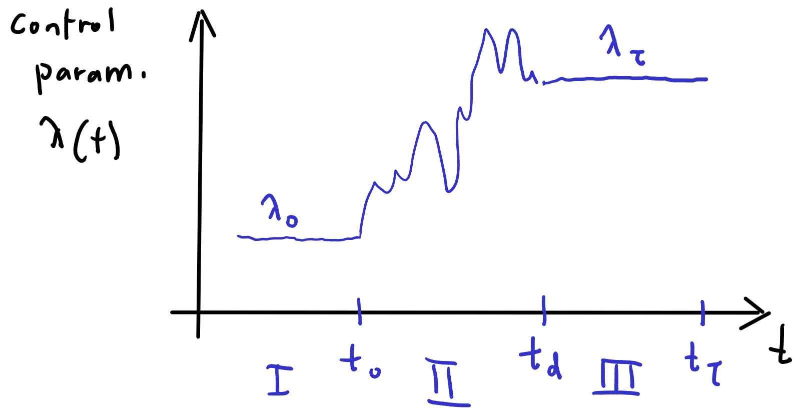


$$Z(\lambda) = \sum_n e^{-\beta E_n(\lambda)}$$

I. $F(t) \to F^{eq}(\lambda_0) = -k_B T \ln Z(\lambda_0)$

III. $F(t) \to F^{eq}(\lambda_\tau) = -k_B T \ln Z(\lambda_\tau)$

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

run same protocol many times $\Rightarrow$ ensemble of exper. trajectories

ΔF^{eq} always same for each exper. run (we may not what its value is)

How to estimate?

Apply: IFT $\left\langle e^{-I(\nu)/k_B} \right\rangle = 1$

for an exper. traj. ν

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

previously looked at avg. $I = \Delta S - \frac{1}{T}\Delta E - \frac{1}{T} W \geq 0$

here we look at full distrib. of $I(\nu)$

Beg. + end we are in Boltzmann equil:

$$p_{n_\tau}(t_\tau) = p^{eq}_{n_\tau} = \frac{e^{-\beta E_{n_\tau}(\lambda_\tau)}}{Z(\lambda_\tau)} \qquad \beta = \frac{1}{k_B T}$$

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

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

$$= -\frac{1}{T}\underbrace{\Delta F^{eq}}_{\text{const. in each run}} - \frac{1}{T}\underbrace{W(\nu)}_{\text{varies b/t runs}}$$

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

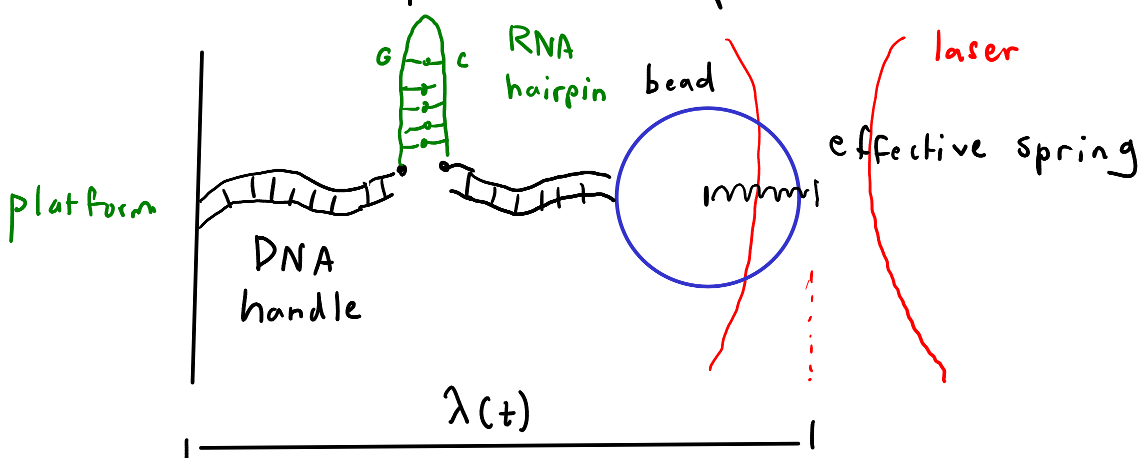
$$\Rightarrow \langle e^{\beta \Delta F^{eq} + \beta W(\nu)} \rangle = 1$$

$$\Rightarrow e^{\beta \Delta F^{eq}} \langle e^{\beta W(\nu)} \rangle = 1$$

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

Jarzynski equality (PRL, 1997)

Experimental proof: Liphardt et al. Science (2002)



controlled by experimentalist (dist. b/t laser + platf.)