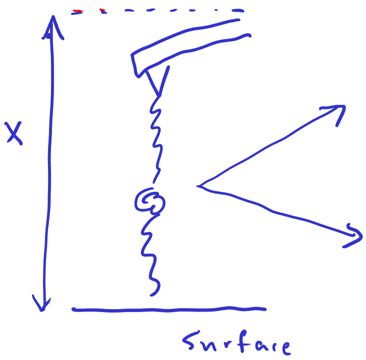
PHYS 414: 4-13-20

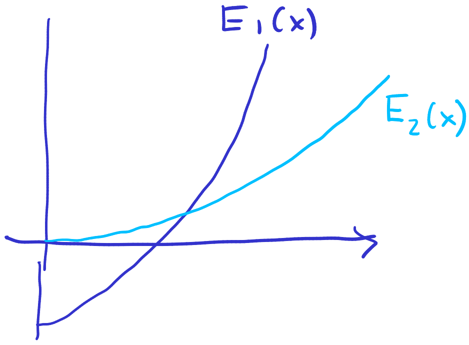


1) folded $E_1(x)$

$W_{21}(x) \downarrow \quad \uparrow W_{12}(x)$

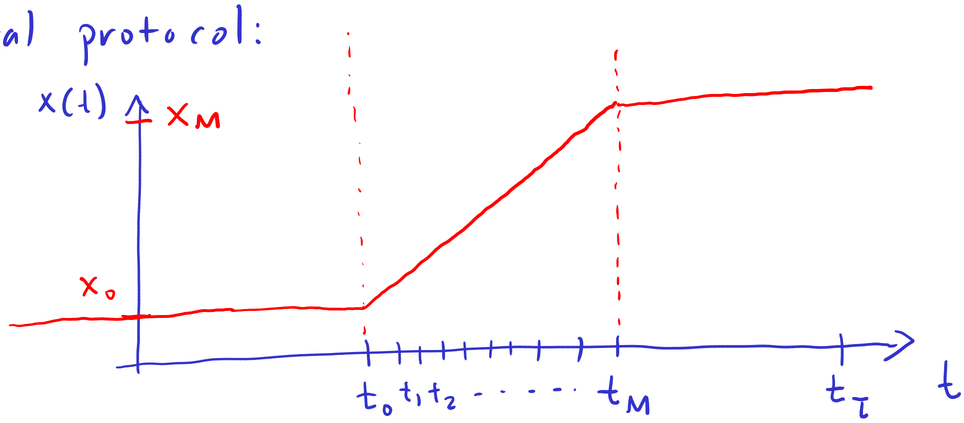
2) unfolded $E_2(x)$

$k_1 > k_2$



$$\text{MR:} \quad \frac{W_{21}(x)}{W_{12}(x)} = e^{-\beta\left(E_2(x) - E_1(x)\right)}$$

Experimental protocol:



regime I: allow sys. to equilibrate at x_0 for a long time before t_0

II: pull the molecule by increasing x

III: allow the sys to find equil. again at final separation of x_M

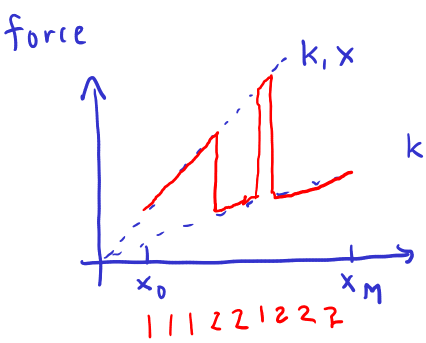
Exper. trajectory:

$\overbrace{t_0 \quad t_1}^{\delta t} \quad t_2 \quad t_3 \cdots t_M \cdots t_\tau$

state: 1 1 2 2 1 2 2 ⋯ 2

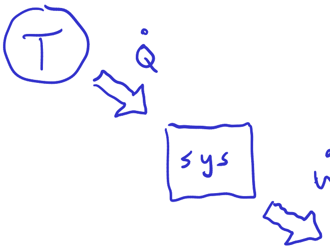
1 1 1 1 2 2 2 ⋯ 1 ⋯ 2

x: x_1 x_2 x_3 ⋯



states: $\underbrace{n_0 \quad n_1 \cdots n_\tau}_{\nu}$

$$e^{\frac{\Delta S^i(\nu)}{k_B}} = \frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} \rightarrow \underbrace{\mathcal{P}(\nu)}_{\text{prob. of traj. running exper. in forw. protocol}} = W_{n_\tau, n_{\tau-1}}(x_\tau) \cdots\cdots W_{n_1, n_0}(x_1)\, p^{eq}_{n_0}(x_0)$$



$$\underbrace{\tilde{\mathcal{P}}(\tilde{\nu})}_{\text{prob. of rev. traj. } \tilde{\nu} \text{ when running exper. in backwards prot.}} = W_{n_0, n_1}(x_1) \cdots\cdots W_{n_{\tau-1}, n_\tau}(x_M)\, p^{eq}_{n_\tau}(x_M)$$

MR: $$\frac{W_{n_{i+1}, n_i}(x_{i+1})}{W_{n_i, n_{i+1}}(x_{i+1})} = e^{-\beta \overbrace{\left(E_{n_{i+1}}(x_{i+1}) - E_{n_i}(x_{i+1})\right)}^{\text{amount of energy (heat) donated from ext. envir. in this state trans.}}}$$

equil $\Rightarrow$ Boltz equil : $$p^{eq}_{n_0}(x_0) = \frac{e^{-\beta E_{n_0}(x_0)}}{Z(x_0)}$$

$$Z(x_0) = e^{-\beta E_1(x_0)} + e^{-\beta E_2(x_0)}$$

$$p^{eq}_{n_\tau}(x_M) = \frac{e^{-\beta E_{n_\tau}(x_M)}}{Z(x_M)}$$

$$\frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} = e^{-\beta \Big[\underbrace{\left(E_{n_\tau}(x_\tau) - E_{n_{\tau-1}}(x_\tau)\right) + \cdots\cdots + \left(E_{n_1}(x_1) - E_{n_0}(x_0)\right)}_{\Delta Q(\nu) \,=\, \text{total amount of heat from ext. env. in traj. } \nu} \Big]}$$

$$\cdot\, e^{\beta \underbrace{\left(E_{n_\tau}(x_M) - E_{n_0}(x_0)\right)}_{\Delta E(\nu) \,=\, \text{total energy diff. from } t_0 \text{ to } t_\tau \text{ in traj. } \nu}} \frac{Z(x_M)}{Z(x_0)}$$

$$\Delta Q(\nu) = \Delta E(\nu) + \underbrace{\Delta W(\nu)}_{\text{work done by sys in traj. } \nu}$$ 1st law energy budget

$$\Rightarrow \quad \frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} = e^{-\beta[\Delta E(\nu) + \Delta W(\nu)]} \, e^{\beta \Delta E(\nu)} \frac{Z(x_M)}{Z(x_0)}$$

$$= e^{-\beta \Delta W(\nu)} \frac{Z(x_M)}{Z(x_0)}$$

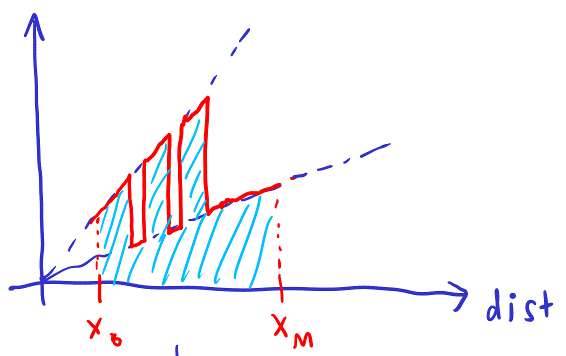
$$F = \bar{E} - TS \quad \underset{\text{in equil.}}{\Rightarrow} \quad F^{eq} = -k_B T \ln Z$$

does not depend on ν

$$\left.\begin{aligned} F^{eq}(x_M) &= -k_B T \ln Z(x_M) \\ F^{eq}(x_0) &= -k_B T \ln Z(x_0) \end{aligned}\right\} \quad \Delta F = F^{eq}(x_M) - F^{eq}(x_0)$$

$$\frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})} = e^{-\beta[\Delta W(\nu) + \Delta F]} = e^{\Delta S^i(\nu)/k_B}$$

$$\Rightarrow \quad \boxed{\underbrace{\Delta S^i(\nu)}_{\text{entropy prod. in traj.}} = -\frac{(\Delta W(\nu) + \Delta F)}{T}}$$



area under curve = work done by ext. deg. of freedom (apparatus) on sys $= -\Delta W(\nu)$