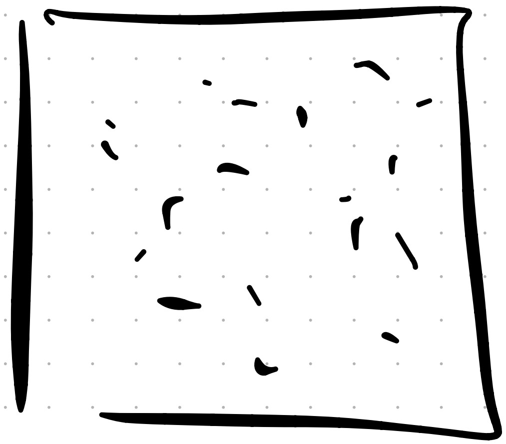
Kinetic Theory of Gasses

Ideal Gas

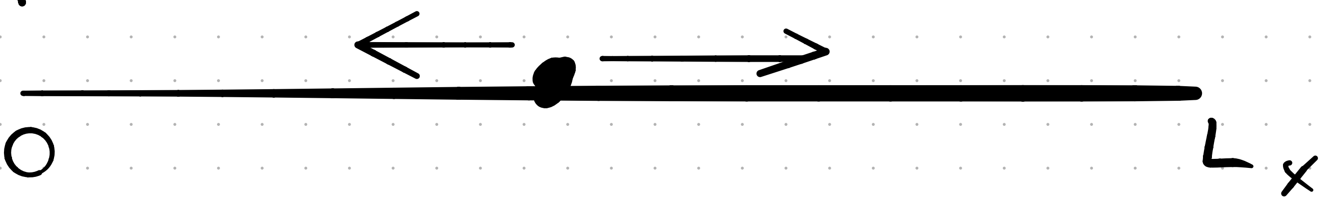


N particles
Volume V
Temperature T

What are gas particles doing?

Total Energy = Kinetic Energy
+ ~~Potential e~~

One particle in 1 dimension



$$KE = \frac{1}{2} m v_x^2$$

Thermodynamics: Prob of state energy $\mathcal{E}$

$$P(\mathcal{E}) \propto e^{-\mathcal{E}/k_B T}$$ (Bolzmann's Law)

Probability of our particle having velocity $= v_x$

$$P(v_x) \propto e^{-\frac{m v_x^2}{2 k_B T}}$$ ⇐ Gaussian Distribution

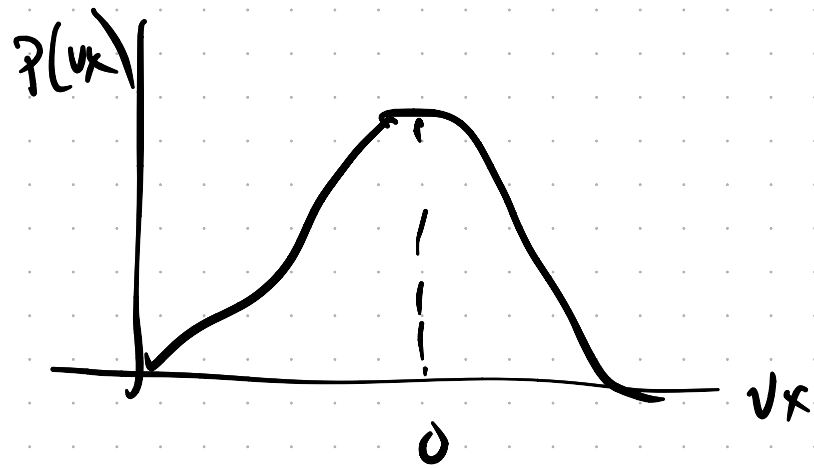
$$e^{-(x-\mu)^2/2\sigma^2}$$

$\mu = 0$

$\sigma^2 = k_B T/m$

$$P(v_x) = \frac{1}{\sqrt{2\pi (k_B T/m)}} e^{-m v_x^2 / 2 k_B T}$$

$$\int_{-\infty}^{\infty} dv_x \, P(v_x) = 1$$



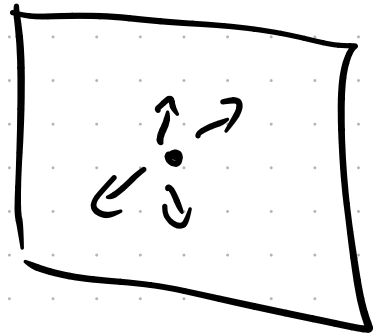
$\langle v_x^2 \rangle = ?$ $\quad$ $\mathrm{Var}(A) = \langle A^2 \rangle - \langle A \rangle^2$ $\;= \mu^2 \rightarrow 0$ $\;\mu = 0$

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

Root mean squared velocity $\sqrt{\langle v_x \rangle^2} = \sqrt{\frac{k_B T}{m}}$

$$\langle \varepsilon \rangle = \langle \tfrac{1}{2} m v_x^2 \rangle = \tfrac{1}{2} m \langle v_x^2 \rangle = \frac{k_B T}{2}$$

What about 3D?



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

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

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

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

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

v_x, v_y, v_z are <u>independent</u>

$$\langle \varepsilon \rangle_{3d} = \frac{1}{2} m \langle \vec{v}^2 \rangle = \frac{1}{2} m (\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle)$$

$$\langle \varepsilon \rangle_{3D} = \frac{1}{2} m \left(\frac{k_B T}{m} + \frac{k_B T}{m} + \frac{k_B T}{m} \right)$$

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

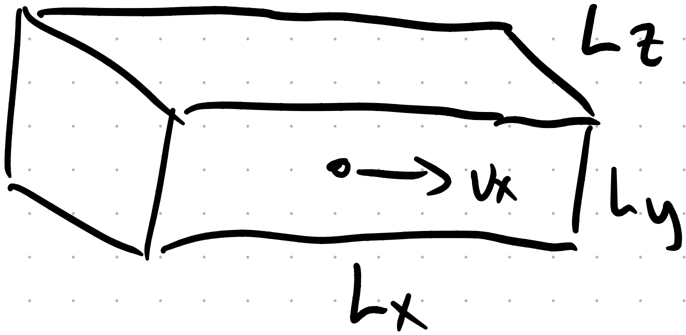
Ideal Gas: Total $\varepsilon = \sum_{i=1}^{N} \frac{1}{2} m_i \vec{v}_i^{\,2}$

Each molecule independent

$$\langle \varepsilon \rangle_{N,3d} = \sum_{i=1}^{N} \left\langle \frac{1}{2} m_i \vec{v}_i^{\,2} \right\rangle = \sum_{i=1}^{N} \left(\frac{3}{2} k_B T \right)$$

$$= \frac{3}{2} N k_B T = \underline{\frac{3}{2} n R T}$$

Ideal Gas Law?



Elastic collision with right wall

$P_x = m v_x$

$\text{force} = \frac{\Delta p}{\Delta t}$

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

$= \frac{d(mv)}{dt}$

$\Delta p = (m v_x) - (-m v_x) = 2 m v_x$

$d = vt \qquad d = 2L_x = v_x \cdot \Delta t$

$\Delta t = 2L_x / v_x$

$F_{\text{right wall}} = (2 m v_x) / (2L_x / v_x) = \frac{2 m v_x^2}{2 L_x} = \frac{m v_x^2}{L_x}$

$$P_i = \frac{F}{A} = \left(\frac{mv_x^2}{L_x}\right) \Big/ (L_y L_z) \qquad L_x L_y L_z = V$$

$$= mv_x^2 / V$$

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

$$P = \sum_{j=1}^{N} P_j = \sum_{i=1}^{N} \frac{m v_j^{x2}}{V} \cdot \frac{N}{N} = \frac{mN}{V} \cdot \underbrace{\left(\frac{1}{N} \sum_{j=1}^{N} v_j^{x2}\right)}_{\langle v_x^2 \rangle}$$

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

$$\boxed{PV = N k_B T = nRT}$$

Speed of molecules in Gas

Avg Speeds!

Root mean squared velocity

3D: $\langle \vec{v}^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = \frac{3 k_B T}{m}$

$$\sqrt{\langle \vec{v}^2 \rangle} = \sqrt{\frac{3 k_B T}{m}}$$

"Speed" = $|v|$, no direction to it

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

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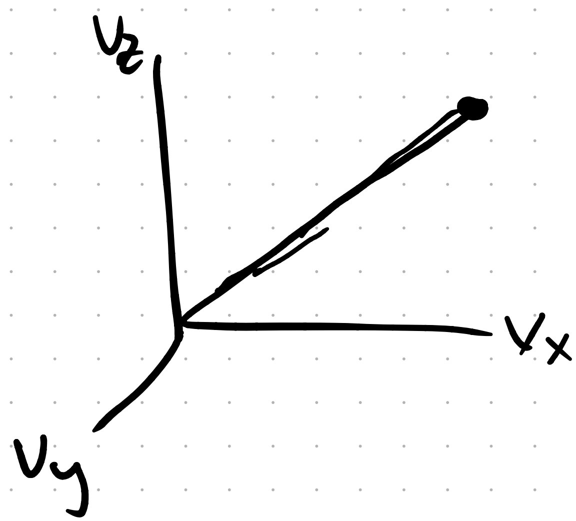
$$P(v_\alpha) = \frac{1}{\sqrt{2\pi \frac{k_B T}{m}}}\, e^{-\frac{1}{2k_B T} v_\alpha^2}$$

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



$$x, y, z \rightarrow \text{"}r\text{"}, \theta, \phi$$

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

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

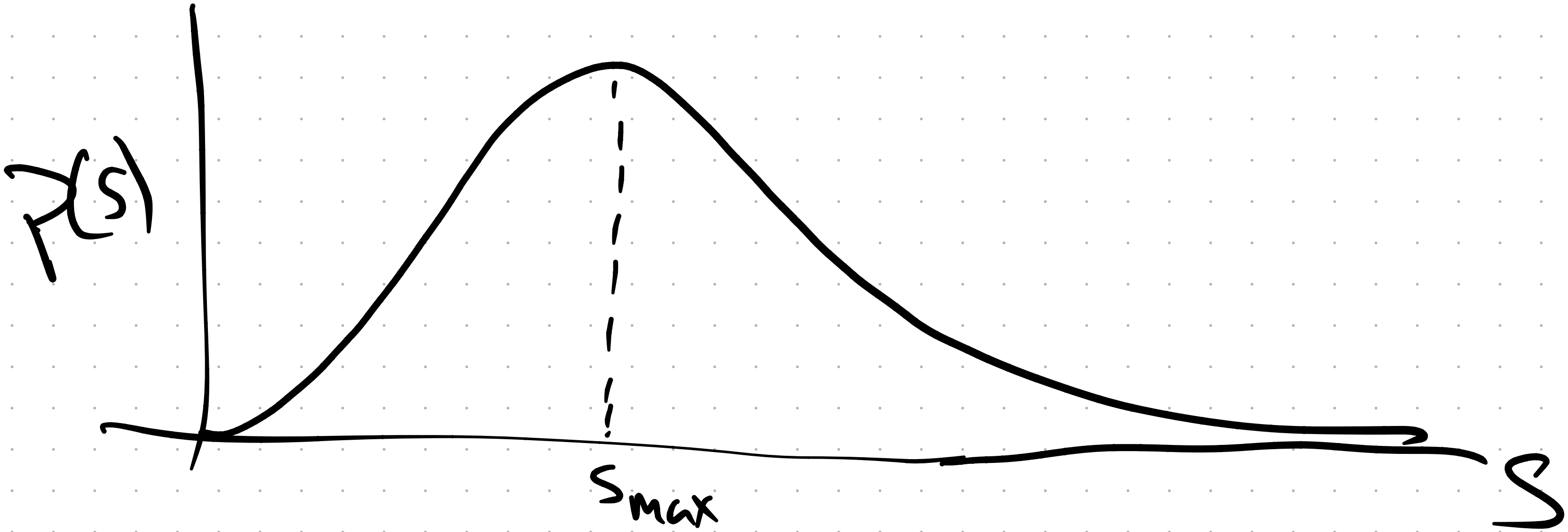
$$P(s,\theta,\phi) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \sin\theta \, s^2 \, e^{-ms^2/2k_BT}$$

$$P(s) = \int_0^{\pi}\int_{-\pi}^{\pi} d\phi \, d\theta \, P(s,\theta,\phi) =$$

$$= \underbrace{4\pi}_{\text{angles}} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \underline{s^2 e^{-\frac{ms^2}{2k_BT}}}$$

$$\underline{s^2 e^{-s^2 A}}$$

Maxwell Boltzmann



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

(pg 1114 McQuarrie)

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

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

$$\propto s^2 e^{-as^2}$$

$$? = 0$$

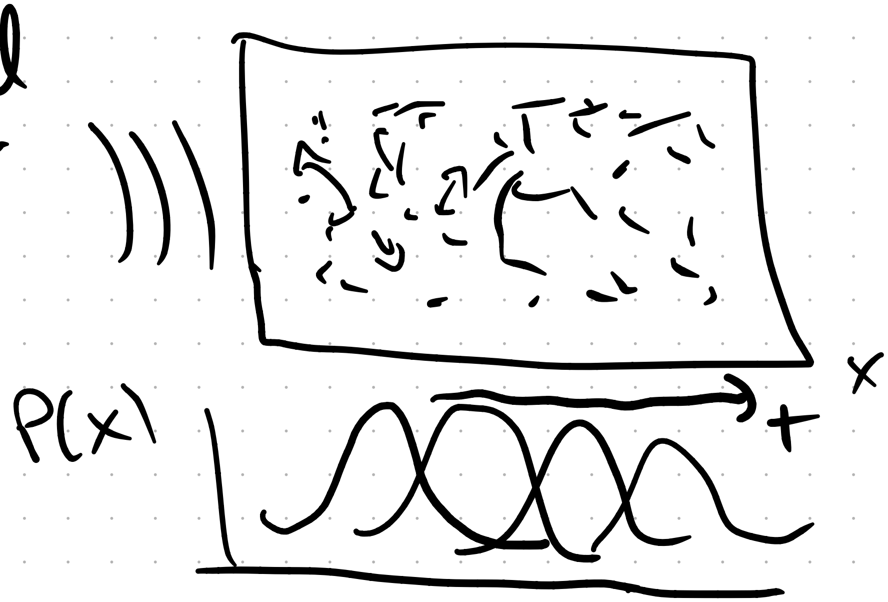
$$\frac{2k_BT}{m} s_{max} = s_{max}^3 \Rightarrow s_{max} = \sqrt{\frac{2k_BT}{m}}$$

3 speeds: $\sqrt{\frac{2k_BT}{m}}$ $\quad \sqrt{\frac{8}{\pi}\frac{k_BT}{m}}$ $\quad \sqrt{\frac{3k_BT}{m}}$

$$s_{max} < \langle s \rangle < \sqrt{\langle s^2 \rangle}$$

$$86.6\% \langle s \rangle < \langle s \rangle < 108.5\% \langle s \rangle$$

Speed of Sound



$$C = \sqrt{\frac{\gamma}{3}}\, s_{rms} \qquad \gamma = c_p / c_v$$

From these speeds: calculate collision frequencies

Reaction rates:

- Proportional to collision frequency

- Energy to exceed some reaction threshold

(Pg 1116–1127 McQuarrie)

Evaporative Cooling

Most cases $\quad \mathcal{E} = KE + PE$

potential

$$P(\mathcal{E}) \propto e^{-\frac{1}{k_BT}(KE+PE)}$$

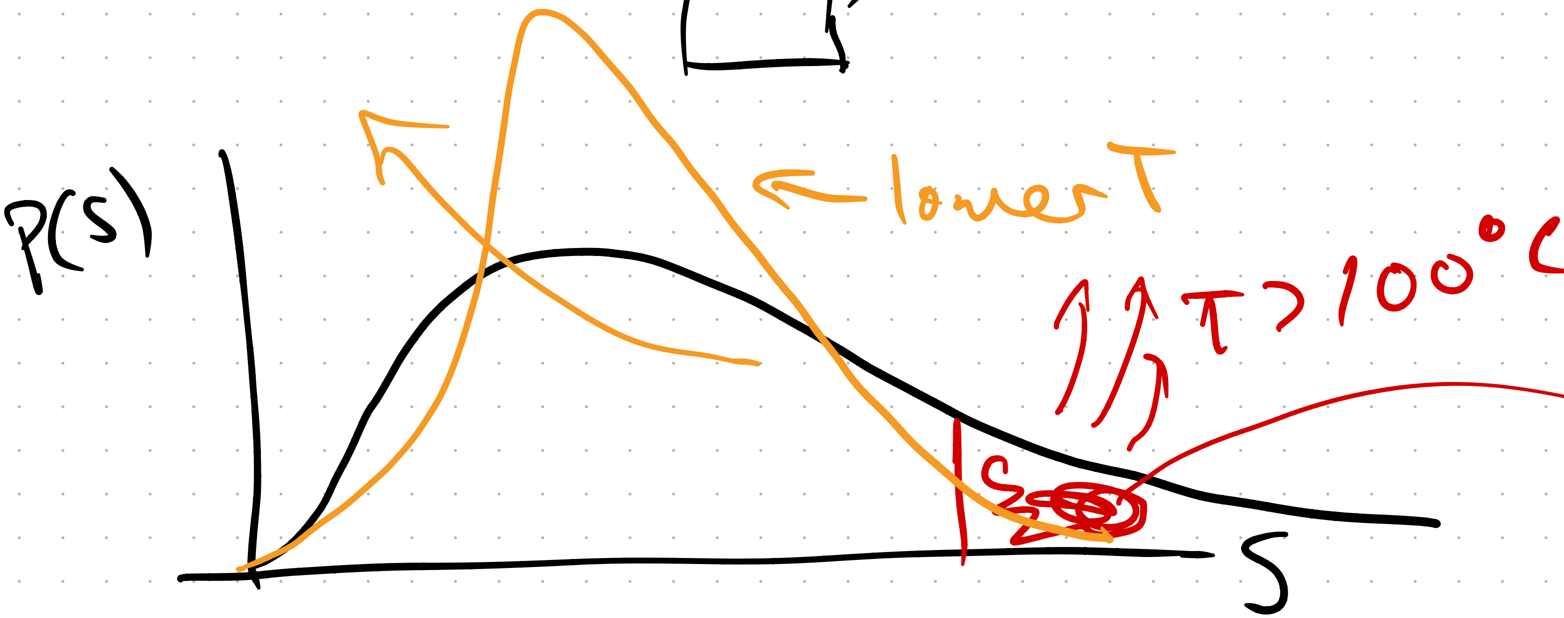
$$e^{-\sum^{4} \frac{1}{2} \frac{mv^2}{k_BT}} \cdot e^{-u(\vec{r})/k_BT}$$

$P(\vec{v}) \propto e^{-\frac{1}{2}\frac{mv^2}{k_BT}}$ even in eg.

a liquid @ Eq

Liquid

H_2O @ 95°C



$$\langle s^2 \rangle = \frac{3k_B T}{m} \Rightarrow T = \frac{m\langle s^2 \rangle}{3k_B}$$

Evaporate & take energy away

$$P(s > s^*) = \int_{s^*}^{\infty} P(s)\,ds$$