$\langle n_E \rangle_t$ $\langle n_S \rangle_t$ $\langle n_S n_E \rangle_t$ $\langle n_{ES} \rangle_t$ $\langle n_{S*} \rangle_t$

digression: imagine two random variables X & Y describing a system

joint prob. distribution $\underbrace{\mathcal{P}(X,Y)}_{\text{frac. of population w/ value } (X,Y)}$

marginal prob. $\mathcal{P}(X) = \sum_Y \mathcal{P}(X,Y)$

$$\mathcal{P}(Y) = \sum_X \mathcal{P}(X,Y)$$

$$\langle X \rangle = \sum_{X,Y} X\,\mathcal{P}(X,Y) = \sum_X X\,\mathcal{P}(X)$$

$$\langle Y \rangle = \sum_{X,Y} Y\,\mathcal{P}(X,Y) = \sum_Y Y\,\mathcal{P}(Y)$$

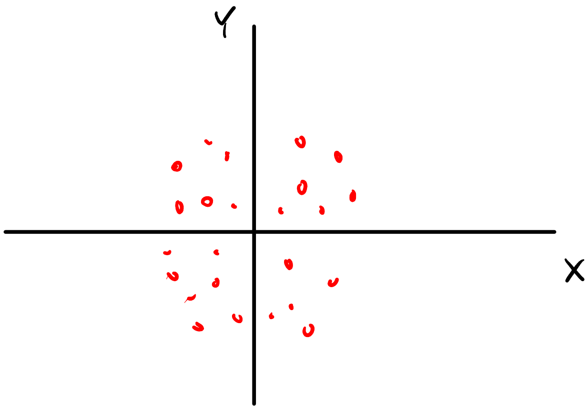
$$\langle XY \rangle = \sum_{X,Y} XY\,\mathcal{P}(X,Y)$$

in general: $\langle XY \rangle \neq \langle X \rangle \langle Y \rangle$ $\neq$

$$\langle X \rangle \langle Y \rangle = \sum_{X,Y} XY\,\mathcal{P}(X)\mathcal{P}(Y)$$

When is $\langle XY \rangle \approx \langle X \rangle \langle Y \rangle$

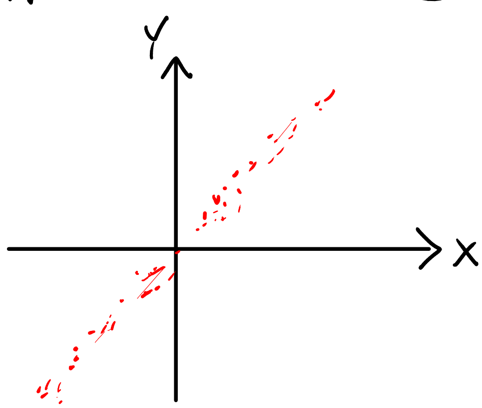
different scenarios: X + Y not strongly correlated



$$\mathcal{P}(X,Y) \approx \mathcal{P}(X)\,\mathcal{P}(Y)$$

$$\langle XY \rangle \approx \langle X \rangle \langle Y \rangle$$

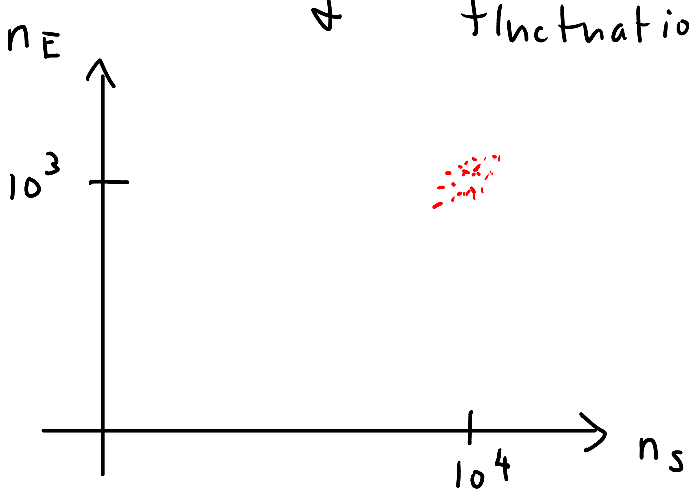
opposite: strong correlations



$$\langle XY \rangle \neq \langle X \rangle \langle Y \rangle$$

Chemical systems: mean #'s of molec's is typically quite high ($10^2 - 10^5$ molec./cell)

& fluctuations $\ll$ mean



precise shape of point cloud is irrelevant

$$\langle n_s n_E \rangle_t \approx \langle n_s \rangle_t \langle n_E \rangle_t$$

define concentrations: $c_s(t) = \dfrac{\langle n_s \rangle_t}{V}$

$$\frac{dc_s}{dt} = -\tilde{k}_b \bar{V} c_s c_E + k_u c_{ES}$$

$$\frac{dc_E}{dt} = -\tilde{k}_b \bar{V} c_s c_E + (k_u + k_{cat}) c_{ES}$$

$$\frac{dc_{ES}}{dt} = \tilde{k}_b \bar{V} c_s c_E - (k_u + k_{cat}) c_{ES}$$

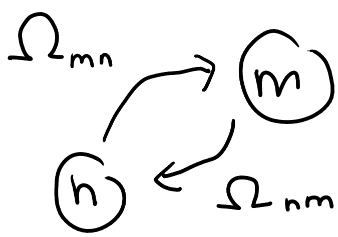
$$\frac{dc_{s^*}}{dt} = k_{cat} c_{ES}$$

4 equ's
4 unk:
c_s
c_E
c_{ES}
c_{s^*}

Next step: think about influence of energy

$\Rightarrow$ biological thermodynamics

system of transitions b/t states



dynamics:

$$\frac{dp_n}{dt} = \sum_m \Omega_{nm} p_m$$

GOAL: connect Ω_{nm} to physical quantities (i.e. energy, chemical potentials, etc.)

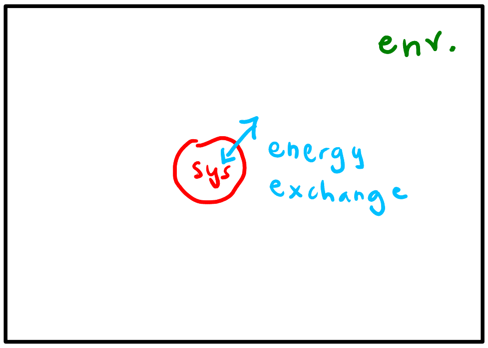
start: consider energy differences b/t states

know: state $n \Rightarrow$ energy E_n
state $m \Rightarrow$ energy E_m

"internal" energy of system

$n \to m$ transition: change in system energy

$$E_m - E_n$$



idea: Ω_{mn} should be related to how likely it is to gain/lose $E_m - E_n$ energy from env.