Lecture 30

Monday, November 6, 2023 9:56 AM

Last Time = $\frac{\partial G}{\partial x} = \Delta G = \Delta G^{(0)} + RT \ln Q$

$z_i(T) \rightarrow Z_i(T) \rightarrow Z(T) \rightarrow \frac{\partial \ln Z}{\partial n_i} \sim \mu_i$

# of microstates of molecule @ temp T — multiply — for n_i moles of molecules — multiply — for all molecules in the rxn

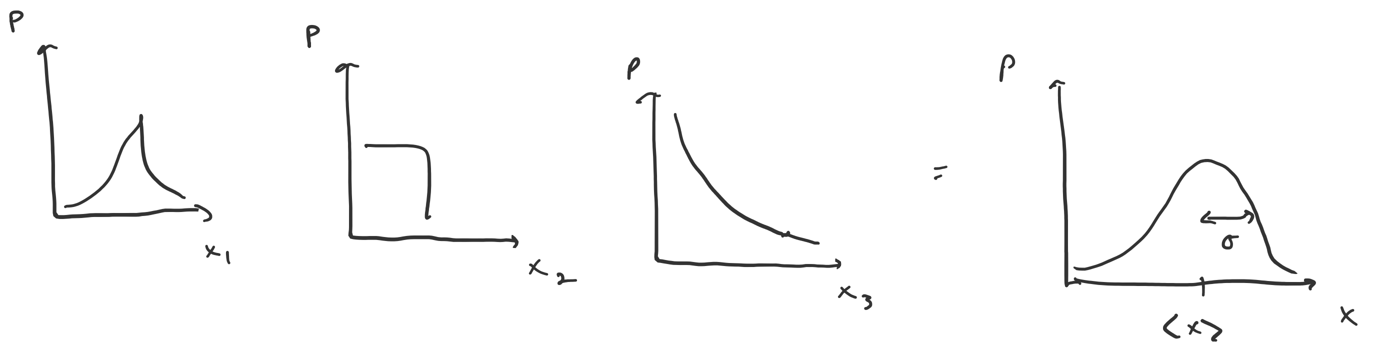
$\Rightarrow \Delta G^{(0)} = \sum \mu_i^{(0)} \cdot \nu_i$ if calculated @ 298 K, 1 atm

Long ago: Central Limit Theorem = CLT

$X_1 + X_2 + X_3 + \ldots = X$

$\langle x \rangle = \sum \langle x_i \rangle$

$\sigma^2 = \sum \sigma_i^2$



Today = Time-dependent stat mech - kinetics & transport

① Brownian Motion ② Drift velocity

① At short times, F=ma predicts where particle goes

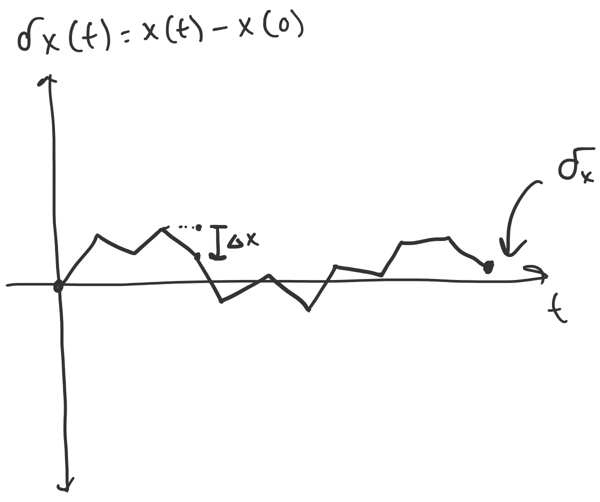
$V = \frac{\Delta x}{\Delta t}$, $F = ma = m\frac{\Delta V}{\Delta t}$

$\Rightarrow \Delta x = V \cdot \Delta t$ $\quad \Delta V = \frac{F}{m} \cdot \Delta t$

$x(t+\Delta t) = x(t) + V \cdot \Delta t$ $\quad V(t+\Delta t) = \frac{F}{m}\Delta t + V(t)$

Long Time = "Butterfly effect" = Chaos

We can use this concept of chaos to see how a particle really moves in time when subject to unpredictable forces:



$\sigma_x(t) = \sigma_x(n \cdot \Delta t) = \sum_{j=1}^{n} \Delta x_j$

σ_x is a gaussian random variable w/ standard deviation given by

$\langle \sigma_x^2 \rangle = \sum_{j=1}^{n} \Delta x_j^2 = n \langle \Delta x_j^2 \rangle$

$$\Rightarrow \langle \sigma x^2 \rangle = n \langle \Delta x_j^2 \rangle = \frac{t}{\Delta t}\langle \Delta x_j^2 \rangle$$

$$= \frac{\langle \Delta x_j^2 \rangle}{\Delta t} \cdot t$$

$$= 2D \cdot t$$

Diffusion — Diffusion Coefficient

$\langle \sigma x^2 \rangle = 2D \cdot t$ in 1-D

$\langle \sigma x^2 \rangle = 6D \cdot t$ in 3-D

Ex. = dermal patch $\Delta x = 2$ mm skin

$D = 100\ \mu m^2/s$ (typical organic molecule)

$t = \frac{\langle \sigma x^2 \rangle}{2D} = \frac{(2000\ \mu m)^2}{2 \cdot 100\ \mu m^2/s} \approx 20{,}000\ s \approx 5\ hr$