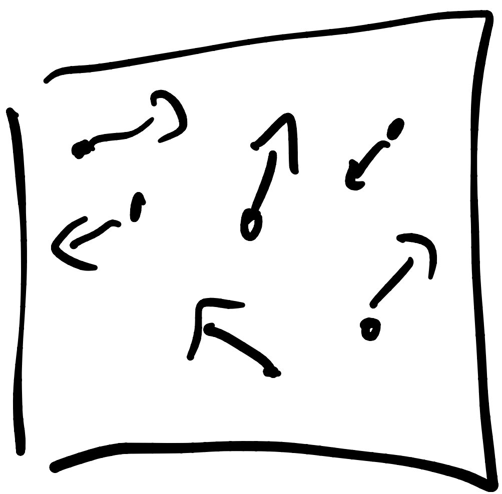
Kinetics / Kinetic theory of gasses



derive average quantities

from motion of molecules

Newton's equations
Classical mechanics

T ~ average kinetic energy

Origin of pressure

How fast are molecules moving?

interact with walls

at constant temperature

$$P(\varepsilon) \propto e^{-\varepsilon/k_B T}$$

Ideal gas, only energy is K.E., 1 mc $\varepsilon = \frac{1}{2} m v^2$

How fast are molecules moving?

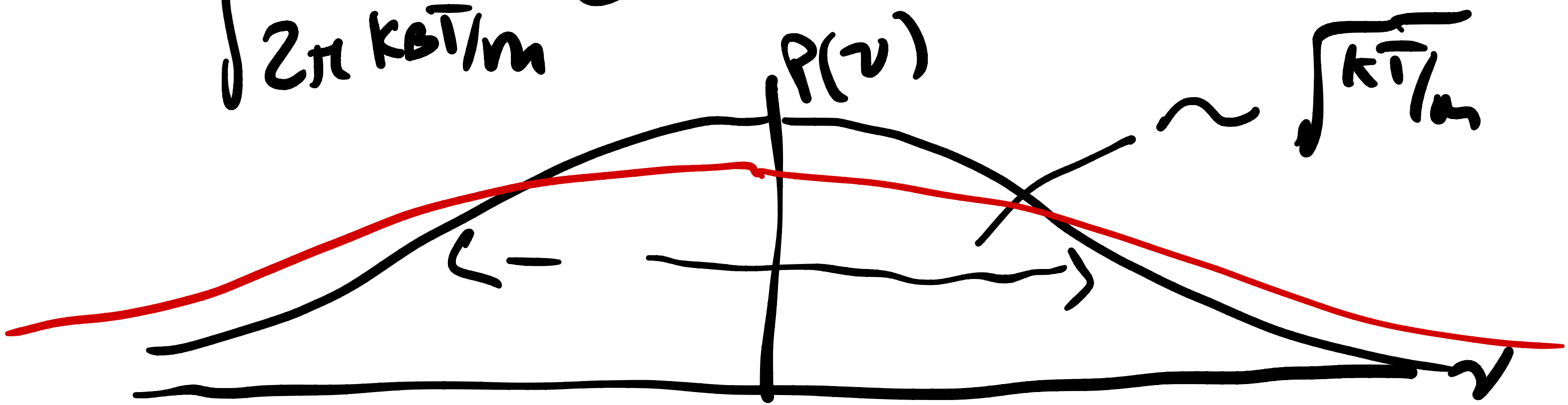
$$P(v) \propto e^{-\frac{1}{2}mv^2/k_BT} \qquad e^{-(x-\mu)^2/2\sigma^2}$$

↑ Normal distribution

$$\mu = 0, \quad \sigma^2 = k_BT/m$$

x, y, or z direction

$$= \frac{1}{\sqrt{2\pi k_BT/m}} e^{-\frac{1}{2}mv^2/k_BT}$$



Average kinetic energy

variance
σ^2

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

$$= \frac{1}{2} m \frac{k_B T}{m} = \frac{k_B T}{2}$$

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

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

$$P(\varepsilon) \propto \underbrace{e^{-\frac{1}{k_BT}\frac{1}{2}m(v_x^2+v_y^2+v_z^2)}}_{e^{-\frac{1}{2k_BT}mv_x^2}\cdot e^{-\frac{1}{2k_BT}}\cdots}$$

$$= P(v_x)P(v_y)P(v_z)$$

Independent directions

$$\langle \varepsilon \rangle = \frac{1}{2}m\langle v_x^2+v_y^2+v_z^2\rangle =$$

$$\langle \varepsilon \rangle = \frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle =$$

$$= \frac{1}{2} m \big(\underbrace{\langle v_x^2 \rangle}_{\sigma^2} + \underbrace{\langle v_y^2 \rangle}_{\sigma^2} + \underbrace{\langle v_z^2 \rangle}_{\sigma^2} \big)$$

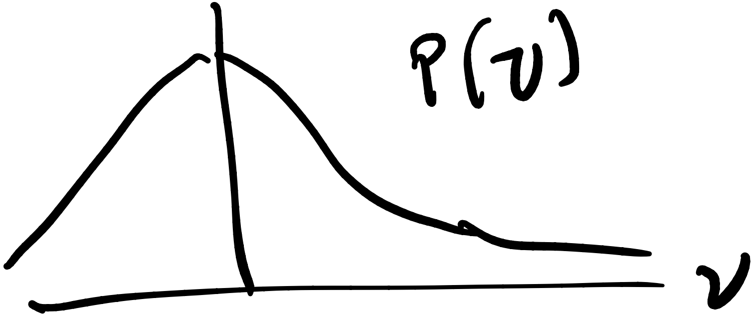
$$= \frac{3}{2} k_B T$$

if N particles

each particle independent

$$KE = \sum_{i=1}^{N} KE_i \Rightarrow \langle KE \rangle = \frac{3}{2} N k_B T$$

$$= 3/2\, nRT$$



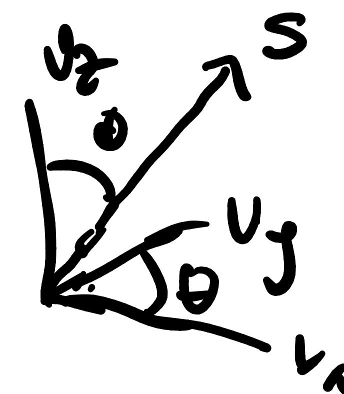
velocity has a direction

"speed", $|v|$

no direction

$$\underbrace{P(\vec{v})}_{dv_x\,dv_y\,dv_z} = \left(\frac{m}{2\pi m k_B T}\right)^{3/2} e^{-\frac{m}{2k_BT}\left(v_x^2+v_y^2+v_z^2\right)}$$

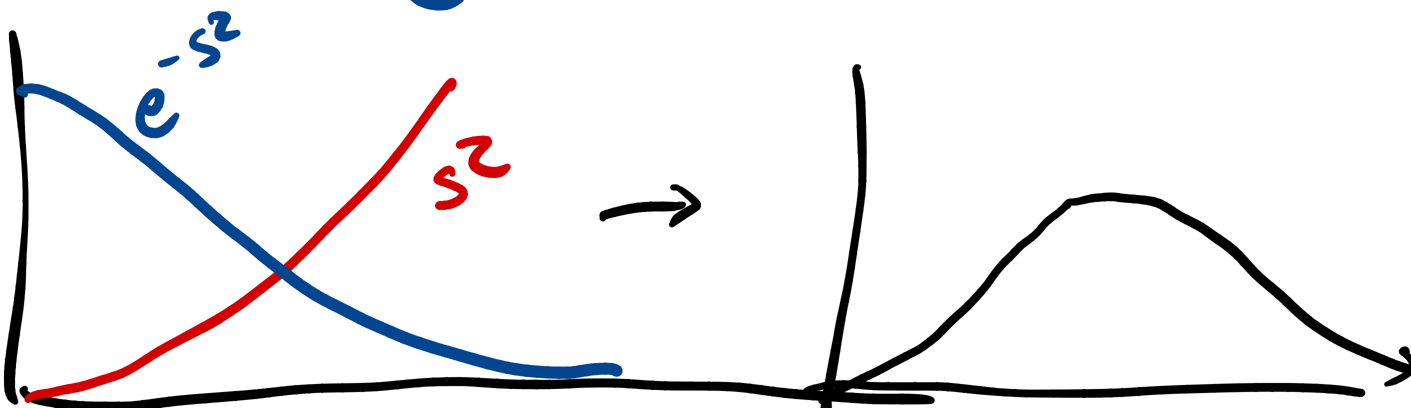
$$s = \sqrt{v_x^2+v_y^2+v_z^2}$$

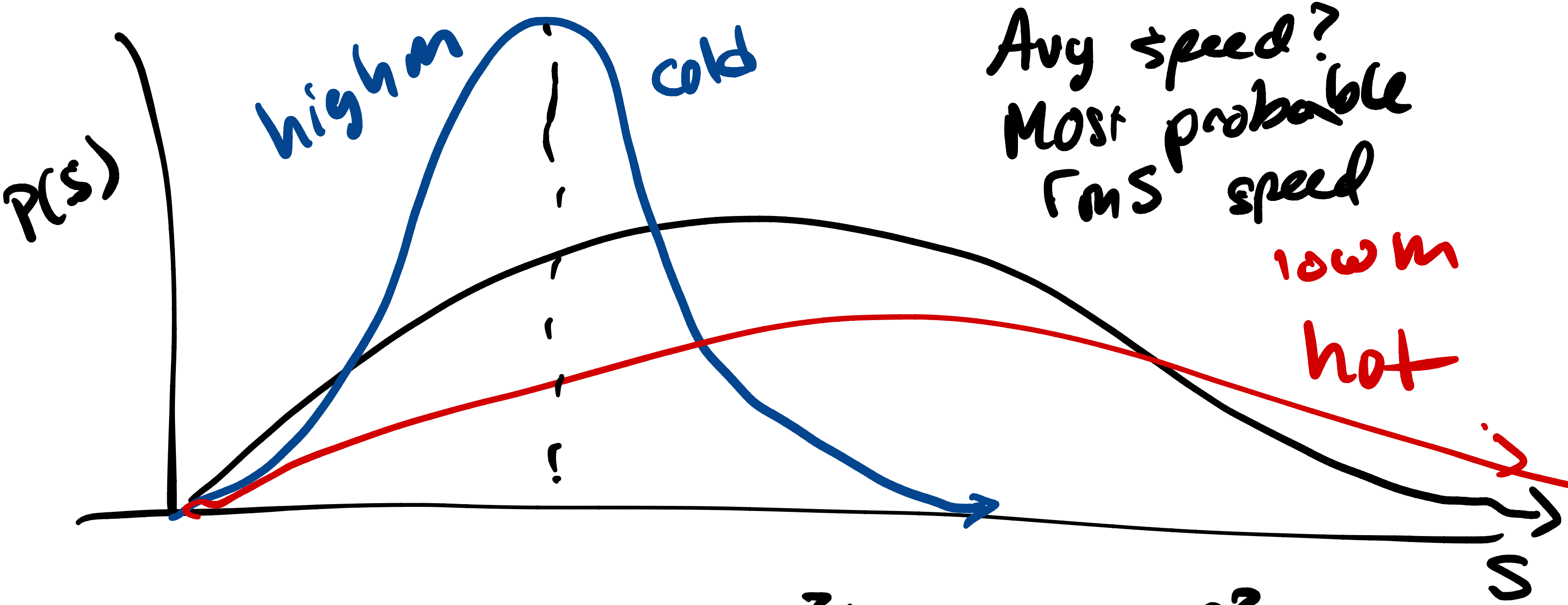


$$P(s) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} s^2 e^{-ms^2/2k_B T}$$

Maxwell-Boltzmann distribution

$$\sim s^2 e^{-ms^2/T}$$





$$P(s) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} s^2 e^{-ms^2/2k_B T}$$

$$\langle s\rangle = \int_0^\infty s P(s)\, ds \rightarrow \int s^3 e^{-s^2}$$

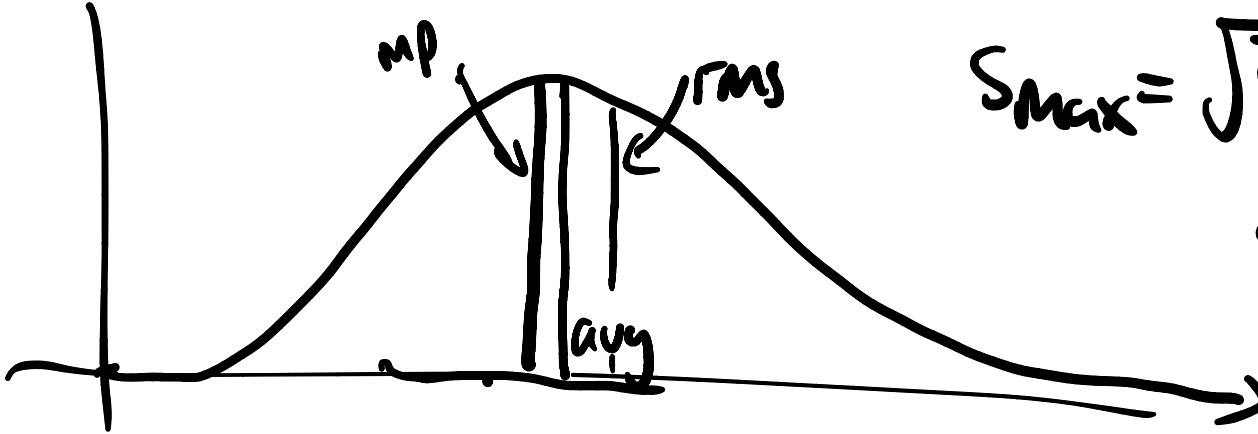
$$= \left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

[see pg 114]

$$v_{rms} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3k_BT}{m}}$$

is avg speed or rms bigger

$\langle s\rangle / v_{rms} = \sqrt{8/3\pi} < 1$, $\langle s\rangle$ smaller



$s_{max} = \sqrt{2k_BT/m}$

squared average
dominated by larger values

most probable "mode"

$$dP(s)/ds = 0 = C\left[s^2 \cdot -\frac{sm}{k_BT} + 2s\right]e^{-ms^2/2k_BT}$$

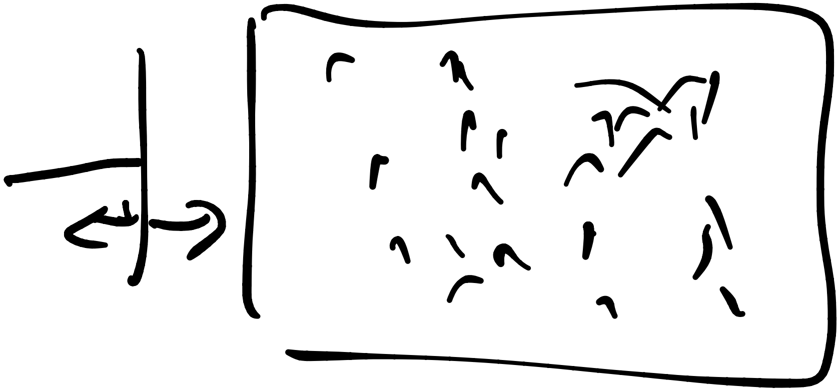
$S_{mode} \approx 86.6\%\, S_{avg} < S_{avg} < 108.5\%\, S_{avg}$
$= S_{rms}$

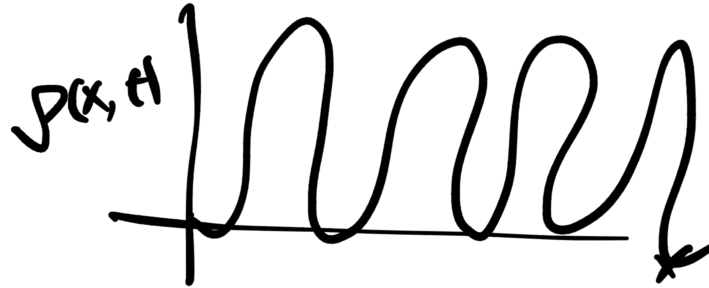
What are these speeds

Eg: speed of N_2 @ 300K

speed of sound

$$C = \sqrt{\gamma/3}\; S_{rms}, \quad \gamma = c_p/c_v$$



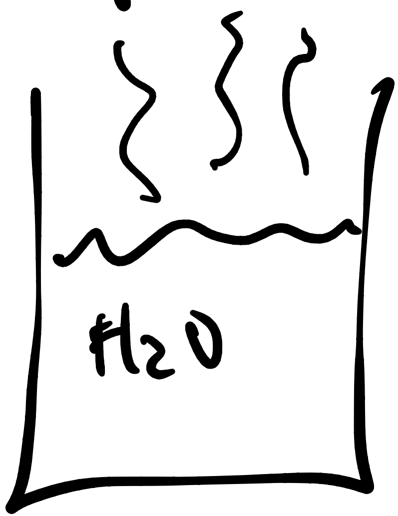


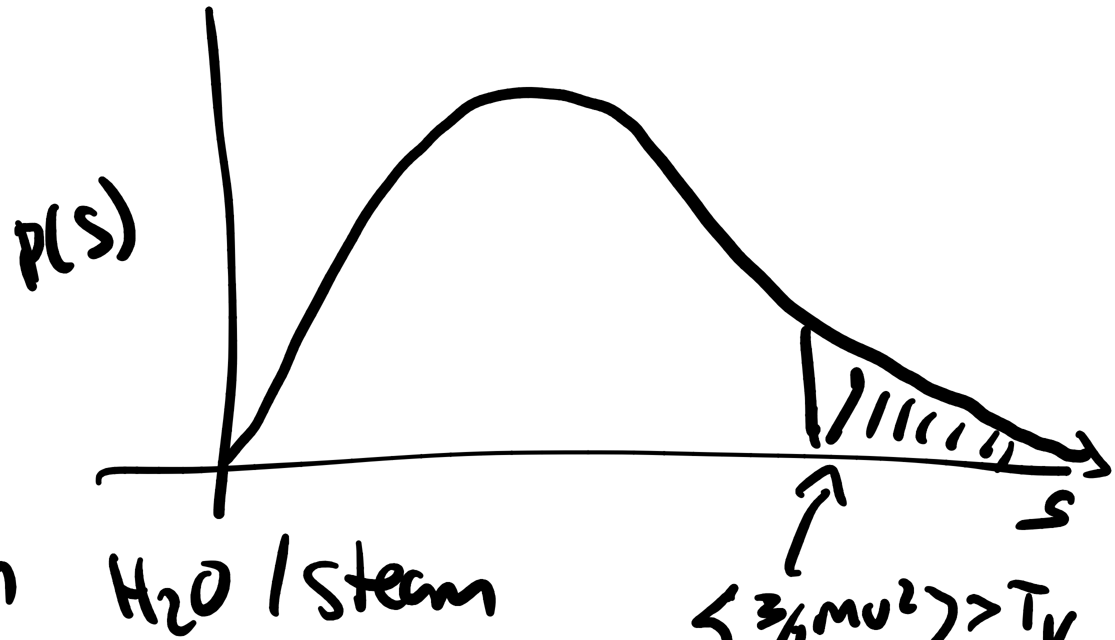
Reaction rate $\propto$ collission rate $\leftarrow$ depends on v_{rms}

[pg 1116 - 1127 Mc Quarrie]

Why does hot stuff cool off

Evaporative cooling

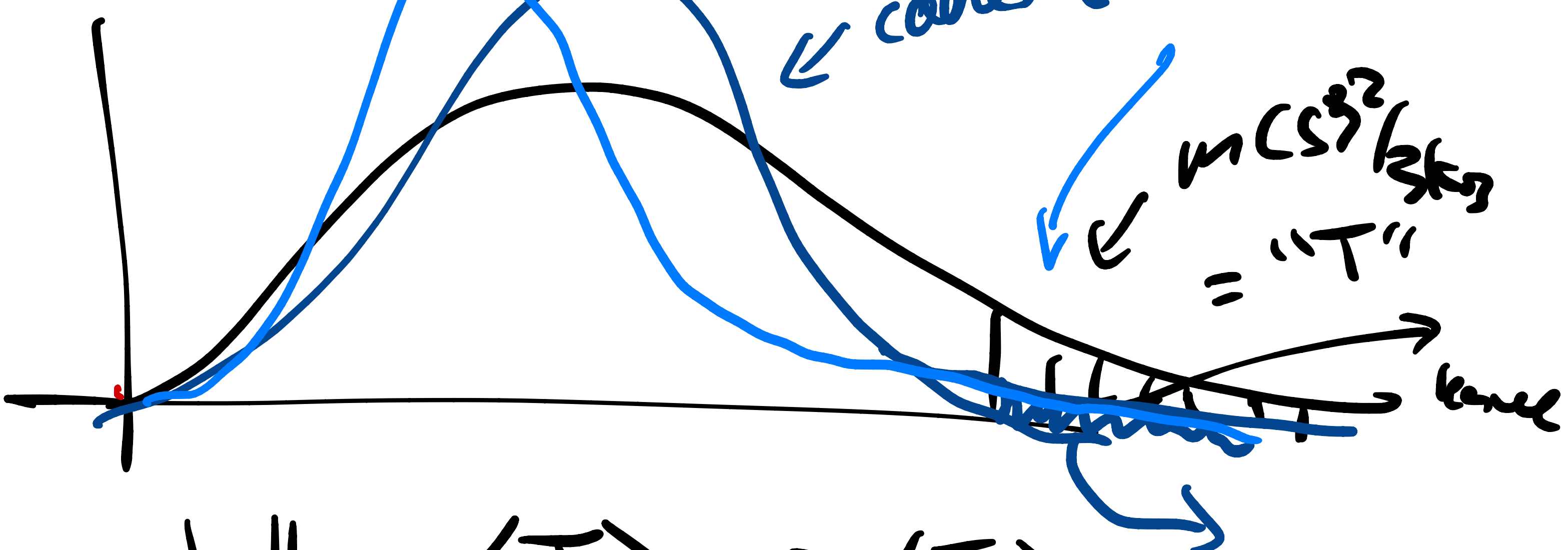




Equilibrium btwn H_2O / steam

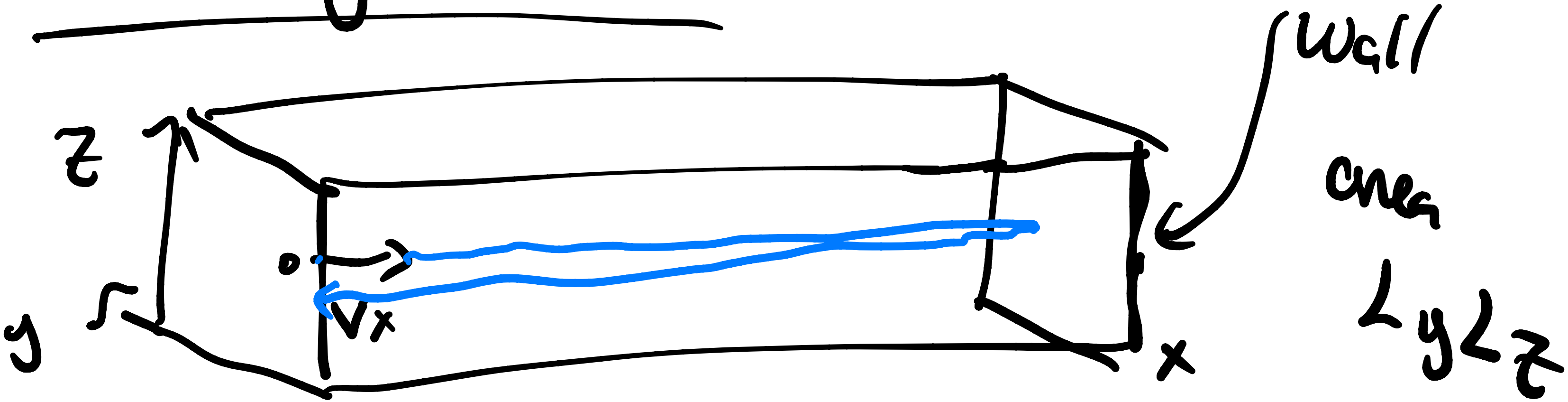
$$\langle v^2 \rangle = \frac{3k_BT}{m}$$

$$T = m\langle s\rangle^2 / 3k_B$$



eventually $\langle T\rangle_{liq} = \langle T\rangle_{surroundings}$

Ideal gas law



$$P = \frac{F_{wall}}{A_{wall}} \leftarrow \frac{\Delta p}{\Delta t} \qquad \Delta t = \frac{2L_x}{v_x}$$

$$\Delta p = mv_x - (-mv_x) = 2mv_x$$

$$F = \Delta p / \Delta t = \frac{2 m v_x}{2 L_x / v_x} = \frac{m v_x^2}{L_x}$$

$$F/A = m v_x^2 / L_x L_y L_z = \frac{1}{V} m v_x^2 = P_i$$

$$P_{tot} = \sum_{i=1}^{N} P_i = \frac{1}{V} \sum_{i=1}^{N} m v_{i}^{x\,2} \cdot \frac{N}{N}$$

$$= N/V \cdot m \cdot \left(\frac{1}{N} \sum_{i=1}^{N} v_i^2 \right) = \frac{Nm}{V} \langle v^2 \rangle = \frac{N k_B T}{V}$$