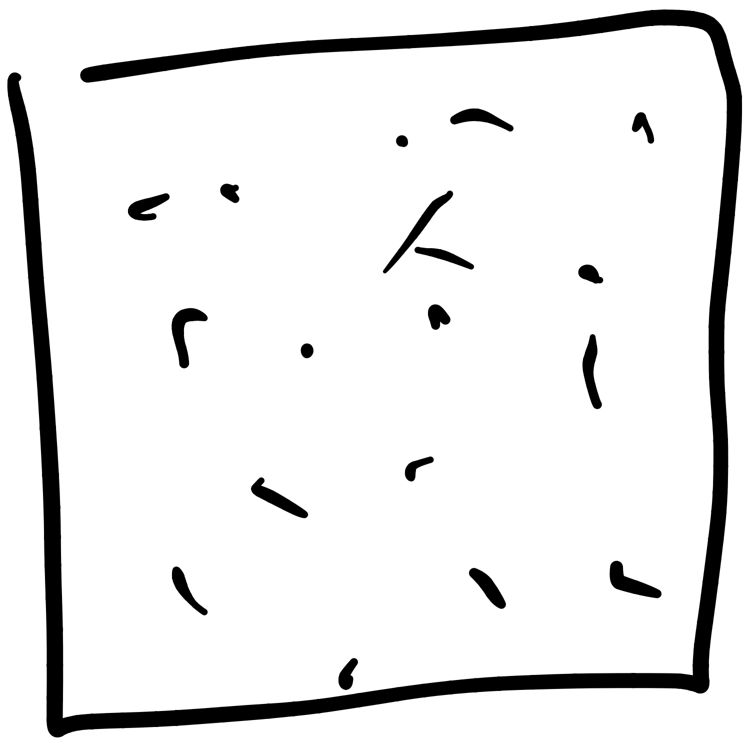
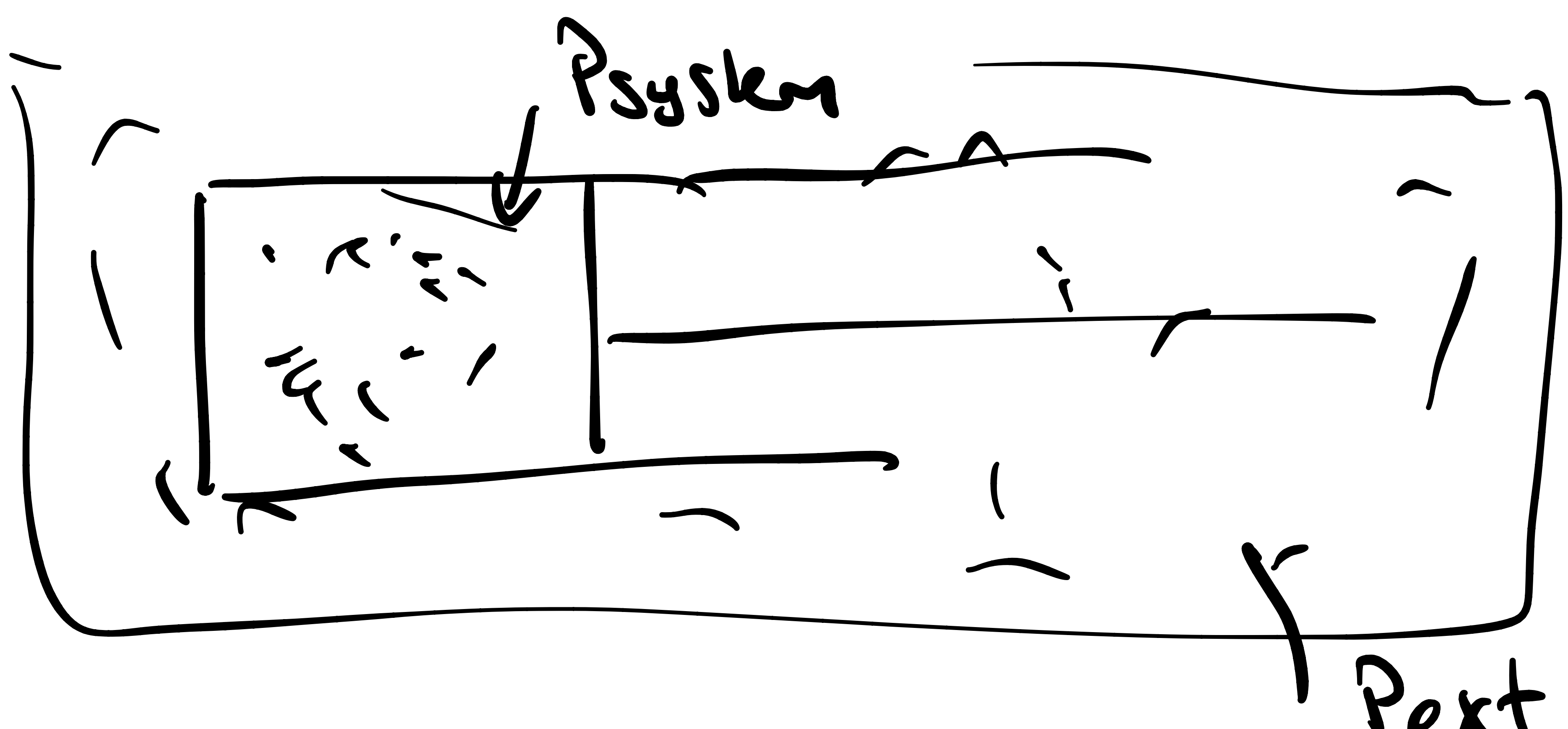
Lecture 17 - Kinetic Theory of Gasses



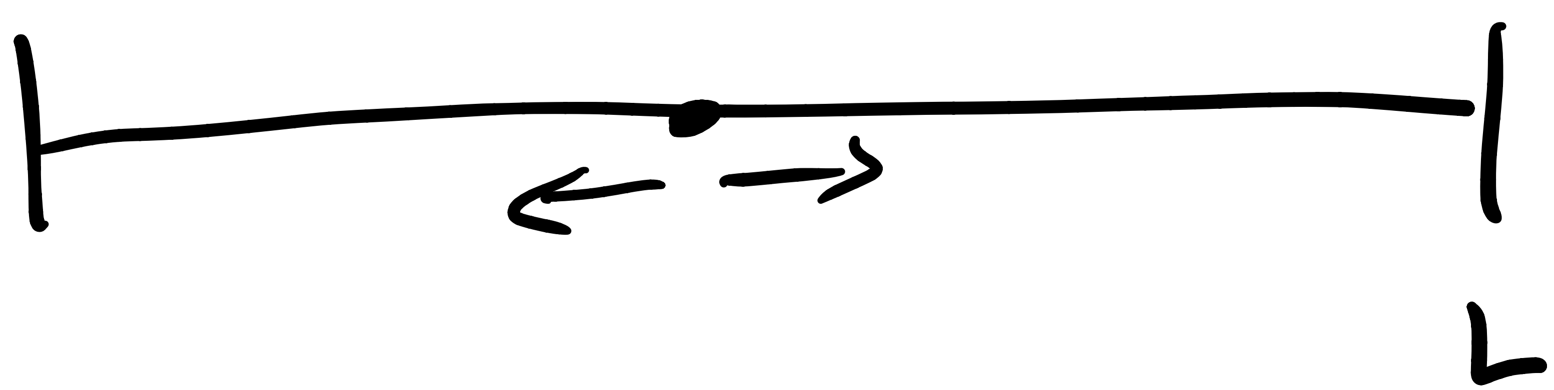
N particles
Box volume V
@ temperature T



what are molecules doing?

ideal gas has only kinetic energy
no particle interaction
-particle

$$\varepsilon_{kinetic} = \frac{1}{2} m v^2 = \frac{p^2}{2m} \qquad p = mv$$



if this is "in a bath", exchanges energy beforehand

$$P(\varepsilon) \propto e^{-\varepsilon/k_BT} = e^{-\frac{1}{2}mv^2 \cdot \frac{1}{k_BT}}$$

$$P(v) = e^{-\frac{1}{2}mv^2/k_BT} / Z$$

$$\mu = \langle v \rangle = 0$$

$$N(\mu, \sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2}$$

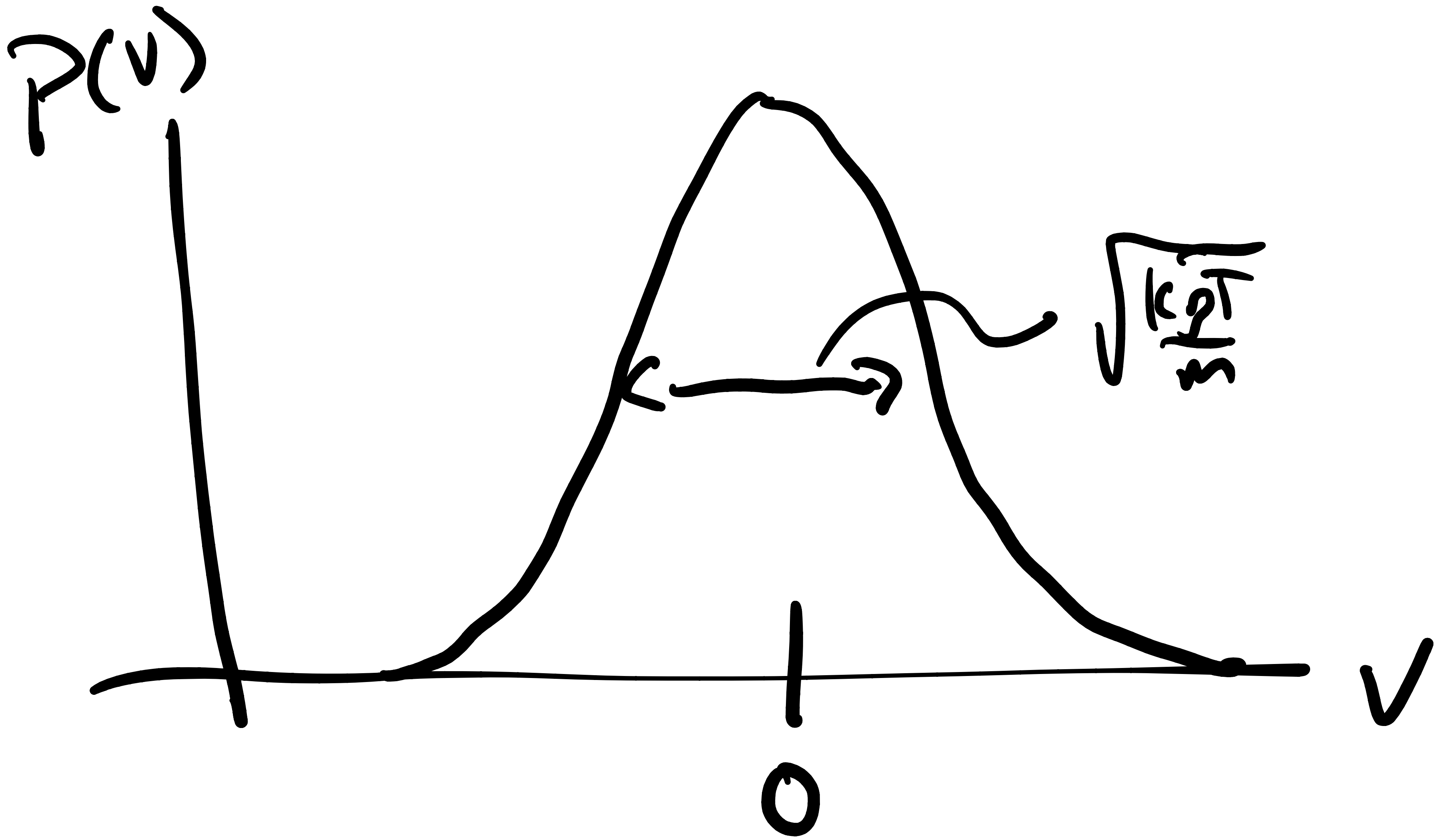
$$\sigma^2 = \langle v^2 \rangle - \mu^2$$
$$= \langle v^2 \rangle$$
$$= k_BT/m$$

$$P(v) = \frac{1}{\sqrt{2\pi\left(\frac{k_B T}{m}\right)}} e^{-\frac{1}{2}\frac{mv^2}{k_B T}}$$

$\mu = 0$

$\langle v^2 \rangle = \frac{k_B T}{m}$

r.m.s. velocity $\sqrt{\langle v^2 \rangle} = \sqrt{\frac{k_B T}{m}}$



wider if $T \uparrow$

$m \downarrow$

$$\langle KE \rangle = \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \frac{k_B T}{m}$$

$$= k_B T / 2$$

$$T = \frac{2 \langle KE \rangle}{k_B}$$

missing 3d, N molecules

$$e^{a+b} = e^a \cdot e^b$$

3d $\vec{v} = (v_x, v_y, v_z)$

$$\vec{x}^2 = \vec{x} \cdot \vec{x}$$

$$KE = \frac{1}{2} m |v|^2 = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$$

$$(a, b, c) \cdot (e, f, g) = ae + bf + cg$$

$$P(KE) \propto e^{-E/k_BT} = e^{-1/k_BT \frac{(v_x^2 + v_y^2 + v_z^2)}{2m}} = e^{\frac{-1 v_x^2}{2m}/k_BT} e^{-v_y^2/k_BT} \cdots$$

$$= P(KE^x)\, P(KE^y)\, P(KE^z)$$

$$\langle KE \rangle = \left\langle \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right) \right\rangle$$

1 mol, 3d

$$= \frac{1}{2} m \left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z \rangle^2 \right)$$

$$= \frac{3}{2} m \cdot \left(\frac{k_B T}{m} \right) = \frac{3}{2} \cdot k_B T$$

N molecules $$KE = \sum_{i=1}^{N} \frac{1}{2} m |\vec{v}_i|^2$$

$$\langle KE \rangle = N \cdot \frac{3}{2} k_B T = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

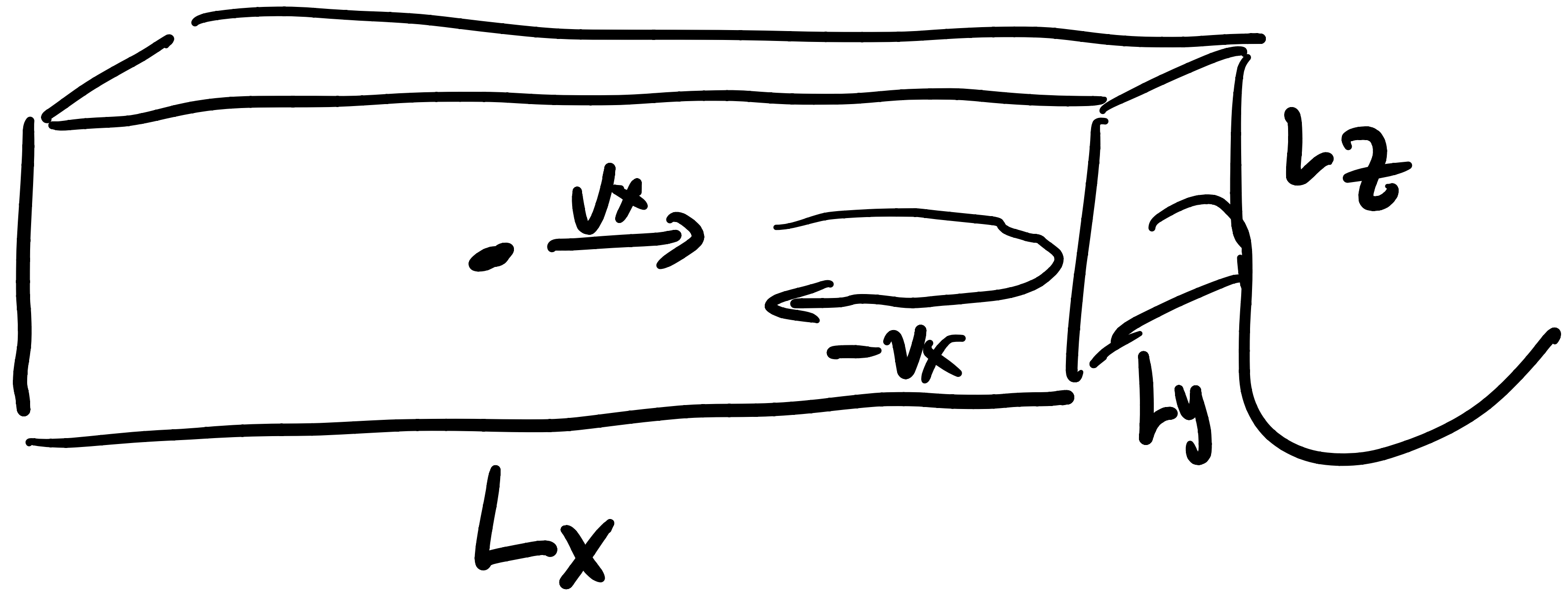
In Liquid

$$\langle \varepsilon \rangle = \langle KE \rangle + \langle PE \rangle$$

$$\uparrow \quad \frac{k_B T}{2} \cdot \underbrace{\#\,\mathrm{dof}}_{3N}$$

Ideal gas law: $PV = nRT$

What is Pressure? Should get $\frac{nRT}{V}$



$$V = L_x L_y L_z$$

$$P = \frac{F}{A}$$

$$F = \frac{dp}{dt} = m\frac{dv}{dt} = ma$$

Change is momentum is $mV_x - (-mV_x)$

$$\Delta p = 2mV_x$$

$$\Delta t = \frac{2L_x}{V_x}$$

$$F_x = \frac{\Delta p}{\Delta t} = \frac{mV_x^2}{L_x}$$

$$P = F_x / L_y L_z = mV_x^2 / V$$

$$P_i V = m v_x^{i^2}$$

$$P_{total} = \sum_{i=1}^{N} \frac{m v_{x,i}^2}{V} \cdot \frac{N}{N} = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{N m v_{x,i}^2}{V} \right)$$

$$P = \frac{Nm}{V} \langle v_x^2 \rangle = \frac{N k_B T}{V} = \frac{nRT}{V}$$

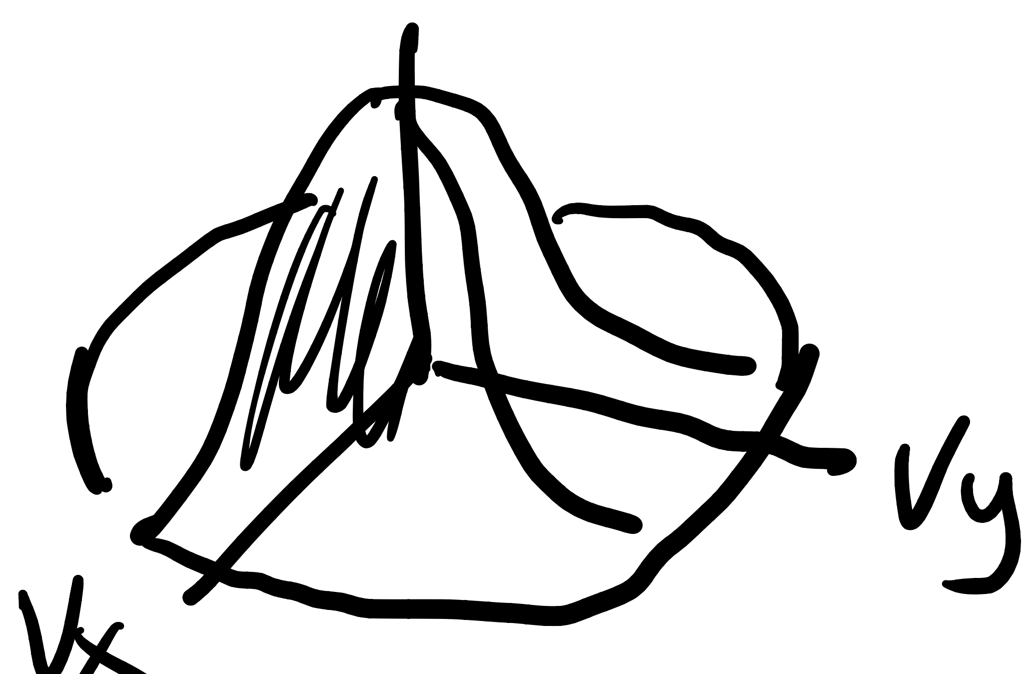
$$\boxed{PV = nRT}$$

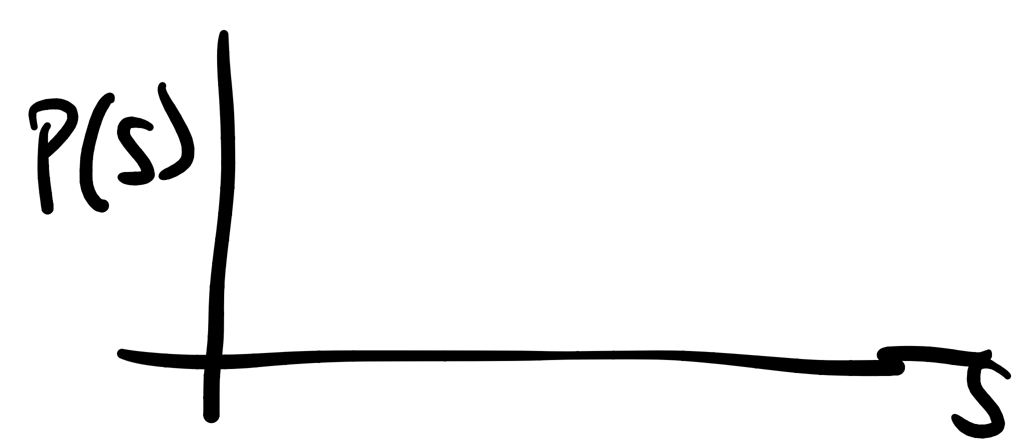
What speed are the molecules going?

speed = $|v|$

$$P(v_x, v_y, v_z) = \frac{1}{\sqrt{2\pi\sigma^2}} \cdot \frac{1}{\sqrt{2\pi\sigma^2}} \frac{1}{\sqrt{2\pi\sigma^2}} \times$$

$$e^{-\frac{m}{2k_BT} v_x^2} e^{-\frac{m}{2k_BT} v_y^2} e^{-\frac{m}{2k_BT} v_z^2}$$





$$f(x,y,z)\,dx\,dy\,dz$$

$$= \tilde{f}(r,\theta,\phi)\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

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

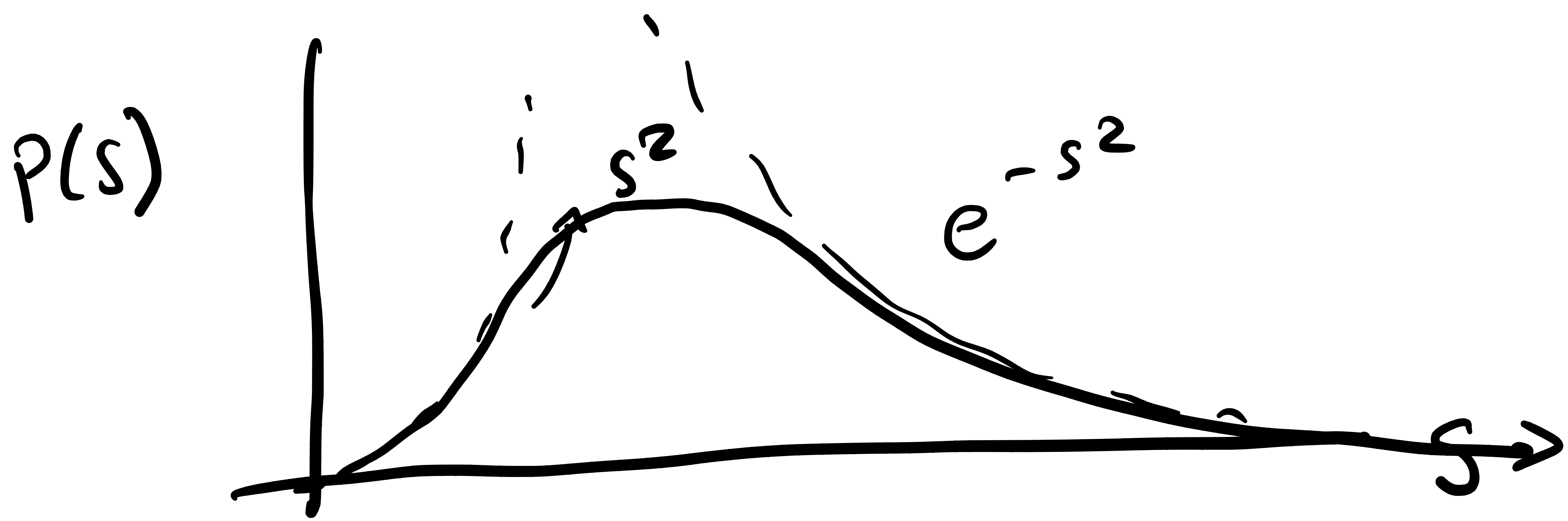
$$S(v_x, v_y, v_z) = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

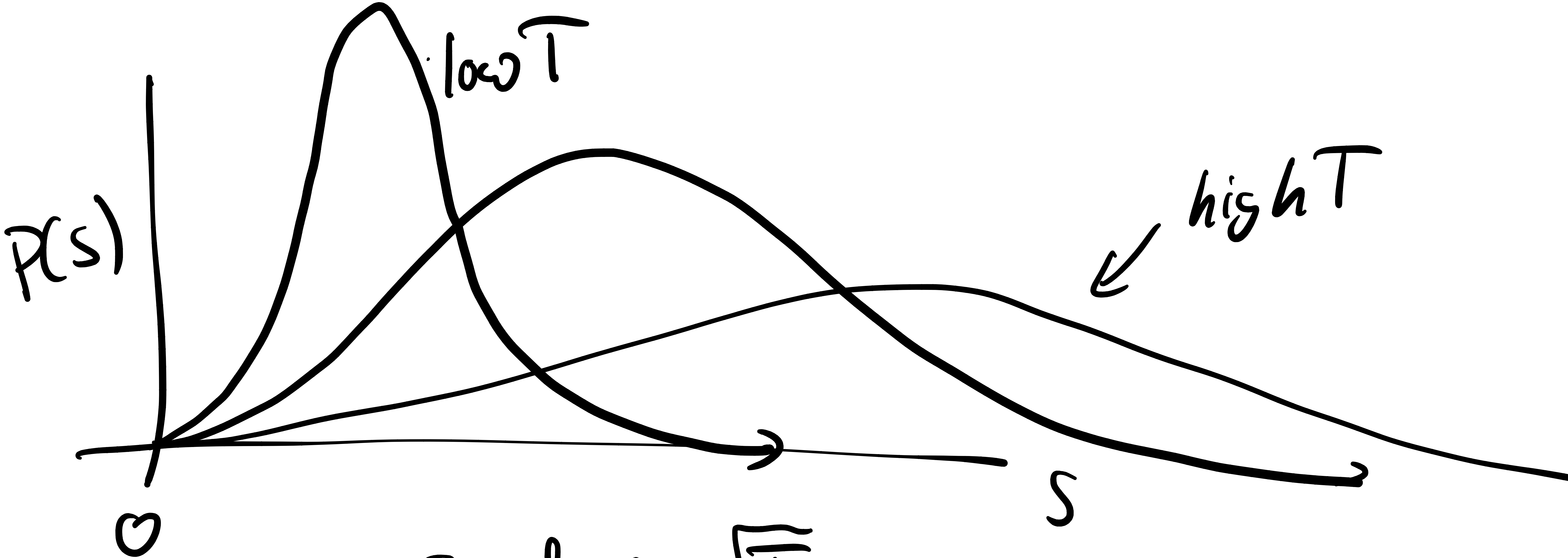
$$\overbrace{\int_0^{\pi}\int_{-\pi}^{\pi} \sin\theta\, d\theta\, d\phi}^{4\pi}$$

$$P(v_x, v_y, v_z) = P(S,\theta,\phi)\, S^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$P(v_x, v_y, v_z) \propto e^{-\frac{1}{2}\frac{m}{k_B T} s^2} \leftarrow \text{no } \theta, \phi$$

$$\underbrace{P(s)\,ds = \underbrace{4\pi}_{\text{integrate over angles}} \left(\frac{m}{2\pi k_B T}\right)^{3/2} s^2 e^{-ms^2/(2k_BT)}}_{\text{Maxwell-Boltzmann distribution}}$$





avg speed $\propto \sqrt{T}$

3 quantities characterize this distribution

avg speed

rms speed

median speed

$$\langle s \rangle = \int_0^\infty s P(s)\, ds = \sqrt{\frac{8 k_B T}{m\pi}}$$

$$v_{rms} = s_{rms} = \sqrt{\frac{3 k_B T}{m}}$$

median speed, $0 = \frac{dP(s)}{ds}$ & solve

$$s_{most\ prob} = \sqrt{\frac{2 k_B T}{m}}$$

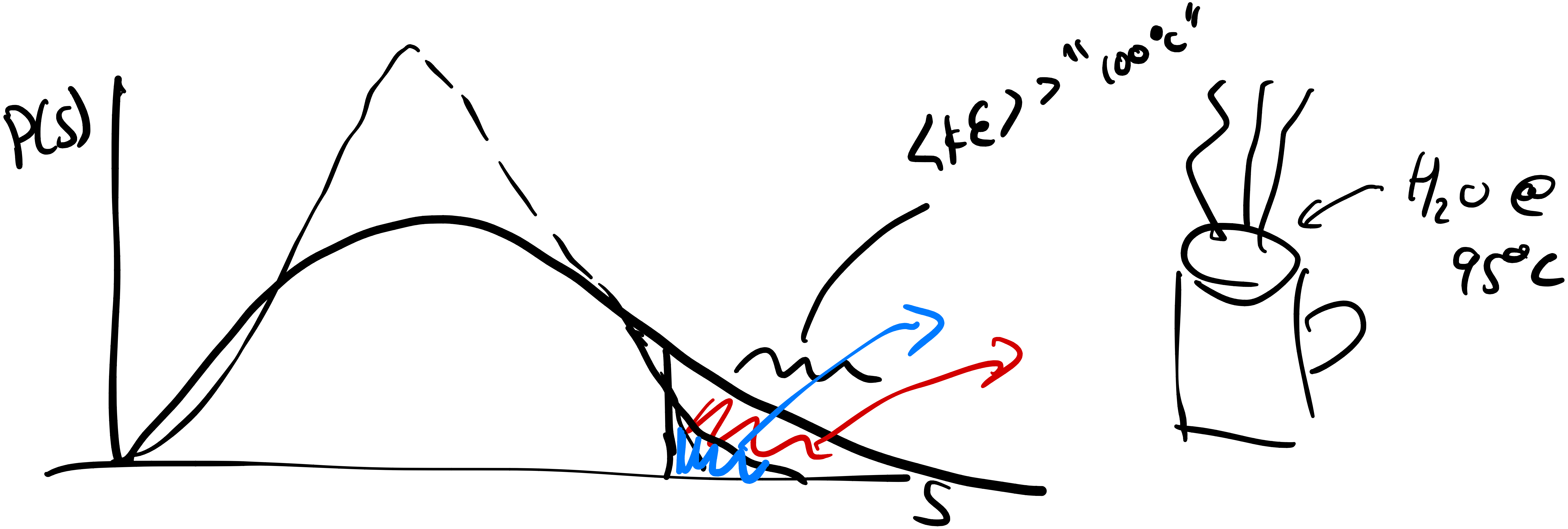
ratios $86.7\% \sim 1 \sim 108.5\%$

What is speed of sound?

$$C = \sqrt{\frac{\gamma}{3}}\, S_{rms} \qquad \gamma = C_P/C_V$$

Reaction rate in gas
how often things collide, & with how much energy

(pg 1116 - 1127 McQ)



evaporative cooling