Jarzynski equality

Recall that at equil,

$$Z = \int d\Gamma \, e^{-\underbrace{\beta}_{(k_B T)^{-1}} \underbrace{H(p,q)}_{\text{Hamiltonian}}}$$

↑ part'n f'n

$$\underbrace{F(T,V)}_{\text{free en}} = -k_B T \log Z$$

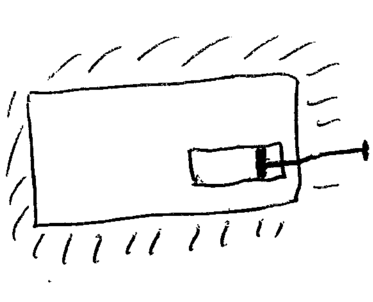
$$d\Gamma = \frac{d^3p_1 \dots d^3p_N \, d^3q_1 \dots d^3q_N}{(2\pi\hbar)^{3N}}$$

Thus $\frac{1}{Z} = e^{\beta F}$, and the prob. that the system resides around $d\Gamma$ is given by

$$\frac{1}{Z} e^{-\beta H(p,q)} d\Gamma = e^{\beta(F - H(p,q))} d\Gamma$$

Now, consider a thermally isolated macroscopic system. External forces can act on the small part of the system. ← so that work done on the system is ≪ its total energy

$$H = H(p, q, \lambda(t))$$



$\lambda_0 = \lambda(0)$ $\lambda(t_f)$

$t=0$ $t=t_f$

not unique!

So, at $t=0$: $H(p_0, q_0, \lambda_0) \equiv H_0$

at $t=t_f$: $H(p_f, q_f, \lambda(t_f)) \equiv H_f$

The work done on the system is given by

$$W = \underbrace{\int_0^{t_f} \frac{\partial H}{\partial \lambda} \frac{d\lambda}{dt} dt}_{\int_{\lambda_0}^{\lambda(t_f)} \frac{\partial H}{\partial \lambda} d\lambda} = H(p_f, q_f, \lambda(t_f)) - H(p_0, q_0, \lambda_0) = H_f - H_0 .$$

For ex., consider

$$H(q, \lambda) = \frac{q^2}{2} - \lambda q$$

HJ eq's: $\begin{cases} \frac{\partial H}{\partial p} = \dot{q}, \\ \frac{\partial H}{\partial q} = -\dot{p}. \end{cases}$

Average work: $\langle W \rangle = \langle H(p_f, q_f, \lambda(t_f)) - H(p_0, q_0, \lambda(0)) \rangle$

$\langle .. \rangle$ over many experiments performed with the same $\lambda(t)$

Now, consider

$$\langle e^{-\beta W} \rangle = \int \underbrace{e^{\beta(F_0 - H_0)}}_{\text{average over initial conditions of the bath}} e^{-\beta \overbrace{(H_f - H_0)}^{W}} d\Gamma_0 =$$

$$= e^{\beta F_0} \int d\Gamma_0 \, e^{-\beta H_f}$$

What to do next? Turns out we can replace $\int d\Gamma_0 \ldots \to$
$\to \int d\Gamma_f \ldots$

Consider canonical transforms:

$$\begin{cases} Q_i = Q_i(\{p\},\{q\},t) \\ P_i = P_i(\{p\},\{q\},t) \end{cases} \quad \text{s.t.} \quad \begin{cases} \dot{q}_i = \dfrac{\partial H(p,q)}{\partial p_i}, \\ \dot{p}_i = -\dfrac{\partial H(p,q)}{\partial q_i} \end{cases}$$

become
$$\begin{cases} \dot{Q}_i = \dfrac{\partial H'(P,Q)}{\partial P_i} \\ \dot{P}_i = -\dfrac{\partial H'(P,Q)}{\partial Q_i} \end{cases}$$

Recall that $\underset{\substack{\uparrow \\ \text{action}}}{S} = \int_{t_1}^{t_2} L\,dt = \overbrace{}^{(\sum_i p_i \dot{q}_i - H)dt}$

$$= \int \underbrace{\left(\sum p_i\, dq_i - H\,dt\right)}_{dS}$$

$\delta S = 0$ gives HJ eq's [easy to show]

So, we require

$$\delta \int \left(\sum_i p_i\, dq_i - H\,dt\right) = 0, \quad \text{"old"}$$

$$\delta \int \left(\sum_i P_i\, dQ_i - H'\,dt\right) = 0 \quad \text{"new"}$$

But then

$$\sum_i p_i\, dq_i - H\,dt = \sum_i P_i\, dQ_i - H'\,dt + d\underbrace{F}_{\substack{F(\{Q\},\{q\},t) \\ \text{some f'n}}}$$

So,

$$dF = \sum p_i dq_i - \sum P_i dQ_i + (H' - H)dt$$

$$\Downarrow$$

$$p_i = \frac{\partial F}{\partial q_i}, \quad P_i = -\frac{\partial F}{\partial Q_i}, \quad H' = H + \frac{\partial F}{\partial t}$$

Legendre transform:

$$\varphi = F + \sum P_i Q_i \qquad \varphi = \varphi(\{q\}, \{P\}, t)$$

$$d(F + \sum P_i Q_i) = \sum p_i dq_i + \sum Q_i dP_i + (H' - H)dt, \text{ or}$$

$$p_i = \frac{\partial \varphi}{\partial q_i} \qquad Q_i = \frac{\partial \varphi}{\partial P_i}$$

$$H' = H + \frac{\partial \varphi}{\partial t}$$

Finally, consider a transform from $p(t), q(t) \to p(t+\tau), q(t+\tau)$

Formally, $\begin{cases} q(t+\tau) = q(q(t), p(t), t, \tau), \\ p(t+\tau) = p(q(t), p(t), t, \tau) \end{cases}$

This transform is <u>canonical</u>:

Indeed,

$$dS = \sum (p(t+\tau) dq(t+\tau) - p(t) dq(t)) - [H(p(t+\tau), q(t+\tau)) - H(p(t), q(t))],$$

$$\underline{\underline{S = -F}}$$

Now, consider

$$\int dQ_1 \dots dQ_s \, dP_1 \dots dP_s = \int dq_1 \dots dq_s \, dp_1 \dots dp_s \; J,$$

where $J = \dfrac{\partial(Q_1 \dots Q_s \, P_1 \dots P_s)}{\partial(q_1 \dots q_s \, p_1 \dots p_s)}$ is the Jacobian.

E.g. $$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}.$$

One can show that

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(t,s)} \, \frac{\partial(t,s)}{\partial(x,y)}.$$

In our case,

$$J = \frac{\partial(Q_1 \dots Q_s \, P_1 \dots P_s)}{\partial(q_1 \dots q_s \, P_1 \dots P_s)} \Big/ \frac{\partial(\overset{q_1 \dots q_s}{p_1 \dots p_s})}{\partial(q_1 \dots q_s \, P_1 \dots P_s)} =$$

e.g. $\dfrac{\partial(Q,P)}{\partial(q,P)} = \begin{vmatrix} \frac{\partial Q}{\partial q} & \frac{\partial Q}{\partial P} \\ \frac{\partial P}{\partial q} & \frac{\partial P}{\partial P} \end{vmatrix} = \dfrac{\partial Q}{\partial q} - \dfrac{\partial Q}{\partial P} \underbrace{\dfrac{\partial P}{\partial q}}_{=0\,(?)}$, $\quad \underbrace{\dfrac{\partial P}{\partial P}}_{=1}$

$$= \underbrace{\frac{\partial(Q_1 \dots Q_s)}{\partial(q_1 \dots q_s)}\Bigg|_{\{P\}=\text{const}}}_{} \Big/ \frac{\partial(p_1 \dots p_s)}{\partial(P_1 \dots P_s)}\Bigg|_{\{q\}=\text{const}}$$

consists of $\dfrac{\partial Q_i}{\partial q_k} = \dfrac{\partial^2 \Phi}{\partial q_k \partial P_i}$ $\quad J_{ik} \rightarrow$

$$\frac{\partial p_i}{\partial P_k} = \frac{\partial^2 \Phi}{\partial q_i \partial P_k}$$

$\uparrow J_{ik}$

One ~~determinant~~ matrix is the transpose of the other $\Rightarrow$ dets same $\Rightarrow$

$$\Rightarrow J = 1$$

So, $\int d\Gamma_0 \to \int d\Gamma_f$, and

$$\langle e^{-\beta W}\rangle = e^{\beta F_0} \underbrace{\int e^{-\beta H_f} d\Gamma_f}_{e^{-\beta F_f}}$$

So, $$\boxed{\langle e^{-\beta W}\rangle = e^{-\beta \underbrace{\Delta F}_{F_f - F_0}}} \quad (*)$$

If the process is cyclic,

$$\lambda(t_f) = \lambda(0) \quad \Rightarrow \quad \Delta F = 0 \quad \Rightarrow \quad \langle e^{-\beta W}\rangle = 1.$$

indeed, $dE = dW + dQ \Rightarrow dW = dE - dQ = = dE - TdS = dF$
in a reversible isothermal process

Now recall that if λ changes slowly, the process is reversible, and $\langle W\rangle = \Delta F$. If λ changes rapidly, $S \uparrow$, and $\boxed{\langle W\rangle > \Delta F}$ (1)

If the subsystem on which the work is done is macroscopic, $N_S \gg 1$, we expect $\langle W\rangle \sim N_S$ and $\frac{|\delta W|}{\langle W\rangle} \sim \frac{1}{\sqrt{N_S}}$.

If fluctuations are neglected entirely,

$$\langle e^{-\beta W}\rangle = 1 - \beta\langle W\rangle + \frac{\beta^2}{2!}\langle W^2\rangle + \dots$$

$$e^{-\beta\langle W\rangle} = 1 - \beta\langle W\rangle + \frac{\beta^2}{2!}\langle W\rangle^2 + \dots$$

or: $W = \langle W\rangle + \delta W \Rightarrow \langle e^{-\beta W}\rangle = e^{-\beta\langle W\rangle} \underbrace{e^{-\beta \delta W}}_{\simeq 1}$

But $\langle \delta W^2 \rangle = \langle W^2 \rangle - \langle W \rangle^2 \approx 0$,
so $\langle W^2 \rangle \approx \langle W \rangle^2$.

So, $\langle e^{-\beta W} \rangle \approx e^{-\beta \langle W \rangle}$ in this case, and

$\langle W \rangle \approx \Delta F$, inconsistent with (1)

So, fluctuations cannot be neglected. Sometimes, $W \ll \langle W \rangle$ by chance, in which case $e^{-\beta W}$ is large & makes a substantial contribution to $\langle e^{-\beta W} \rangle$.

So, eq'n (*) is dominated by large (rare) fluctuations. $\Rightarrow$ need mesoscopic experimental systems to verify (*)

Finally, note that since

$$\langle e^{x} \rangle \geq e^{\langle x \rangle},$$

$$e^{-\beta \Delta F} = \langle e^{-\beta W} \rangle \geq e^{-\beta \langle W \rangle}$$

$$\Downarrow$$

$$\underline{\underline{\Delta F < \langle W \rangle}}.$$

---

when fluct's are small, we can expand (*) & compute the 1st fluctuation correction to ΔF:

$$\Delta F = -k_B T \log \langle e^{-\beta W} \rangle \underset{W = \langle W \rangle + \delta W}{\approx}$$

$$\approx -k_B T \log \left(e^{-\beta \langle W \rangle} \left(1 - \underbrace{\beta \langle \delta W \rangle}_{=0} + \frac{\beta^2}{2} \langle \delta W^2 \rangle \right)\right) =$$

$$= \langle W \rangle - \beta^{-1} \log \left(1 + \frac{\beta^2}{2} \langle \delta W^2 \rangle \right) \approx$$

$$\approx \langle W \rangle - \frac{\beta}{2} \langle \delta W^2 \rangle .$$

Crooks relations [G.E. Crooks]

Direct process: $\lambda^A(t)$

Reverse process: $\lambda^R(t) = \lambda^A(t_f - t)$

(runs from $\lambda(t_f)$ to λ_0 in reverse order)

Consider time evolution

$p_0, q_0 \to p_f, q_f$ in the phase space; work W is delivered during this process

The prob. of this process is

$$dP^A = e^{\beta(F_0 - H(p_0, q_0, \lambda_0))} d\Gamma_0$$

[system at equil. @ $t=0$]

For the reverse process, let us assume that the system is @ equilibrium with $\lambda = \lambda(t_f)$.

Now, consider initial conditions $-p_f, q_f$ @ $t=0$.

Since $H(-p, q) = H(p, q)$, [no magnetic field]

$$dP^R = e^{\beta(F_f - H_f)} d\Gamma_f$$

Clearly, $(p^R, q^R)\big|_t = (-p^A, q^A)\big|_{t_f - t}$

@ $t = t_f$ for the <u>reverse</u> process,

$(p^R, q^R)\big|_{t_f} = (-p_0, q_0) \Rightarrow H = H_0$,

and the work delivered is

$H_0 - H_f = -W$.

$$\text{So, } \frac{dP^A(W)}{dP^R(-W)} = \frac{e^{\beta(F_0 - H_0)} d\Gamma_0}{e^{\beta(F_f - H_f)} d\Gamma_f} =$$

$$= e^{\beta(\overbrace{H_f - H_0}^{W})} e^{-\beta(\overbrace{F_f - F_0}^{\Delta F^A})} \underbrace{\frac{d\Gamma_0}{d\Gamma_f}}_{=1 \text{ as before}}$$

$$\text{So, } \left[\frac{dP^A(W)}{dP^R(-W)} = e^{\beta(W - \Delta F^A)} \right]$$

Reversible process: in a macroscopic system $W \approx \langle W \rangle = \Delta F^A$,

and

$dP^A(W) = dP^R(-W)$.

Note that one can have $W = \Delta F^A$ in a non-equil. process, just by chance

Define $W_d = W - \Delta F^A \Leftarrow$ energy dissipation in a given realization of the process, "dissipated work"

$\langle W \rangle > \Delta F^A \Rightarrow \langle W_d \rangle > 0$,

but in some realizations one

may have $w_d < 0$.

Eq'n (*) can be written as

$$\langle e^{-\beta W_d} \rangle = 1$$

This is consistent with

$$e^{-\beta W} dP^A(W) = e^{-\beta \Delta F^A} dP^R(-W);$$

integrate over the phase space to get the $\langle \ldots \rangle$:

$$\langle e^{-\beta W} \rangle = \int dP^A(W) e^{-\beta W} =$$

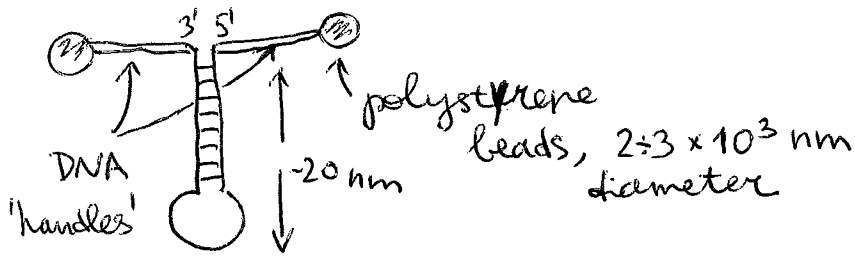
$$= e^{-\beta \Delta F^A} \underbrace{\int dP^R(-W)}_{=1}, \text{ or}$$

$$\langle e^{-\beta W_d} \rangle = 1.$$

Experiments with RNA molecules

(C. Bustamante, Berkeley)

Idea: measure work needed to fold/unfold a single-stranded RNA molecule:



immersed in aqueous solution

One bead anchored on a glass micropipette, the other one confined by an optical trap. You control the displacement of the RNA molecule (λ), and can measure forces acting on the bead.

Maximum unfolding (50–250 nm), max unfolding force (15–20 pN)

[Slow/fast deformations : 1–5 pN/s, 30–50 pN/s]

Typically, $W \simeq 50-200\ k_B T$,

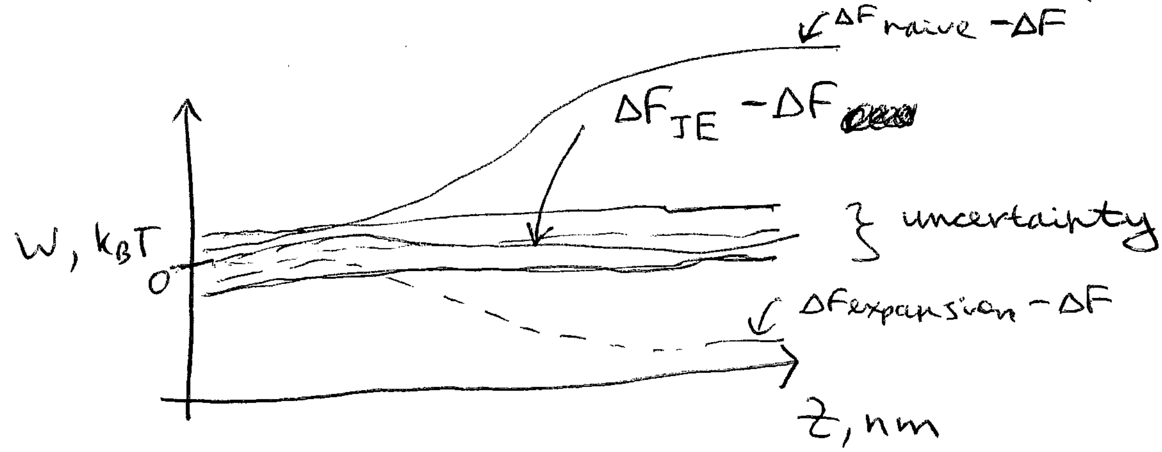
$W_d = W - \Delta F$ dissipated work

Can verify $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$ using this setup

First, compute $\langle e^{-\beta W} \rangle$ directly by doing irreversible exps

Second, unfold the molecule slowly (i.e. reversibly) to get $W_A^{rev} = \Delta F \approx 60\, k_B T$

Two deformation rates: 34 pN/s, 52 pN/s



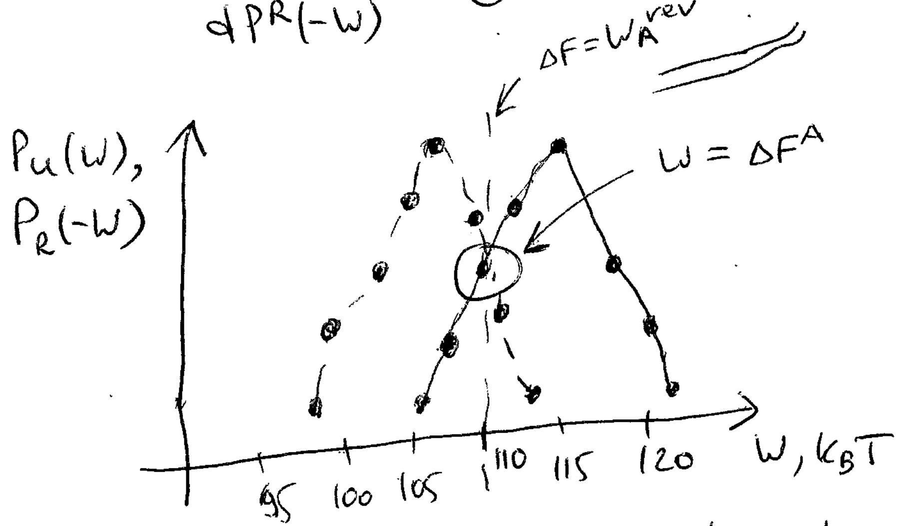
$$\Delta F_{JE} = -k_B T \log \langle e^{-\beta W} \rangle$$

$$\Delta F_{naive} = \langle W \rangle$$

$$\Delta F_{expansion} = \langle W \rangle - \frac{\beta}{2} \langle (\delta W)^2 \rangle$$

Can use the optical trap setup to verify Crooks ~~eq~~ equality:

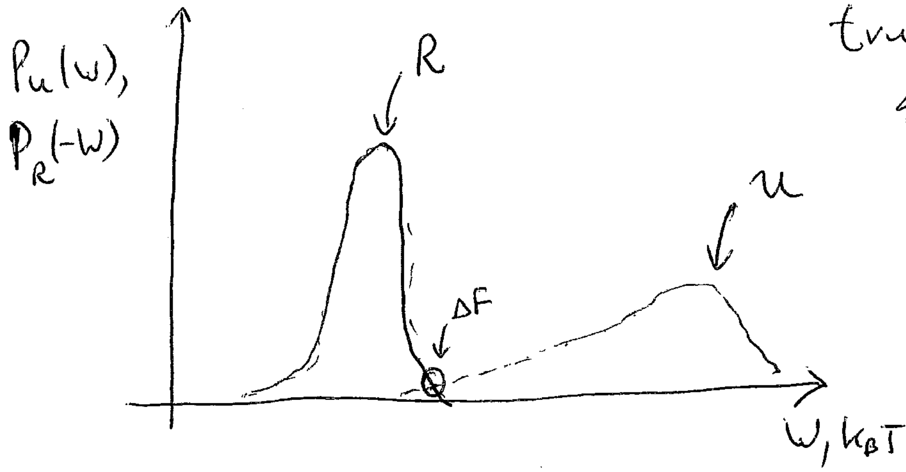
$$\frac{dP^A(W)}{dP^R(-W)} = e^{\beta(W - \Delta F^A)}$$



True for different deformation rates: 1.5 pN/s, 7.5 pN/s, 20 pN/s

$\Delta F = 110.3\, k_B T$ here

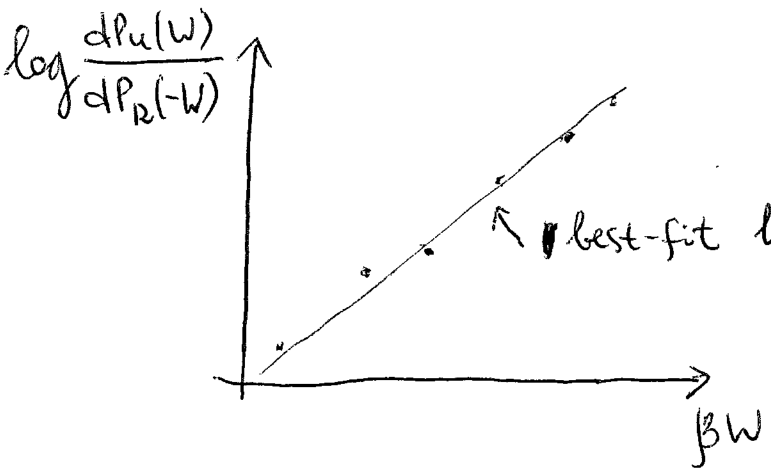
Nonequil. processes in nanosystems do not have to be gaussian:



true for WT & mutants

$$\log \frac{dP_u(W)}{dP_R(-W)} = \cancel{\quad} = \beta W - \beta \Delta F_u$$

slope ~~[illegible]~~ of 1 wrt βW



best-fit line: slope 1.06