CHEM 440

Lecture 1 8/21/23

Welcome to pchem!

→ Our goal: a quantifiable understanding of molecules and chemical rxns from "first principles"

First 3 Lectures: the math of pchem

① Averages

Ex: Consider a series of measurements

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

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

$$= \underbrace{\left(\tfrac{1}{6}\right)}_{\text{prob. } P_1 \text{ of getting } y_i = 1}(1) + \left(\tfrac{2}{6}\right)(3) + \left(\tfrac{1}{6}\right)(2) + \left(\tfrac{2}{6}\right)(4) \approx 2.83$$

$$= \sum_{i=1}^{6} P_i \, y_i$$

Quick aside: $\sum_{i=1}^{N} P_i = 1$ always

If $y_i \to y(x)$, a continuous function (instead of a discrete set of values) then the sum becomes an integral:

$$\bar{y} = \int \underbrace{P(x)}_{\text{"probability distribution"}} \cdot y(x) \, dx$$

Ex: Single Molecule Rxn (eg protein folding)

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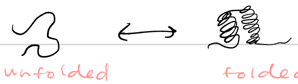
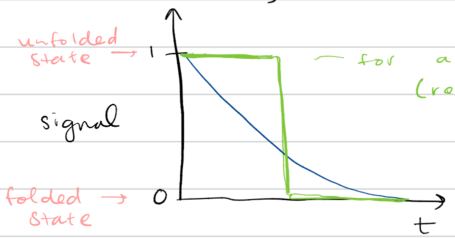
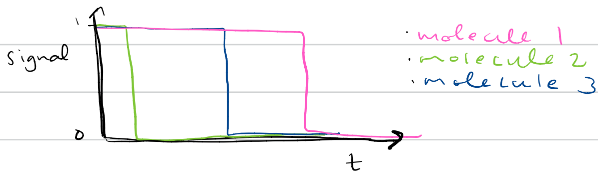


watching a single molecule:

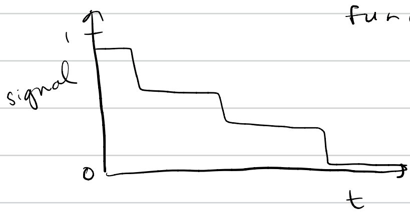


— for a single molecule (reaction for 1 molecule is essentially instantaneous)

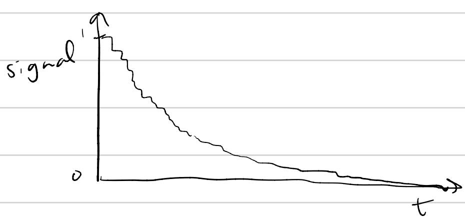
watching several molecules



⇓ average signal as a function of time



⇓ many molecules



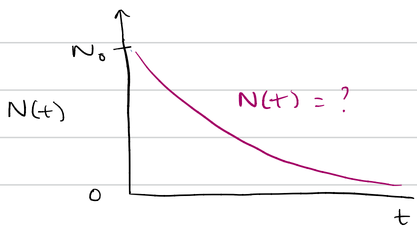
② Derivative Models

Ex: $$\frac{\partial x}{\partial t} = f(x,t)$$

The irony: chemical systems are actually discrete molecules, so

$$\text{"approx."}\left\{\frac{\partial x}{\partial t}\right. \approx \left.\frac{\Delta x}{\Delta t}\right\}\text{"exact"}$$

Ex: we start w/ $N_0 >> 1$ molecules of unfolded proteins. How many are left at time t?



Thought Experiment.

Claim: "The rate at which unfolded proteins fold is proportional to the number of unfolded proteins."

Turning this thought into an equation:

$$\text{rate} = \frac{\partial N}{\partial t} \underbrace{\sim}_{\text{"is proportional to"}} N$$

OR

$$= \frac{\partial N}{\partial t} = \underbrace{-k}_{\text{proportionality constant, unknown}} N$$

Q = why did we pick a minus sign?

A: because we want k to be positive (so -k is negative), but our slope is negative

⟶

solving:

$$\frac{\partial N}{\partial t} = -kN$$

$$\Rightarrow \frac{\partial N}{N} = -k\,dt$$

$$\Rightarrow \int_0^{N(t)} \frac{1}{N}\,\partial N = -k \int_0^t dt'$$

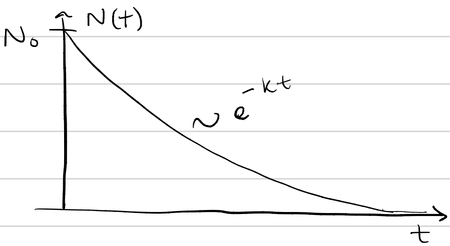
$$\Rightarrow \ln N \Big|_0^{N(t)} = -kt'\Big|_0^t$$

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

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

$e^{AB} = e^A e^B$

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



thought: for a rxn $A + B \rightarrow C$

$$\hookrightarrow \frac{\partial [C]}{\partial t} \sim [A][B]$$

if $A = B$ $(2B \rightarrow C)$

$$\hookrightarrow \frac{\partial [C]}{\partial t} \sim [B]^2$$