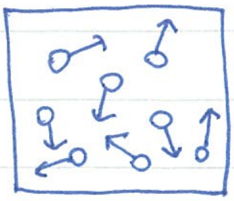
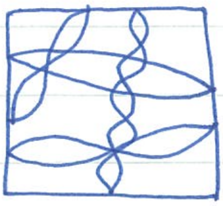
HH0045 Kinetic Theory for Ideal Gas

We will give a kinetic derivation of the ideal gas law $PV = N\tau$, and also introduce the notion of mean free path ℓ. There're two different views to describe an ideal gas: moving particles or standing waves. Let us start with the "classical" point of view first.



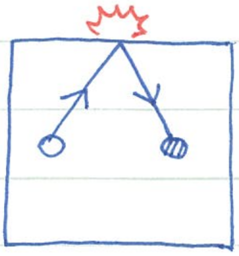
moving particles



standing waves

$$\boxed{P = \left(\text{momentum change / molecule}\right) \times \left(\begin{array}{l}\text{number of molecules striking}\\ \text{unit arear per unit time}\end{array}\right)}$$

Suppose a molecule is reflected specularly



$$\left(\begin{array}{l}\text{momentum change}\\ \text{per molecule}\end{array}\right) = \underbrace{2M|v_z|}$$

The number of molecules per unit volume between v_z and $v_z + dv_z$ is $a(v_z)dv_z$ with the relation $\int a(v_z)dv_z = n$ ← particle density.

$$\left(\begin{array}{l}\text{number of molecules striking}\\ \text{unit area per unit time}\end{array}\right) = \underbrace{a(v_z)\cdot dv_z \cdot |v_z|} \leftarrow \text{only for } (v_z, v_z + dv_z)$$

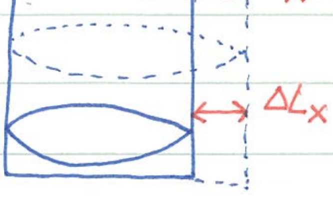
Thus, the total pressure can be found by integration,

$$p = \int_0^\infty 2Mv_z^2 a(v_z)dv_z = M\int_{-\infty}^{+\infty} v_z^2 a(v_z)dv_z = Mn\langle v_z^2\rangle$$

$$\rightarrow \boxed{p = Mn\langle v_z^2\rangle}$$

For an ideal gas, equipartition of energy tells us $\langle \frac{1}{2}Mv_z^2\rangle = \frac{1}{2}\tau$. It is easy to see that $p = n\tau$, or $PV = N\tau$.

One can try to look at the same problem in the "quantum" point of view. Pressure can be viewed as "squeezing the wave functions" without changing the occupation distribution P_n, i.e. $\sigma = \text{const}$.



Consider the pressure caused by one particle, P_1, first.

$$\Delta U = \sum_n \left(\frac{\partial \varepsilon_n}{\partial L_x}\cdot \Delta L_x\right)\cdot P_n = P_1 A(-\Delta L_x)$$ ← $\Delta L_x < 0$ here.

Thus, we obtain $\boxed{P_1 = \frac{1}{A}\sum_n P_n\left(-\frac{\partial \varepsilon_n}{\partial L_x}\right)}$ The energy spectrum is simple $\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{n_x^2\pi^2}{L_x^2}+\frac{n_y^2\pi^2}{L_y^2}+\frac{n_z^2\pi^2}{L_z^2}\right)$

$$-\frac{\partial \varepsilon_n}{\partial L_x} = \frac{\hbar^2\pi^2 n_x^2}{2M}\,\frac{2}{L_x^3} = \frac{2}{L_x}\cdot\left(\frac{\hbar^2\pi^2 n_x^2}{2ML_x^2}\right) \longrightarrow \underline{\frac{2}{L_x}\cdot\frac{1}{2}\tau}$$ ← after thermal average.

Therefore, the pressure caused by one particle is

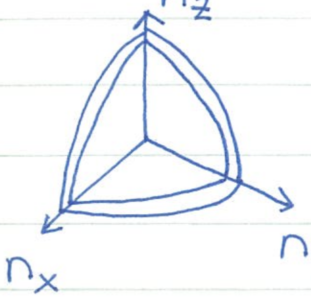
$$P_1 = \frac{1}{A}\left\langle -\frac{\partial \varepsilon_n}{\partial L_x}\right\rangle = \frac{1}{L_yL_z}\cdot\frac{2}{L_x}\cdot\frac{1}{2}\tau = \underline{\frac{1}{V}\cdot\tau}$$

For an ideal gas, the quantum statistics is not important → $P = NP_1 = N\tau/V$. The ideal gas law is derived again.

Q: The total pressure is assumed, $P = NP_1$. Is it always true? Why?

⊘ Maxwell velocity distribution: For an ideal gas, the distribution function is $\underline{f(\varepsilon_n) = \lambda e^{-\varepsilon_n/\tau}}$ with $\lambda = n/n_Q$.

For simplicity, take $L_x = L_y = L_z = L$ → $\varepsilon_n = \frac{\hbar^2}{2M}\left(\frac{n\pi}{L}\right)^2$, $n = (n_x, n_y, n_z)$



$$\begin{pmatrix}\text{number of atoms}\\ \text{btn } n,\ n+dn\end{pmatrix} = \begin{pmatrix}\text{number of orbitals}\\ \text{btn } n,\ n+dn\end{pmatrix} \times f(\varepsilon_n)$$

$$= \left(\frac{1}{8}\cdot 4\pi n^2\cdot dn\right)\cdot\left(\lambda e^{-\varepsilon_n/\tau}\right) = \underline{\frac{1}{2}\pi\lambda n^2 e^{-\varepsilon_n/\tau}\,dn.}$$

Now we are ready to derive the Maxwell velocity distribution

$$N P_M(v)\,dv = \frac{1}{2}\pi\lambda n^2 e^{-\varepsilon_n/\tau}\,dn$$ ← now need to find the relation $n = n(v)$

The kinetic energy $\frac{1}{2}Mv^2$ is related to its quantum version,

$$\frac{1}{2}Mv^2 = \frac{\hbar^2}{2M}\left(\frac{n\pi}{L}\right)^2 \longrightarrow \boxed{n = \frac{ML}{\pi\hbar}\, v}$$

linear dependence ☺

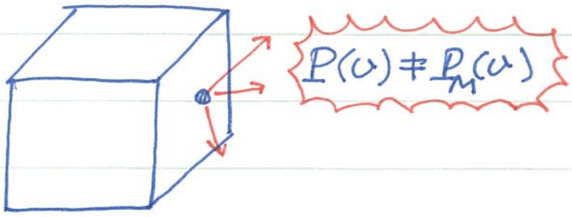
The velocity distribution is $P_M(v) = \frac{1}{N}\cdot\frac{1}{2}\pi\lambda n^2 e^{-\varepsilon_n/\tau}\frac{dn}{dv}$

Recall that $\lambda = n/n_Q = (N/L^3)(2\pi\hbar^2/M\tau)^{3/2}$, the above can be brought into the form,

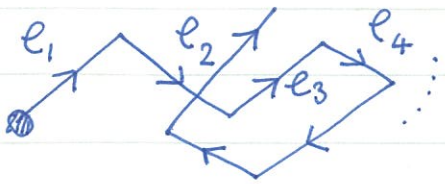
$$\boxed{P_M(v) = \underbrace{4\pi\left(\frac{M}{2\pi\tau}\right)^{\frac{3}{2}}}_{\text{just some "const" for normalization}} \underbrace{v^2}_{\text{phase space (multiplicity)}} \underbrace{e^{-\frac{Mv^2}{2\tau}}}_{\text{Boltzmann factor}}}$$

with $\int_0^\infty P_M(v)\,dv = 1$

⊘ Measure $P_M(v)$ experimentally ☺



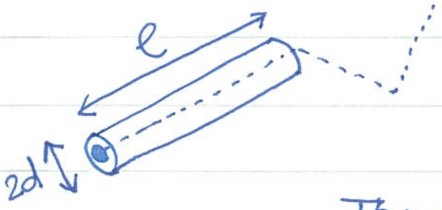
One can make a hole on the box and try to measure the velocity distribution $P(v)$. BUT! It is not going to be Maxwell distribution $P_M(v)$. To make the situation clear, we need to introduce the notion of mean free path ℓ.



$$\boxed{\ell \equiv \text{average length between collisions}}$$

It's easy to guess $\ell = \ell(\underbrace{d}_{\text{molecular size}}, \underbrace{n}_{\text{density}})$

Suppose the diameter of a molecule is d. Molecules within the distance d will collide.

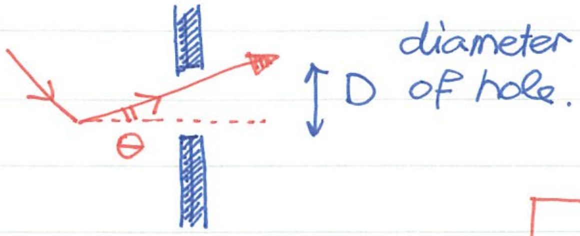


$$(\pi d^2 \cdot \ell)\cdot n = 1 \leftarrow \text{1 colliding atom.}$$

Thus, the mean free path $\boxed{\ell = \frac{1}{n\pi d^2}}$

$\ell \approx 100\,\text{nm}$ for normal air, about 1000 times of molecular size. $\longrightarrow \ell \sim \frac{1}{n}$ (not $\frac{1}{n^{\frac{1}{3}}}$)

Two different transport regimes:



$\ell \gg D$

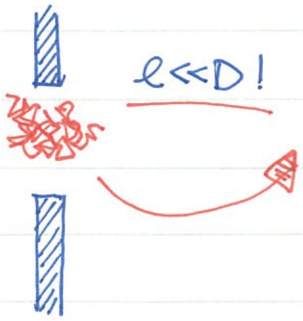
effusive regime

(collisionless!)

Fast molecules strike the hole more often → additional $v\cos\theta$ factor appears.

$$\boxed{\begin{aligned} P(v) &\propto (v\cos\theta)\,P_M(v) \\ &\propto v^3 e^{-Mv^2/2\tau} \end{aligned}}$$

On the other hand, if the mean free path is much shorter, $\ell \ll D$, the transport property is rather different.



$$\begin{cases} \text{local temperature} & \tau(\vec{r}) \\ \text{local density} & n(\vec{r}) \\ \text{local flow velocity} & u(\vec{r}) \end{cases}$$

the notion of steady state

hydrodynamic regime

In the hydrodynamic regime, it is more convenient to introduce various smooth varying fields and describe the system by classical/quantum field theory.

Happy

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