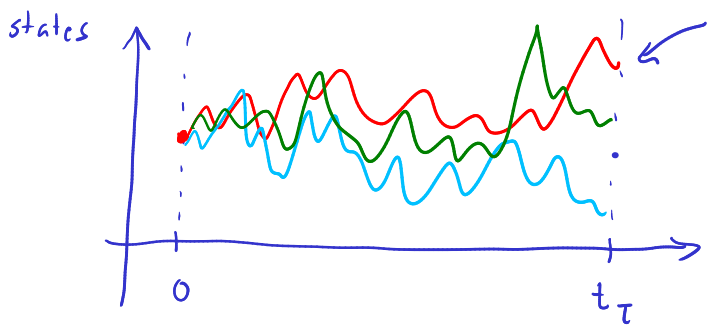
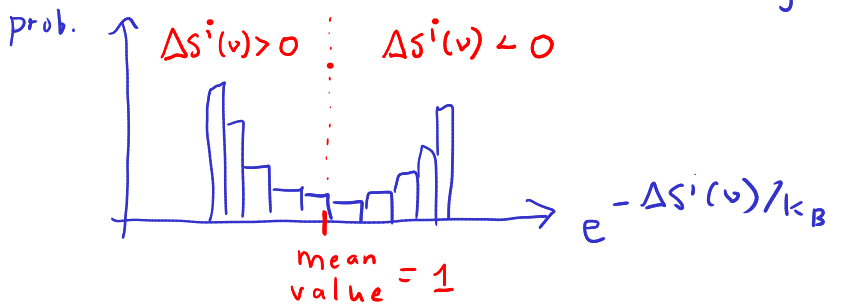
PHYS 414: 4-10-20



associated w/ each traj. ν

$\Rightarrow \Delta S^i(\nu)$ entropy production

$\Rightarrow e^{-\Delta S^i(\nu)/k_B}$ collect histogram



If $\Delta S^i(\nu) > 0$ traj. exist, there must be enough $\Delta S^i(\nu) < 0$ traj. that also exist to compensate + allow IFT to hold.

IFT: $\langle e^{-\Delta S^i(\nu)/k_B} \rangle = 1$

$\Delta S^i(\nu) > 0$: entropy producing trajectories

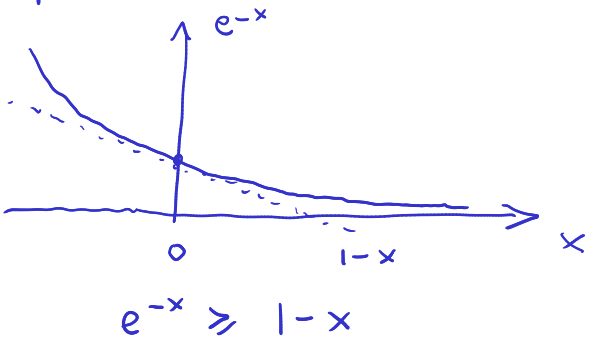
$\Delta S^i(\nu) < 0$: entropy destroying trajectories

Another property: first do a small inequality proof (Jensen's inequality)

arbitrary quantity x_n w/ prob. p_n

$$\langle x \rangle = \sum_n x_n p_n$$

$\langle e^{-x} \rangle$



$$\langle e^{-x} \rangle = \sum_n p_n e^{-x}$$

$e^{-x} \geq 1 - x$

$$\geq \sum_n p_n (1 - x) = \sum_n p_n - \sum_n p_n x = 1 - \langle x \rangle$$

$$\Rightarrow \langle e^{-x} \rangle \geq 1 - \langle x \rangle$$

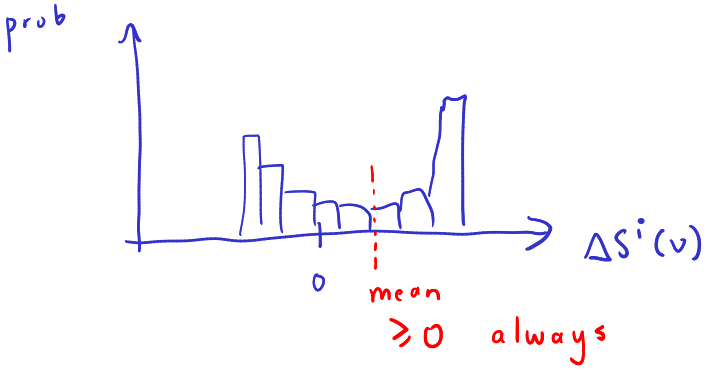
$$1 = \left\langle e^{-\Delta S^i(\nu)/k_B} \right\rangle \geq 1 - \frac{\left\langle \Delta S^i(\nu) \right\rangle}{k_B}$$

$$\Rightarrow \boxed{\left\langle \Delta S^i(\nu) \right\rangle \geq 0}$$

Second law of thermodynamics (another version)

$$\left[\dot{S}^i \geq 0 \text{ always} \right]$$

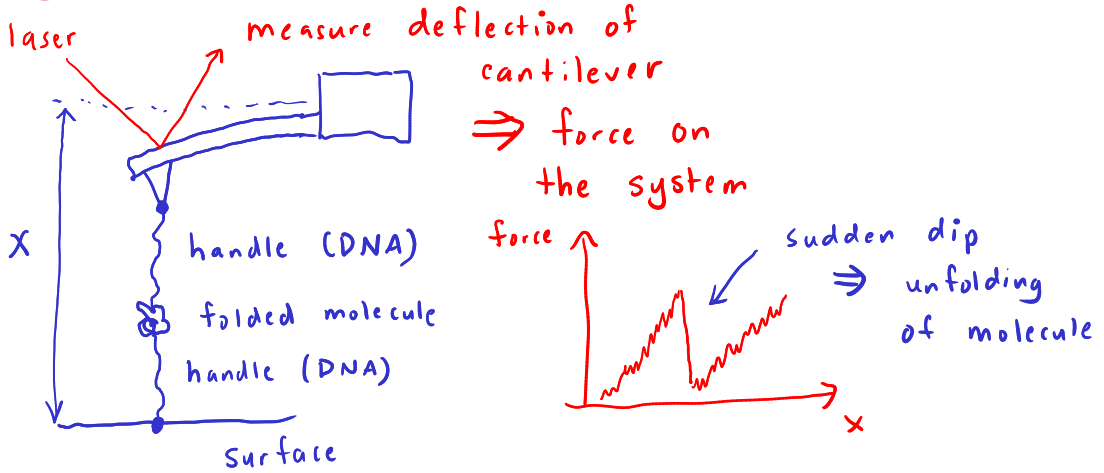
$$\Delta S^i(\nu) = \int_0^{t_\tau} dt\, \dot{S}^i(\nu) \geq 0$$



Goal: figure out how to experimentally test this?

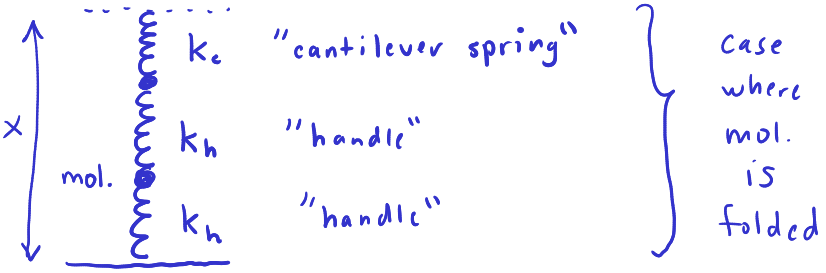
$\Rightarrow$ figure out a platform where we can measure $\Delta S^i(\nu)$ for each traj (out of equil., since $\Delta S^i(\nu) = 0$ for equil. traj.)

AFM (atomic force microscope) unfolding of a biomolecule



x(t) can be controlled by experimentalist (surface can be moved up or down)

spring model:



$\Rightarrow$ $=$ $k_1 \approx \dfrac{1}{\frac{1}{k_c}+\frac{1}{k_h}+\frac{1}{k_h}}$

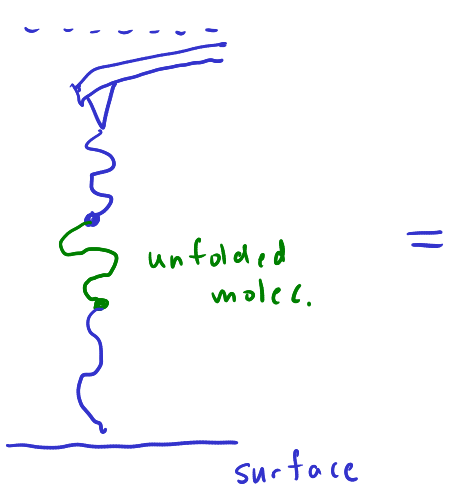
single effect. spring

state 1: folded molecule

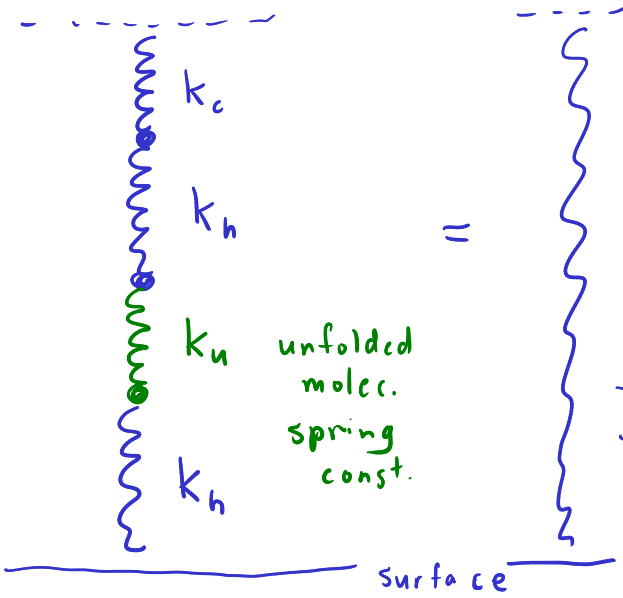
$E_1(x) = \frac{1}{2} k_1 x^2 - \epsilon$

ϵ: energy of folded molec. relative to unfolded state

state 2: unfolded molec.

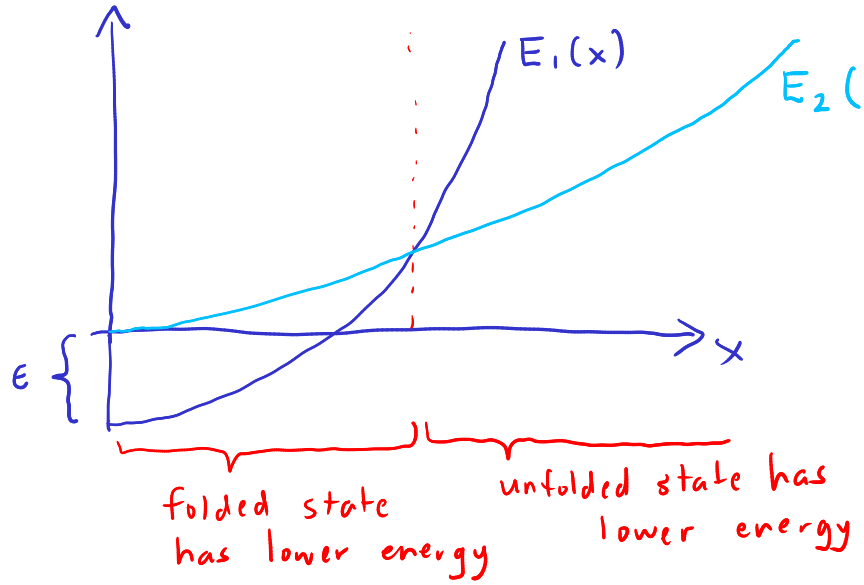


$=$



$=$ $k_2 = \dfrac{1}{\frac{1}{k_c}+\frac{1}{k_h}+\frac{1}{k_h}+\frac{1}{k_u}}$

$\Rightarrow k_2 < k_1$ $\quad E_2(x) = \frac{1}{2} k_2 x^2$



typical exper. protocol