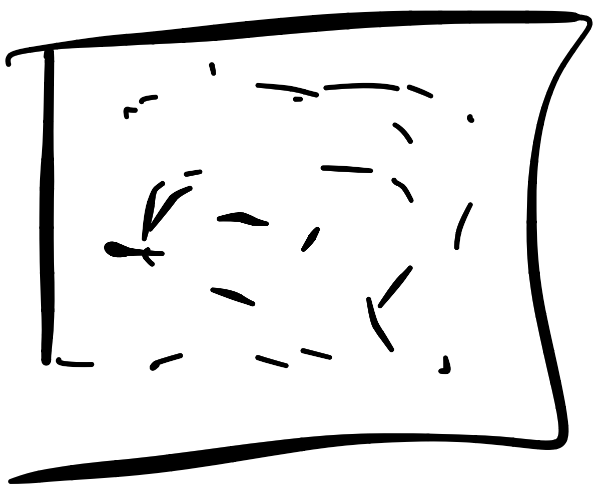
Kinetic Theory of Gasses
Brief overview

Spent a lot of time on ideal gas



N particles
Box volume V
@ temp T

or in piston

where pressure matches external pressure

But what are gas molecules doing?

In ideal gas, only energy is kinetic energy, and no particle interacts, so we can consider one molecule/atom in 1d to start

$$\mathcal{E} = \frac{1}{2} m v^2$$

Said before, will discuss more the Bolzmann equation for constant temperature $P(\mathcal{E}) \propto e^{-\mathcal{E}/k_B T}$

Prob of this system having energy $\mathcal{E}$ is exponential in $\mathcal{E}$

The prob of a particular velocity is related to the energy of the system at that v

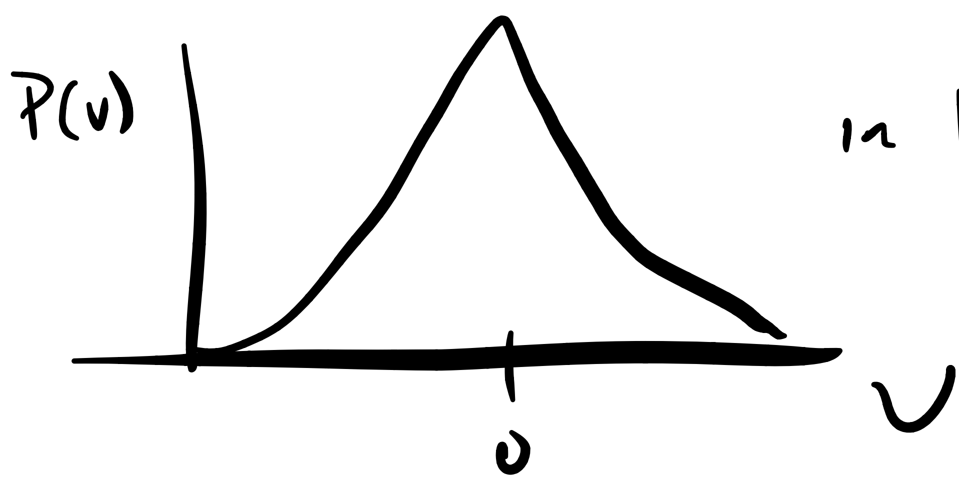
$P(v) \propto e^{-\frac{1}{2}mv^2/k_BT}$ ← gaussian $\mu = 0$, $\sigma^2 = k_BT/m$

Learned at beginning of class:

$$P(v) = \frac{1}{\sqrt{2\pi k_BT/m}} e^{-\frac{mv^2}{2k_BT}}$$ has

$$\int_{-\infty}^{\infty} dv\, P(v) = 1$$

so



in 1d

$$\langle v^2 \rangle = \int_{-\infty}^{\infty} dv\, v^2 P(v) = \frac{k_BT}{m}$$ ← variance

so $\langle \varepsilon \rangle = \langle \frac{1}{2}mv^2 \rangle = \frac{1}{2}m\langle v^2 \rangle = k_BT/2$

what about 3d?

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

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

So $P(\mathcal{E}) \propto e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z$

$\propto P(v_x) P(v_y) P(v_z)$ independent

$$\langle \mathcal{E} \rangle = \langle \frac{1}{2} m \vec{v}^2 \rangle = \frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle$$

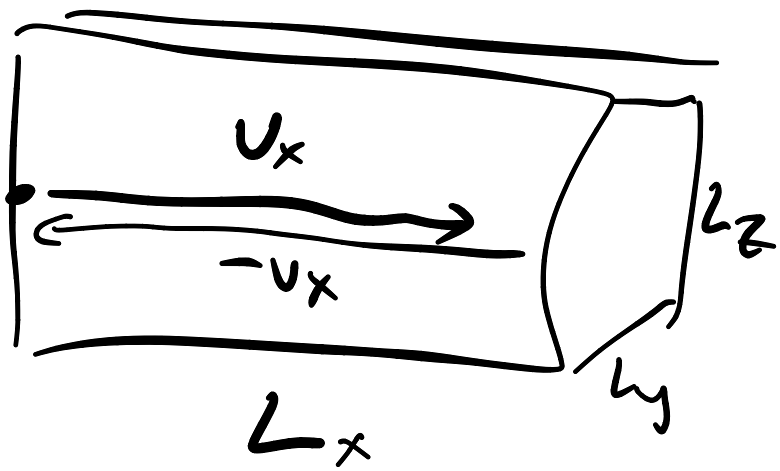
$$= \frac{3}{2} m \cdot \frac{k_BT}{m} = \frac{3}{2} k_B T$$

For N independent particles

$$\langle \mathcal{E} \rangle = \frac{3}{2} N k_B T = \underline{\frac{3}{2} nRT}$$

Ideal gas energy from microscopics

What about ideal gas law?



change in momentum is

$$mv_x - (-mv_x) = 2mv_x$$

time passed is $2L_x / v_x$ $\quad (d = vt)$

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

$$\text{Pressure} = F/A = F_x / L_y L_z$$

$$P = \frac{mv_x^2}{L_x L_y L_z} = mv_x^2 / V$$

$$P_i V = m v_x^{i\,2}$$ one particle

Total pressure

$$P = \sum P_j = \sum_{i=1}^{N} \frac{m v_j^{x2}}{V} = \frac{Nm}{V} \cdot \underbrace{\frac{1}{N} \sum_{i=1}^{N} v_j^{x2}}_{\langle v_j^x \rangle^2}$$

$$= \frac{N}{V} m \frac{k_B T}{m}$$

so $PV = N k_B T = nRT$ ✓

What do the speeds of molecules look like in the gas

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

RMS speed/velocity $\sqrt{v^2} = \sqrt{3 k_B T / m}$

Speed is $|v|$, no direction

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

$$= \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m}{2k_BT}(v_x^2+v_y^2+v_z^2)}$$

u^2

Spherical coordinates

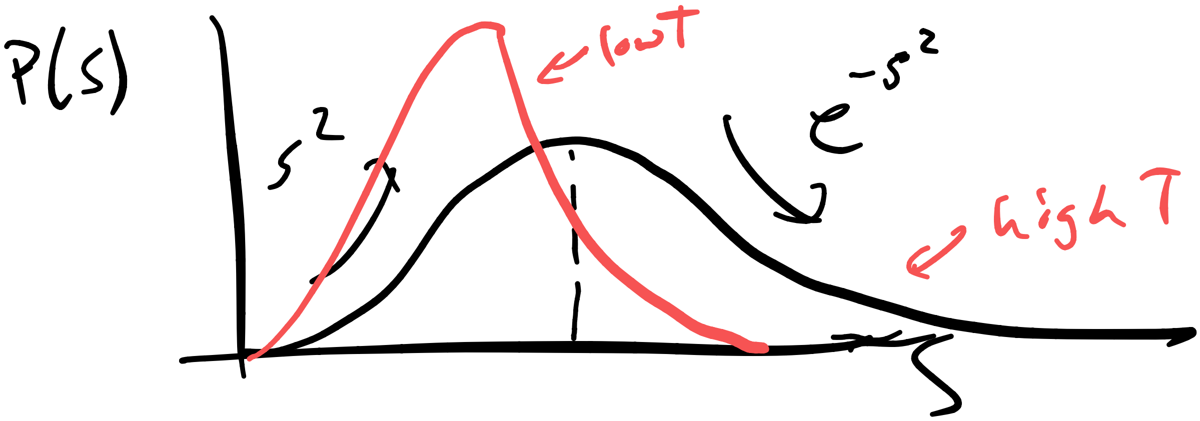
$x, y, z \to \theta, \phi, r$

$$r = \sqrt{x^2+y^2+z^2}$$

Here $P(s,\theta,\phi) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \sin\theta \, s^2 e^{-\frac{ms^2}{2k_BT}}$

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

check normalized



Avg speed?

$$\langle s \rangle = \int_0^\infty s\,P(s)\,ds = \left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

check, see pg 1114

Is this bigger or smaller than v_{rms}

$$v_{rms} = \sqrt{3k_BT/m} \qquad \frac{\langle s \rangle}{v_{rms}} = \sqrt{\frac{8}{3\pi}}$$

avg speed smaller

What is most probable speed / mode?

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

$$\frac{2k_BT}{m}s_{max} = s_{max}^3 \Rightarrow s_{max} = \sqrt{2k_BT/m}$$

smaller than avg speed

$S_{max} < S_{avg} < S_{rms}$!

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

What are these values for
a real molecule?

Eg N_2 @ 300K?

speed of sound must be related
to how fast molecules move

turns out to be

$$c = \sqrt{\gamma/3}\, S_{rms} \quad \text{where } \gamma = C_p/C_v$$

from before

For N_2 approximating air, what
is the speed of sound at 1atm
& 300K?

From these considerations, can derive collision frequency of molecules

★ Reaction rate proportional to collision frequency, & prob energy exceeds a reaction threshold

(Pg 1116 - 1127 McQuarrie)

Evaporative cooling

If $\varepsilon = \varepsilon_{kinetic} + \varepsilon_{potential}$, then

$P(\varepsilon) \propto e^{-(K\varepsilon + P\varepsilon)/k_BT} = e^{-K\varepsilon/k_BT} e^{-P\varepsilon/k_BT}$

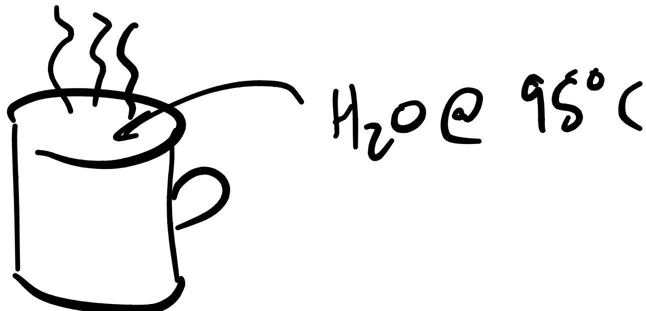
So even not in gasses, $P(v) \propto e^{mv^2/2k_BT}$

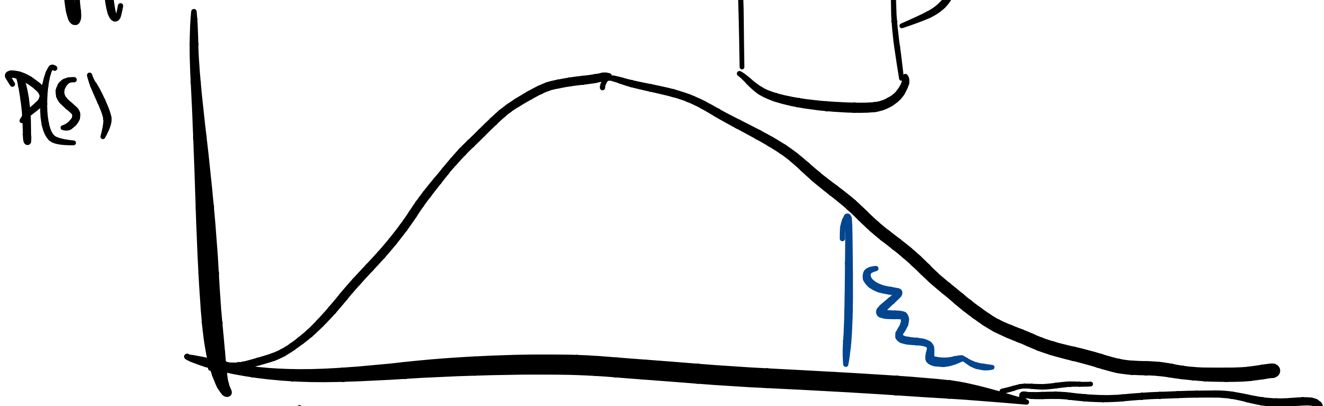
Maxwell Boltzmann is true in liquids @ Eq

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

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

Suppose we have





Make this plot

what is S_{RMS}^{100} for $T = 100°C$?

Prob of $S > S_{RMS}^{100}$

$$P(s > S_{rms}) = \int_{s_{rms}}^{\infty} P(s)\,ds$$ ↙ calculate

These can evaporate taking their energy away (could approximately calculate)

new dist