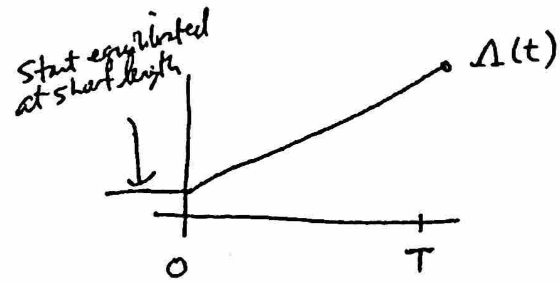
Nonequilibrium Work Relations

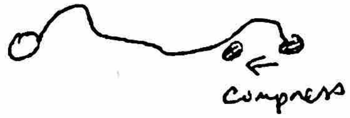
Experiment

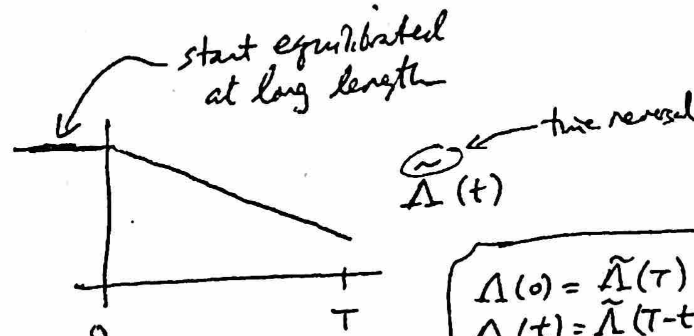
$\leftarrow \Lambda(t) \rightarrow$

a time-dependent protocol



Time-reversed experiment:





$$\boxed{\begin{aligned}\Lambda(0) &= \tilde{\Lambda}(T) \\ \Lambda(t) &= \tilde{\Lambda}(T-t)\end{aligned}}$$

These plots are only the time dependence of the controlled degree of freedom (Λ), but there is also a high-dimensional trajectory $\vec{x}(t)$ telling the positions of all the interior beads as a function of time.

How probable is any one possible $\vec{x}(t)$?

- The answer depends on the nature of the dynamics, i.e. are the beads moving according to Newton's laws? Or a Langevin dynamics that mimics the effect of solvent through random kicks?
  For the simplest illustration, we will assume Newton's laws (Hamiltonian dynamics).

Key Idea: Let's think not only of the time-reversal of protocols

$$\Lambda(t) \longleftrightarrow \tilde{\Lambda}(t)$$

but also of the time-reversed trajectories (remember, high dimensions)

$$\underline{\vec{x}(t)} \longleftrightarrow \underline{\tilde{\vec{x}}(t)}$$

Both pass through the exact same sequence of polymer configurations but in reversed order.

$$P(\vec{x}(t) \mid \Lambda(t)) = P_F(\vec{x}(t))$$

$$P(\tilde{\vec{x}}(t) \mid \tilde{\Lambda}(t)) = P_R(\tilde{\vec{x}}(t))$$

What is the relative probability of these two? $\dfrac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))}$

$$P_F(\vec{x}(t)) = \underbrace{\frac{e^{-\beta E(\vec{x}(0))}}{Q(\Lambda(0))}}_{\text{Probability of the initial condition } \vec{x}(0)} \times \underbrace{P(\vec{x}(t) \mid \Lambda(t), \vec{x}(0))}_{\text{Probability that a trajectory initialized at } \vec{x}(0) \text{ and subject to protocol } \Lambda(t) \text{ will yield } \vec{x}(t)\text{. For Hamiltonian dynamics this is like a delta function -- either 1 or 0.}}$$

$$P_R(\tilde{\vec{x}}(t)) = \frac{e^{-\beta E(\tilde{x}(0))}}{Q(\tilde{\Lambda}(0))} \times P(\tilde{\vec{x}}(t) \mid \tilde{\Lambda}(t), \tilde{\vec{x}}(0))$$

$Q(\Lambda(0))$ and $Q(\tilde{\Lambda}(0))$ are different!

$Q(\Lambda(0))$ is the normalization constant for all polymer configurations with Λ = short distance

$Q(\tilde{\Lambda}(0))$ is the normalization constant for all polymer configurations with Λ = long distance.

$$\Rightarrow \quad \frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))} = \frac{e^{-\beta E(\vec{x}(0))}/Q_{short}}{e^{-\beta E(\tilde{\vec{x}}(0))}/Q_{long}}$$

$$= \frac{e^{-\beta E(\vec{x}(0))}/Q_{short}}{e^{-\beta E(\vec{x}(T))}/Q_{long}}$$

Is $E(\vec{x}(0))$ the same as $E(\vec{x}(T))$ for Hamiltonian dynamics?

Careful! Because we're controlling $\Lambda(t)$, we can do work on the system, adding or removing energy.

$E(\vec{x}(T)) - E(\vec{x}(0)) = W$ done on the system over time T.

$$\frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))} = e^{\beta W[x(t)]} e^{-\beta \Delta A} \quad \text{, where} \quad \frac{Q_{long}}{Q_{short}} = e^{-\beta \Delta A}$$

$$\boxed{\Delta A = A(\text{long}) - A(\text{short}) = W_{rev}(\text{short} \to \text{long}) = -k_B T \ln \frac{P(\text{long})}{P(\text{short})}}$$

ΔA is the reversible work, but $W[\vec{x}(t)]$ is the work measured in trajectory $\vec{x}(t)$, which was driven non-reversibly by protocol $\Lambda(t)$!

We now have the relationship

$$\frac{P_F(\vec{x}(t))}{P_R(\tilde{\vec{x}}(t))} = e^{\beta W_{diss}[\vec{x}(t)]}$$

dissipated work for trajectory $\vec{x}(t)$.

We'd like to re-express the left-hand side in terms of the work. What's the difference?

$P_F(\vec{x}(t))$ is super high dimensional

Specifies the locations of every monomer at every moment of time

$$P_F(W) = \underbrace{\int d\vec{x}(t)\, P_F(\vec{x}(t))\, \delta(W - W[\vec{x}(t)])}$$ is a function of one variable

Add up the probability of every possible trajectory $\vec{x}(t)$ that yields work W. W is ~~actual~~ a collective variable of the trajectory.

$$= \int d\vec{x}(t)\, P_R(\tilde{\vec{x}}(t))\, e^{\beta W_{diss}[\vec{x}(t)]}\, \delta(W - W[\vec{x}(t)])$$

$$= e^{\beta(W - \Delta A)} \int d\vec{x}(t)\, P_R(\tilde{\vec{x}}(t))\, \delta(W - W[\vec{x}(t)])$$

$\downarrow$ Change of variables – Instead of summing over forward paths $\vec{x}(t)$, sum over time-reversals

$$= e^{\beta W_{diss}} \int d\tilde{\vec{x}}(t)\, P_R(\tilde{\vec{x}}(t))\, \delta(W + W[\tilde{\vec{x}}(t)])$$

Time-reversal flips the sign of work

$$= e^{\beta W_{diss}}\, P_R(-W)$$

from that sign flip

$$\Rightarrow \boxed{\frac{P_F(W)}{P_R(-W)} = e^{\beta W_{diss}}}$$

Or for a cyclic protocol with $F = R$ and $\Delta A = 0$,

$$\frac{P(W)}{P(-W)} = e^{\beta W}.$$