

Distribuição de Velocidades $f(v_x, v_y, v_z)$

$$pV = nRT \text{ (Lei dos Gases Ideais)}$$

$$p(z) = p_0 \exp\left(-g \frac{\rho}{p_0} z\right) \text{ (Lei de Halley)}$$

$$E = \frac{m}{2} v^2 + mgh \text{ (cons. de energia mecânica)}$$

Boltzmann (1876)

$$\text{Boltzmann: } \frac{p(z)}{p_0} = \frac{p(z)'}{p_0} = \exp\left[-g \frac{\rho_0}{p_0} z\right]$$

$\rho \rightarrow$ dens. do gás (kg/m^3)
 $p \rightarrow$ pressão ($\text{Pa} = \text{N/m}^2$)

$$p \cdot V = n R T = M \cdot \frac{R T}{M_m}$$

$n \rightarrow$ moles

$M_m \rightarrow$ massa molar, massa de 1 mol
molécula-grama

$$M_m = N_0 \cdot m$$

$m \rightarrow$ massa da molécula

$N_0 \rightarrow$ n. de Avogadro

$$p = \frac{M}{V} \frac{R T}{M_m} = p \frac{R \cdot T}{N_0 \cdot m}$$

$$p = \frac{p}{m} k_B T \Rightarrow \frac{p}{p_0} = \frac{p_0}{p_0} = \frac{m}{k_B T} \rightarrow \text{massa} \rightarrow \left[\frac{1}{v^2}\right]$$

\rightarrow Energia

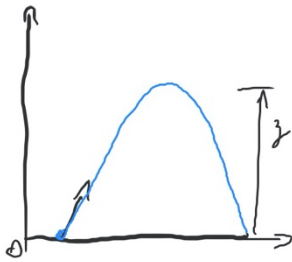
$$\frac{\rho(z)}{\rho(0)} = \exp\left[-\frac{m}{k_B T} g z\right]; \rho(z) = N(z) \cdot m \quad \left| \quad \frac{N(z)}{N(0)} = \exp\left(-\frac{m g z}{k_B T}\right)\right.$$

dens. molecular

Ignorar colisões

$$E_p + E_k = \text{cte}$$

Calcular $f(v_z)$



$$m g z = \frac{m v_z^2}{2}$$

↓
alt.
máxima

$$v_z = v$$

Para deixar a notação mais leve

Velocidade w , $f_1(w)$; $\int_{-\infty}^{\infty} f_1(w) dw = 1 \rightarrow$ distribuição bem comportada

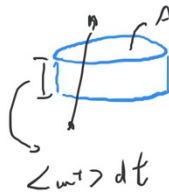
Moléculas ascendentes: $w > 0 \rightarrow w^+$

$$\langle w^+ \rangle = \int_0^{\infty} f_1(w) w dw = -\langle w^- \rangle$$

$$\langle w \rangle = \int_{-\infty}^{\infty} f_1(w) w dw = \int_{-\infty}^0 f_1(w) w dw + \int_0^{\infty} f_1(w) w dw = 0$$

$\langle w^- \rangle + \langle w^+ \rangle = 0$

Número médio de moléculas cruzando uma seção de área A



Quantas moléculas temos? $N(z) \cdot \underbrace{\langle u \rangle dt}_{\text{altura}} \cdot A$

$N(z)$ por unid. de tempo

Média cruzando a área A $N(z) \langle u \rangle \quad [s^{-1}]$

Trabalhando por classe de velocidades

$$n(z) \underbrace{f_1(u) du}_{\text{Fração de moléculas}} \cdot u$$



N' de moléculas, em função da velocidade

$$z=0 \quad N(z) \cdot \underbrace{f_1(u) du}_{\text{transformação}} \cdot u$$



$$mgz = \frac{mv^2}{2}$$

$$mg dz = d\left(\frac{1}{2} mv^2\right) = mv dv$$

Variação de densidade molecular

$$[N(z) - N(z+dz)] \cdot \langle u \rangle = n_0 \underbrace{f_1(u) du}_{\text{Fração de moléculas}} \cdot u$$

Dif. do fluxo de moléculas \rightarrow n_0 de moléculas que atravessam 1, mas não cruzam a região 2

$$\underline{N(z) - N(z+dz)} = -\frac{\partial N(z)}{\partial z} dz$$

$$-\frac{\partial N(z)}{\partial z} \langle w^2 \rangle = N(z) f_1(w) m \frac{dw}{dz}$$

$$-\frac{\partial N(z)}{\partial z} = \frac{N_0}{\langle w^2 \rangle} \cdot f_1(w) \cdot g$$

indep. de z

$$g dz = m dw$$

$$\langle w^2 \rangle = \int_{-\infty}^{\infty} f(w) w^2 dw$$

distribuição

→ $\propto T \rightarrow K$
por molécula

$f(w)$ torna-se independente de z !

Lei de Maxwell: $n(z) = n_0 \exp\left(-\frac{mgz}{k_B T}\right)$

$$\frac{d}{dz} n(z) = -\frac{mg}{k_B T} \cdot n_0 \exp\left(-\frac{mgz}{k_B T}\right)$$

$$\frac{d}{dz} n = -\frac{mg}{k_B T} n(z) \exp\left(-\frac{mgz}{k_B T}\right) \quad / \quad \frac{d}{dz} n = -n(z) g \frac{f_1(w)}{\langle w^2 \rangle}$$

Maxwell ↙

$$\frac{f_1(w)}{\langle w^2 \rangle} = \frac{m}{k_B T} \exp\left(-\frac{mgz}{k_B T}\right) \quad \rightarrow \quad mgz = \frac{m w^2}{2}$$

$$f_1(w) = \frac{m \langle w^2 \rangle}{k_B T} \exp\left(-\frac{1}{2} \frac{m w^2}{k_B T}\right)$$

Calcular $\langle w^2 \rangle$

→ Normalização de $f_1(w)$...

$$\int_{-\infty}^{\infty} f_1(m) dm = 1$$

$$\int_{-\infty}^{\infty} \frac{m \langle m^2 \rangle}{kT} \exp\left(-\frac{1}{2} \frac{m \omega^2}{kT}\right) dm$$

$$\rightarrow x^2 = \frac{m \omega^2}{2kT}$$

$$x = \sqrt{\frac{m}{2kT}} \cdot m$$

$$dx = \sqrt{\frac{m}{2kT}} dm$$

$$= \frac{m \langle m^2 \rangle}{kT} \cdot \sqrt{\frac{2kT}{m}} \int_{-\infty}^{\infty} \exp(-x^2) dx$$

$$= \sqrt{\frac{2m}{kT}} \cdot \langle m^2 \rangle \cdot \int_{-\infty}^{\infty} e^{-x^2} dx$$

Software
tablas de integración

Calculando explícitamente

$$\int_{-\infty}^{\infty} e^{-x^2} dx = A \Rightarrow A^2 = \int_{-\infty}^{\infty} e^{-x^2} dx \cdot \int_{-\infty}^{\infty} e^{-y^2} dy$$

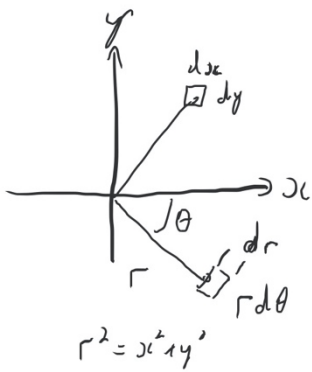
$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy$$

$$= \int_0^{2\pi} \left[\int_0^{\infty} e^{-r^2} r dr \right] d\theta = 2\pi \int_0^{\infty} e^{-r^2} r dr$$

$$= -\pi [e^{-r^2}]_0^{\infty}$$

$$= \pi$$

$$\therefore A = \sqrt{\pi}$$



Portanto $\sqrt{\frac{2m}{kT}} \cdot \langle w^2 \rangle \cdot \sqrt{\pi} = 1 \Rightarrow \langle w^2 \rangle = \sqrt{\frac{kT}{2m\pi}}$

$$f_1(w) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{1}{2} \frac{mw^2}{k_B T}\right)$$

$$\begin{cases} pV = nRT \\ p(z) = p_0 e^{-\left(g \frac{\rho_0 z}{p_0}\right)} \\ mgz = \frac{m \overline{w^2}}{2} \end{cases}$$

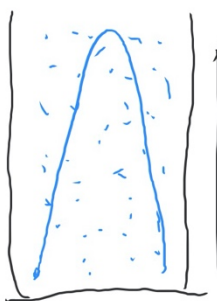
\downarrow alt. m. v. \hookrightarrow comp. 2 da velocidade em $z=0$

Gaussiana

$$e^{i\pi} + 1 = 0$$

Tratamento de Boltzmann \rightarrow Gaussiana

Distr. de Maxwell \Rightarrow



$v_x, v_y, v_z \rightarrow$ distribuição isotrópica em \vec{v}

g foi instrumento de cálculo

$z \rightarrow$ mudança na densidade

Hipótese \rightarrow sujeita à confirmação experimental

$$\underbrace{f(v_x, v_y, v_z) dv_x dv_y dv_z}_{\text{probabilidade } \in (\vec{v}, \vec{v}+d\vec{v})} = f_1(v_x) dv_x \cdot f_1(v_y) dv_y \cdot f_1(v_z) dv_z$$

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \cdot \exp\left(-\frac{1}{2} \frac{m(v_x^2 + v_y^2 + v_z^2)}{k_B T}\right)$$

$$= \left(\frac{m}{2\pi k_B T} \right)^{3/2} \cdot \exp\left[-\frac{1}{2} \frac{m v^2}{k_B T}\right]$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$f_1(v_x) dv_x \rightarrow$ Integração marginal

$$\underbrace{f_1(v_x)}_{\text{prob. 1D}} dv_x = dv_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \underbrace{f(\vec{v})}_{\text{Integração nos outros 2 dim.}} dv_y dv_z$$

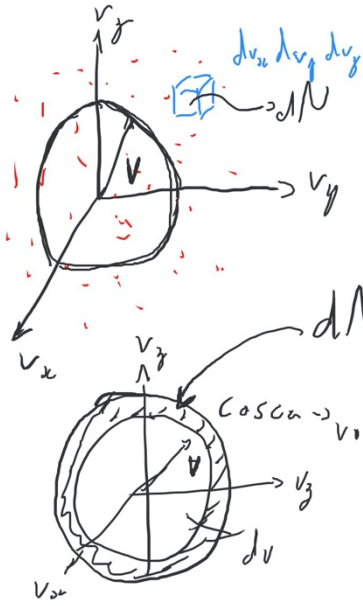
$$\frac{m v^2}{2} = K \quad \text{en. cinética}$$

$$f(\vec{v}) = \sqrt{\frac{m}{2\pi k_B T}} \cdot \exp\left(-\frac{K}{k_B T}\right)$$

\hookrightarrow distr. de Maxwell
Boltzmann

energia \rightarrow relacionada com
temperatura

Espaço de velocidades



Fração de Moléculas

$$\frac{dN(v_x, v_y, v_z)}{N} = \underbrace{f(\vec{v})}_{f(v)} \underbrace{dv_x dv_y dv_z}_{\text{3 coord}}$$

$$dN(v_x, v_y, v_z) = N \cdot F(v) dv = N f(\vec{v}) 4\pi v^2 dv$$

distribuição
módulo da
velocidade

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

$$F(v) = 4\pi \cdot v^2 f(\vec{v})$$

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

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

$v \rightarrow$ valor absoluto da velocidade

v_{qm}^2, v mais provável, $\langle v \rangle$

Distr. de Maxwell

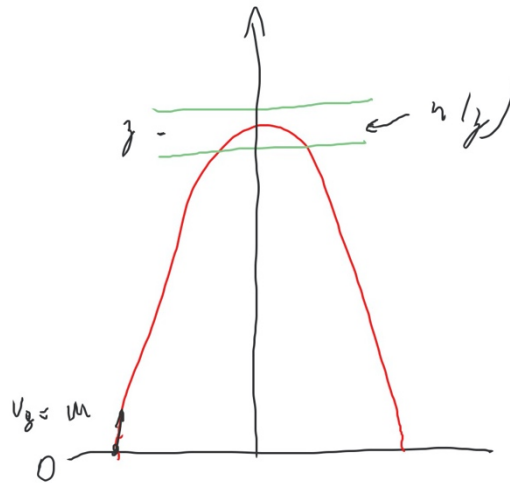
Lei de Holey

$$n(z) = n(0) \exp\left(-\frac{mgz}{kT}\right)$$

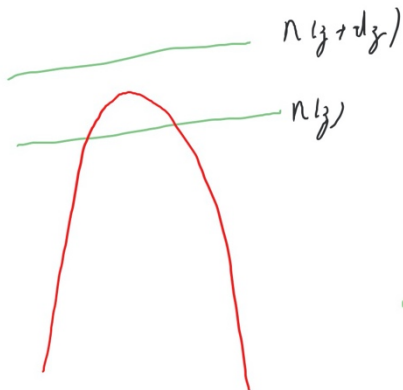
↓
dens.
atômica

$$\frac{mv^2}{2} = mg \cdot z$$

Boltzman



moleculas que atingem z
e não saem por $z+dz$



$$\underbrace{[n(z) - n(z+dz)]}_{\uparrow \Delta z} \langle w^2 \rangle = n_0 \underbrace{f_1(w)}_{\uparrow \Delta z} dm m$$

moleculas que atingem a
ascensão máxima em z

moleculas que
partiram de $z=0$
com velocidade w

$$\lim_{\Delta z \rightarrow 0} \rightarrow -\frac{dn(z)}{dz} \langle w^2 \rangle = n(0) f_1(w) \frac{dm m}{dz}$$

$$\frac{m}{2} \frac{dm^2}{dz} = mgz$$

$$\frac{1}{2} \frac{d}{dz} (m^2) = \frac{2}{2} m \frac{dm}{dz} = g$$

$$\frac{d}{dz} n(z) \langle m^2 \rangle = n_0 f_1(m) \cdot g$$

$$\frac{d n(z)}{dz} = -\frac{mg}{kT} \cdot n_0 \exp\left(-\frac{mg}{kT} \cdot z\right)$$

$$f_1(m) = \frac{m \langle m^2 \rangle}{kT} \exp\left(-\frac{1}{2} \frac{m m^2}{kT}\right)$$

↳ gaussiana

$$\int_{-\infty}^{\infty} f_1(m) dm = 1$$

$$f_1(m) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{1}{2} \frac{m m^2}{kT}\right)$$

$$f(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot \exp\left[-\frac{1}{2} \frac{m(v_x^2 + v_y^2 + v_z^2)}{kT}\right]$$

↳ densidade de probabilidade em \vec{v}

$$\int_{-\infty}^{\infty} f(\vec{v}) dv_x dv_y dv_z = 1 \rightarrow \text{isotropia}$$

$$F(v)$$

$$\int_0^{\infty} F(v) dv = 0$$

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$F(v) = 4\pi \cdot \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot \frac{1}{\pi} \cdot \left(\frac{m v^2}{2kT}\right) \cdot \exp\left(-\frac{m v^2}{2kT}\right)$$

$$= 4 \cdot \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot \left(\frac{m v^2}{2kT}\right) \exp\left(-\frac{m v^2}{2kT}\right)$$

$$\frac{m v^2}{2kT} = x^2$$

$$F(x) \propto x^2 e^{-x^2}$$

Calcular velocidades características \rightarrow Distr. Maxwell-Boltzmann

$$v_{qm}^2 = \langle v^2 \rangle = \int_0^{\infty} v^2 F(v) dv$$

$$F(v) = \frac{4\pi}{\pi^{3/2}} \cdot \left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{m v^2}{2kT}\right) = \frac{4}{\sqrt{\pi}} \cdot \lambda^{3/2} v^2 \exp(-v^2 \lambda)$$

$\lambda = m/2kT$

Normalizazio

$$\int_0^{\infty} F(v) dv = \frac{4}{\sqrt{\pi}} \lambda^{3/2} \int_0^{\infty} v^2 e^{-\lambda v^2} dv = 1$$

O polo do zero $\frac{d}{d\lambda} \left(\lambda^{3/2} \int_0^{\infty} v^2 \exp^{-\lambda v^2} dv \right) = \frac{d}{d\lambda} (1) = 0$

$$\frac{3}{2} \cdot \lambda^{1/2} \int_0^{\infty} v^2 e^{-\lambda v^2} dv + \lambda^{3/2} \int_0^{\infty} v^2 \frac{d}{d\lambda} (e^{-\lambda v^2}) dv = 0$$

$$\frac{3}{2} \lambda^{1/2} \int_0^{\infty} v^2 e^{-\lambda v^2} dv - \lambda^{3/2} \int_0^{\infty} v^2 \cdot v^2 e^{-\lambda v^2} dv = 0$$

$$\frac{3}{2} \lambda^{1/2} \frac{\sqrt{\pi}}{4} \cdot \frac{1}{\lambda^{3/2}} = \lambda^{3/2} \int_0^{\infty} v^4 e^{-\lambda v^2} dv$$

$$v_{qm}^2 = \int_0^{\infty} v^2 F(v) dv = \frac{4}{\sqrt{\pi}} \int_0^{\infty} \lambda^{3/2} v^4 e^{-\lambda v^2} dv$$

$$= \frac{4}{\sqrt{\pi}} \cdot \frac{5}{2} \frac{\sqrt{\pi}}{4} \cdot \frac{1}{\lambda} = \frac{3}{2} \cdot \frac{1}{1} = \frac{3}{2} \frac{kT}{m}$$

$$\therefore v_{qm} = \sqrt{\frac{3kT}{m}}$$

\rightarrow equipartição de energia $\frac{1}{2} m v_{qm}^2 = 3 \frac{kT}{2}$
 teoria cinética dos gases \downarrow en. cinética \downarrow 3. en. de
 total \downarrow 1 grau de liberdade

$$\begin{aligned}
 \langle v_{qm}^2 \rangle &= \int_{-\infty}^{\infty} (v_x^2 + v_y^2 + v_z^2) \cdot f(v_x, v_y, v_z) dv_x dv_y dv_z \\
 &= \int_{-\infty}^{\infty} v_x^2 f_1(v_x) dv_x \cdot \int_{-\infty}^{\infty} f_1(v_y) dv_y \cdot \int_{-\infty}^{\infty} f_1(v_z) dv_z \\
 &+ \int_{-\infty}^{\infty} v_y^2 f_1(v_y) dv_y \cdot \int_{-\infty}^{\infty} f_1(v_x) dv_x \cdot \int_{-\infty}^{\infty} f_1(v_z) dv_z \\
 &+ \int_{-\infty}^{\infty} v_z^2 f_1(v_z) dv_z \cdot \int_{-\infty}^{\infty} f_1(v_x) dv_x \cdot \int_{-\infty}^{\infty} f_1(v_y) dv_y = \frac{3}{2} kT
 \end{aligned}$$

$\frac{1}{2} kT$

Velocidad media $\langle v \rangle = \int_{-\infty}^{\infty} f(v_x, v_y, v_z) \cdot v dv_x dv_y dv_z = 0$

Para $F(v)$

$$\langle v \rangle = \int_0^{\infty} v \cdot F(v) dv = \int_0^{\infty} v \cdot \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$= \frac{4}{\sqrt{\pi}} \int_0^{\infty} \left(\frac{mv^2}{2kT} \right) \cdot \exp\left(-\frac{mv^2}{2kT}\right) \frac{m}{\sqrt{2kT}} v dv$$

$$\frac{4}{\sqrt{\pi}} \cdot \sqrt{\frac{kT}{2m}} \int_0^{\infty} x e^{-x} dx$$

$$\begin{aligned}
 x &= \frac{mv^2}{2kT} \\
 \frac{dx}{dv} &= \frac{m \cdot v}{kT}
 \end{aligned}$$

$$\int_0^{\infty} x e^{-x} dx = x \cdot (-e^{-x}) \Big|_0^{\infty} - \int_0^{\infty} 1 \cdot (-e^{-x}) dx = \int_0^{\infty} e^{-x} dx = -e^{-x} \Big|_0^{\infty} = 1$$

$\begin{matrix} \downarrow & \downarrow \\ F & g \end{matrix}$

 $\begin{matrix} \downarrow & \downarrow \\ F & G \end{matrix}$

 $\begin{matrix} \downarrow & \downarrow \\ L & G \end{matrix}$

$$\langle v \rangle = \frac{4}{\sqrt{\pi}} \sqrt{\frac{kT}{2m}} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{kT}{m}} = \sqrt{\frac{8}{3\pi}} \cdot v_{qm} \approx 0,92 v_{qm}$$

Qual a velocidade mais provável?

$$v_p / \frac{d}{dv} [F(v)] = 0 \quad \frac{d}{dv} F = \frac{d}{dx} \left[\frac{4}{\sqrt{\pi}} \sqrt{\frac{2kT}{m}} x^2 e^{-x^2} \right] \cdot \frac{dx}{dv} = 0$$

\downarrow
 $\neq 0$

$$\frac{d}{dx} (x^2 e^{-x^2}) = 2x e^{-x^2} - x^2 \cdot 2x e^{-x^2} = 0$$

$$\rightarrow x = 1$$

$$x = \frac{m v^2}{2kT}$$

$$v_p = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2}{3}} v_{qm} \approx 0,82 v_{qm}$$

$$v_p < \langle v \rangle < v_{qm}$$

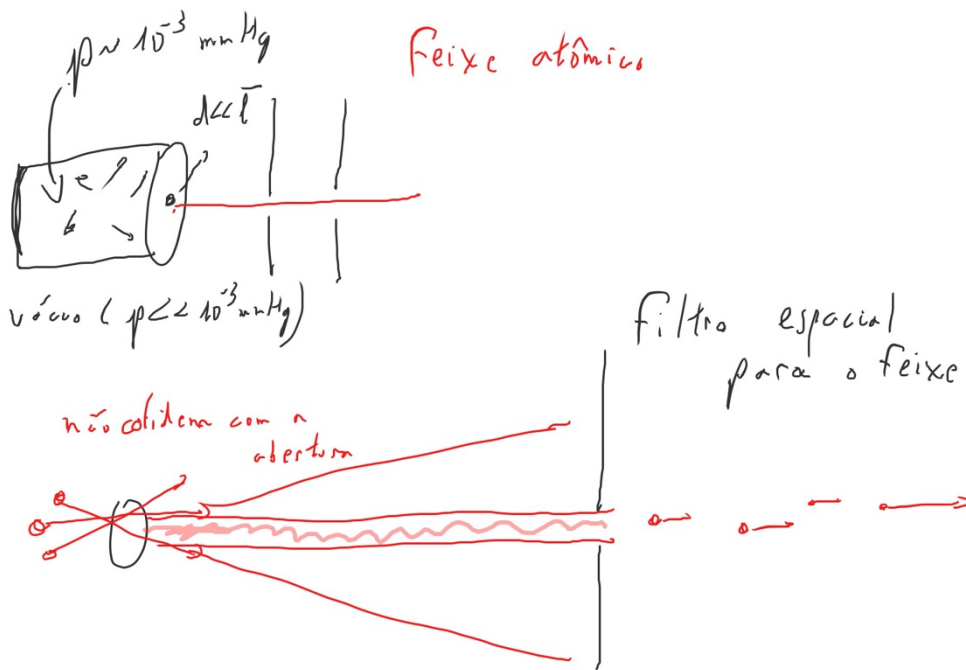
$$F(v) dv \rightarrow v_p \Rightarrow \underbrace{F(v_p) dv}_{\text{máxima}} \rightarrow \begin{matrix} \text{unidade} \\ \text{probabilidade} \end{matrix}$$

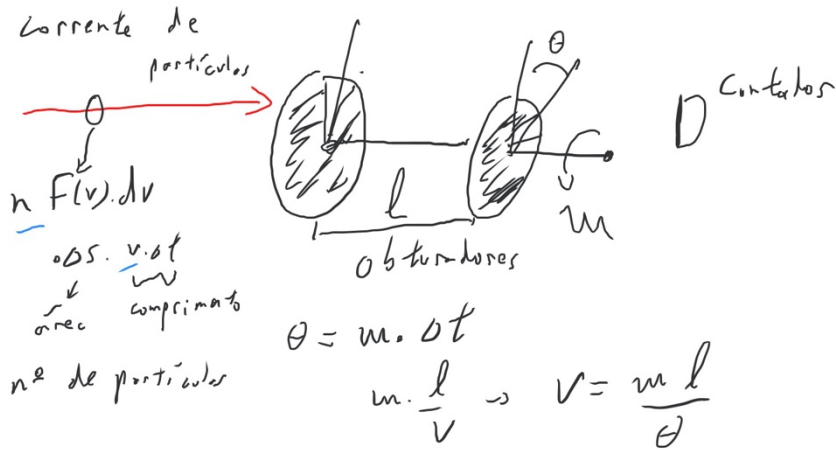
$$n(z) = n(0) e^{-\frac{mgz}{kT}} \rightarrow \begin{matrix} \text{V}_{\text{sub}} \\ e^{\text{exp}} \left(\frac{-mv^2}{2kT} \right) \end{matrix}$$

Função geral: $F(x, y, z, v_x, v_y, v_z) = C \exp \left[\frac{-mgz + \frac{mv^2}{2}}{kT} \right]$

$= C \exp \left(\frac{E}{kT} \right)$ Distr. de Boltzmann

$\underbrace{\hspace{10em}}_{\text{energia}} \quad C \rightarrow \int F d\vec{r} d\vec{v} = 1$





Densidade de corrente. $j(v) \propto F(v) \cdot n \cdot v \propto v^3 \exp\left(\frac{-mv^2}{2kT}\right)$

Movimento Browniano: (1827) para partículas inorgânicas



$$\theta \approx 1 \mu\text{m}$$

partícula \rightarrow macromolécula

$$\frac{3}{2} kT = \frac{m}{2} v_{\text{qm}}^2 = \frac{M \langle v^2 \rangle}{2}$$

$$\frac{v_{\text{qm}}}{v_{\text{qm}}} \sim \sqrt{\frac{m}{M}}$$

$$\frac{m}{M} \sim 10^{-8}$$

$$\sqrt{\frac{m}{M}} \sim 10^{-4}$$

$$v \sim 10^4 v_{\text{qm}} \sim 10^{-4} \cdot 400 \text{ m/s} \sim 4 \text{ cm/s} \rightarrow \text{rápido}$$

Deslocamento $\sim 0,1 \text{ mm/minuto}$. Por quê?

Movimento não é balístico \rightarrow Deslocamento aleatório



longo, $v \sim v_{qm}$, aleatório \rightarrow choques

Passo do bebado

passo
à frente

$x_0 = 0$	$+l$	$-l$	passo atrás
-----------	------	------	----------------

$$x_1 = \pm l$$
$$\langle x_1 \rangle = 0$$
$$\langle x_1^2 \rangle = l^2$$

$$x_2 = x_1 \pm l$$
$$\langle x_2 \rangle = \langle x_1 \pm l \rangle = \langle x_1 \rangle \pm l$$
$$\langle x_1 \rangle = 0 \rightarrow \langle x_2 \rangle = \pm l$$

$$\langle x_2^2 \rangle = \langle x_1^2 + l^2 \pm 2x_1 l \rangle = \langle x_1^2 \rangle + l^2 + 2\langle x_1 \rangle \langle l \rangle = 2l^2$$

$$\langle x_n \rangle = 0$$

$$\langle x_n^2 \rangle = n \cdot l^2$$

$$x_{qm} = \sqrt{n} \cdot l$$

\hookrightarrow Tabuleiro de Galton

Processo difusivo

1D

Processo difusivo \rightarrow passos $\rightarrow l \sim v \cdot \bar{t} \rightarrow \frac{l}{\bar{t}} \sim v$

Molécula $\bar{t} \rightarrow$ livre caminho médio

$v \sim v_{qm}$ $\bar{t} \sim$ intervalo entre colisões

$$\begin{aligned} \langle x^2 \rangle &= N \cdot l^2 & v &\sim 5 \cdot 10^2 \text{ m/s} \\ &= \frac{l}{\bar{t}} \cdot l = l \cdot v \cdot t = 2D \cdot t & D &\sim 10^{-5} \text{ cm}^2/\text{s} \end{aligned}$$

difusividade (m^2/s)

Difusão de um gás

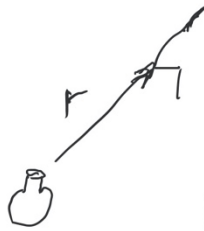
$$D \sim 1 \text{ cm}^2/\text{s}$$

Em 3 Dim

$$\begin{aligned} 2D &\sim l \cdot v \\ \leftarrow D &\sim \frac{l \cdot v}{2} \end{aligned}$$

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle$$

$$\begin{aligned} \langle r^2 \rangle &= 3 \cdot \langle x^2 \rangle \\ &= 6 \cdot D \cdot t \end{aligned}$$



$$r_{qm} = \sqrt{6D \cdot t}$$

Crescimento com \sqrt{N}

\rightarrow partículas pequenas \rightarrow "macro" moléculas
 \rightarrow Forças aleatórias \rightarrow grãos $\sim 1 \mu\text{m}$? \rightarrow 1905 Einstein