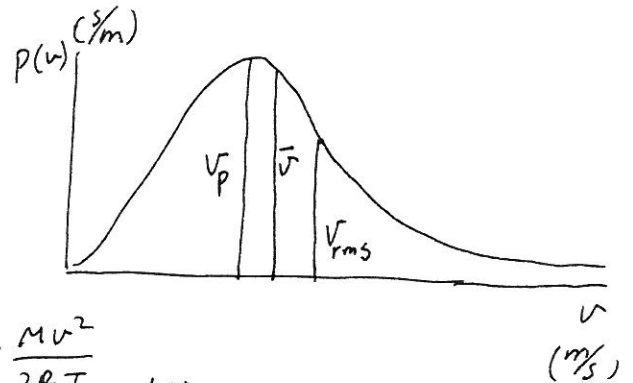
Maxwell's speed distribution

5.

SP-20-7

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

Average speed of Oxygen
at $T = 300\text{K}$



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

$$= \int_0^{\infty} v \cdot 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}} dv$$

$$= \sqrt{\frac{8RT}{\pi M}} \quad \text{--- Average speed.}$$

$$\textcircled{2} \quad v_{\text{rms}} = \sqrt{\overline{v^2}} = \left[\int_0^{\infty} v^2 P(v) dv \right]^{1/2} = \sqrt{\frac{3RT}{M}} \quad \text{--- rms speed,}$$

$\textcircled{3} \quad v_p$ --- most probable speed.

$$\frac{dP(v)}{dv} = 0 \rightarrow v_p = \sqrt{\frac{2RT}{M}}$$

5. Molar specific heat.

Internal energy of nN_A molecules is just the sum of all the kinetic energy if we assume monatomic molecules.

$$E_{\text{int}} = nN_A \cdot \frac{3}{2} kT = \frac{3}{2} nRT$$

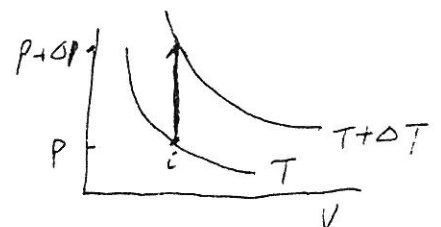
$\textcircled{1}$ Constant volume C_v

$$Q = nC_v \Delta T, \quad \text{and from 1st law, } dW = PdV = 0$$

$$\Delta E_{\text{int}} = Q - W = nC_v \Delta T - 0$$

$$\rightarrow \frac{3}{2} nRT = nC_v \Delta T$$

$$\rightarrow \boxed{C_v = \frac{3}{2} R}$$



if the number of molecules per unit volume is n_v

$(\pi d^2 \bar{v} \Delta t) n_v =$ number of point-size molecules in the cylinder

$$l \equiv \text{mean free path} = \frac{\bar{v} \Delta t}{(\pi d^2 \bar{v} \Delta t) n_v} = \frac{1}{\pi d^2 n_v}$$

$$f = \frac{\pi d^2 \bar{v} \Delta t n_v}{\Delta t} = \text{collision frequency}$$

Actually, $l = \frac{1}{\sqrt{2} \pi d^2 n_v}$ (take into the relative motion of the molecules)

$$f = \sqrt{2} \pi d^2 \bar{v} n_v = \frac{\bar{v}}{l}$$

$$l = \frac{\bar{v} \Delta t}{\pi d^2 \bar{v} \Delta t n_v} = \frac{v_{\text{ave}} \Delta t}{\pi d^2 v_{\text{rel}}} \quad v_{\text{relative}}$$

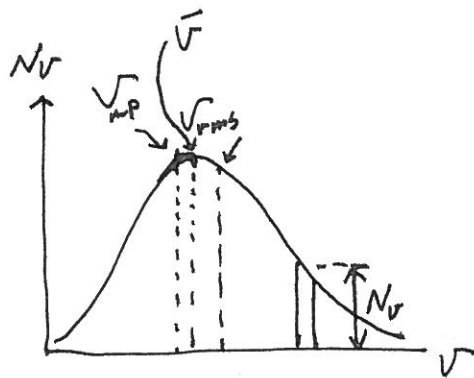
$$\textcircled{1} \quad v_{\text{ave}} = \int_0^{\infty} v N_v = \int_0^{\infty} 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^3 e^{-\frac{mv^2}{2RT}} dv = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\textcircled{2} \quad v_{\text{rms}} = \sqrt{\bar{v}^2}$$

$$\textcircled{3} \quad v_{\text{mp}} \Rightarrow \frac{d}{dv} N(v) = 0 \quad v = \sqrt{\frac{2RT}{M}}$$

21.6 Distribution of Molecular Speed

- Maxwell-Boltzmann distribution N_v



$$v_{rms} > \bar{v} > v_{mp}$$

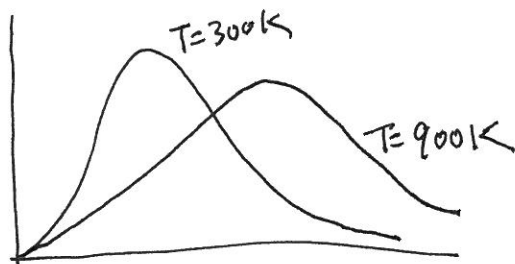
$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}$$

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m}} = 1.73 \sqrt{\frac{k_B T}{m}}$$

$$\bar{v} = \sqrt{\frac{8k_B T}{m}} = 1.60 \sqrt{\frac{k_B T}{m}}$$

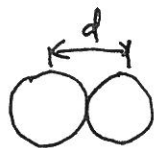
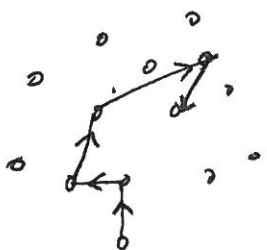
$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = 1.41 \sqrt{\frac{k_B T}{m}}$$

P39. P65



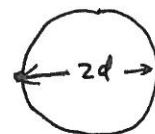
21.7 Mean free path

- The average distance between collisions is called mean free path



Actual collision

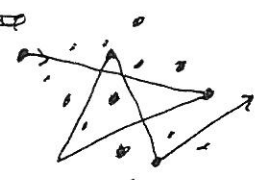
or



Equivalent collision

$\pi d^2 \cdot \bar{v} \Delta t =$ A volume of cylinder a molecule sweeps in Δt

4. Mean free path - due to the presence of other molecules, a molecule may not wander very far before hitting other molecules,



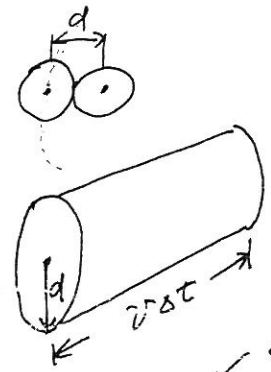
- Between collisions, molecule moves in a straight line
- Mean free path is the average distance traversed by a molecule between collisions. λ .

$\lambda \propto \frac{1}{\frac{N}{V}}$ - the more of the molecule volume density the shorter the mean free path is

$\lambda \propto \frac{1}{d^2}$ - the bigger the size is, the smaller the mean free path is.

- Assume molecules are spheres of diameter d
- A collision will happen when two molecules come within the distance d

- Within this cylinder there are total,



$V = \pi d^2 \cdot v \Delta t$

$(\frac{N}{V}) (\pi d^2 v \Delta t)$ molecules

speed of molecules relative to the container

Assume only one molecule is moving

$$\lambda = \frac{\text{total length}}{\text{number of collisions}} = \frac{v \Delta t}{\frac{N}{V} \pi d^2 \bar{v}_{rel} \Delta t} = \frac{1}{\pi d^2 \frac{N}{V}}$$

← mean speed relative to other molecules

$$= \frac{1}{\sqrt{2} \pi d^2 \frac{N}{V}}, \quad \bar{v}_{rel} = \sqrt{2} \bar{v}$$

take into the speed distribution of the molecules

- λ (air, at sea level) $\approx 0.1 \mu\text{m}$
- λ (air, at 100 km altitude) $\approx 16 \text{ cm}$
- λ (air, at 300 km altitude) $\approx 300 \text{ km}$

for ideal gas $\Delta E_{int} = n C_v \Delta T$, at const. volume. 6.
 Therefore, the change in internal energy is independent of the path taken, and only depends on the temperature.

② Constant pressure

$$Q = n C_p \Delta T$$

$$\Delta E_{int} = Q - W \quad , \quad \text{Since pressure = const.}$$

We must also do work to keep the volume increase

$$= n C_p \Delta T - P \Delta V$$

$$\Delta E_{int} = n C_p \Delta T - n R \Delta T$$

$$\frac{\Delta E_{int}}{n \Delta T} = C_p - R$$

$$C_v = C_p - R$$

$$\rightarrow \boxed{C_p = C_v + R}$$

$$\boxed{Sp \ 20-8}$$

$$E_{int} = \frac{3}{2} n R T = n C_v T \quad \text{— ideal gas, any process.}$$

6 Degree of freedom — According to Maxwell, each degree of freedom will store an average of $\frac{1}{2} kT$ energy per molecule. — equipartition theorem

1) translation 3 degree of freedoms

2) Rotation $\left\{ \begin{array}{l} \text{diatomic } f=2 \\ \text{polyatomic } f=3 \end{array} \right.$

$$\rightarrow E_{int} = \frac{3}{2} n R T = \frac{f}{2} n R T$$

$$\rightarrow C_v = \frac{f}{2} R$$

7. Adiabatic process $PV^\gamma = \text{const.}$ $\gamma = C_p/C_v$

$$dE_{\text{int.}} = dQ - dW$$

$$= Q - PdV, \quad Q=0 \text{ for adiabatic process}$$

$$nC_v dT = -PdV$$

$$ndT = -\left(\frac{P}{C_v}\right)dV$$

$$\frac{PdV + VdP}{C_p - C_v} = -\left(\frac{P}{C_v}\right)dV$$

$$\frac{dP}{P} + \left(\frac{C_p}{C_v}\right)\frac{dV}{V} = 0$$

$$\ln P + \gamma \ln V = \text{const}$$

$$\boxed{PV^\gamma = \text{const.}}$$

— for adiabatic process of ideal gas, $Q=0$

$$PV = nRT$$

$$PdV + VdP = nRdT$$

$$\frac{PdV + VdP}{R} = ndT$$

$$\frac{PdV + VdP}{C_p - C_v} = ndT$$

8. Free Expansion — $Q = W = 0$

$$\text{since } T_i = T_f$$

$$\rightarrow P_i V_i = P_f V_f$$

Maxwell distribution

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

the probability $P(r, p) d^3r d^3p$

$$P(r, p) d^3r d^3p \propto e^{-\frac{p^2}{2m} \beta} d^3r d^3p$$

$$\text{But } v = \frac{p}{m}$$

$$\therefore P(r, v) d^3r d^3v \propto e^{-\frac{1}{2} \beta v^2} d^3r d^3v$$

let $f(v) d^3v \equiv$ the mean number of molecules (of the specified kind) per unit volume, which have a velocity between v and $v + dv$

$$f(v) d^3v = \frac{N P(r, v) d^3r d^3v}{d^3r}$$

$$= c e^{-\frac{1}{2} \beta m v^2}$$

$$c \int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_x^2} dv_x \int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_y^2} dv_y \int_{-\infty}^{\infty} e^{-\frac{1}{2} \beta m v_z^2} dv_z = n$$

$$c = n \left(\frac{\beta m}{2\pi} \right)^{3/2}$$

$$\therefore f(v) d^3v = n \left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\left(\frac{1}{2}\right) \beta m v^2} d^3v$$

$$\text{But } F(v) dv = \int f(v) d^3v$$

$$= 4\pi f(v) v^2 dv$$

$$\therefore F(v) dv = 4\pi c e^{-\left(\frac{1}{2}\right) \beta m v^2} \cdot v^2 dv$$

positions x, y, z

linear momentum p_x, p_y, p_z

The range of position and momentum variables corresponding to a volume of phase

space of size $dx dy dz dp_x dp_y dp_z$

$$d^3r = dx dy dz$$

$$d^3p = dp_x dp_y dp_z$$

Mean free path

$$l = \bar{v} \tau = \frac{\bar{v}_{\text{rel}}}{\bar{v}_{\text{rel}}} \frac{1}{n\sigma}$$



$$\vec{v}_{\text{rel}} = v - v'$$

$$v_{\text{rel}}^2 = v^2 + v'^2 - 2v \cdot v'$$

$$\overline{v_{\text{rel}}^2} = \overline{v^2} + \overline{v'^2} - 2 \overline{v \cdot v'}$$

$$= 0$$

since $v \cdot v' = v v' \cos \theta$

$$= v v' \cos \theta$$

The average of $\cos \theta = 0$

$$\therefore \overline{v_{\text{rel}}^2} = \overline{v^2} + \overline{v'^2}$$

$$\approx \overline{v^2} + \overline{v'^2}$$

(neglecting the distinction of the average of square and the square of the average)

if all the molecules are identical, $\overline{v^2} = \overline{v'^2}$

$$\overline{v_{\text{rel}}^2} = 2 \overline{v^2}$$

$$\therefore \overline{v_{\text{rel}}} = \sqrt{2} \overline{v}$$

Chap 20. 49p

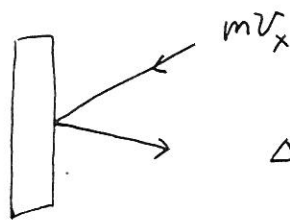
(a) $\bullet \pm \sim 0.5 \text{ mm}$ $A_p = \pi \frac{D^2}{4} \approx 2 \times 10^{-7} \text{ m}^2$

$\textcircled{\text{air}}$ molecule $d_{\text{air}} = 2 \times 10^{-10}$, $A_{\text{air}} = \frac{\pi}{4} d^2 \sim 3 \times 10^{-20} \text{ m}^2$

$\therefore \frac{A_p}{A_{\text{air}}} = \frac{2 \times 10^{-7}}{3 \times 10^{-20}} \sim 10^{13}$

Remember $d_{\text{atom}} \sim 1 \text{ \AA}$

(b)



$\Delta p = 2mV_x$ momentum change

$p = \text{pressure} = \frac{2m\bar{V}_x N}{A \Delta t}$

= Total pressure exert on the area

$\therefore N = \frac{PA \Delta t}{2m\bar{V}_x}$

$\Delta t = 1 \text{ sec}$

$\bar{V}_x \sim \sqrt{\bar{V}_x^2} = v_{\text{rms}} / \sqrt{3}$

$m = \frac{M}{N_A}$

$M = 6 \times 10^{-23}$

$\therefore N = \frac{\sqrt{3} p A N_A \Delta t}{2 M v_{\text{rms}}} = \frac{p A N_A \Delta t}{2 \sqrt{M R T}} \sim 7 \times 10^{20}$

$\bar{V} = \sqrt{\frac{8RT}{\pi M}}$

$v_{\text{rms}} = \sqrt{\bar{V}^2} = \sqrt{\frac{3RT}{M}}$