L1: Welcome to Pchem!

our goal: quantitative understanding of molecules and chemical reactions from "first principles"

TAs will make notes available.

Course policies: see our course website:

gruebele-group.chemistry.illinois.edu/courses/chem-440

The math of Pchem

① averages, e.g:

$y_i = 1, 2, 3, 3, 4, 4$; $N = 6$

$$\bar{y} = \frac{1+3+2+3+4+4}{6} \approx 2.83$$

or

$$\bar{y} = \underbrace{\frac{1}{6}\cdot 1 + \frac{2}{6}\cdot 3 + \frac{1}{6}\cdot 2 + \frac{2}{6}\cdot 4}_{\sum p_i \cdot y_i} \approx 2.83$$

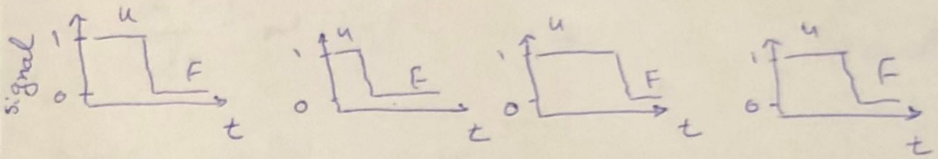
p_i → probability, y_i → value

if $y_i \to y(x)$, i.e a continuous function, then the sum becomes an integral:

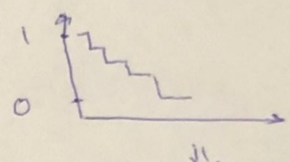
$$\bar{y} = \int p(x) \cdot y(x)\, dx$$

Example: Single molecule reaction, e.g. protein folding: $u \to F$

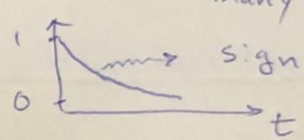
Various measurements:



⇓ average



⇓ many measurements from many molecules

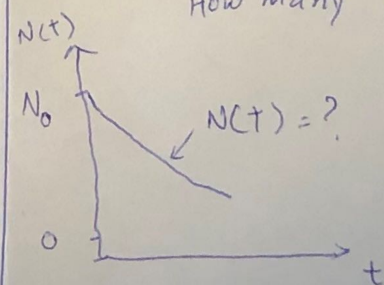


signal begins to look smooth

② Derivative models, e.g. $\frac{\partial x}{\partial t} = f(x, t)$

the irony: chemical systems are discrete molecules, so it is $\frac{\Delta x}{\Delta t}$, and $\frac{\partial x}{\partial t}$ is an approximation.

Example: start with many ($N_0 \gg 1$) unfolded proteins. How many are left at time t?



thought: "the rate at which unfolded proteins fold is proportionate to the number of unfolded proteins"

Turning the words into equation:

$$\frac{\partial N}{\partial t} \sim N \quad \text{or} \quad \frac{\partial N}{\partial t} = \underbrace{-k}_{\text{Proportionality constant}} N$$

(Q: why the minus sign?)

solving,

$$\frac{dN}{N} = -k\,dt \Rightarrow \int_{N_0}^{N(t)} \frac{dN'}{N'} = \int_0^t -k\,dt'$$

dummy variables

$$\Rightarrow \ln N(t) - \ln N_0 = -kt - (-0)$$

$$\Rightarrow N(t) = N_0\, e^{-kt}$$

Sometimes observations from real systems does not yield an exact exponential like the one solved here → come up with a different hypothesis, i.e "verbal conjecture"

Thought: what does the differential equation look like for (I) A+B → C? or (II) 2A → C

(I) $\frac{d[C]}{dt} \sim [A][B]$; reaction is ~~[illegible]~~ first-order in A and B

(II) $\frac{d[C]}{dt} \sim [A]^2$; reaction is second-order in A

higher-order reactions are less likely to occur as it is unlikely that three or more molecules can collide simultaneously to react.