Jarzynski equality: start in equil. λ_0

$\Downarrow$

drive system arbitrarily (fast)

out-of-equilib.

$\Downarrow$

wait for equil. λ_τ

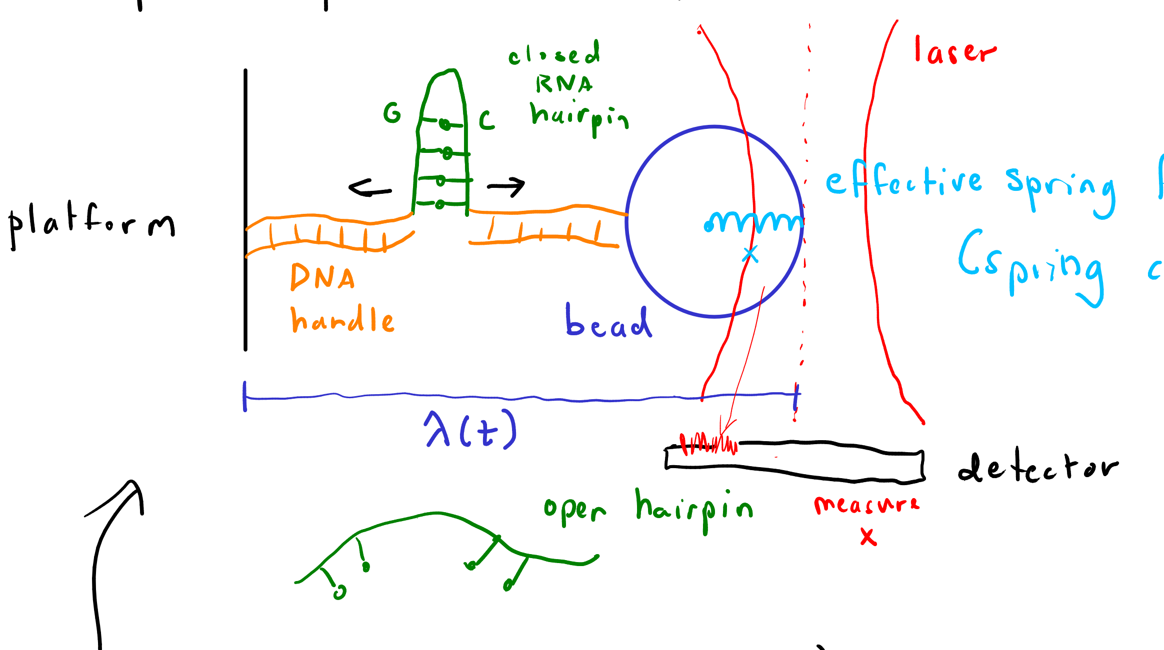
$\Bigg\} \Delta F^{eq}$

$W(v)$ = work done by sys. in one exper. run

$$\langle e^{\beta W(v)} \rangle = e^{-\beta \Delta F^{eq}} \qquad \text{[PRL 1997]}$$

$\Rightarrow$ allows you to estimate ΔF^{eq} from many short, fast experimental (or simulation) run

Exper. proof: Liphardt et al, Science (2002)



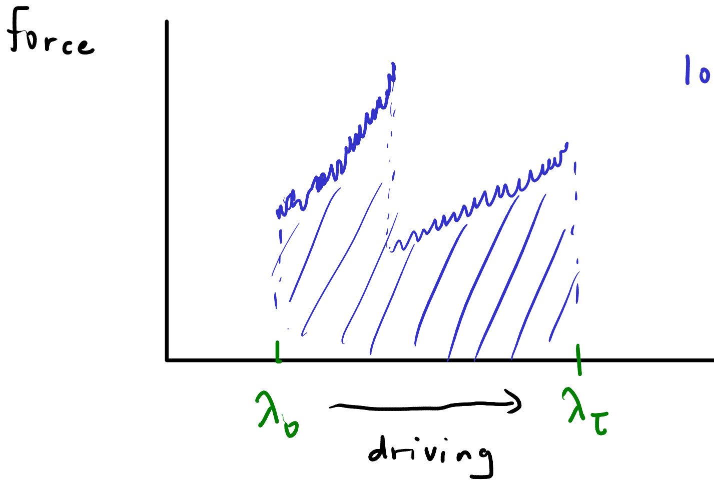
$U(x) = \frac{1}{2}kx^2$

$p^{eq}(x) = \dfrac{e^{-\beta \frac{1}{2}kx^2}}{Z}$

distance: control variable $\lambda(t)$

(measure how far bead is out of laser trap $\Rightarrow$ get force)

Single experimental run ν:



look somewhat diff. for every run ν (stochastic opening of hairpin)

$$\overline{W}(\nu) = \text{work done by sys}$$
$$= - \int \text{force} \cdot d\lambda$$
$$= - (\text{area under curve})$$

calc. avg. over 100's of short exper. runs

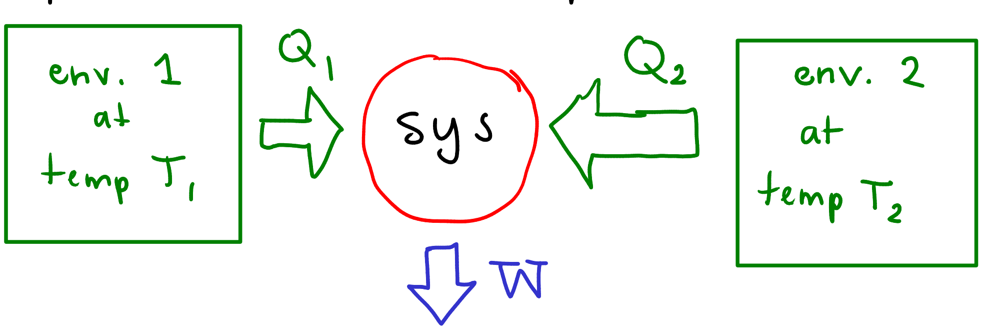
$\Rightarrow$ get $\langle e^{\beta \overline{W}(\nu)} \rangle$ LHS

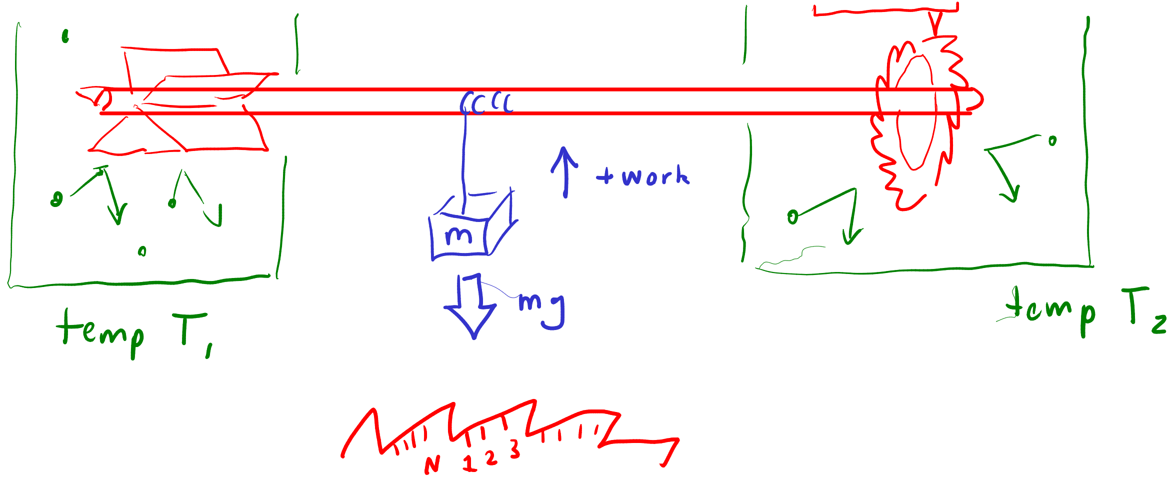
if you known seq. of hairpin (G, C, A, U seq.)

$\Rightarrow$ computational tools can be used to estimate ΔF^{eq} RHS

check LHS = RHS

What about systems coupled to multiple temperatures (multiple diff. environments)?





two transition matrices (for sys. connected to each env.)

$W^{(1)}_{nm}$ = prob. of $m \to n$ trans. due to exchange of energy w/ env. 1

$W^{(2)}_{nm}$ = " " env. 2

LDB: $\alpha = 1, 2$ $\qquad \beta_\alpha = \dfrac{1}{k_B T_\alpha}$

$$\frac{W^{(\alpha)}_{nm}}{W^{(\alpha)}_{mn}} = e^{-\beta_\alpha (E_n - E_m + \omega_{nm})}$$

imagine δt is small enough so that in each time step energy exchange happens w/ only one environment

prob. of $m \to n$ trans. due to env. 1 alone $\quad W^{(1)}_{nm}\left(1 - W^{(2)}_{nm}\right) \approx W^{(1)}_{nm}$ to leading order (assuming W's are small for small δt)

p_α = prob. that in time step δt, the trans. occurs due to env. α

$\rho_1 + \rho_2 = 1$

$$\text{traj. } \nu = (\underbrace{n_0, n_1}_{\alpha_0}, \underbrace{n_1, \ldots}_{\alpha_1} \ldots, \underbrace{\ldots, n_\tau}_{\alpha_{\tau-1}})$$

env. labels

$\alpha_0 \in$ 1 or 2