Ex velocity distr. in a gas according to Maxwell (1866), $\rho : \mathbb{R}^3 \to [0, \infty)$

$$\rho(\underline{v}) = \mathcal{N} \exp\left(-\frac{m|\underline{v}|^2}{2kT}\right)$$

m = mass of 1 molecule

k = Boltzmann constant $\approx 10^{-23}$ J/K

T = abs. Temp.

N_2, O_2, Ar, H_2O

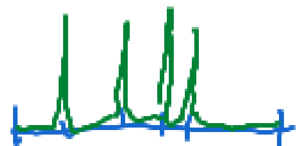
$$\boxed{\underline{\mu} = \underline{0}, \quad A = \begin{pmatrix} -\frac{m}{2kT} & & \\ & -\frac{m}{2kT} & \\ & & -\frac{m}{2kT} \end{pmatrix} \qquad C = \begin{pmatrix} \frac{kT}{m} & & \\ & \frac{kT}{m} & \\ & & \frac{kT}{m} \end{pmatrix}.}$$

The Law of Large Numbers

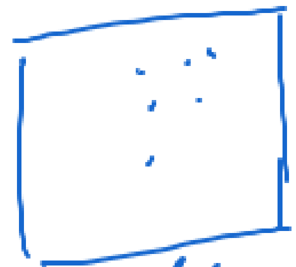
Notation $\delta_x(A) = \begin{cases} 1 & \text{if } x \in A \\ 0 & \text{if } x \notin A \end{cases}$ measure

Def $\mathcal{M}$-valued r.v.s $X_1 \dots X_n$, their empirical distribution

is $\mu^{emp} = \frac{1}{n}\sum_{k=1}^{n} \delta_{X_k}$.



$\mathcal{M}$

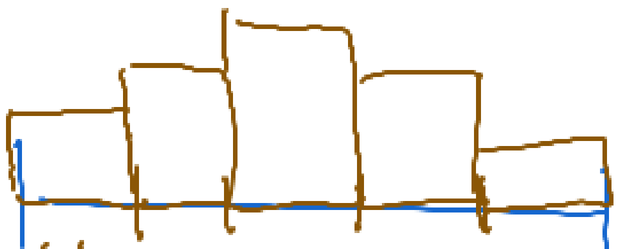


$\mathcal{M}$

histogram

partition $\mathcal{M}$

$\mathcal{A} = \{A_1 \dots A_r\}$



bins

coarse-grained distribution

$\mu(A_1), \dots, \mu(A_r)$

LLN: if $X_1 \dots X_n$ indep. and identically distr. (i.i.d.)

$n \gg 1$, then $\mu^{\text{emp}} \approx \mu^{\text{marg}} = \mu^{\text{theor.}}$

$$\mu^{\text{emp}}(A_i) = \frac{1}{n}\sum_{k=1}^{n} \underbrace{\delta_{X_k}(A_i)}_{} \qquad \mathbb{1}_{X_k \in A_i} = \begin{cases} 1 & \text{if } X_k \in A_i \\ 0 & \text{otherwise} \end{cases}$$

$$= \frac{1}{n} \# \{ k \in \{1 \dots n\} : X_k \in A_i \}$$

$\overset{\text{rel.}}{=}$ freq. of occurences in A_i.

LLN: Jacob Bernoulli

<u>Thm</u> (weak law of large numbers)

Let $\mathcal{M}$ be a measurable space

$X_1 \dots X_n$ i.i.d. $\mathcal{M}$-valued r.v.s

$\mathcal{A} = \{A_1 \dots A_r\}$ partition of $\mathcal{M}$

$\underline{P} = (P_1, \dots, P_r) \in \mathbb{R}^r$ coarse-grained theor. distr.,

i.e., $P_i = \mathbb{P}(X_k \in A_i)$,

$\underline{F} = (F_1 \dots F_r)$, $F_i = \frac{1}{n} \# \{ k \in \{1 \dots n\} : X_k \in A_i \}$

Then $\forall \varepsilon > 0 : \mathbb{P}\left(\forall i : |F_i - P_i| < \varepsilon \right) \geq 1 - \frac{1}{n\varepsilon^2}$.

Cor $X_1, X_2, \ldots$ i.i.d.

$$\underline{F}_n = (F_{n1} \ldots F_{nr}), \quad F_{ni} = \frac{1}{n} \#\{k \in \{1 \ldots n\} : X_k \in A_i\}$$

Then $\forall \varepsilon > 0$:

$$\mathbb{P}\left(\| \underline{F}_n - \underline{P} \|_\infty < \varepsilon \right) \xrightarrow{n \to \infty} 1$$

with $\| \underline{x} \|_\infty = \max\{ |x_1|, \ldots, |x_r| \}$ maximum norm.

for $\underline{x} \in \mathbb{R}^r$

also in $\| \cdot \|_2$ b/c $\| \underline{x} \|_2 \le \sqrt{r}\, \| \underline{x} \|_\infty$

Pf of thm: Markov ineq.: If $Y \geq 0$ and $a > 0$

then $\mathbb{P}(Y \geq a) \leq \frac{\mathbb{E}Y}{a}$

"In a population with average income 1000, no more than 10% can have income ≥ 10000."

Chebychev ineq.

$$\mathbb{P}(|X - \mathbb{E}X| < \varepsilon) \geq 1 - \frac{\operatorname{Var} X}{\varepsilon^2}.$$

Pf: $Y = (X - \mathbb{E}X)^2$, $a = \varepsilon^2$

$X = F_i$

$$F_i = \frac{1}{n} \sum_{k=1}^{n} 1_{X_k \in A_i}$$

$$\Rightarrow \mathbb{E} F_i = \frac{1}{n} \sum_{k=1}^{n} \mathbb{E}\, 1_{X_k \in A_i} = \frac{1}{n} \sum_{k=1}^{n} \underbrace{\mathbb{P}(X_k \in A_i)}_{p_i} = p_i$$

$$\operatorname{Var} F_i = \frac{1}{n^2} \operatorname{Var} \sum_{k} 1_{X_k \in A_i} \overset{X_k \text{ indep.}}{=} \frac{1}{n^2} \sum_{k} \underbrace{\operatorname{Var} 1_{X_k \in A_i}}_{p_i(1-p_i)}$$

$$= \frac{1}{n} p_i (1 - p_i)$$

Cheb.

$$\Rightarrow \mathbb{P}\left(|F_i - p_i| \overset{\geq}{<} \varepsilon \right) \overset{\leq}{\geq} \cancel{1 -} \frac{p_i(1-p_i)}{n\, \varepsilon^2}$$

$$\mathbb{P}\left(\dot{\bigcup_{i=1}^{r}}\{|F_i - p_i| \geq \varepsilon\}\right) \leq \sum_{i=1}^{r} \mathbb{P}(|F_i - p_i| \geq \varepsilon)$$

$$\overset{\text{Ch.}}{\leq} \sum_{i=1}^{r} \frac{p_i(1-p_i)}{n\varepsilon^2} \leq \sum_{i=1}^{r} \frac{p_i}{n\varepsilon^2} = \frac{1}{n\varepsilon^2}$$

$\square$

<u>Thm</u> (strong law of large numbers)

$X_1, X_2, \ldots$ i.i.d. $\mathcal{U}$-valued r.v.s

$$F_{ni} = \frac{1}{n} \# \{ k \in \{1 \ldots n\} : X_k \in A_i \}$$

$$\mathbb{P}\left(\forall i : \lim_{n \to \infty} F_{ni} = p_i \right) = 1 .$$

Pf: Émile Borel in 1909.

$$\boxed{Z_k = \mathbb{1}_{X_k \in A_i}}$$

LLN also:

Thm (weak law) $Z_1, Z_2, \dots$ i.i.d. real-valued with finite $\mathbb{E}$ and Var.

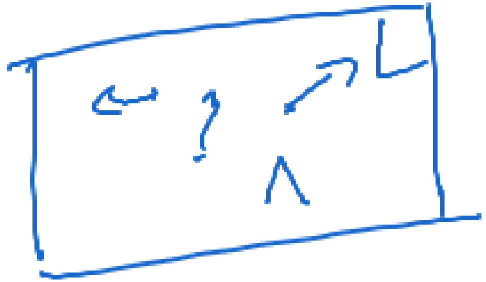
$$\mathbb{P}\left(\left|\frac{1}{n}\sum_{j=1}^{n} Z_j - \mathbb{E} Z_1\right| < \varepsilon\right) \geq 1 - \frac{\operatorname{Var} Z_1}{n\varepsilon^2}$$

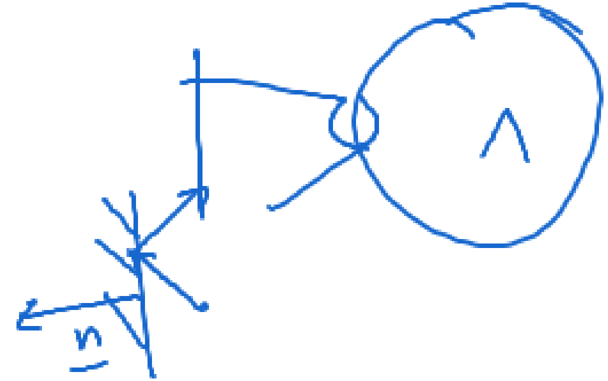
Thm (strong law)

$$\mathbb{P}\left(\lim_{n\to\infty} \frac{1}{n}\sum_{j=1}^{n} Z_j = \mathbb{E} Z_1\right) = 1$$

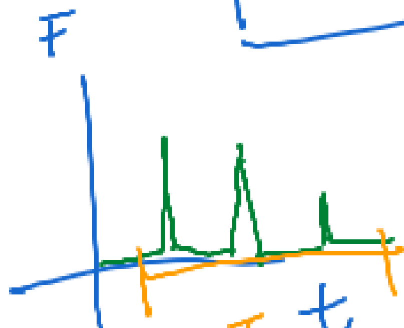
The Maxwellian Distribution

Pressure



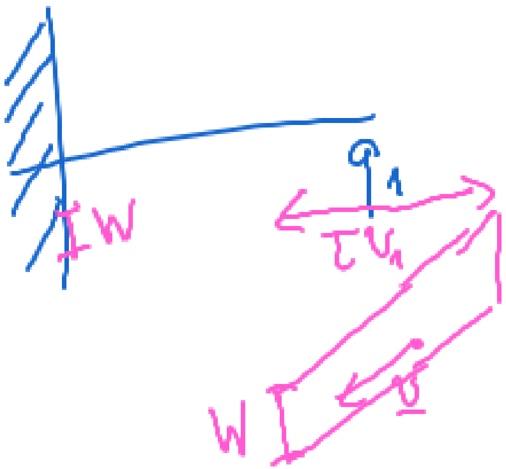


$$p = \frac{\underline{F}\cdot\underline{n}}{A}$$



$$F = \frac{P_n}{t}$$

$$F := \frac{P_n(\tau)}{\tau}$$



$\frac{N}{\mathrm{vol}(\Lambda)}\rho(\underline{v})\, d^3\underline{x}\, d^3\underline{v}$ = no. of mol.
in $d^3\underline{x} \times d^3\underline{v}$

$$d^3\underline{x} = \tau v_1\, \mathrm{area}(W)$$

momentum transferred $2mv_1$

$$p = \frac{P_n(\tau)}{\text{area}(W)\tau} = \frac{1}{\text{area}(W)} \int_{-\infty}^{0} dv_1 \int_{\mathbb{R}} dv_2 \int_{\mathbb{R}} dv_3 \; 2mv_1 \frac{N}{\text{vol}(\Lambda)} \rho(\underline{v}) \times \text{area}(W)\tau v_1$$

$$= \frac{m N \cancel{\text{area}(W)\tau}}{\text{vol}(\Lambda)} \underbrace{\int_{\mathbb{R}^3} d^3\underline{v} \; v_1^2 \rho(\underline{v})}_{\langle v_1^2 \rangle}$$

$$\mathbb{E} v_1 = 0$$

$$\langle v_1^2 \rangle = \operatorname{Var} v_1 = \frac{kT}{m}$$

Daniel Bernoulli (1700–1782) *Hydrodynamica* 1738.

$$\Longrightarrow \quad p = \frac{NkT}{\operatorname{vol}(\Lambda)} = \frac{NkT}{V}$$

$$\Longrightarrow \quad pV = NkT.$$

state eq. of the ideal gas.

By-product: average kinetic energy per molecule

$$\bar{e} = \int_{\mathbb{R}^3} \frac{m}{2} \underline{v}^2 \rho(\underline{v})\, d^3\underline{v} = \frac{3m}{2} \int_{\mathbb{R}^3} v_1^2 \rho(\underline{v})\, d^3\underline{v} = \frac{3\cancel{m}}{2} \frac{kT}{\cancel{m}}$$