Non-Equilibrium Work Theorem

aka "Jarzynski's equality": & Jarzynski, PRL 78:2690(1997)

\[ w = \int F(x) dx = \Delta U - Q \]

For slow, reversible processes:

\[ \Delta A = \Delta U - T \Delta S = \frac{w}{Q_{\text{rev}}} \]

For irreversible processes, \( w_{\text{irr}} > w_{\text{rev}} \) (otherwise violation of 2nd law). The overbar "" denotes averages over all possible paths.

Jarzynski's equality states that

\[ e^{-\frac{w}{T}} = e^{-\Delta A} \]

for any process, reversible or irreversible!

**Proof**: Consider switch of Hamiltonian over time \( t_s \)

So that at \( t=0 \), \( \lambda=0 \), \( H = H_0 \), state \( \Gamma(0) = \{ \bar{\phi}^0, \nu^0 \} \)

\( t = t_s \), \( \lambda = 1 \), \( H = H_1 \), state \( \Gamma(t_s) = \{ \bar{\phi}^1, \nu^1 \} \)

Probability \( P_0(\Gamma(0)) = \frac{\exp(-B H_0(\Gamma(0))}{\omega_0} \)

\[ \exp[-B W(t_s)] = \int d\Gamma(0) P_0(\Gamma(0)) \exp(-B W(t_s, \Gamma(0))) = \text{over all init states} \]

\[ = \int d\Gamma(0) \frac{\exp(-B H_0(\Gamma(0)))}{\omega_0} e^{-B W(t_s, \Gamma(0))} = \int d\Gamma(0) \frac{e^{-B H_0}}{\omega_0} \cdot \frac{e^{-B H_1 + B H_0}}{Q_0} = H_1 - H_0 \]
Now using that Hamiltonian equations of motion are area-preserving, 
\[ df(t) = df(0) = exp(-Bw(t)) = Sdf(t) e^{-\beta H_1(f(t))} \]
\[ Q_0 = \frac{Q}{Q_0} = exp(\delta A) \]

Limiting case (of fast switching) → wisdom insertion

Key limitation: If fluctuations in \( w \) over different paths are \( \Rightarrow KT \), average is dominated by rare events that we almost never sampled!

E.g. dense liquid 

\[ \implies large \Delta^2 \delta \]

\[ \Delta A = 0 \]

but \( w \gg 0 \)

for most attempts!


Bead \( \implies \) Bead

Stretch RNA using optically trapped beads; variable switching rate