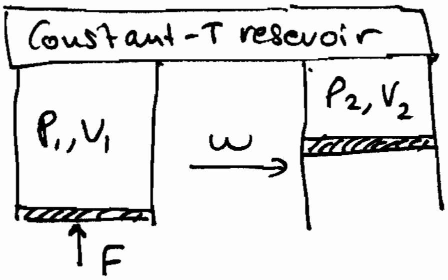
Non-Equilibrium Work Theorem

aka "Jarzynski's equality": { Jarzynski, PRL 78:2690(1997)
Crooks, J. Stat. Phys. 90:1481(1998)



$$w = \int F\,d\ell = \Delta U - Q$$

for slow, reversible processes:

$$\Delta A = \Delta U - \underbrace{T\Delta S}_{Q_{rev}} = w_{rev}$$

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

Jarzynski's equality states that $\boxed{\overline{e^{-\beta W}} = e^{-\beta\Delta A}}$

for any process, reversible or irreversible!

Proof: Consider switch of Hamiltonians over time t_s

So that at $t=0$ $\lambda=0$ $H=H_0$ State $\Gamma(0) = \{\vec{p}^N, \vec{r}^N\}_0$

$t=t_s$ $\lambda=1$ $H=H_1$ State $\Gamma(t_s) = \{\vec{p}^N, \vec{r}^N\}_{t_s}$

Probability $P_0[\Gamma(0)] = \dfrac{\exp(-\beta H_0(\Gamma(0)))}{Q_0}$

$$\overline{\exp[-\beta W(t_s)]} = \underbrace{\int d\Gamma(0)}_{\text{over all init states}} P_0\{\Gamma(0)\}\exp(-\beta W(t_s,\Gamma(0))) =$$

$$= \int d\Gamma(0)\frac{\exp(-\beta H_0(\Gamma(0)))}{Q_0}e^{-\beta W(t_s,\Gamma(0))} = \int d\Gamma(0)\frac{e^{-\beta H_0}}{Q_0}\cdot \underbrace{e^{-\beta H_1+\beta H_0}}_{\substack{\text{work} = \\ = H_1 - H_0}}$$

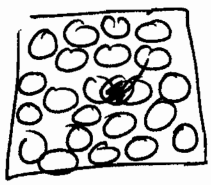
Now using that Hamiltonian equations of motion are area-preserving, $d\Gamma(t_s) = d\Gamma(0)$ $\Rightarrow$

$$\overline{\exp(-\beta W(t_s))} = \int d\Gamma(t_s)\, e^{-\beta H_1(\Gamma(t_s))}/Q_0 = \frac{Q_1}{Q_0} = \exp(-\beta\Delta A)$$

QED

Limiting case (of ∞ fast switching) $\rightarrow$ widom insertion

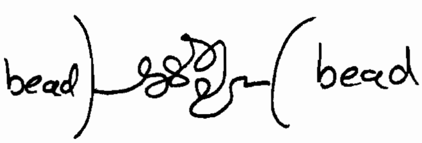
<u>Key limitation</u>: If fluctuations in W over different paths are $\gg kT$, average is dominated by rare events that are almost never sampled!

E.g.  $\rightarrow$ large $\Delta\vec{r}$  $\Delta A = 0$,

but $w \gg 0$ for <u>most</u> attempts!

dense liquid

<u>Experimental Validation</u>: Liphardt et al., Science, <u>296</u>: 1832 (2002)



Stretch RNA using optically trapped beads; variable switching rate