MATH327: StatMech and Thermo

Thursday, 29 January 2026

42 73 55

Something to consider

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

Recap

Probability space $(A, \mathcal{F}, P)$

Today

Law of large numbers

Prob. distribution

Central limit theorem

Random walks

Consider finite $\Omega = \{\omega_1, \omega_2, \dots \omega_N\}$

$\rightarrow$ finite $A = \{X_1, X_2, \dots X_n\}$ all X_i distinct

$n \leq N$

Usually $n < N$ if $X(\omega_i) = X(\omega_j)$ $\omega_i \neq \omega_j$

$\therefore P(X_i \text{ or } X_j) = P(X_i) + P(X_j) = p_i + p_j$ $i \neq j$

Examples

Fair die

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

page 12

Four ~~flips~~ fair coin flips

$\searrow p = 1/16$

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

$$\boxed{\left.\begin{matrix} HHTT, & HTHT, & HTTH \\ TTHH, & THTH, & THHT \end{matrix}\right\} \quad \begin{matrix} P_{equal} = \frac{6}{16} = \frac{3}{8} \\ P_{diff} = 1 - \frac{3}{8} = \frac{5}{8} \end{matrix}}$$

page 12

Assigning probs. to events is "modelling"

Fixed by symmetries in examples above

More generally data driven

Repeat $\mathcal{E}$ many time

Monitor outcomes X_i

Infer prob. p_i

$\llcorner$ justified by law of large numbers

$\mathcal{F} = A = \{X_1, X_2, \cdots X_n\}$ $\qquad \sum_{x \in A} P(X) = 1$

<u>Expectation value</u>

$$\langle f(X) \rangle = \sum_{x \in A} f(x)\, P(x) \qquad \text{(linear operation)}$$

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

<u>Variance</u> $\sigma^2 = \langle (X-\mu)^2 \rangle = \sum_{x \in A} (X-\mu)^2\, P(x)$

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

page 14

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

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

$\searrow A = \{X_1, X_2, \ldots X_n\}$ n elements

$\downarrow$

Outcome space $\mathcal{B}$

For $R=4$, $\mathcal{B} = \{X_1 X_1 X_1 X_1,\ X_1 X_2 X_{99} X_1,\ \ldots\}$ page 14

Number of elements? $n \cdot n \cdot n \cdots n = n^R$

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

$$\therefore P_{\mathcal{B}}(X_i X_j X_k \cdots X_z) = P_A(X_i) \cdot P_A(X_j) \cdot P(X_k) \cdots P_A(X_z)$$

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

(arithmetic mean)

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

Consider fluctuations of random var. around μ assuming μ, σ^2 finite

$$\langle (\overline{X}_R - \mu)^2 \rangle_{(\mathcal{B})} = \langle (\tfrac{1}{R} \textstyle\sum_r X^{(r)} - \mu)^2 \rangle_A$$

$\mu = \frac{1}{R} \sum_r \mu$

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

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

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

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

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

page 15

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

$$\lim_{R\to\infty} \overline{X}_R = \mu$$ Law of large numbers

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

Generalize to continuous X with uncountable A

To get probability must integrate over prob. distribution

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

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 $\sigma^2 = \underbrace{\langle x^2 \rangle}_{l=2} - \mu^2$

Central limit Theorem (CLT)

Consider N random variables $x_1, x_2, \dots x_N$
all with same finite μ, σ^2
("i.i.d." – independent & identically distributed)

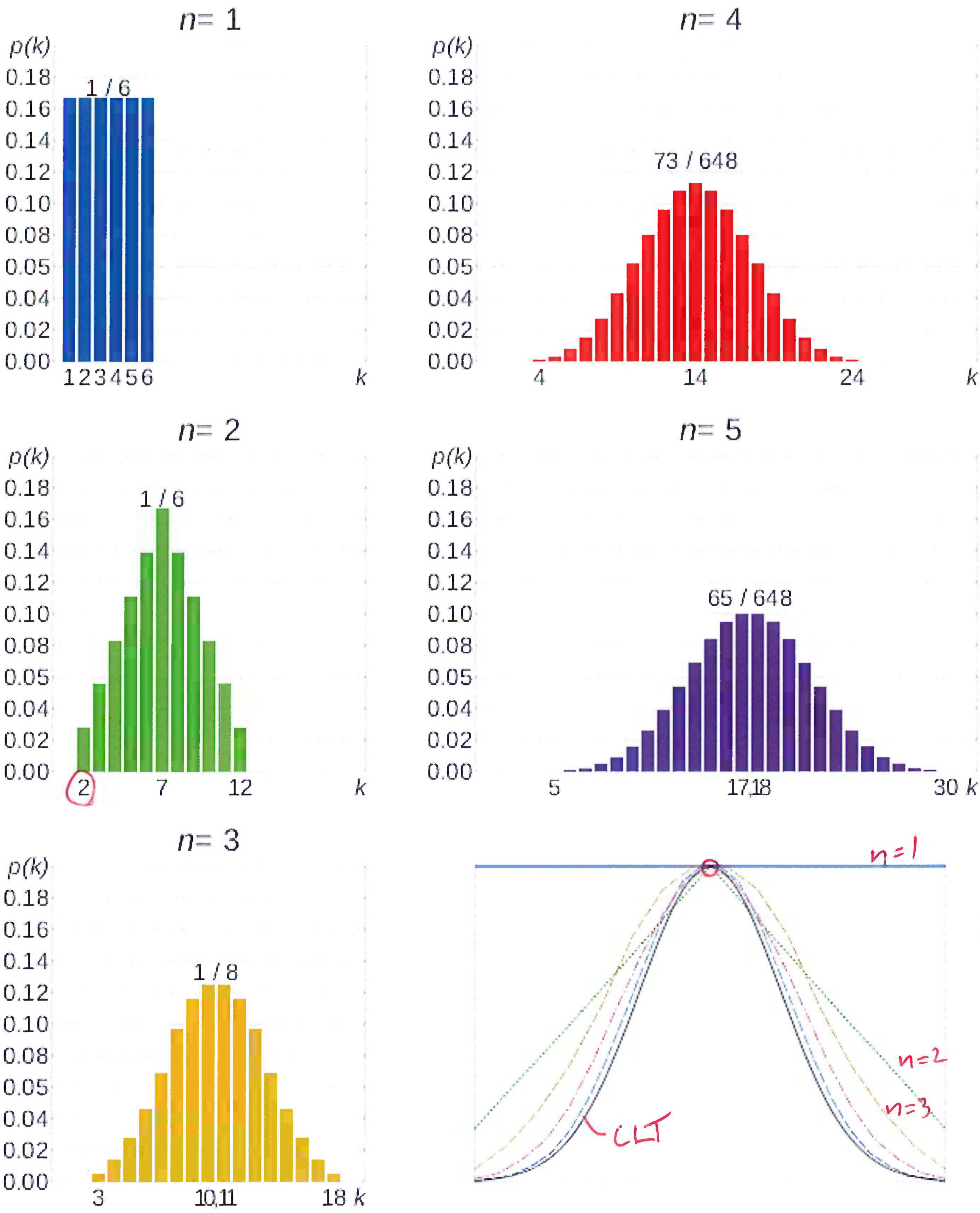
Sum $x = \sum_{i=1}^{N} x_i$ is collective random variable

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

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

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

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



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

CLT application: Random walks

General modelling tool – Brownian motion, roulette game, stock prices, genetic drift

Idea: Object takes random step

current state → new state

Repeat many times

"Markov process" produced Markov chain

Simple examples

Step only right ($+\ell$) or left ($-\ell$) along line

prob. p prob. $q = 1-p$

Set $\ell = 1$ and step every δt (time interval)

N steps → total time $t = N\,\delta t$

$N = 6$ LRLRRR   final $x = 2 = \sum_{i=1}^{N} x_i$

start at $x_0 = 0$

RLRLLL $\to x = -2$, $p^2 q^4$

page 18

How many 6-step walks? $2 \cdot 2 \cdots 2 = 2^N \to 64$

$P(\text{LRLRRR}) = qpqppp = p^4 q^2$

Prob. for N-step walk with r steps to right, $N-r$ to left

$\propto p^r q^{N-r}$

order doesn't matter

page 19

How many 6-step walks end at $x = 4$?

RRRRRL, RRRRLR, ...

$$6 = \binom{6}{5} = \binom{N}{r} = \binom{N}{N-r} = \frac{N!}{r!\,(N-r)!}$$

$\therefore$ overall $P_r = \binom{N}{r} p^r q^{N-r}$

Predict expectation value $\langle x \rangle = \sum_{s=\pm 1} s\, P(s)$

and fluctuations $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

Convert $x, P(s) \longleftrightarrow r, P_r$ for special case $l=1$ 1d

$$\boxed{x = (+1)r + (-1)(N-r) = 2r - N}$$

$-N \le x \le N$ ✓

page 19

$$\boxed{\begin{aligned} \langle x \rangle &= \sum_{r=0}^{N} (2r-N) P_r = 2\langle r \rangle - N \\ \langle x^2 \rangle &= \sum_{r} (2r-N)^2 P_r = 4\langle r^2 \rangle - 4N\langle r \rangle + N^2 \end{aligned}}$$

page 20

Trick to get $\langle r \rangle, \langle r^2 \rangle, \ldots \langle r^n \rangle$

generating function: $G(\theta) = \sum_{r=0}^{N} e^{r\theta} P_r$ $G(0) = 1$