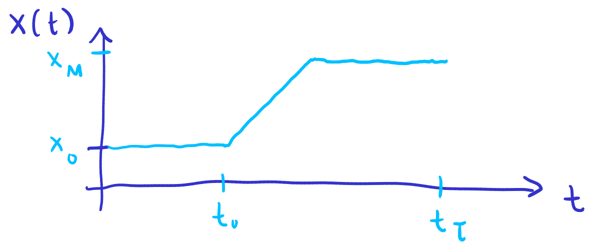
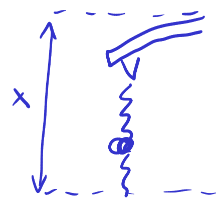
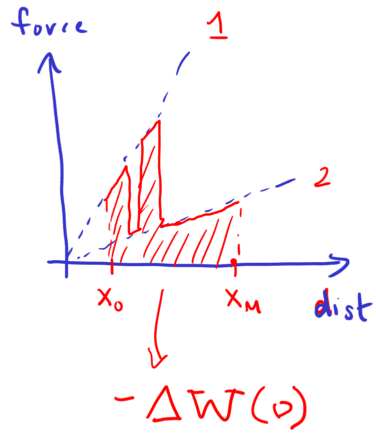
PHYS 414: 4-15-20

$$\Delta S^i(\nu) = \frac{-\Delta W(\nu) - \Delta F}{T}$$







$$F^{eq}(x_M) - F^{eq}(x_0) \equiv \Delta F$$

fluct. theorem: $\quad \dfrac{\tilde{\mathcal{P}}(\tilde{\nu})}{\mathcal{P}(\nu)} = e^{-\Delta S^i(\nu)/k_B}$

$\downarrow$

Crooks fluct. theorem (1998)

$$\left\langle e^{-\Delta S^i(\nu)/k_B} \right\rangle = \sum_\nu \mathcal{P}(\nu) e^{-\Delta S^i(\nu)/k_B}$$

avg. over many traj.

$$= \sum_\nu \mathcal{P}(\nu) \frac{\tilde{\mathcal{P}}(\tilde{\nu})}{\mathcal{P}(\nu)}$$

$$= \sum_\nu \tilde{\mathcal{P}}(\tilde{\nu})$$

$$= \sum_{\tilde{\nu}} \tilde{\mathcal{P}}(\tilde{\nu}) = 1$$

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

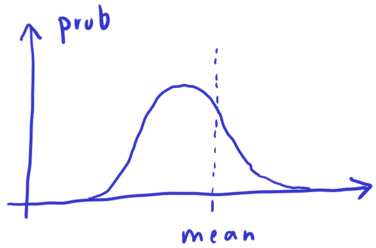
$$\Rightarrow \quad \left\langle e^{\beta[\Delta W(\nu) + \Delta F]} \right\rangle = 1$$

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

Jarzynski equality (1997)

many experiments: each one calculate $\Delta W(v)$

histogram:



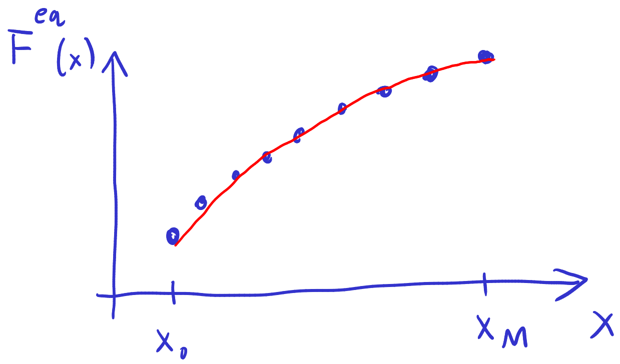
$e^{\beta \Delta W(v)}$

$= e^{-\beta \Delta F}$

from mean

$\Rightarrow$ extract

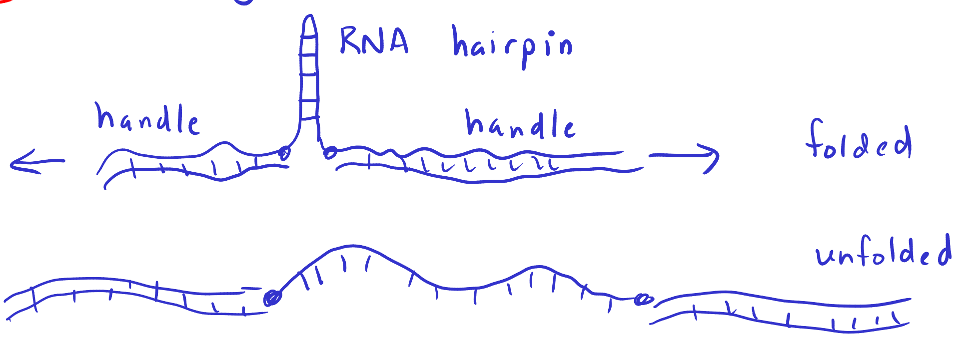
$\Delta F = F^{eq}(x_M) - F^{eq}(x_0)$



change ending dist. x_M and vary it to get entire curve of $F(x)$

experimental proofs:

pulling RNA (sys of interest)



RNA free energy can be known to good approx. from seq. of base pairs $\Rightarrow$ know ΔF + can check Jarzynski equal.

- Jarzynski validation: 2002 (Liphardt et al., Science)

- Crooks validation: 2005 (Collin et al, Nature)

$\Rightarrow$ can be generalized to quantum as well

- quantum Jarzynski: 2015 (An et al., Nature Phys.)

Everything so far: ensembles + probabilities + master equations } classical systems

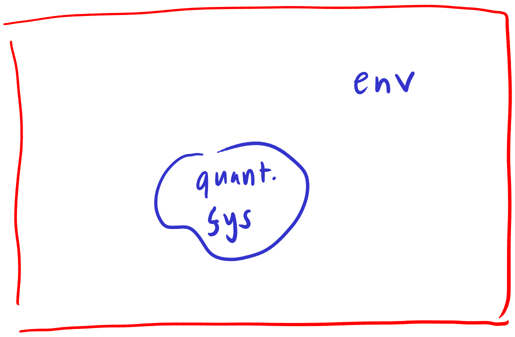
⇓

quantum mechanics:

GOAL: to derive a "quantum master equation" for a system coupled to environ. } open quantum systems

⇒ Lindblad-Kossakowski equation (1976)

⇒ foundation of our understanding of decoherence



interactions b/t env + system:

- example: "measurement" where this interaction leads to proj. sys onto one eigenstate
- in general: "generalized measurement" that does not lead to collapse onto one eigenstate

LAST PART: Open questions!

⇒ def'n of thermo quantities like work

⇒ meaning of "chaos" in QM + its relation to equilibration

Quantum stat. mech

return to the idea of <u>ensemble</u>:

many copies of the system prepared at $t=0$

classical ensemble: $P_n(0)$ = fraction of ensemble prepared in state n

quantum ensemble: $P_n(0)$ = frac. of ensemble prepared in quantum state $|\psi_n\rangle$

Here $\{|\psi_n\rangle\}$, $n = 1, 2, \ldots$ is some arbitrary set of quantum states in a Hilbert space

Note: $\{|\psi_n\rangle\}$ does not have to be orthogonal to each other, or form a complete

<u>but</u> we will require normalization:

$$\langle\psi_n|\psi_n\rangle = 1$$

copies:

$$\text{ensemble:} \quad \underbrace{|\psi_1\rangle \quad |\psi_1\rangle \quad |\psi_1\rangle}_{P_1(0)} \quad \underbrace{|\psi_2\rangle \quad |\psi_2\rangle}_{P_2(0)} \quad |\psi_3\rangle \cdots$$

probabilities:

$$P_n(0) \geq 0 \quad + \quad \sum_n P_n(0) = 1$$

Classical state n is charact. by a definite set of physical quantities: E_n, x_n, N_n, etc.

Quantum state $|\psi_n\rangle$ is different:

observable ($\hat{A}$ operator):

in state $|\psi_n\rangle$ the mean value $\langle A\rangle = \langle\psi_n|\hat{A}|\psi_n\rangle$

for a general ensemble:

$$\langle A\rangle = \sum_n p_n \langle\psi_n|\hat{A}|\psi_n\rangle$$

$\hat{A}$ is Hermitian, e-vecs $|a\rangle$ such that $\hat{A}|a\rangle = a|a\rangle$

↳ complete basis ↑ e-vals

$$\langle A\rangle = \sum_{n,a} p_n \langle\psi_n|\hat{A}|a\rangle\langle a|\psi_n\rangle$$

$\sum_a |a\rangle\langle a| = \hat{I}$

$$= \sum_{n,a} p_n\, a \langle\psi_n|a\rangle\langle a|\psi_n\rangle$$

$$= \sum_{n,a} a\, \underbrace{p_n\, |\langle a|\psi_n\rangle|^2}_{\text{two contrib. to prob:}}$$

- p_n from choosing state $|\psi_n\rangle$ from ensemble
- $|\langle a|\psi_n\rangle|^2$ prob. to get result a when doing measurement of A in state $|\psi_n\rangle$