Far-from-equilibrium Statistical Dynamics of Small Systems: Past, Present & Future

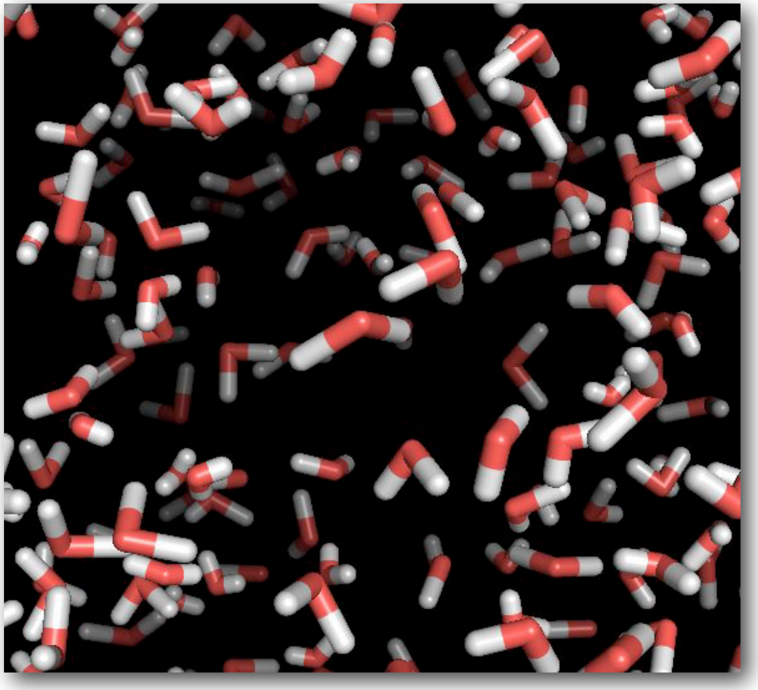
Forward Through Backwards Time by RocketBoom

Gavin E. Crooks

The Past

Life is divided into three periods: that which has been, that which is, that which will be.

Seneca the Younger



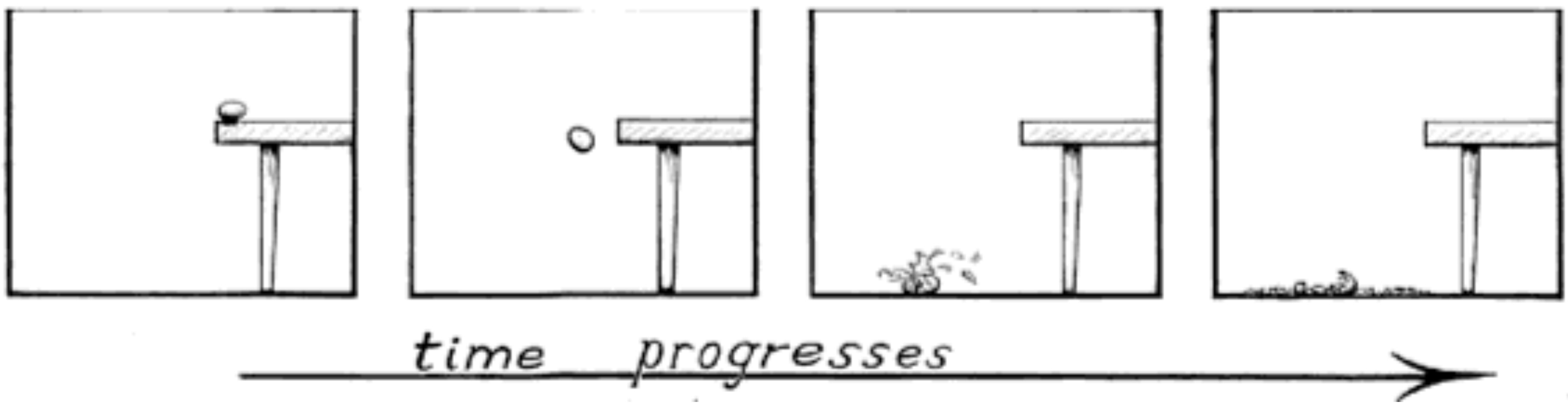
Thermodynamic Equilibrium:
Future, past and present are indistinguishable

The 2nd Law of Thermodynamics

Clausius inequality
(1865)

$$\Delta S_{\text{total}} \geq 0$$

Total Entropy
increases
as time progresses



Cycles of time
R.Penrose (2010)

The (improved) 2nd Law of Thermodynamics

Clausius inequality
(1865)

Jarzynski Identity
(1997)

$$\langle \Delta S_{\text{total}} \rangle \geq 0$$

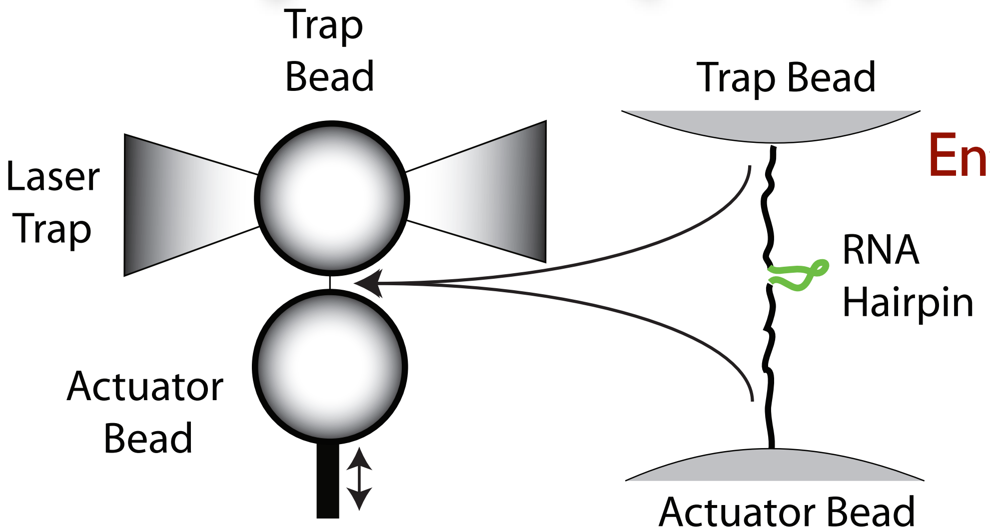
$$\left\langle e^{-\Delta S_{\text{total}}} \right\rangle = 1$$

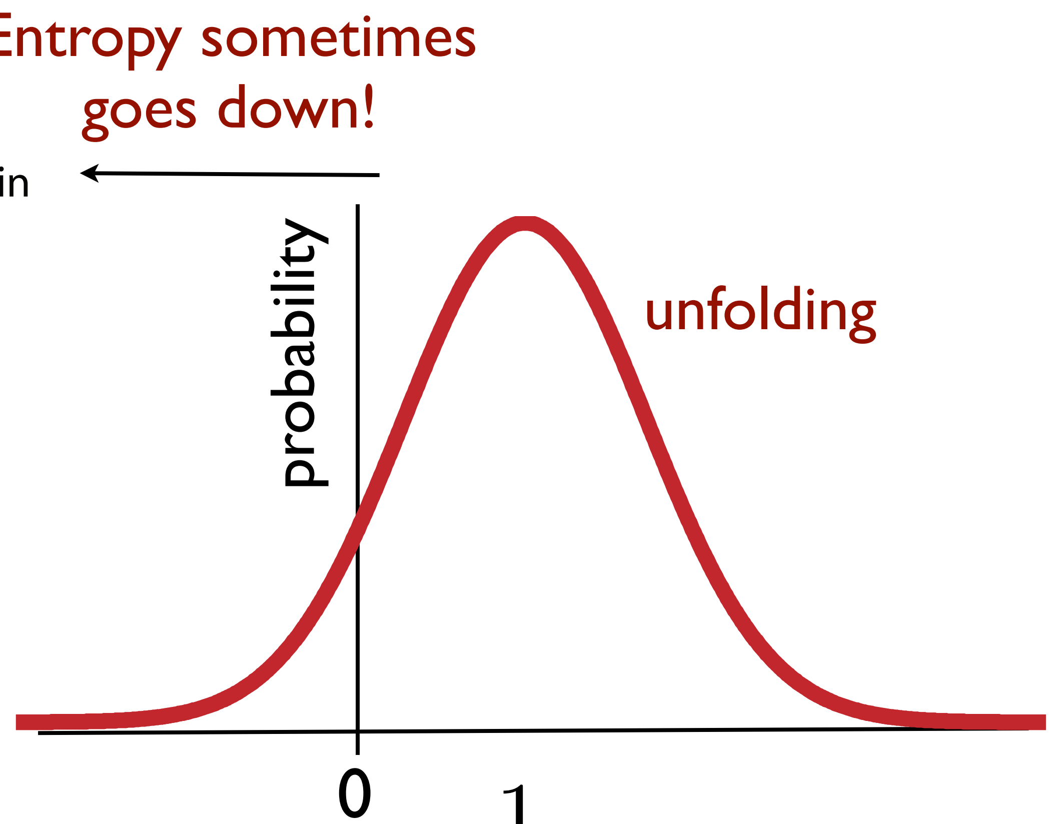
equality only for
reversible process

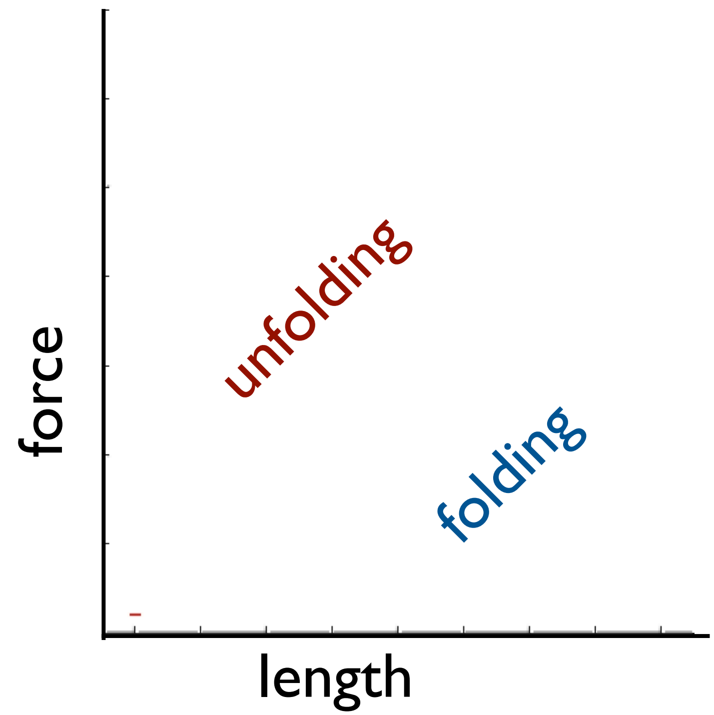
equality far-from-equilibrium

$$\Delta S_{\text{total}} = \frac{1}{T}(W - \Delta F)$$

Experiments (c2000): unfolding of RNA hairpins.





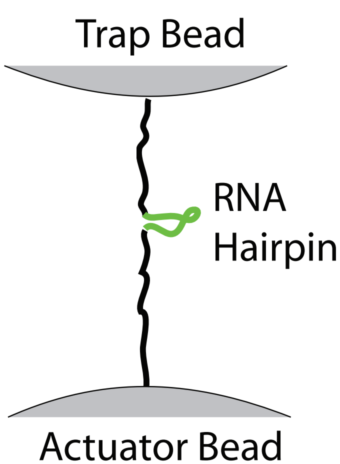


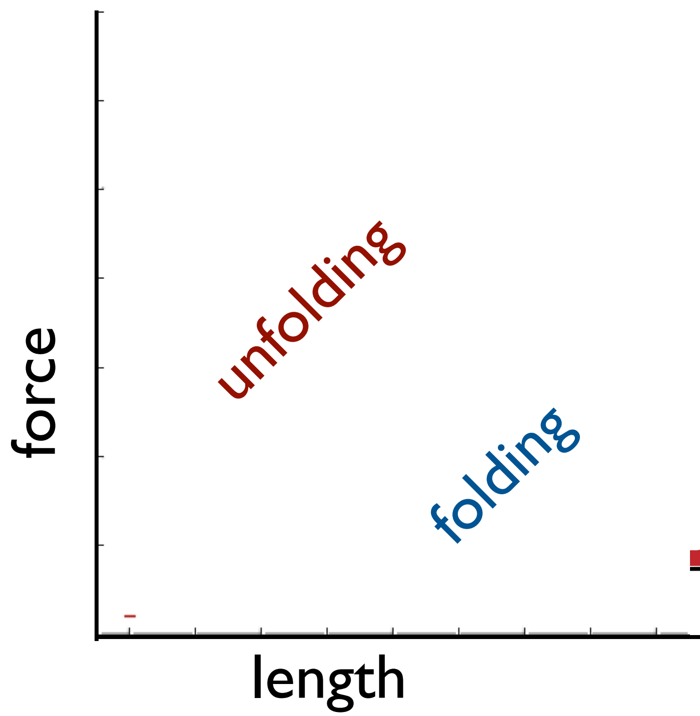
$$\Delta S_{\text{total}} = \frac{1}{T}\left(W - \Delta F\right)$$

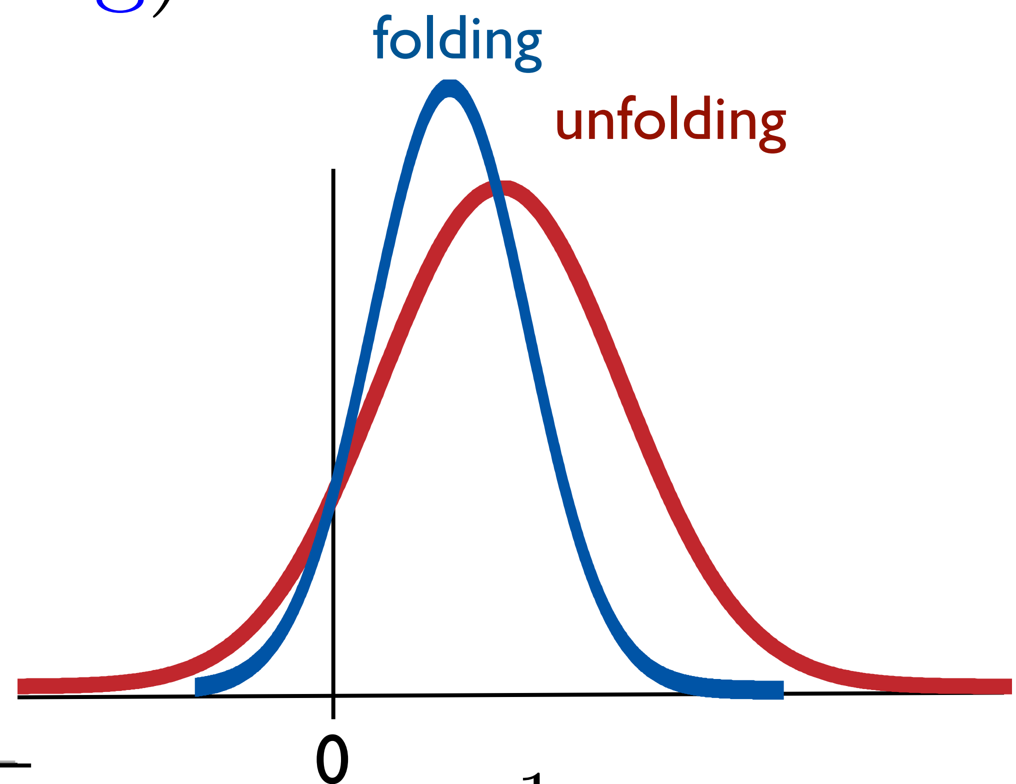
total entropy change — temperature — work — free energy change

Fluctuation Theorems (c1993-1999)

$$\frac{P(+\Delta S_{\mathrm{total}}|\mathrm{unfolding})}{P(-\Delta S_{\mathrm{total}}|\mathrm{folding})} = e^{\Delta S_{\mathrm{total}}}$$







$$\Delta S_{\mathrm{total}} = \frac{1}{T}(W - \Delta F)$$

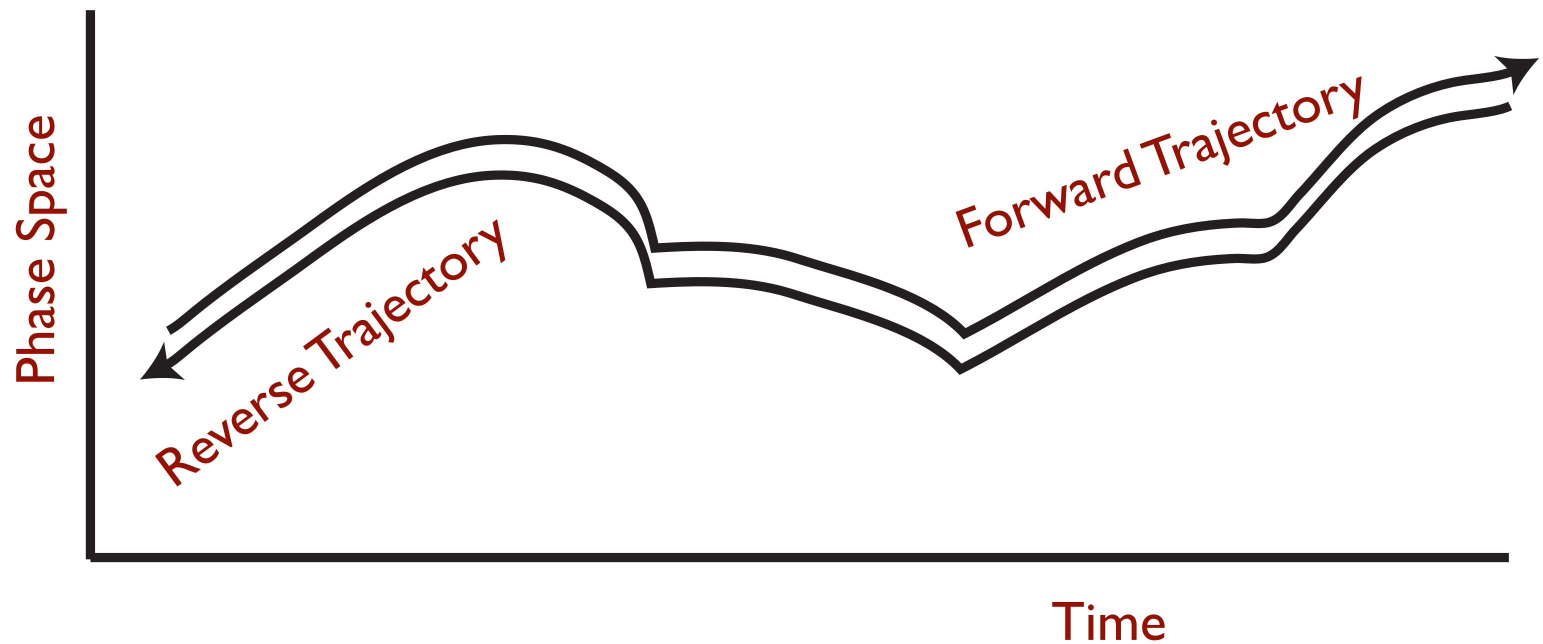
Dissipation (entropy increase) breaks time-reversal symmetry

$$\frac{P[\text{trajectory}]}{P[\text{time reversed trajectory}]} = e^{\text{dissipation}} = e^{\beta W - \beta \Delta F}$$

Work

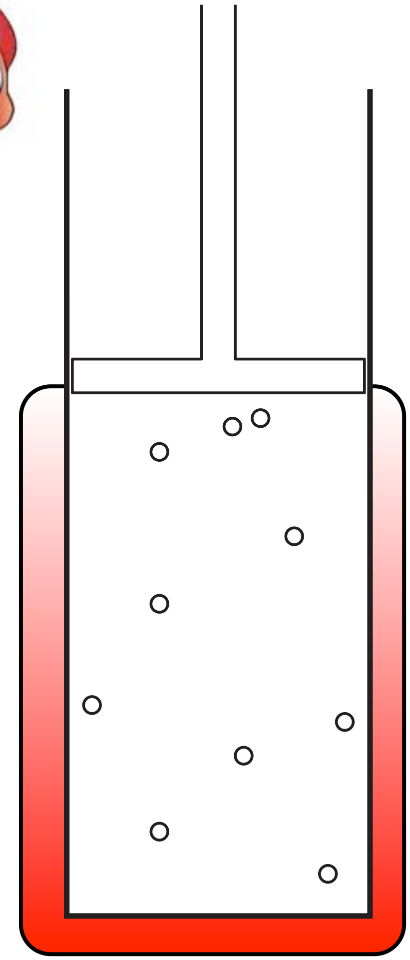
Free Energy Change

Inverse Temperature



Feedback Fluctuation Theorems (c2010)

$$\left\langle e^{-\frac{1}{T}(W-\Delta F)-I} \right\rangle = 1$$

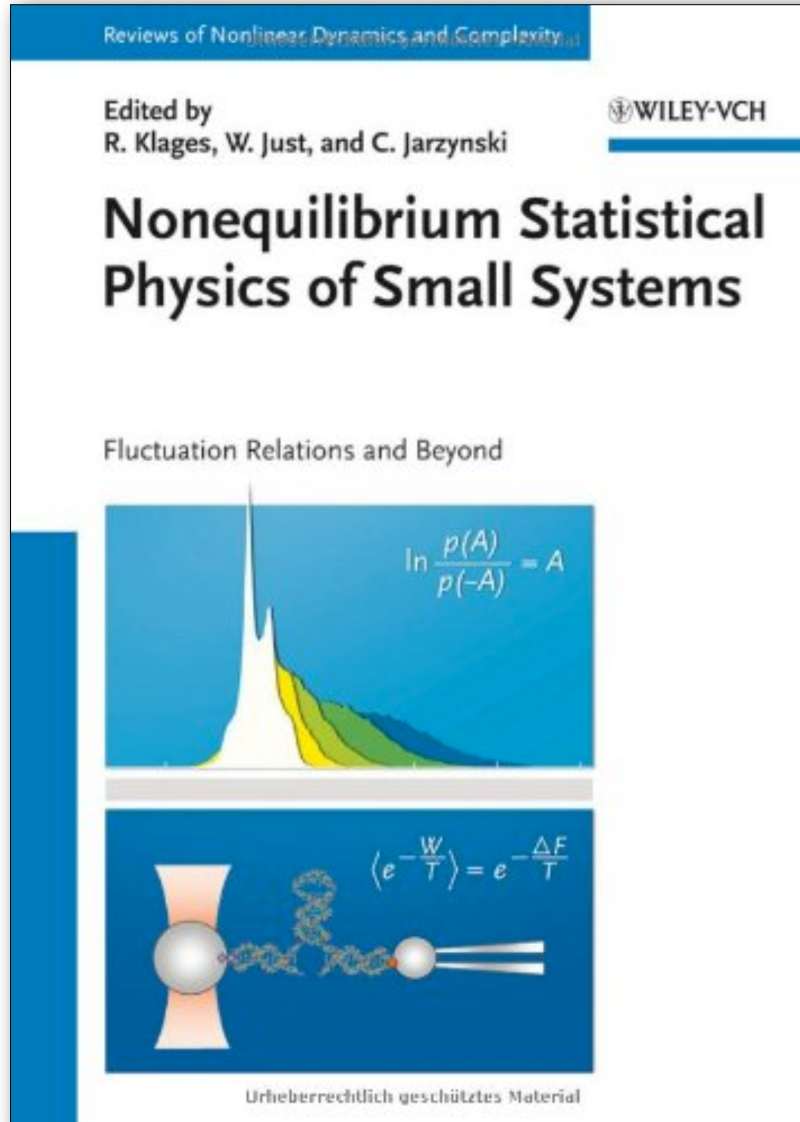


Demon-system information

Sagawa & Ueda (2008) (2010)
Horowitz & Vaikuntanathan (2010)

The Present

Of these the present is fleeting,
the future is doubtful,
the past is certain.
Seneca the Younger



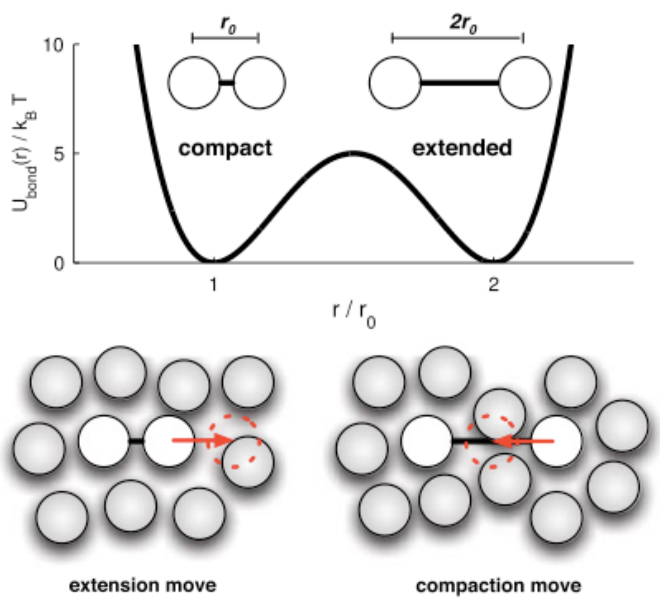
What have we learned?

$$\langle e^{-\Delta S_{\text{total}}} \rangle = 1$$

- Exact, general relations for driven systems, far-from-equilibrium
- Fluctuations matter
- *Trajectories* primary objects (rather than *states*)
- Entropy change breaks time reversal symmetry, quantitatively.
- Relevant at small dissipation (<10s kT)
- Coupled systems: Information flow is as important as work and heat flow.

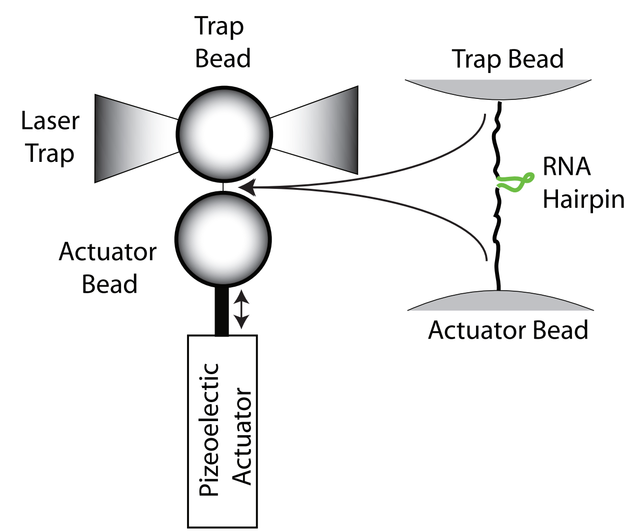
Where are we useful?

computer simulations



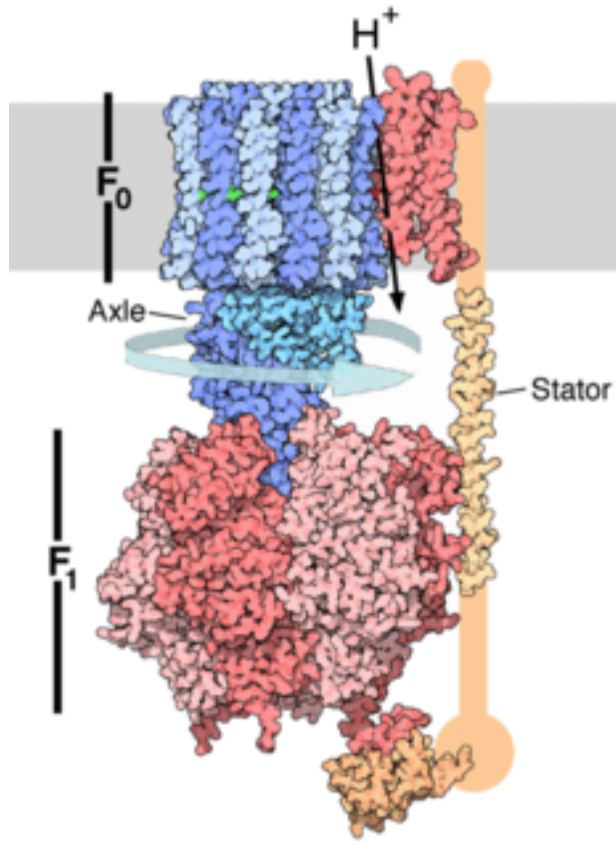
(e.g. Free energy calculations, Nonequilibrium candidate Monte Carlo, Langevin dynamics simulation)

experiments



Free energies of unfolding

The Future



It's tough to make predictions, especially about the future.

Yogi Berra

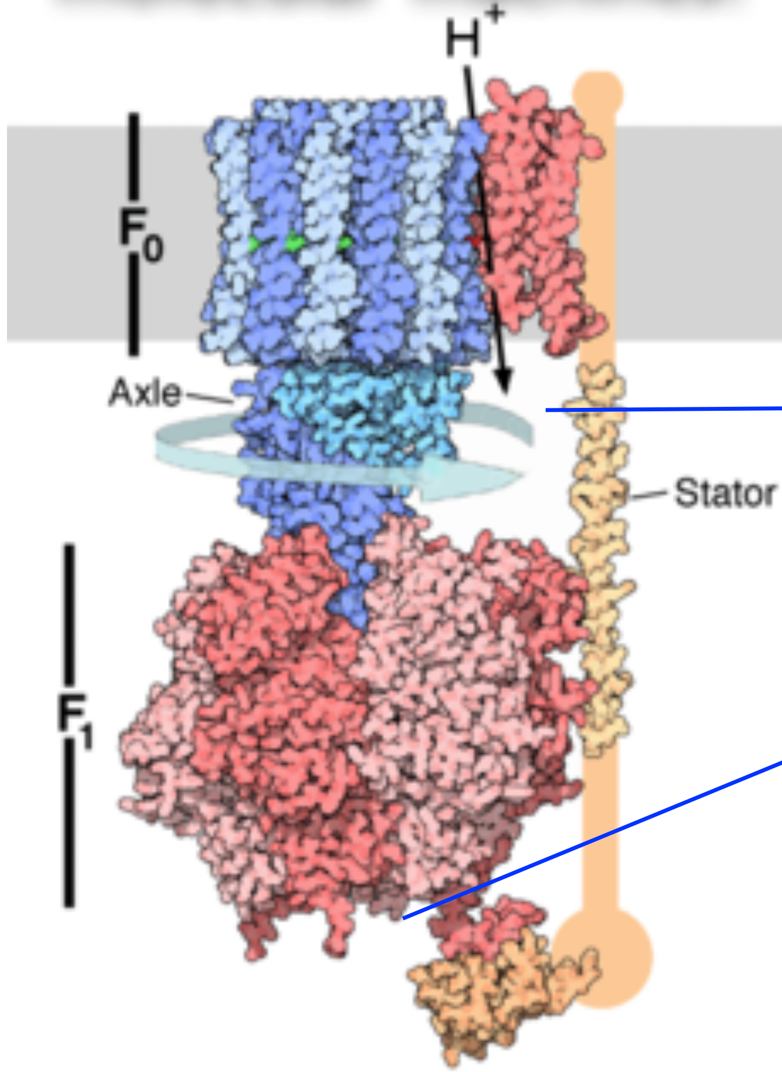
What are the fundamental operational principles of molecular machines?

information processing

"info-engine"

$1\ kT = 25\ meV$

$= 2.5\ kJ/mol$



proton gradient

mechanical energy

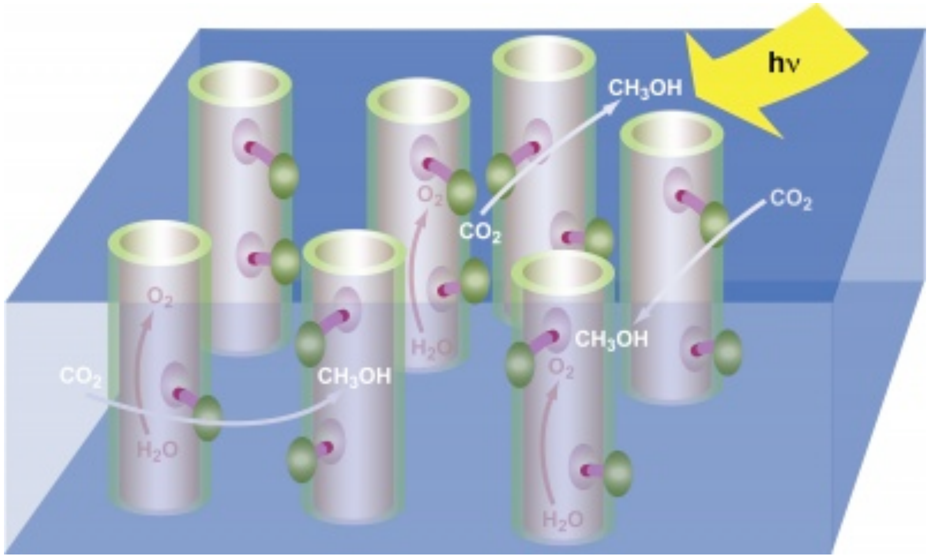
chemical energy

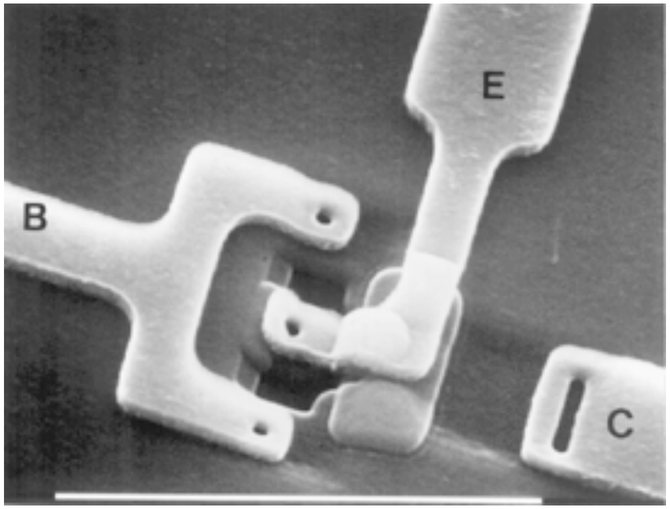
ATP synthase

Free Energy ATP = 20 kT

= 0.5 eV

Gavin E. Crooks



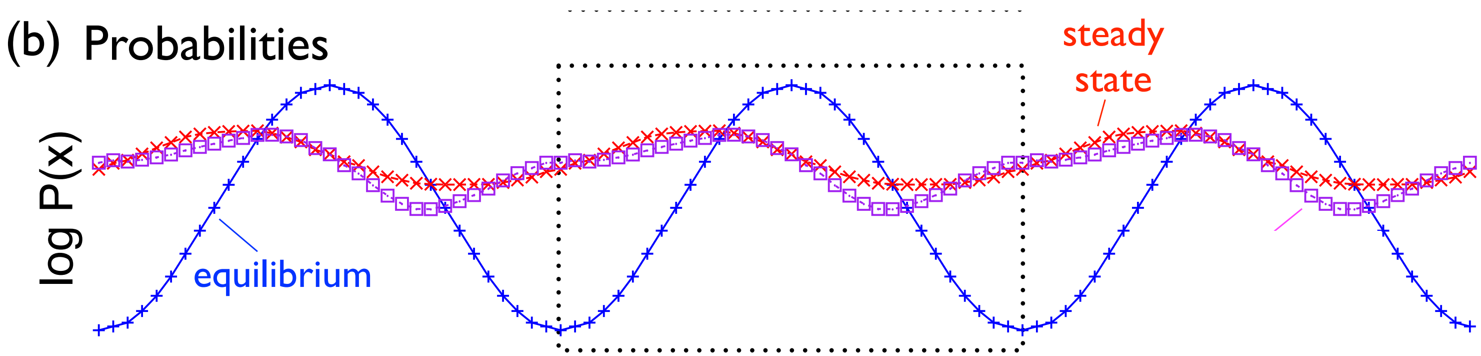


nano-scale
engineering

low energy
computation

(1) The Measurement Problem

- Example: Hanata-Sasa Relation



Fluctuation theorem for transitions between steady states.

Total heat = Housekeeping heat + Excess Heat

Hatano & Sasa (2001)
Massimiliano & Van den Broeck (2010)
"Three detailed fluctuation theorems"

(1) The problem of measuring entropy out-of-equilibrium

$$S = -\sum_i p_i \ln p_i$$

1 natural unit of entropy
equivalent to
1 kT of thermal energy

T : Temperature (ambient 300K)
k : Boltzmann's constant

1 kT = 25 meV
= 2.5 kJ/mol
= 0.6 kcal/mol

(2) Not-so-near equilibrium statistical dynamics?

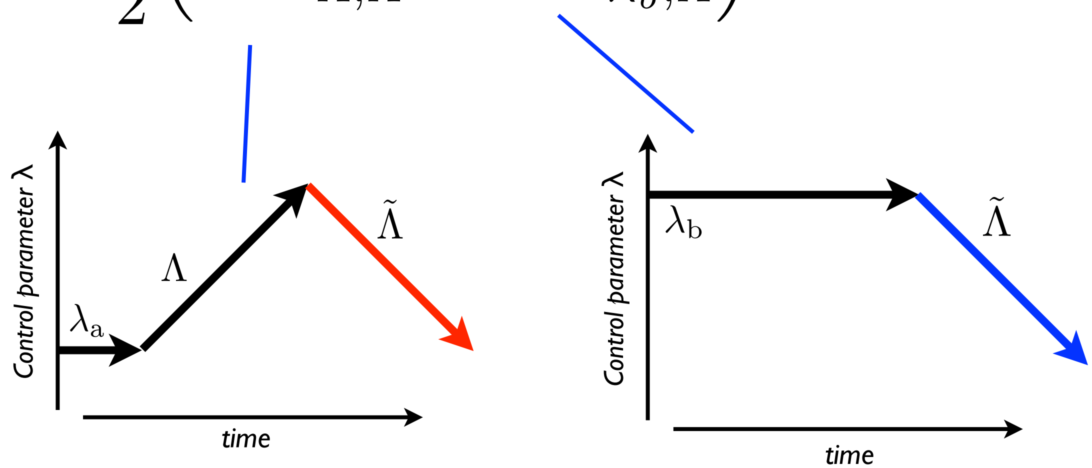
Thermodynamic Equilibrium	Near equilibrium	Not-so-near equilibrium?	Far from equilibrium
Statistical mechanics	Linear Response	Almost-linear response?	Fluctuation theorems, Jarzynski equality
(c1900)	(1950s)	(<2034?)	(1990s)

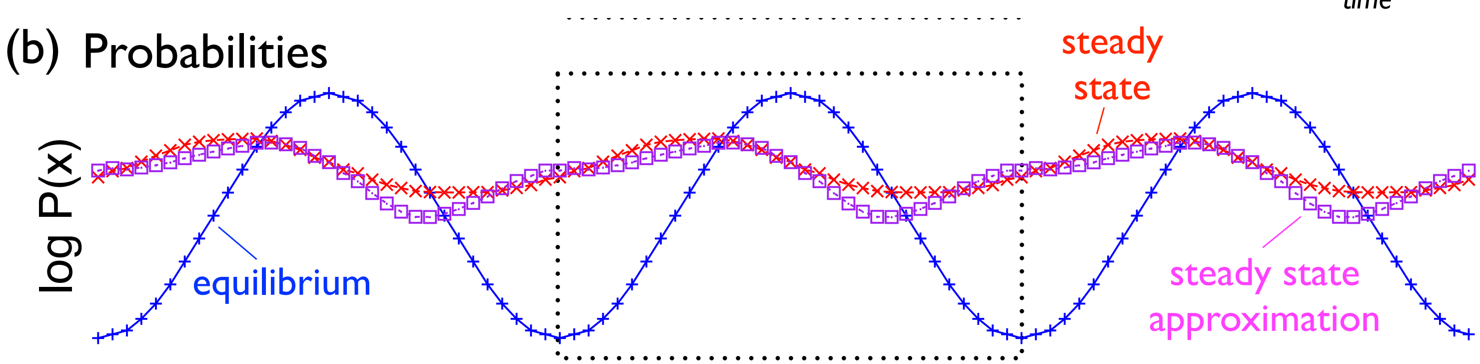
Near-equilibrium measurements of free energy

- Practical method for measuring free energies in near-equilibrium regime. Applicable to existing single-molecule experiments

Free energy change — Mean Excess Work

$$F_{\lambda_a,\Lambda} - F_{\lambda_b} \approx -\frac{1}{2}\left(\langle\mathcal{W}\rangle_{\Lambda;\widetilde{\Lambda}} - \langle\mathcal{W}\rangle_{\lambda_b;\widetilde{\Lambda}}\right)$$





(3) Optimization principles

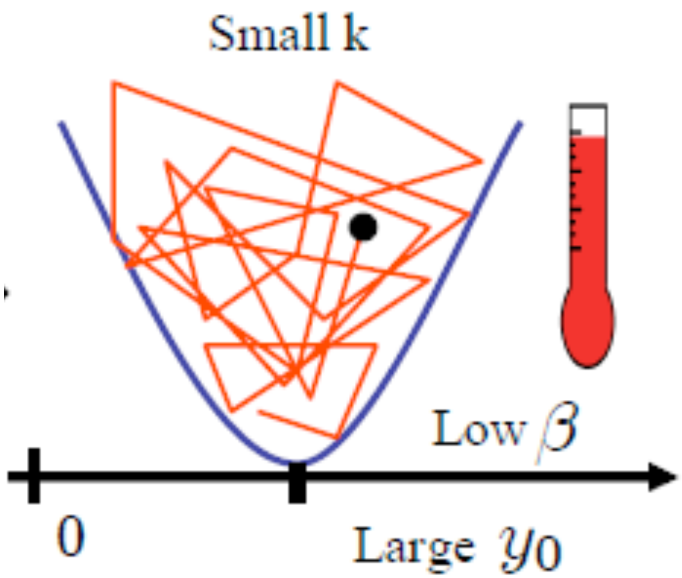
- How does one design a machine to:
  minimize dissipation?
  maximize rate (or power)?
  maximize fidelity?

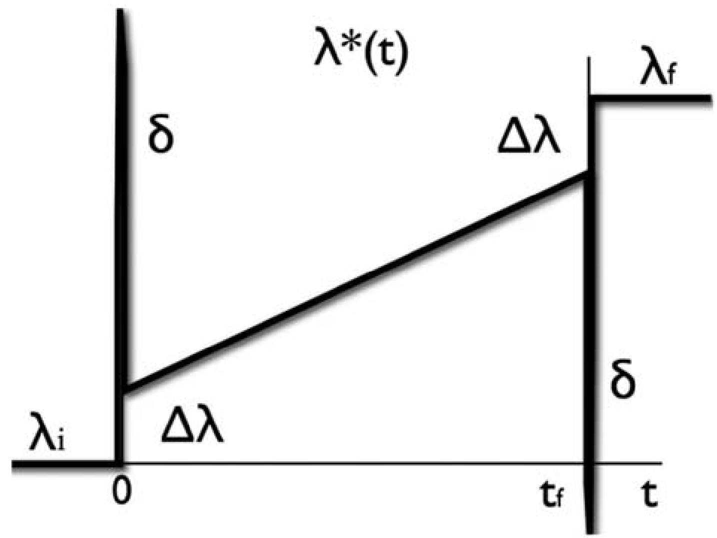
  rate / dissipation / fidelity tradeoff?

- What are the optimal principles relevant to operation of biological molecular machines?

ATP synthase

Minimum dissipation protocols





Schmiedl & Seifert PRL (2007)

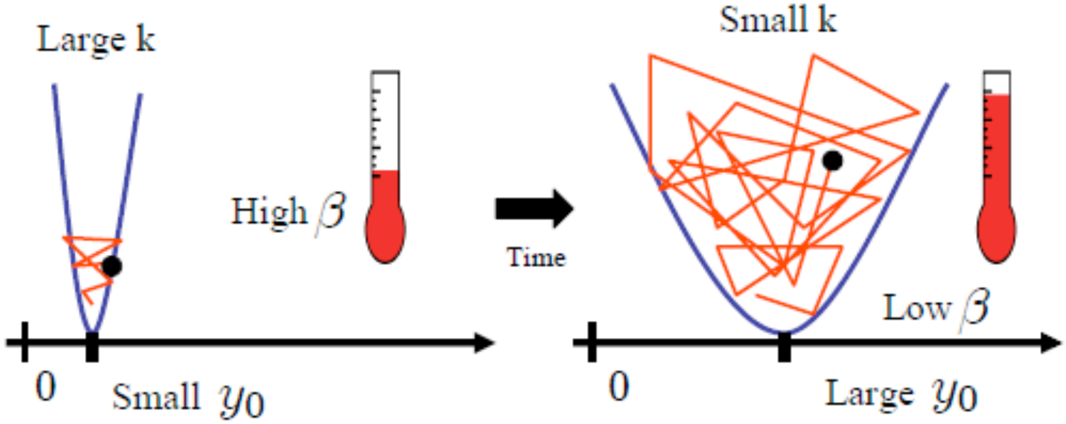
Geometry of thermodynamic control

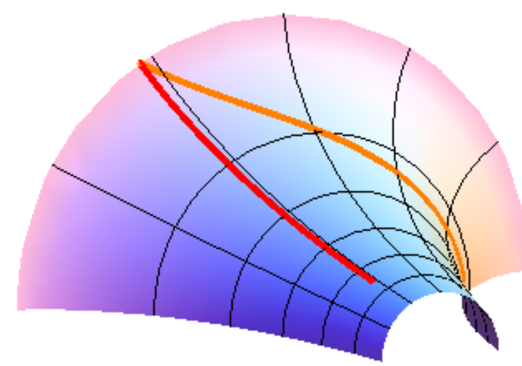
- Finite time thermodynamics with linear response friction tensor
- Riemannian metric, minimum dissipation paths are *geodesics*

nonequilibrium excess power imposed by protocol Λ

linear response friction tensor

$$\mathcal{P}^{\mathrm{ex}}_{\Lambda}(t_0) = \left[\frac{\mathrm{d}\boldsymbol{\lambda}^T}{\mathrm{d}t}\right]_{t_0} \cdot \zeta\big(\boldsymbol{\lambda}(t_0)\big) \cdot \left[\frac{\mathrm{d}\boldsymbol{\lambda}}{\mathrm{d}t}\right]_{t_0}$$

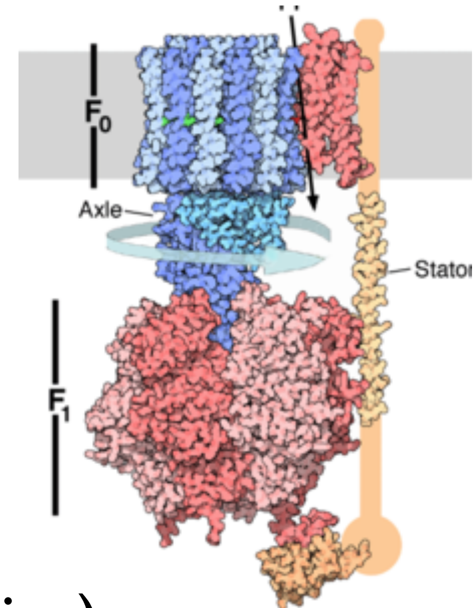




Hyperbolic geometry

Sivak & Crooks, *Phys. Rev. Lett.*, 2012
Zulkowski, Sivak, Crooks & DeWeese Phys. Rev. E 2012

The future: Summary



- What are the fundamental operational principles of molecular scale machines?
  - (1) How do we measure entropy (and probabilities) away from thermodynamics equilibrium
  - (2) Not-so-near equilibrium, almost linear response?
  - (3) Optimization principles
    - rate / dissipation / fidelity tradeoff?
    - minimum dissipation protocols

Time flies like an arrow; Fruit flies like a banana Groucho Marks