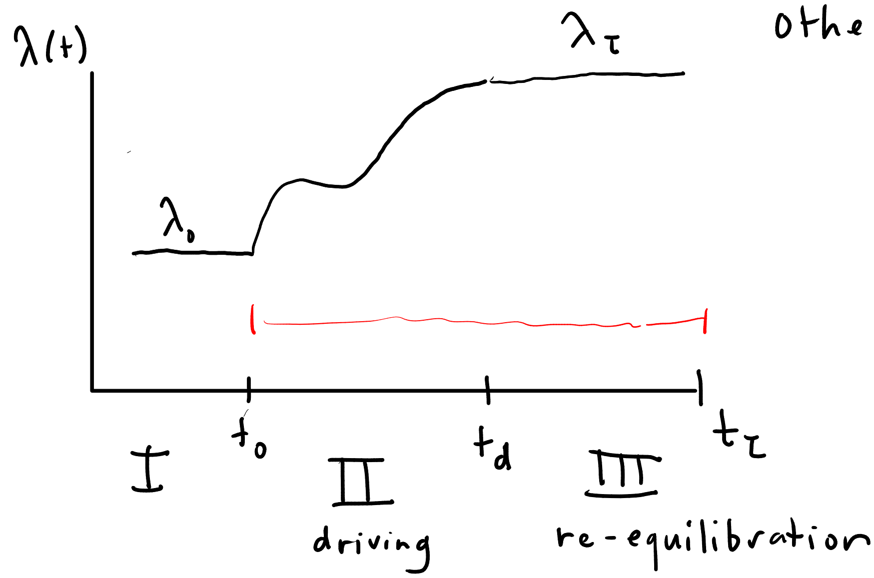
non-periodic $\lambda(t)$: case considered in 1990's by Jarzynski, Crooks, & others

$\uparrow$
control protocol

$\Downarrow$

$W(\lambda(t))$



I: before t_0 system has reached equil.

$$F(t_0) = F^{eq}(\lambda_0)$$

$$= -k_B T \ln Z(\lambda_0)$$

$$Z(\lambda_0) = \sum_n e^{-\beta E_n(\lambda_0)}$$

II: arbitrary driving w/ $\lambda(t)$

III: at $t \gg t_d$ system re-equilibrates to new equilibrium

$$F(t_\tau) \simeq F^{eq}(\lambda_\tau) \quad \text{for } t_\tau \gg t_d$$

will prove: $\mathcal{W}(\nu)$ = net work done by system in traj. ν from t_0 to t_τ

Jarzynski equality

$$\langle e^{\beta W(\nu)} \rangle = e^{-\beta \Delta F^{eq}}$$

related to nonequil. driving

related to equil. free energies

$$\Delta F^{eq} = F^{eq}(\lambda_\tau) - F^{eq}(\lambda_0)$$

PROOF: Start w/ IFT: $\langle e^{-I(\nu)/k_B} \rangle = 1$

$$I(\nu) = -k_B \left(\ln p_{n_\tau}(t_\tau) - \ln p_{n_0}(t_0) \right) - \frac{1}{T}\left(E_{n_\tau}(\lambda_\tau) - E_{n_0}(\lambda_0) \right) - \frac{1}{T} W(\nu)$$

$$W(\nu) = \sum_{i=1}^{\tau-1} \omega_{n_{i+1} n_i}$$

at beg. + end we are in Boltzmann equ.

$$p_{n_\tau}(t_\tau) = p_{n_\tau}^{eq} = \frac{e^{-\beta E_{n_\tau}(\lambda_\tau)}}{Z(\lambda_\tau)}$$

$$p_{n_0}(t_0) = p_{n_0}^{eq} = \frac{e^{-\beta E_{n_0}(\lambda_0)}}{Z(\lambda_0)}$$

$$\Rightarrow I(\nu) = k_B \ln Z(\lambda_\tau) - k_B \ln Z(\lambda_0) - \frac{1}{T} W(\nu)$$

$$= -\frac{1}{T} \Delta F^{eq} - \frac{1}{T} W(\nu)$$

every run beg's + ends w/ same λ_0 + λ_τ $\Rightarrow$ ΔF^{eq} is same for every run

potentially varies w/ each run + so depends on ν

avg. over v $\rightarrow$ $$\left\langle e^{-I(v)/k_B} \right\rangle = 1$$

$$\left\langle e^{\beta \Delta F^{eq} + \beta \bar{W}(v)} \right\rangle = 1$$

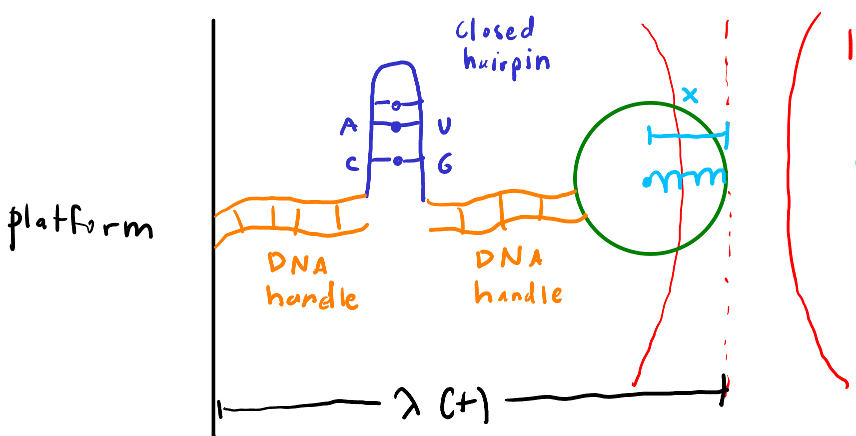
$$e^{\beta \Delta F^{eq}} \left\langle e^{\beta \bar{W}(v)} \right\rangle = 1$$

$$\Rightarrow \boxed{\left\langle e^{\beta \bar{W}(v)} \right\rangle = e^{-\beta \Delta F^{eq}}}$$

Jarzynski equal. [PRL 1997]

note: $\bar{W}(v) > 0 \Rightarrow$ net work done by sys.

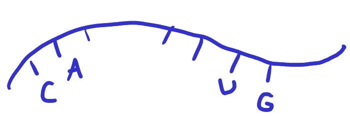
Experimental proof: Liphardt et al Science (2002)



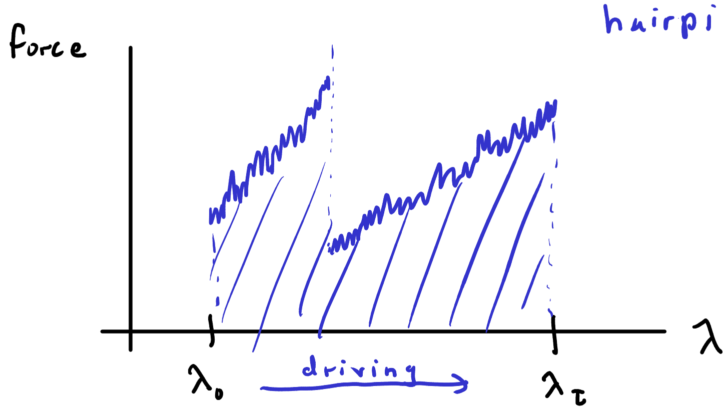
effective spring force due to laser light refracted thru bead

measure x, know spring constant k $\Rightarrow$ measure instant. force kx in system

control param: dist. b/t platform + beam axis



open RNA hairpin



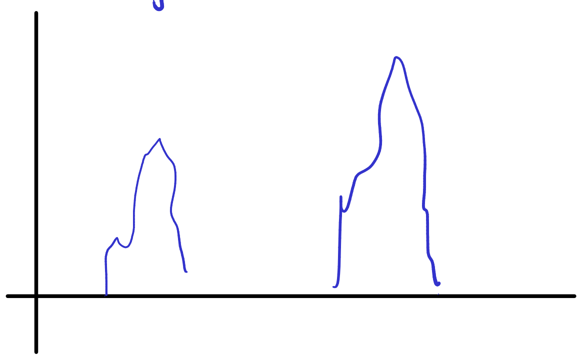
typical experimental run v

integral under curve $= \int \text{force} \cdot d\lambda$

$= \text{work done on sys.}$

$\simeq -\underbrace{\overline{W}(v)}_{\text{work done by sys.}}$

histogram of $\overline{W}(v)$ values



$\Rightarrow$ histog. of $e^{\beta \overline{W}(v)}$

$\Rightarrow$ avg. $\langle e^{\beta \overline{W}(v)} \rangle$

LHS of Jarzynski

for known seq. of hairpin $\Rightarrow$

computationally predict ΔF^{eq} RHS

$\Rightarrow$ check LHS = RHS