

$$① \langle n \rangle = \frac{\int_0^{\infty} n f(n) dn}{\int_0^{\infty} f(n) dn} = \frac{A \int_0^{\infty} n^3 e^{-\alpha V} dn / V A}{A \int_0^{\infty} n^2 e^{-\alpha V} dn / V A} = \langle \bar{n} \rangle \quad (1)$$

$$(1) \int_0^{\infty} n^2 e^{-\alpha V} dn = \int_0^{\infty} n^2 e^{-\alpha V} d(n) = -\frac{d}{dV} \left(\int_0^{\infty} e^{-\alpha V} d(n) \right) = -\frac{1}{2} \sqrt{\pi} \frac{d}{d\alpha} \alpha^{-1/2}$$

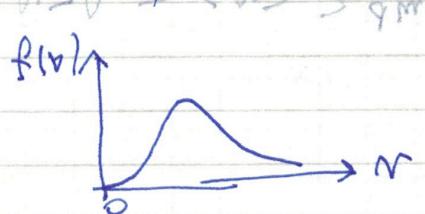
$$(1) \int_0^{\infty} n^2 e^{-\alpha V} dn = \int_0^{\infty} n^2 e^{-\alpha V} \frac{d(\alpha V)}{2} = \frac{1}{2} \sqrt{\pi} \alpha^{-1/2} \int_0^{\infty} \bar{n} e^{-\alpha \bar{n}} d\bar{n} = \frac{1}{2} \sqrt{\pi} \alpha^{-1/2} \int_0^{\infty} u e^{-u} du$$

$$\int_0^{\infty} u e^{-u} du = \boxed{1/2\alpha^2} = \frac{1}{2} \sqrt{\pi} \alpha^{-1/2} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \cdot \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{8} \pi^{1/2} \alpha^{-1/2}$$

$$\langle \bar{n} \rangle = \frac{(1/2\alpha^2)}{\left(\frac{\sqrt{\pi}}{4}\right)^2} = \frac{4\alpha^{3/2}}{\sqrt{\pi}} \cdot \frac{1}{2\alpha^2} = \frac{2}{\sqrt{\pi}} \frac{1}{\alpha^{1/2}} = \langle \bar{n} \rangle \approx \frac{2}{\sqrt{\pi}} \frac{1}{\alpha^{1/2}}$$

$$= \frac{2}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}} = \sqrt{\frac{8kT}{\pi m}} \quad \text{but } \langle \bar{n} \rangle > \frac{2}{\sqrt{\pi}} \frac{1}{\alpha^{1/2}}$$

$$② f(n) = A n^2 e^{-\alpha V}$$



$$0 = f'(n) = 2n e^{-\alpha V} + n^2 e^{-\alpha V} (-2\alpha) = e^{-\alpha V} [2n - 2\alpha n^2] = 0$$

$$\Rightarrow 2\alpha n^2 = 2n \Rightarrow \alpha n^2 = 1 \Rightarrow n = \frac{1}{\sqrt{\alpha}} = \sqrt{\frac{2kT}{m}}$$

$$(3) \quad \langle v^2 \rangle = \frac{\int_0^\infty A V^4 e^{-\alpha V} b dV \cdot V^2}{\int_0^\infty A V^2 e^{-\alpha V} b dV} = \frac{\int_0^\infty V^4 e^{-\alpha V} dV}{\int_0^\infty V^2 e^{-\alpha V} dV} = \frac{V^4 - \alpha^4}{V^2 - \alpha^2}$$

$$\begin{aligned} \int_0^\infty V^4 e^{-\alpha V} dV &= \frac{d}{d\alpha^2} \left(\int_0^\infty e^{-\alpha V} dV \right) = \frac{d}{d\alpha^2} \left(\frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) = \frac{\sqrt{\frac{\pi}{\alpha}}}{2} \frac{d}{d\alpha^2} (\alpha^{-1/2}) \\ &= \frac{\sqrt{\frac{\pi}{\alpha}}}{2} \frac{d}{d\alpha} \left(-\frac{1}{2} \alpha^{-3/2} \right) = -\frac{\sqrt{\frac{\pi}{\alpha}}}{4} \frac{d}{d\alpha} (\alpha^{-3/2}) = -\frac{\sqrt{\frac{\pi}{\alpha}}}{4} \cdot \left(-\frac{3}{2} \right) \alpha^{-5/2} \\ &\quad \text{nb. } \int_0^\infty \frac{1}{x^5} = \frac{3}{8} \sqrt{\pi} \alpha^{-8/2} \end{aligned}$$

$$\begin{aligned} \langle v^2 \rangle &= \frac{(3/8) \sqrt{\frac{\pi}{\alpha}} \alpha^{-3/2}}{\frac{(\pi/4)}{2} \alpha^{-3/2}} = \frac{3}{2} \alpha^{-1} = \frac{3}{2\alpha} = \frac{3}{2} \frac{2kT}{m} = \\ &\Rightarrow \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} \end{aligned}$$

$$v_{mp} < \langle v \rangle < \sqrt{\langle v^2 \rangle}$$

Integrals

$$I_n = \int_0^\infty v^n e^{-\alpha v^2} dv \quad (1)$$

$n = 2p+1$

$$I_n = \int_0^\infty v^{2p} v e^{-\alpha v^2} dv = \frac{1}{2} \int_0^\infty (v^2)^p e^{-\alpha (v^2)} d(v^2) = \frac{1}{2} \int_0^\infty x^p e^{-\alpha x} dx$$

$$= \frac{1}{2\alpha^{p+1}} \cdot \underbrace{\int_0^\infty s^p e^{-s} ds}_{p!} = \boxed{\frac{p!}{2\alpha^{p+1}}} \quad (2)$$

$n = 2p$

$$I_n = \int_0^\infty v^{2p} e^{-\alpha v^2} dv = (-1)^p \frac{d^p}{da^p} \underbrace{\int_0^\infty e^{-av^2} dv}_{\frac{1}{\sqrt{a}} \int_0^\infty e^{-x^2} dx}$$

$$I = \int_0^\infty e^{-x^2} dx$$

$$I^2 = \int_0^\infty e^{-x^2} dx \int_0^\infty e^{-y^2} dy = \int_0^\infty \int_0^\infty e^{-(x^2+y^2)} dx dy$$

$$r^2 = x^2 + y^2$$

$$r dr d\phi = dx dy$$

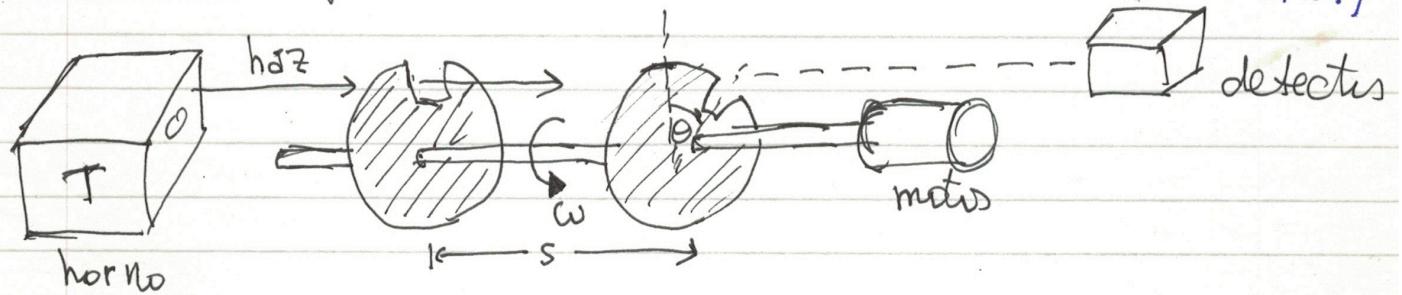
$$\begin{aligned} I^2 &= \int_0^{\pi/2} d\phi \int_0^\infty dr r e^{-r^2} = \frac{\pi}{2} \int_0^\infty r e^{-r^2} dr = \\ &= \frac{\pi}{4} \int_0^\infty e^{-r^2} dr^2 = \frac{\pi}{4} \int_0^\infty e^{-s} ds = \frac{\pi}{4} \end{aligned}$$

$$\boxed{I = \frac{\sqrt{\pi}}{2}}$$

$$\therefore \boxed{I_n = (-1)^p \frac{\sqrt{\pi}}{2} \frac{d^p}{dx^p} (-1/2)} \quad (n = 2p).$$

comprobac. experimental (I.F. Zartman, 1931)

PR 37, 383-39
(1931)



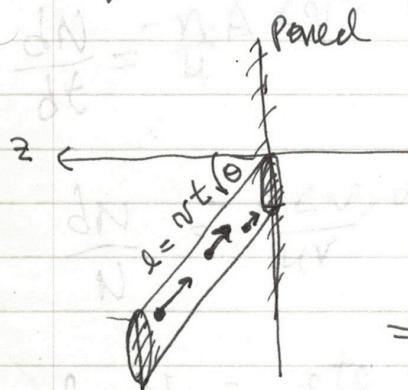
Para ω dado, sólo pase al detector aquellas moléculas que cumplen: $t = \frac{s}{\omega} = \frac{\theta}{\omega}$

$\Rightarrow N = \frac{s\theta}{\omega}$. Variando ω y θ , se puede medir directamente el # de moléculas en un largo de N dodo. Los resultados concuerdan con **M-B**

Ejercicios: Dado **M-B** calcular como función de T:

- (a) \bar{v} (rapidez promedio) = $\sqrt{\frac{3k_B T}{\pi m}}$ ✓
- (b) rapidez más probable v_{mp}
- (c) Veloc. cuadrática media: $\sqrt{\bar{v}^2}$ ✓

Calcular la tasa de escape de moléculas desde una pequeña abertura de área A en un contenedor.



$$\Delta N = nAvt \cos \theta f(\vec{v})$$

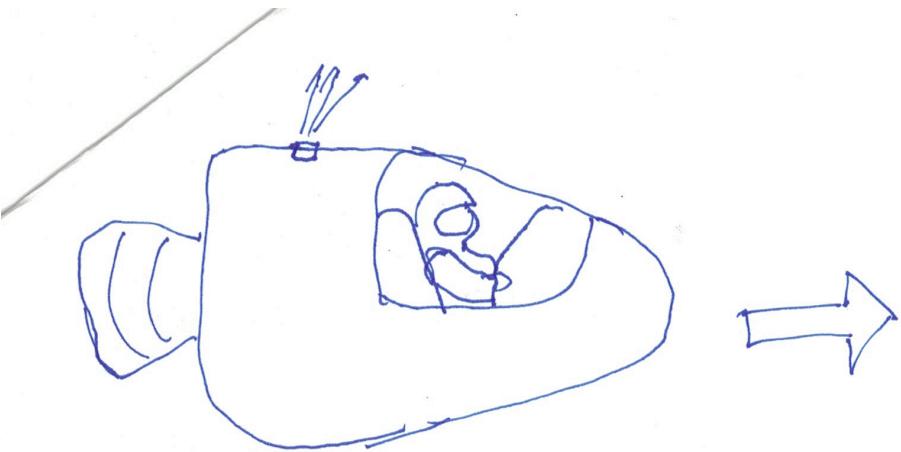
$$\frac{\Delta N}{\Delta t} = n v \cos \theta f(\vec{v})$$

$$\Rightarrow \text{Fluxo} = \int n v \cos \theta f(\vec{v}) d\vec{v}$$

$$= n \left(\frac{m}{2\pi kT} \right)^{3/2} \int \int \int -\frac{mv^2}{2kT} v^3 e^{-\frac{mv^2}{2kT}} \cos \theta \sin \theta dv d\theta d\phi$$

$$= 2\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} \underbrace{\int_0^{\pi/2} \sin \theta \cos \theta}_{1/2} \underbrace{\int_0^{\infty} v^3 e^{-\frac{mv^2}{2kT}} dv}_{\frac{1}{2} \left(\frac{kT}{m} \right)^{3/2}} = n \sqrt{\frac{kT}{2\pi m}}$$

Es el colección de tiempo de escape.



$$\frac{dN}{dt} = -\frac{n}{4} A \langle v \rangle = -\frac{NA}{4V} \langle v \rangle$$

$$\frac{dN}{N} = -\frac{A \langle v \rangle}{4V} dt$$

$$\ln N = \text{cte} + \frac{A \langle v \rangle t}{4V}$$

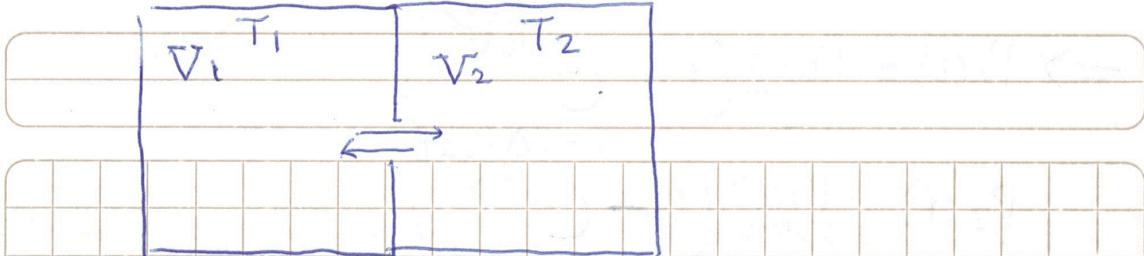
$$N = N(0) e^{-\frac{A \langle v \rangle t}{4V}}$$

$$P = P(0) e^{-\frac{A \langle v \rangle t}{4V}}$$

$$P = P(0) e^{-\frac{A}{4V} \sqrt{\frac{kT}{2\pi m}} t}$$

EJ: calc. tiempo de vaciado.





$$\frac{dN_1}{dt} = -A_1 \left(\frac{N_1}{V_1} \right) \frac{< N >_1}{4} + A_2 \left(\frac{N_2}{V_2} \right) \frac{< N >_2}{4}$$

$$\frac{dN_2}{dt} = -A_2 \left(\frac{N_2}{V_2} \right) \frac{< N >_2}{4} + A_1 \left(\frac{N_1}{V_1} \right) \frac{< N >_1}{4}$$

Sup: $A_1 = A_2$, $V_1 = V_2$ y $T_1 = T_2$

$$\begin{aligned} \dot{N}_1 &= -\alpha N_1 t + N_2 \\ \dot{N}_2 &= \alpha N_1 - \alpha N_2 \end{aligned} \quad \begin{aligned} N_1(0) &= N_0 \\ N_2(0) &= 0 \end{aligned}$$

$$\Rightarrow \dot{N}_1 + \dot{N}_2 = 0 \Rightarrow \frac{d}{dt}(N_1 + N_2) = 0 \Rightarrow [N_1 + N_2 = N_0] \quad (1)$$

$$\Rightarrow N_2 = N_0 - N_1$$

$$\begin{aligned} \dot{N}_1 &= -\alpha N_1 + \alpha(N_0 - N_1) \\ &= -2\alpha N_1 + \alpha N_0 \end{aligned}$$

$$\frac{d}{dt} N_1 = \alpha N_0 - 2\alpha N_1 \Rightarrow N_1 = \frac{N_0}{2} + A e^{-2\alpha t}$$

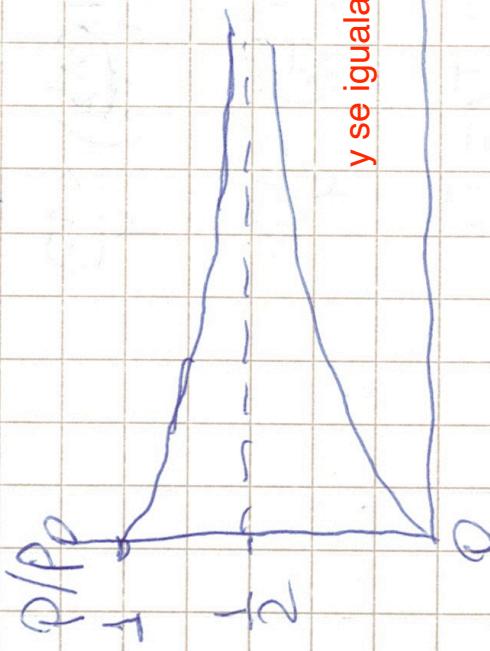
y cuando $N_1(0) = N_0 \Rightarrow [N_1(t) = \frac{N_0}{2} (1 + e^{-2\alpha t})]$

$$N_2 = N_0 - N_1 = N_0 - \frac{N_0}{2} - \frac{N_0}{2} e^{-2\alpha t} = \frac{N_0}{2} - \frac{N_0}{2} e^{-2\alpha t}$$

$$\Rightarrow [N_2(t) = \frac{N_0}{2} (1 - e^{-2\alpha t})]$$

$$\Rightarrow P_1(t) = \frac{P_1(0)}{2} \left(1 + C \frac{-2A \ln v}{4\pi r^2 t} \right)$$

$$P_2(t) = \frac{P_1(0)}{2} \left(1 + C \frac{-2A \ln v}{4\pi r^2 t} \right)$$



se equilibran las presiones

y se iguala el numero de partículas en ambos containers