MATH327: StatMech and Thermo

Wednesday, 5 February 2025

25 55 13

Something to consider

How can we apply the framework of probability spaces to analyse the $\sim 10^{25}$ molecules that compose the air in this room?

Recap

Random walk example

$\hookrightarrow \langle x \rangle = N(2p-1) = \frac{2p-1}{\delta t} t = v_{dr} t \leftarrow$ drift velocity

$$\Delta x = \underbrace{2\sqrt{Npq} = 2\sqrt{\frac{pq}{\delta t}}}_{\text{special case}} \sqrt{t} = \underbrace{D\sqrt{t}}_{\text{general results}} \leftarrow \text{law of diffusion}$$

Today

Tutorial wrap-up

Wrap up diffusion & CLT connection

Ensembles & equilibrium

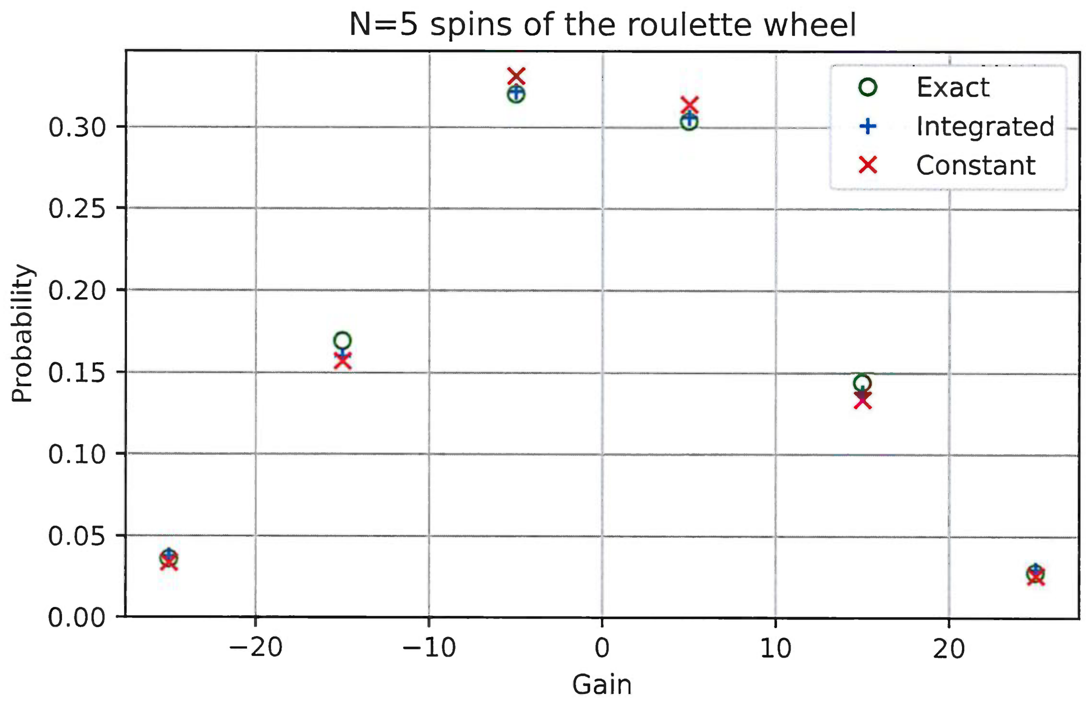
Tutorial random walk just sets $\ell = 5$ $\quad p = 18/37 \quad q = 19/37$

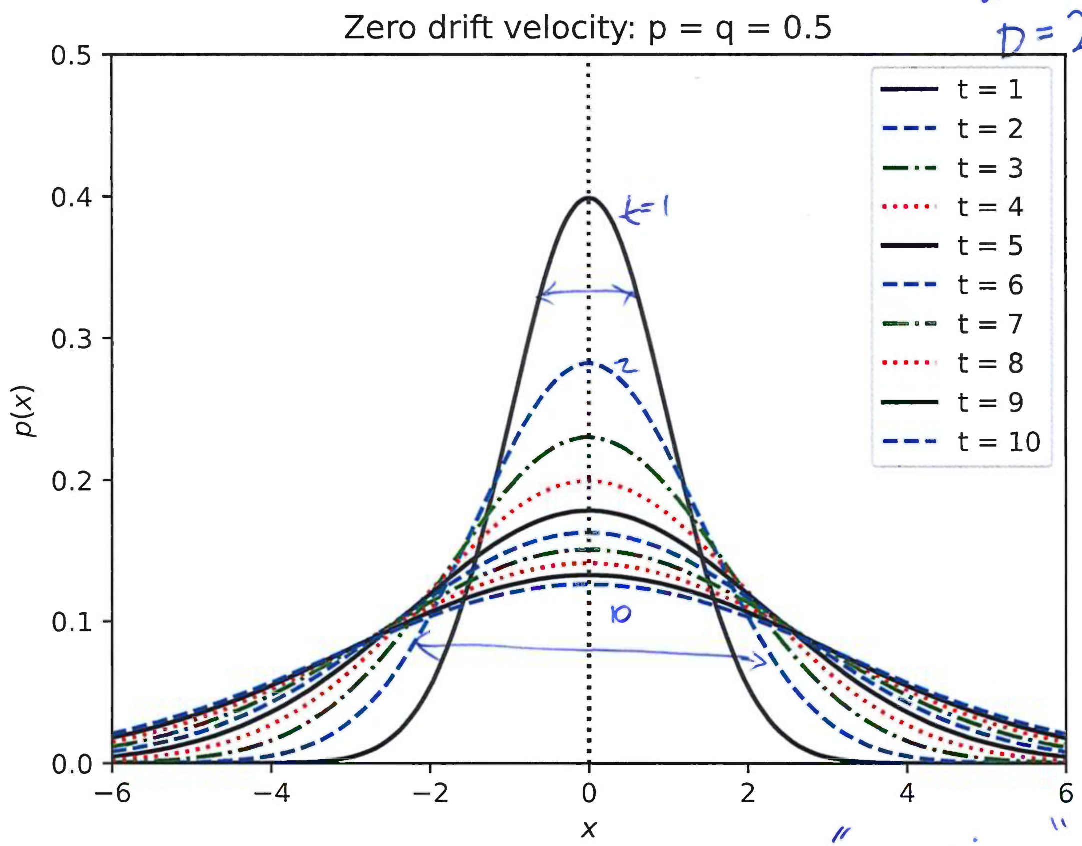
CLT needs $\mu = \sum x_i p(x_i) = -5/37 \approx -0{,}135$

$$\sigma^2 = \langle x_i^2 \rangle - \langle x_i \rangle^2 = 25 - \frac{25}{37^2} = 25\left(1 - \frac{1}{37^2}\right) \approx 24{,}98$$

$$\hookrightarrow (5)^2\left(\frac{18}{37}\right) + (-5)^2\left(\frac{19}{37}\right) = 1 \cdot (25) = 25$$

$$p(g) \approx \frac{1}{\sqrt{49{,}96\,\pi N}} \exp\left[-\frac{(g + 0{,}135N)^2}{49{,}96\,N}\right] \qquad N \gg 1$$


N=5 spins of the roulette wheel
Exact
Integrated
Constant
Probability
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Gain
−20
−10
0
10
20



$V_{dr} = 0$

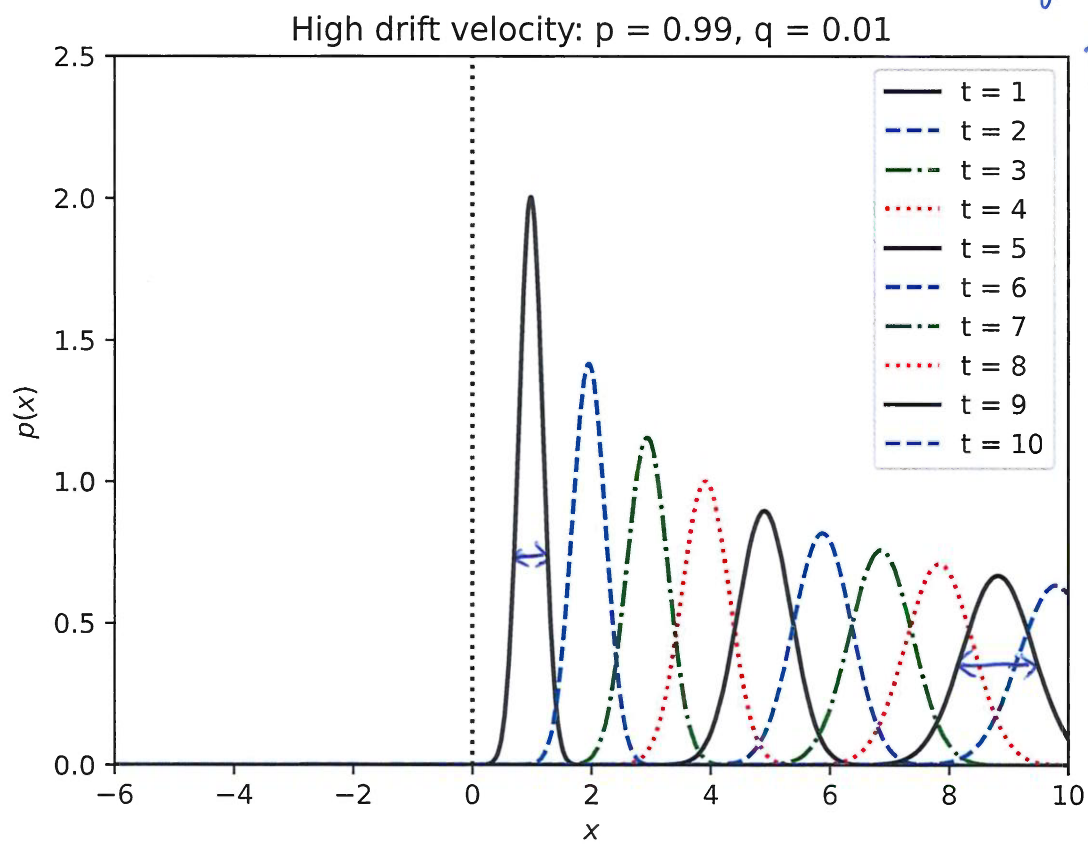
$D = 2\sqrt{\frac{1/4}{\delta t}} = 1$

$\delta t \to 1$

$\langle x \rangle = 0$

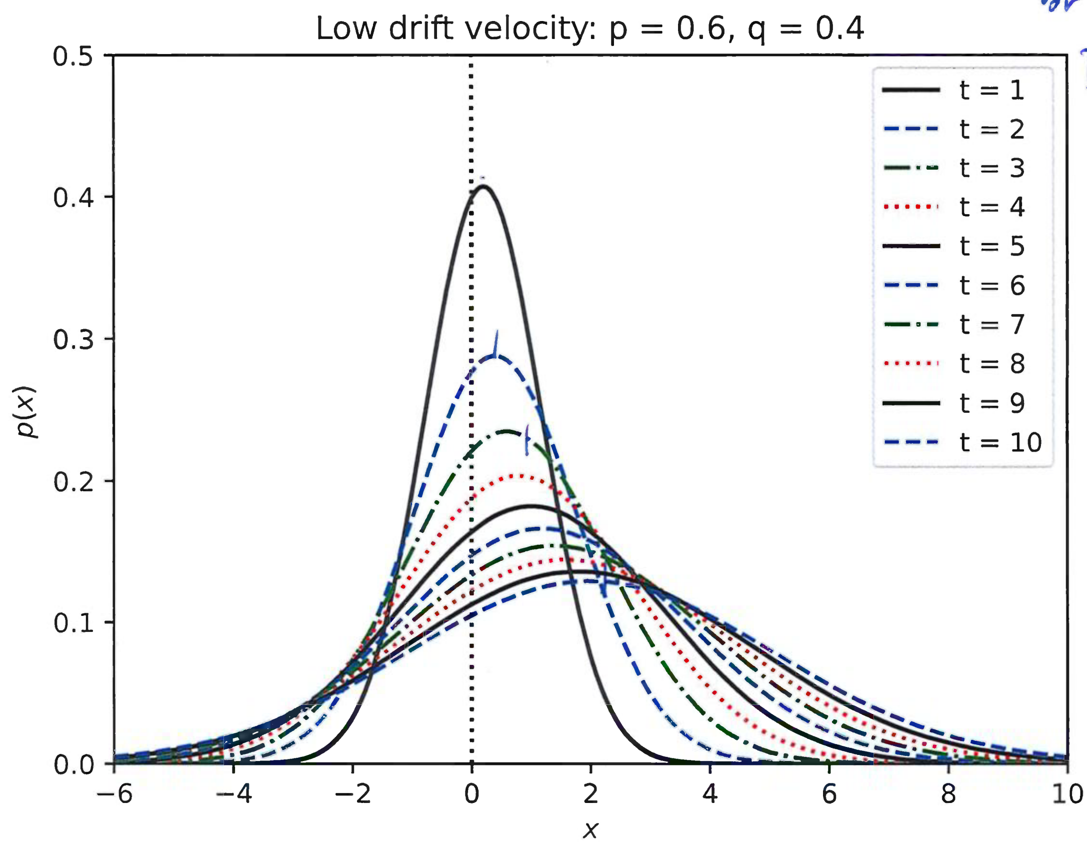
"one-sigma" ~ 68%

$-D\sqrt{t} \le x \le D\sqrt{t}$



$v_{dr} = 2p - 1 = 0.98$

$D = 2\sqrt{pq} \approx 0.199$



$V_{dr} = 0.2$

$D = \sqrt[2]{0.24} \approx 0.98$

Diffusion ~ "spreading out" as time passes

Repeat random walk many times → t-dependent prob. dist.

Connect diffusion to $(N \gg 1)$ CLT

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

Need single-step mean μ and variance σ^2

$$\boxed{\begin{aligned} \mu &= \langle x_i \rangle = \sum_i x_i P_i = (+1)p + (-1)\overset{1-p}{q} = 2p-1 \\ \langle x_i^2 \rangle &= p + q = 1 \\ \sigma^2 &= \cancel{1} - (4p^2 - 4p + \cancel{1}) = 4p(1-p) = 4pq \end{aligned}}$$

Special case

page 24

General results: $\mu = V_{dr}\,\delta t = \frac{V_{dr} \cdot t}{N} = \frac{\langle x \rangle}{N}$

$$\sigma^2 = D^2 \delta t = \frac{D^2 t}{N} = \frac{(\Delta x)^2}{N}$$

$$p(x) \approx \frac{1}{\sqrt{2\pi D^2 t}} \exp\left[\frac{-(x - V_{dr} t)^2}{2D^2 t}\right]$$

↳ Peak at $x = V_{dr} t = \langle x \rangle$

width increases $\propto D\sqrt{t}$

height decreases $\propto 1/D\sqrt{t}$

Drift vs. diffusion (assume $V_{dr} \neq 0$)

$$\left.\begin{aligned} \langle x \rangle &\propto t \\ \Delta x &\propto \sqrt{t} \end{aligned}\right\} \quad \boxed{\frac{\Delta x}{\langle x \rangle} \propto \frac{1}{\sqrt{t}} \to 0 \quad \text{as } t \propto N \to \infty}$$

page 23

Although absolute diffusion length grows $\propto \sqrt{t}$

relative fluctuation become negligible ~~com~~

compared to non-zero drift

Final key ~~result~~ result

Law of diffusion $\longleftrightarrow$ central limit theorem

Both hold wherever single-step μ & σ^2 finite

Statistical ensemble

Idea: Proba space, observe many particles
evolving in time
subject to constraints

Time $t_1, t_2, t_3, \ldots$ $\to$ states $\omega_1, \omega_2, \omega_3, \ldots$

Powerful example: Spin system
"Particles" either point up $\uparrow \sim +1$
or point down $\downarrow \sim -1$

Motivation from magnetic molecules, many uses

Example configuration of $N=8$ spins fixed in a line

$$\boxed{\begin{array}{l} \uparrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow \\ \text{In total } 2\cdot 2\cdot \cdots 2 = 2^N \text{ configs } (256 \text{ for } N=8) \end{array}}$$

page 26

All 256 micro-states have $N=8$ spins
$\to$ N is conserved quantity same for all ω_i

Also conserved: Internal energy of "isolated/"closed" system
$E(\omega_i) = E(\omega_j)$ for all i,j

Historically empirical observations
$\to$ "First law of thermodynamics"

Equivalently: Changing E of system Ω
$\to$ equal & opposite change in E of its surroundings

Spin system energy from external "magnetic field" $H > 0$

H

$\uparrow$ $\delta E = -H$ n_+

$\downarrow$ $\delta E = +H$ $n_- = N - n_+$

Internal energy $E = (-H)n_+ + H(N-n_+) = -H(2n_+ - N)$

$E(\uparrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow) = -4H < 0$

Fraction of micro-states allowed:

$$\frac{\#\text{ allowed}}{\#\text{ total}} = \frac{\binom{8}{6}}{256} = \frac{8\cdot 7/2}{256} = \frac{28}{256} = \frac{7}{64} \approx 11\%$$

page 27

Another example: $N \sim 10^{25}$ point particles of mass m

$$E = \frac{m}{2}\sum_{n=1}^{N} \vec{v}_n^{\,2} = \frac{1}{2m}\sum_n \vec{p}_n^{\,2}$$

Conserved energy $\rightarrow$ constrain accessible momenta

Don't work with $\sim 10^{25}$ time-evolution equations

Instead treat time evolution as stochastic process

$w_1 \rightarrow w_2 \rightarrow w_3 \rightarrow \cdots$

micro-states w_i

Formal definition: A statistical ensemble is set $\Omega = \{w_1, w_2, \ldots\}$ of all micro-states accessible through time evolution

Each w_i has probability $p_i > 0$ of being adopted

$\rightarrow$ prob. space

$\sum_i p_i = 1$ so that system in some micro-state at any time

Conserved quantities unchanged under time evolution
→ characterize statistical ensembles

<u>Micro - canonical</u> ensemble charactized by
conserved internal energy E
and particle number N } implies isolation

Connect to physical experience
→ smooth behaviour stable over time
equilibrium
(focus in this module)

air in room

A micro-canonical system Ω with M micro-states ω_i
is in <u>thermodynamic equilibrium</u> if and only if
all probabilities p_i are equal

Finite M → $p_i = \frac{1}{M}$ $\qquad \sum_i p_i = M\left(\frac{1}{M}\right) = 1$