MATH327: StatMech and Thermo

Wednesday, 29 January 2025

83 26 94

Something to consider

What are some ways we can estimate the probability of an event?

Recap

Emergence from many particles

Random experiment $\mathcal{E} \to$ state $\omega \in \Omega = \{\omega\}$

Today

Prob. spaces

Law of large number

Central limit theorem

Random walks (?)

Measurement $X(\omega)$ extracts info. of interest

Repeat $\mathcal{E} \to X(\omega_i)$ is random variable

$X: \Omega \to A = \{X(\omega)\}$ outcome space

Finite, countable, or continuous

Examples

$\mathcal{E}$: Rolling a die $\qquad X$: Measure number on top

$A = \{1, 2, 3, 4, 5, 6\}$

state ω could also include position, time, temperature, ...

page 10

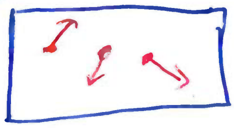
$\mathcal{E}$: Four coin flips $\quad$ X: Measure all four H vs T

page 10

$A = \{HTHT,\ HHHH,\ TTTT,\ HHTT, \ldots\}$

Number of elements in A? $16 = 2^4$ all distinct

$\mathcal{E}$: 10^{23} argon atoms in container



page 11

state could include 10^{23} position velocities, electronic states, isotopes

Measure?

Pressure, temperature, energy, heat capacity, currents, ...

Define <u>event</u> as any subset of outcome space A

Ex: Possible events from rolling die

- Rolling 6
- Rolling 1-5
- Rolling even #

<u>Event space</u> $\mathcal{F}$ is set of all events of interest

Finally <u>probability</u> is measure function $P: \mathcal{F} \to [0,1]$

Number for each events in $\mathcal{F}$

Requirements: 1) $P(x \text{ or } y \text{ or } z) = P(x) + P(y) + P(z)$

countable, mutually exclusive

2) $P(A = \mathcal{F}) = 1$

Must have some measurable outcome

Put it all together: <u>probability space</u> $(A, \mathcal{F}, P)$

prob. for all subsets of outcomes

Suppose finite $\Omega = \{w_1, w_2 \cdots w_N\}$

$\rightarrow$ Finite $A = \{X_1, X_2, \cdots X_n\}$ $\quad n \leq N$

Usually $n < N$ because measurement X can give same outcome for different state

$$X(w_i) = X(w_j) \qquad w_i \neq w_j$$

All X_i distinct $\rightarrow$ $\underset{i \neq j}{P(X_i \text{ or } X_j)} = P(X_i) + P(X_j) = p_i + p_j$

<u>Example</u>: <u>Fair</u> die

page 12

$$\boxed{\begin{array}{l} p_1 = p_2 = \cdots = p_6 = p \qquad p = 1/6 \\ \mathcal{F} = A \qquad P(A) = \sum_{i=1}^{6} p_i = 6p = 1 \ \checkmark \end{array}}$$

<u>Example</u>: Four fair coin flips $\rightarrow$ $\underline{p = 1/16}$

$\mathcal{F} = \{$equal H/T, different H/T$\}$

page 12

$$\boxed{\begin{array}{l} P_{equal} = P(HHTT \text{ or } HTHT \text{ or } HTTH \text{ or } H \leftrightarrow T) = 6/16 \\ P_{diff} = 1 - P_{equal} = 5/8 \end{array}}$$

<u>Modelling</u> assigns probabilities to events

Fixed by symmetries in examples above

More generally data driven

Repeat experiment many times

Monitor outcome X_i

Infer probabilities p_i

justified by law of large numbers

Back to finite $A = \{X_1, X_2, \dots X_n\}$ $\qquad \sum_{X \in A} P(X) = 1$

<u>Expectation value</u> $\qquad \langle F(X) \rangle = \sum_{X \in A} f(X)\, P(X)$ $\qquad$ (linear op)

<u>Mean</u> of prob. space $\qquad \mu = \langle X \rangle = \sum_{X \in A} X\, P(X)$

Variance $\sigma^2 = \langle (X-\mu)^2 \rangle = \sum_{X \in A} (X-\mu)^2 P(X)$

$$= \langle (X - \langle X \rangle)^2 \rangle = \langle X^2 - 2X\langle X\rangle + \langle X \rangle^2 \rangle$$

page 14

$$= \langle X^2 \rangle - \cancel{2}\langle X \rangle\langle X\rangle + \langle X \rangle^{\cancel{2}} = \langle X^2 \rangle - \langle X \rangle^2$$

Standard deviation (of prob. space) $\sigma = \sqrt{\sigma^2} = \sqrt{\langle X^2 \rangle - \langle X \rangle^2}$

Repetition

New experiment: Repeat $\mathcal{E}$ and X R times

$\hookrightarrow A = \{X_1, X_2, \dots X_n\}$ n elem.

$\hookrightarrow$ outcome space B

For $R=4$, $B = \{X_1 X_1 X_1 X_1,\ X_1 X_2 X_9 X_1, \dots\}$

Number of elements: $n \cdot n \cdot n \cdots n = n^R = n^4$

page 14

Each element of B built from R elements of A, $X^{(r)}$

$\therefore P_B(X_j X_i X_k \cdots X_z) = P_A(X_j) \cdot P_A(X_i)\, P_A(X_k) \cdots P_A(X_z)$

Arithmetic mean $\bar{X}_R = \frac{1}{R} \sum_{r=1}^{R} X^{(r)}$ is random variable of repeated expt.

Relate $\bar{X}_R$ to mean $\mu = \langle X^{(r)} \rangle$ of single-expt. prob. space

Consider random var. Fluctuations around μ (assume μ, σ^2 finite)

$$\langle (\bar{X}_R - \mu)^2 \rangle = \left\langle \left(\frac{1}{R} \sum_r X^{(r)} - \mu \right)^2 \right\rangle \qquad \mu = \frac{1}{R}\sum_r \mu$$

$$= \frac{1}{R^2} \left\langle \left(\sum_r (X^{(r)} - \mu) \right)^2 \right\rangle$$

$$= \frac{1}{R^2} \left\langle \left(\sum_r (X^{(r)} - \mu) \right) \left(\sum_s (X^{(s)} - \mu) \right) \right\rangle$$

$$\left(\sum_r a_r\right)\left(\sum_s b_s\right) = \sum_{r,s} a_r b_s$$

page 15

$$= \frac{1}{R^2} \sum_{r,s} \underbrace{\langle (X^{(r)} - \mu)(X^{(s)} - \mu) \rangle}_{\sigma^2 \delta_{rs}}$$

$$= \frac{1}{R^2}\sum_{r,s}\sigma^2\delta_{rs} = \frac{\sigma^2}{R^2}\sum_r 1 = \frac{\sigma^2}{R}$$

$$\lim_{R\to\infty}\langle(\overline{X}_R-\mu)^2\rangle = 0$$ Vanishing sum of squares

$\to$ every term zero

$$\lim_{R\to\infty}\overline{X}_R = \mu$$ <u>Law of large number</u>

$$\overline{X}_R \approx \mu \quad \text{for } R \gg 1$$

Generalize to continuous X with uncountable A

To get probability must integrate over <u>prob. distribution</u>

$$P(a \le X \le b) = \int_a^b p(x)\,dx \qquad x\in\mathbb{R}$$

Expectation values become integrals over entire domain

$$\langle f(x)\rangle = \int_{-\infty}^{\infty} f(x)\,p(x)\,dx \qquad \int p(x)\,dx = 1$$

$$\langle x^l\rangle = \int x^l\,p(x)\,dx$$

$l=1 \to$ mean $\mu = \langle x\rangle$

variance $\sigma^2 = \langle x^2\rangle - \mu^2$

$l=2$

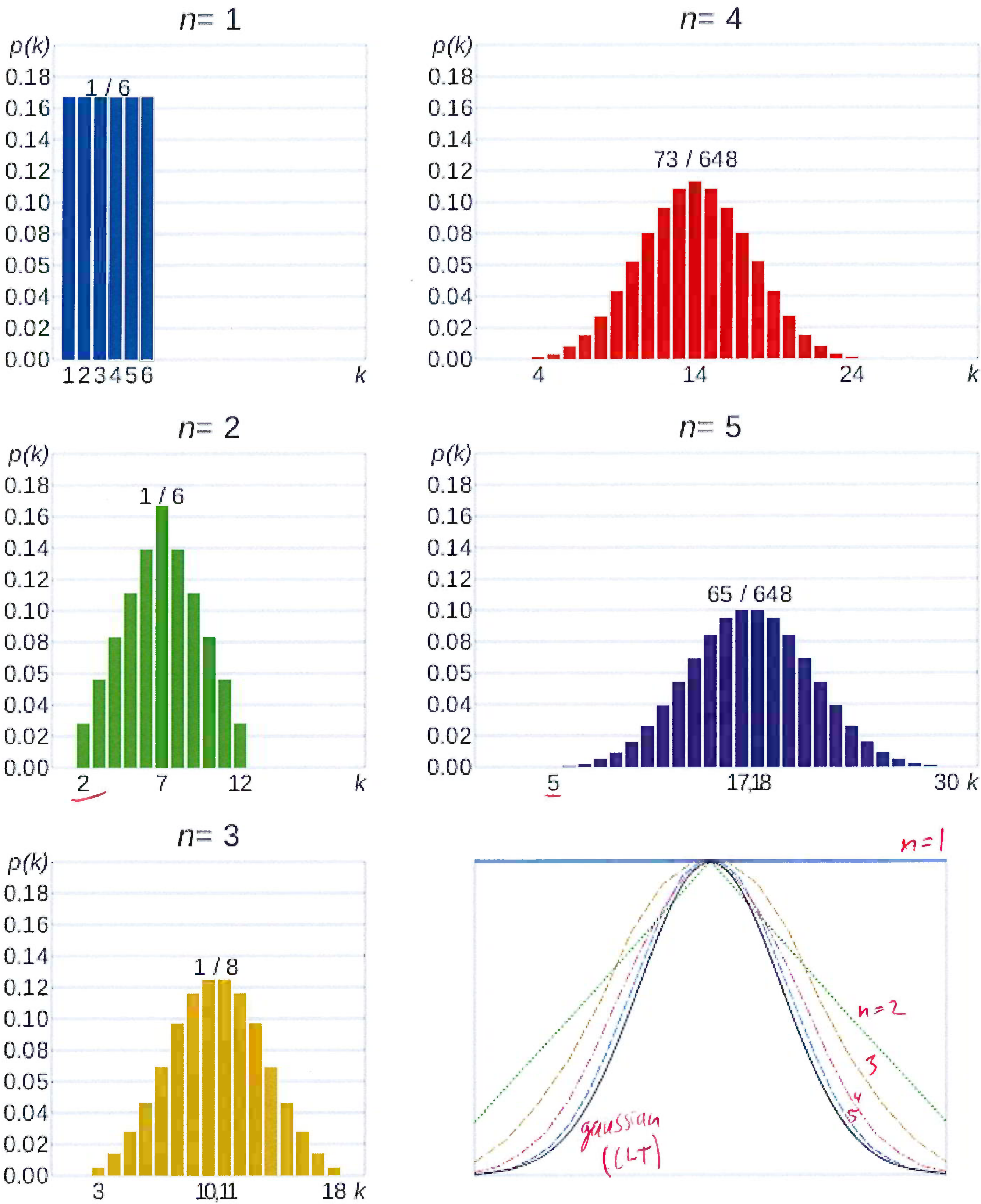
<u>Central limit theorem</u> (CLT)

Consider N random variables $X_1, X_2, \dots X_N$

all with same finite μ, σ^2

("i.i.d." – "independent and identically distributed)

Sum $X = \sum_{i=1}^{N} X_i$ is collective random variable



commons.wikimedia.org/wiki/File:Dice_sum_central_limit_theorem.svg

CLT: For $N \gg 1$, prob. distribution $p(x)$ becomes gaussian

$$p(x) \approx \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left[-\frac{(x - N\mu)^2}{2N\sigma^2} \right] \qquad \text{(equality as } N \to \infty)$$

$\int p(x)\, dx = 1$

Collective behaviour of many particles governed by single-particle μ, σ^2

CLT application: Random walks

General modelling tool – brownian motion, stock prices, genetic drift

Idea: Object takes random step

current state → new state

Repeat many times

"Markov process" produces Markov chain