Nonequilibrium thermodynamics at the microscale

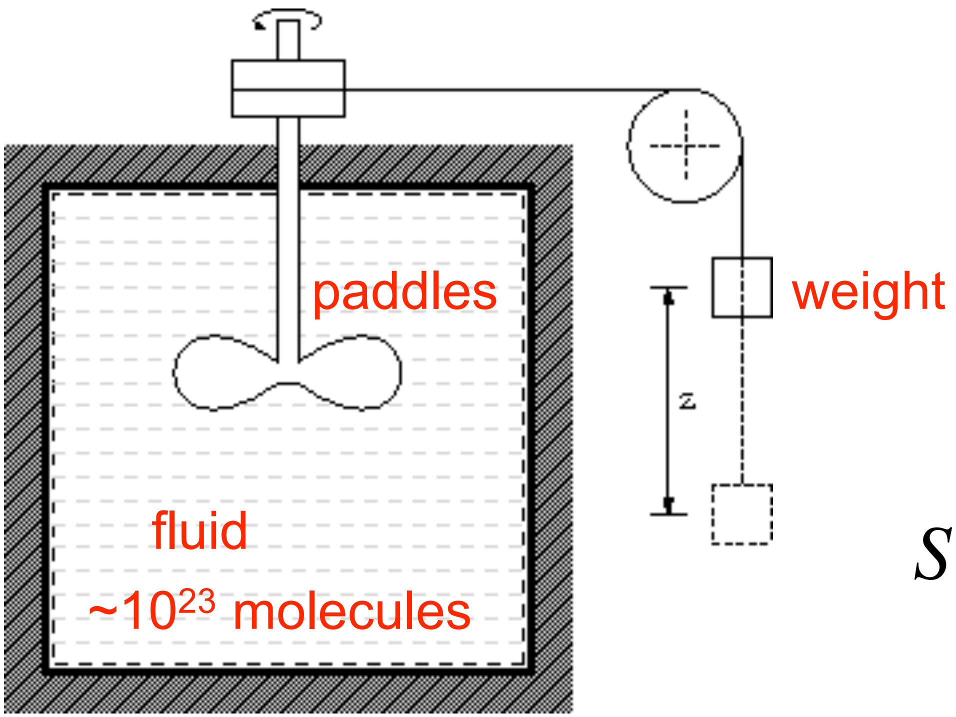
C. Jarzynski

T-13 Complex Systems , LANL

- The entropy of a closed system never decreases.
- Clausius inequality
- Carnot limit on the efficiency of heat engines

LAUR-05-2386

The entropy of a closed system never decreases.

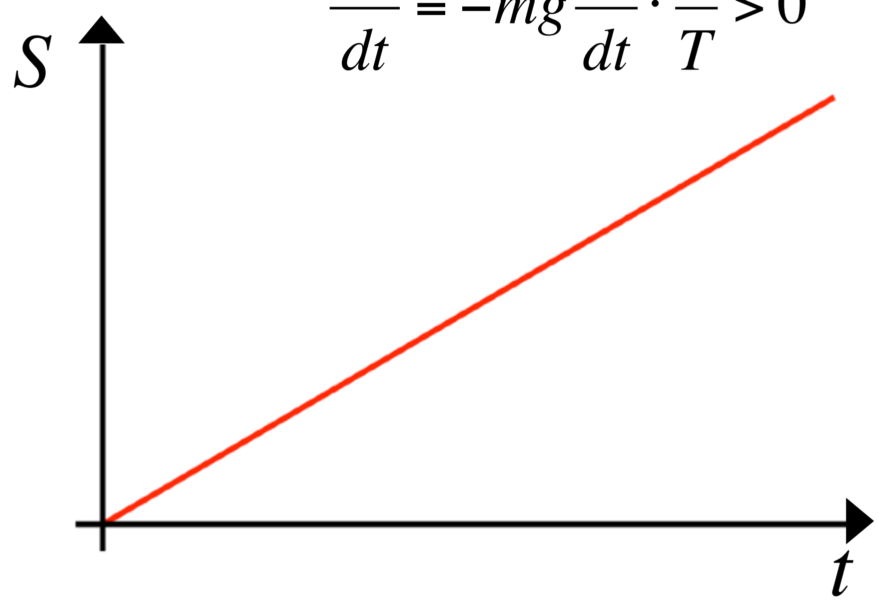


Joule experiment
(1845)

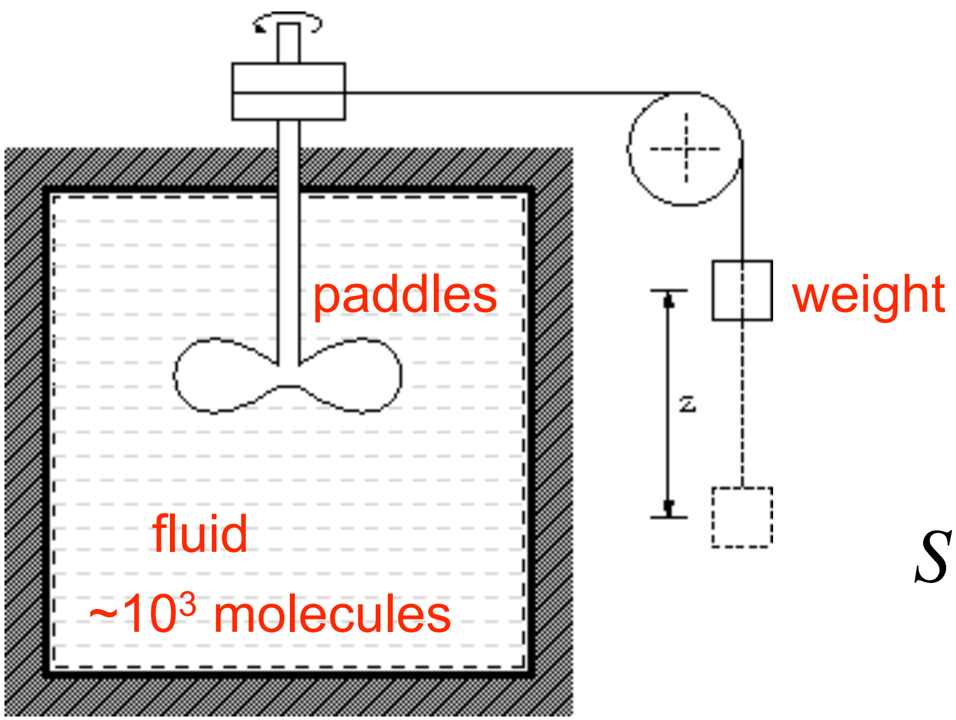
potential energy of weight

→ thermal energy of fluid

$$\frac{dS}{dt} = -mg\frac{dz}{dt} \cdot \frac{1}{T} > 0$$

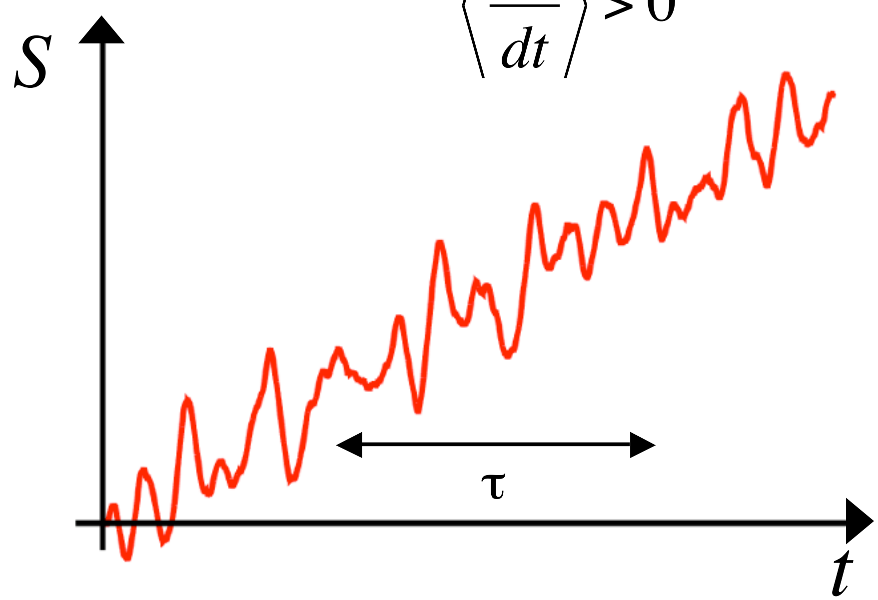


Scale down to the microscopic level …



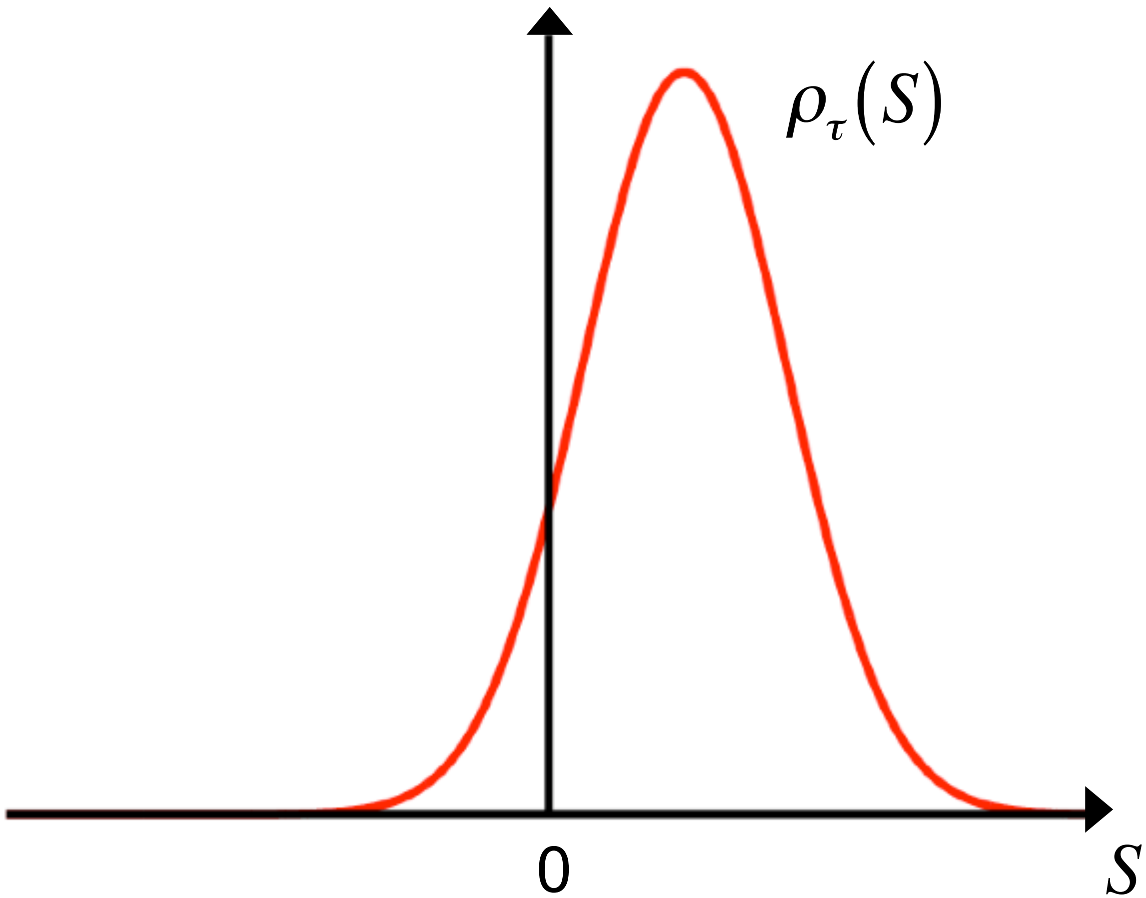
potential energy of weight → thermal energy of fluid

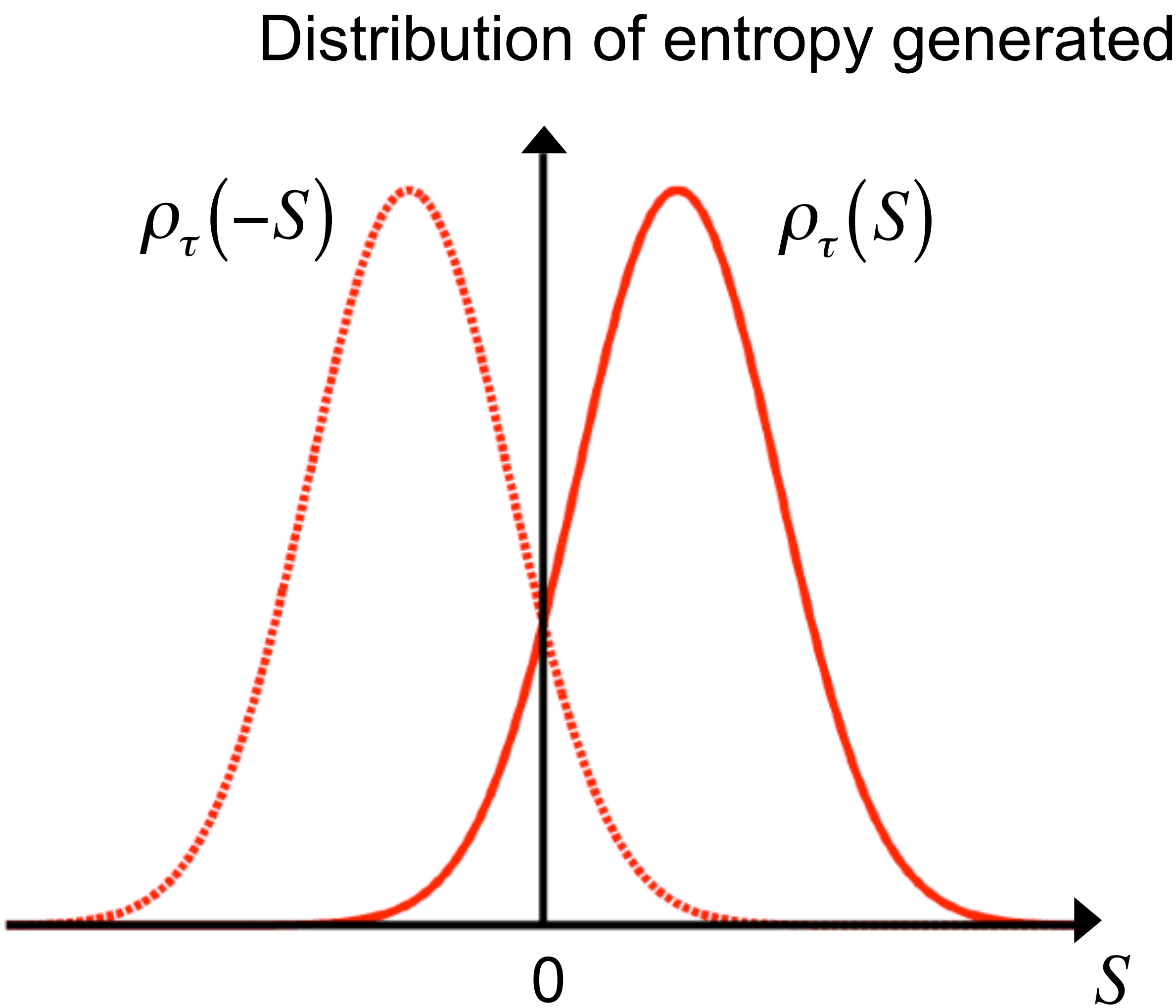
$$\left\langle \frac{dS}{dt} \right\rangle > 0$$



Quantify the fluctuations!

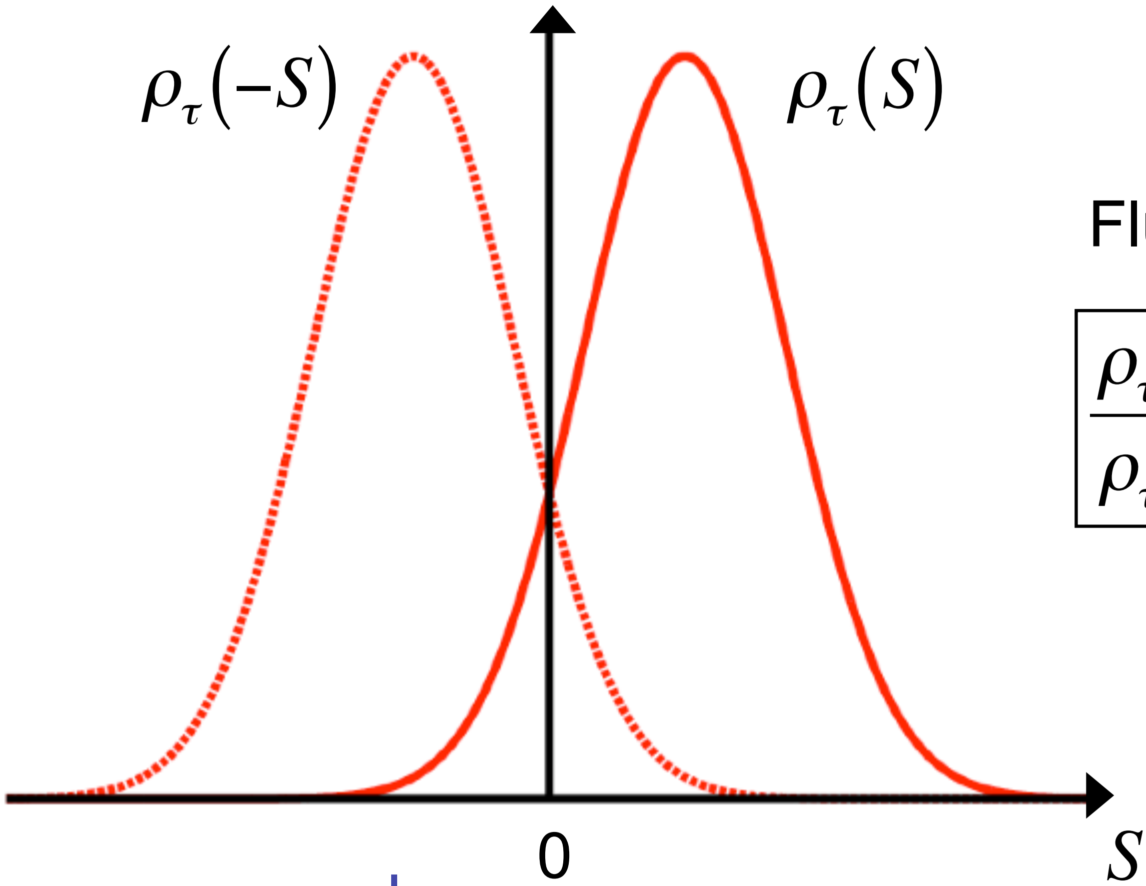
Distribution of entropy generated





Distribution of entropy generated
$\rho_\tau(-S)$
$\rho_\tau(S)$
0
S

Distribution of entropy generated



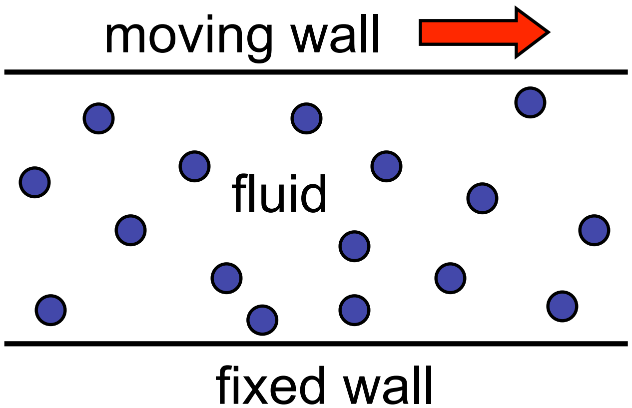
Fluctuation Theorem

$$\frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp(S/k_B)$$

- very general
- valid far from equilibrium
- reduces to linear response near equilibrium

Evans & Searles, PRE 1994
Gallavotti & Cohen PRL 1995
Kurchan, 1998
Lebowitz & Spohn, J Stat Phys 1999
+ *many* others

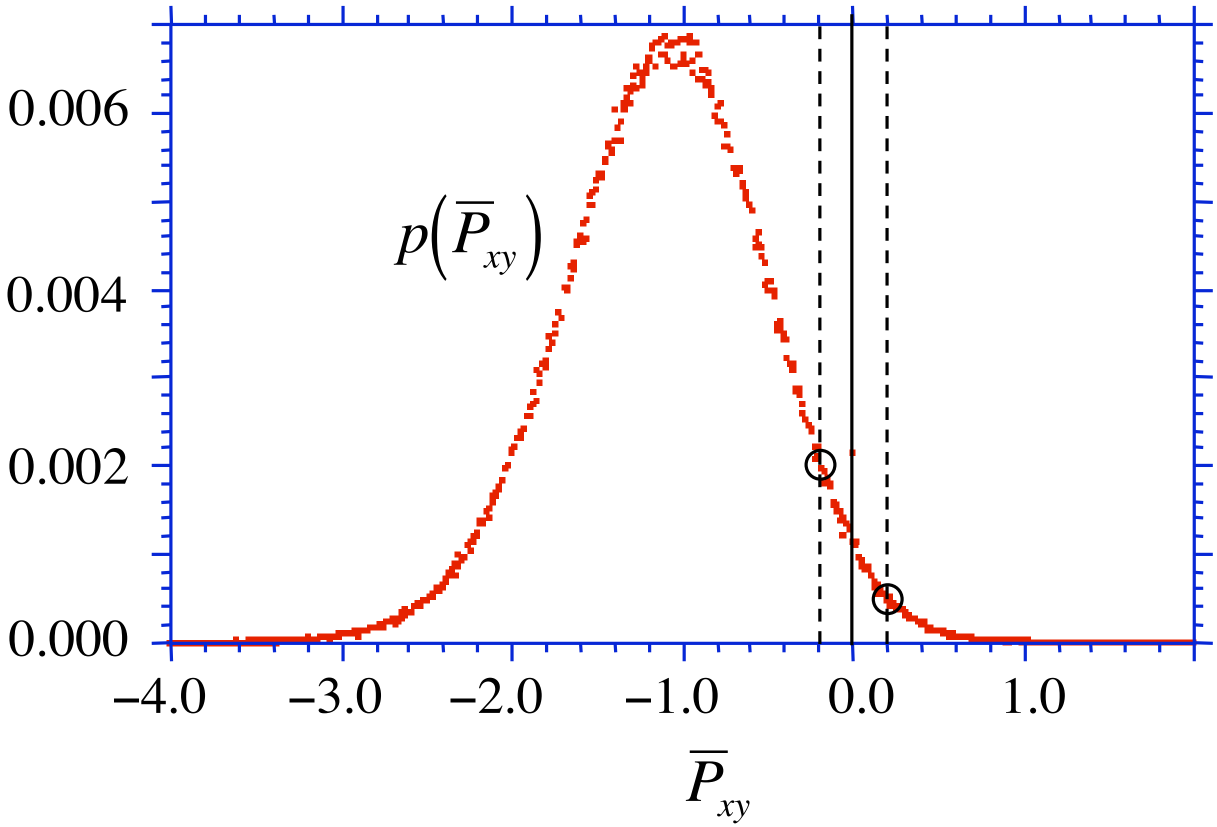
Sheared fluid



shear rate, volume, pressure tensor

$$\frac{dS}{dt} = -\frac{1}{T} \cdot \gamma V P_{xy}(t)$$

$$\Rightarrow \quad S \propto -\overline{P}_{xy}$$

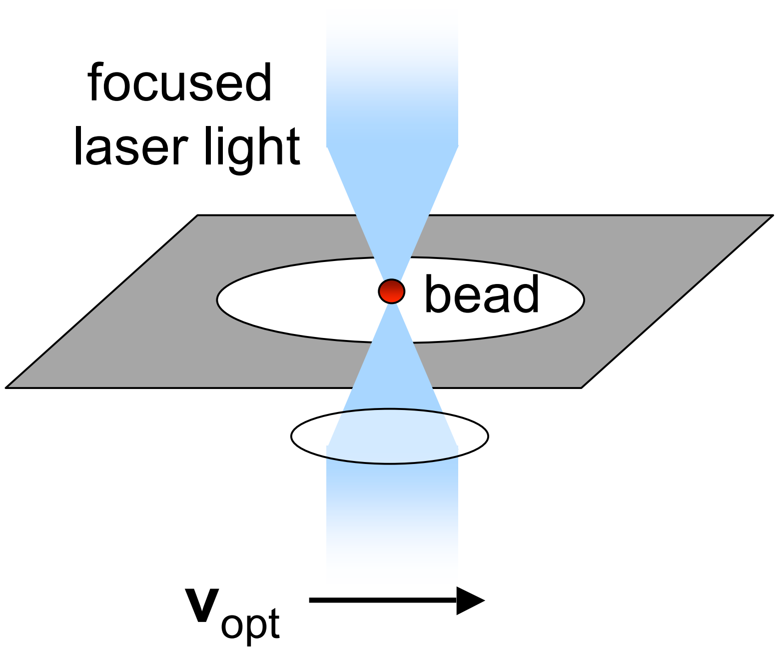


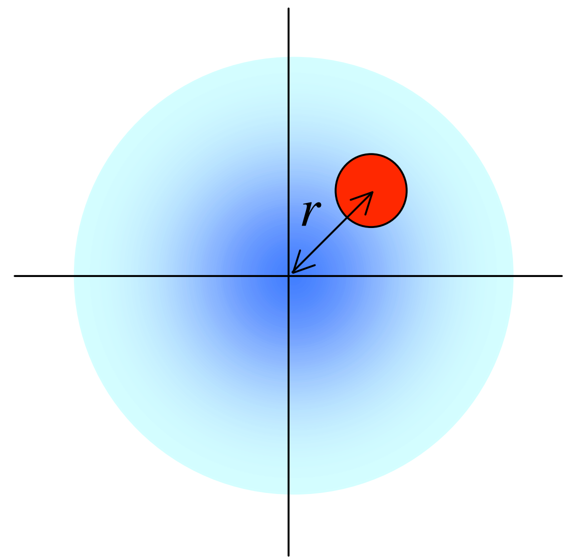
$$\frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp(S/k_B)$$

Evans, Cohen, Morriss, Phys Rev Lett (1993)

Optically dragged beads

Wang *et al*, Phys Rev Lett (2002)

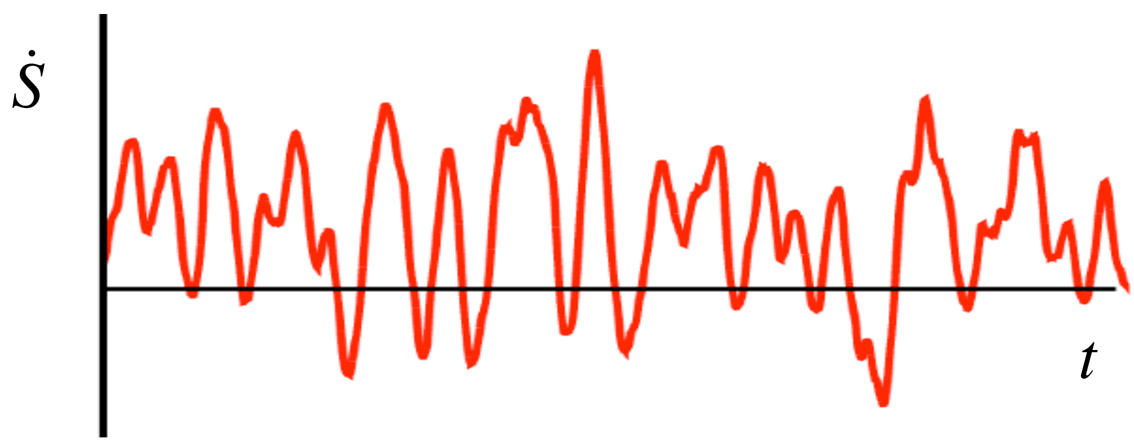




$$\mathbf{F}_{opt} = -k\mathbf{r}$$

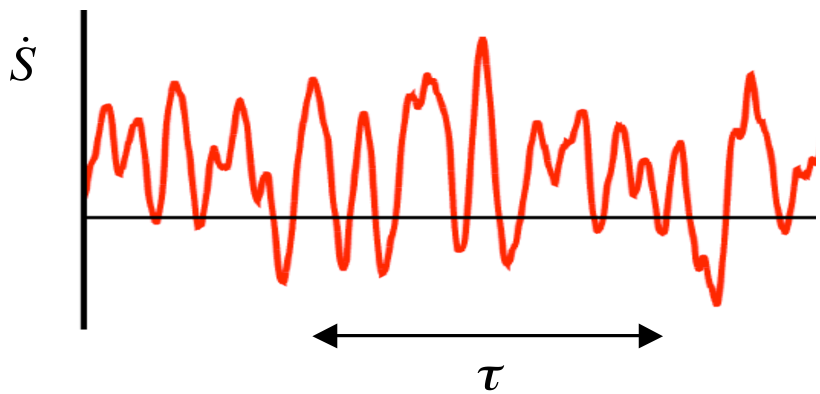
$$k \sim 0.1 \text{ pN/}\mu\text{m}$$

$$\frac{dS}{dt} = \frac{1}{T}\vec{F}_{opt} \cdot \vec{v}_{opt}$$



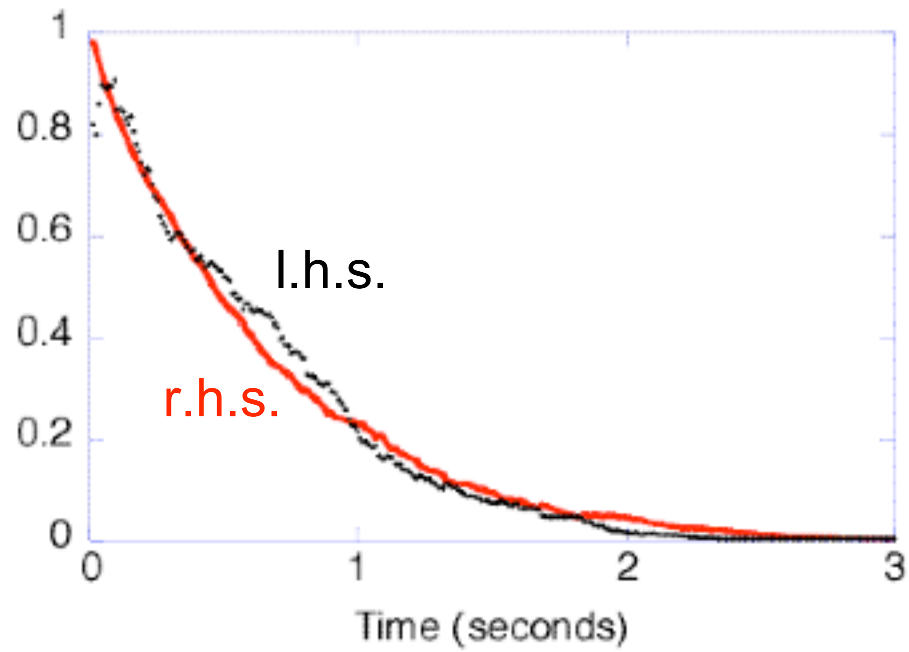
Demonstration of (integrated) Fluctuation Theorem

$$\frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp(S/k_B) \quad \Rightarrow \quad \frac{P(S_\tau < 0)}{P(S_\tau > 0)} = \left\langle \exp(-S_\tau/k_B) \right\rangle_{S_\tau > 0}$$



Ideally: divide the trajectory into many segments of duration τ, compute S for each segment, & construct histogram …

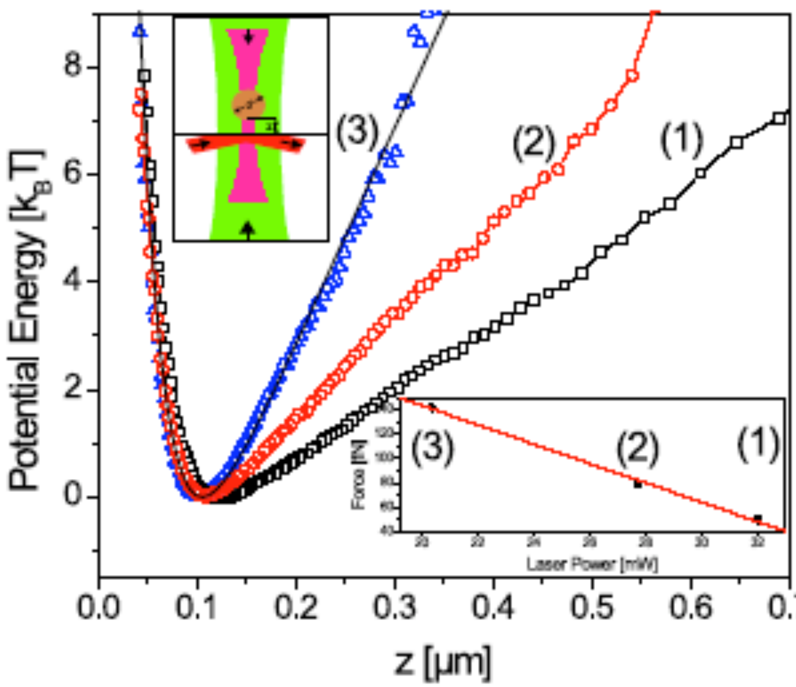
not enough data !



Wang *et al*, Phys Rev Lett (2002)

More recently …

Blickle *et al*, Phys Rev Lett (2006)



Parameter-dependent potential:

$$V(z;I) = A \cdot \exp(-\kappa z) + (B + CI) \cdot z$$

laser intensity

displacement of bead from wall

Drive the system away from equilibrium with a time-symmetric pulse (*squeeze*, then *relax*) … measure the work performed on the bead

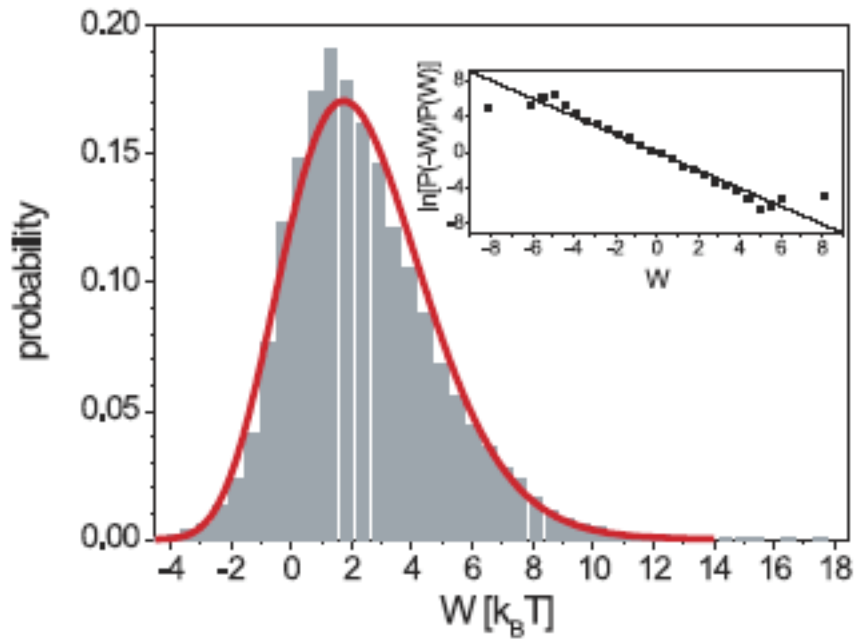
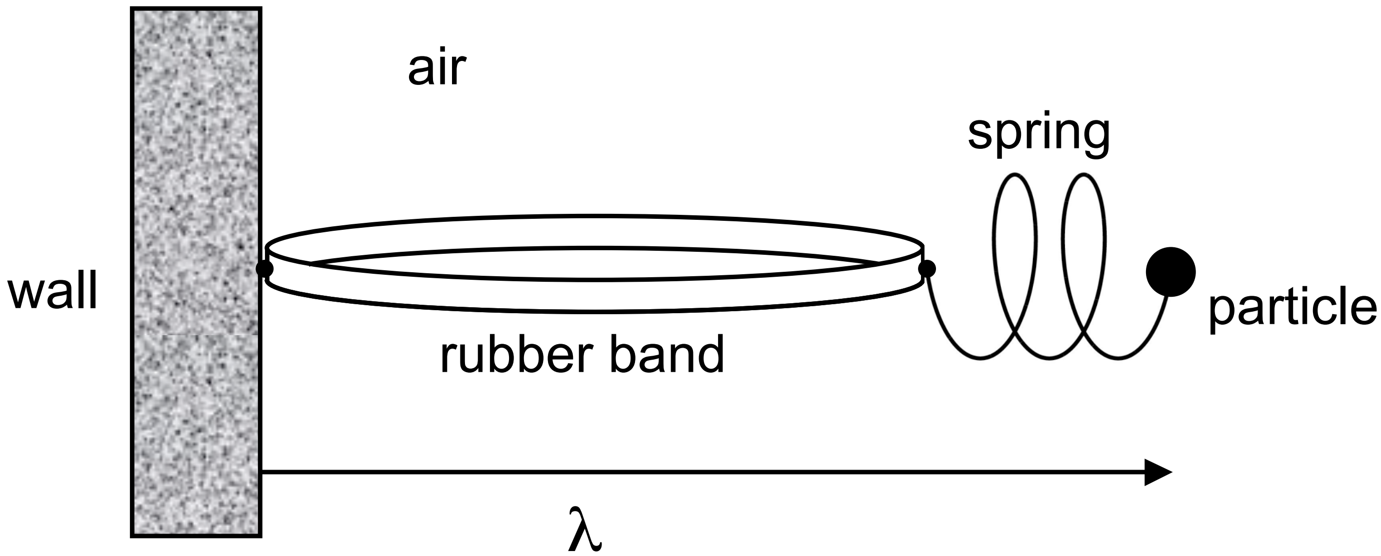
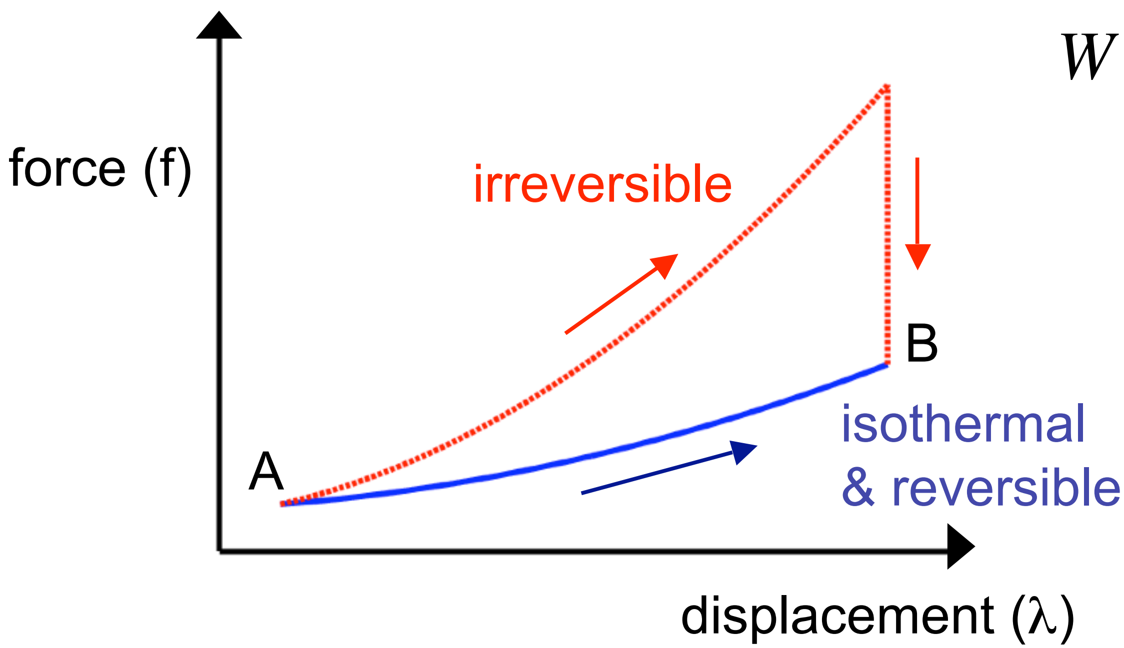


Illustration of *Clausius inequality*: stretched rubber band

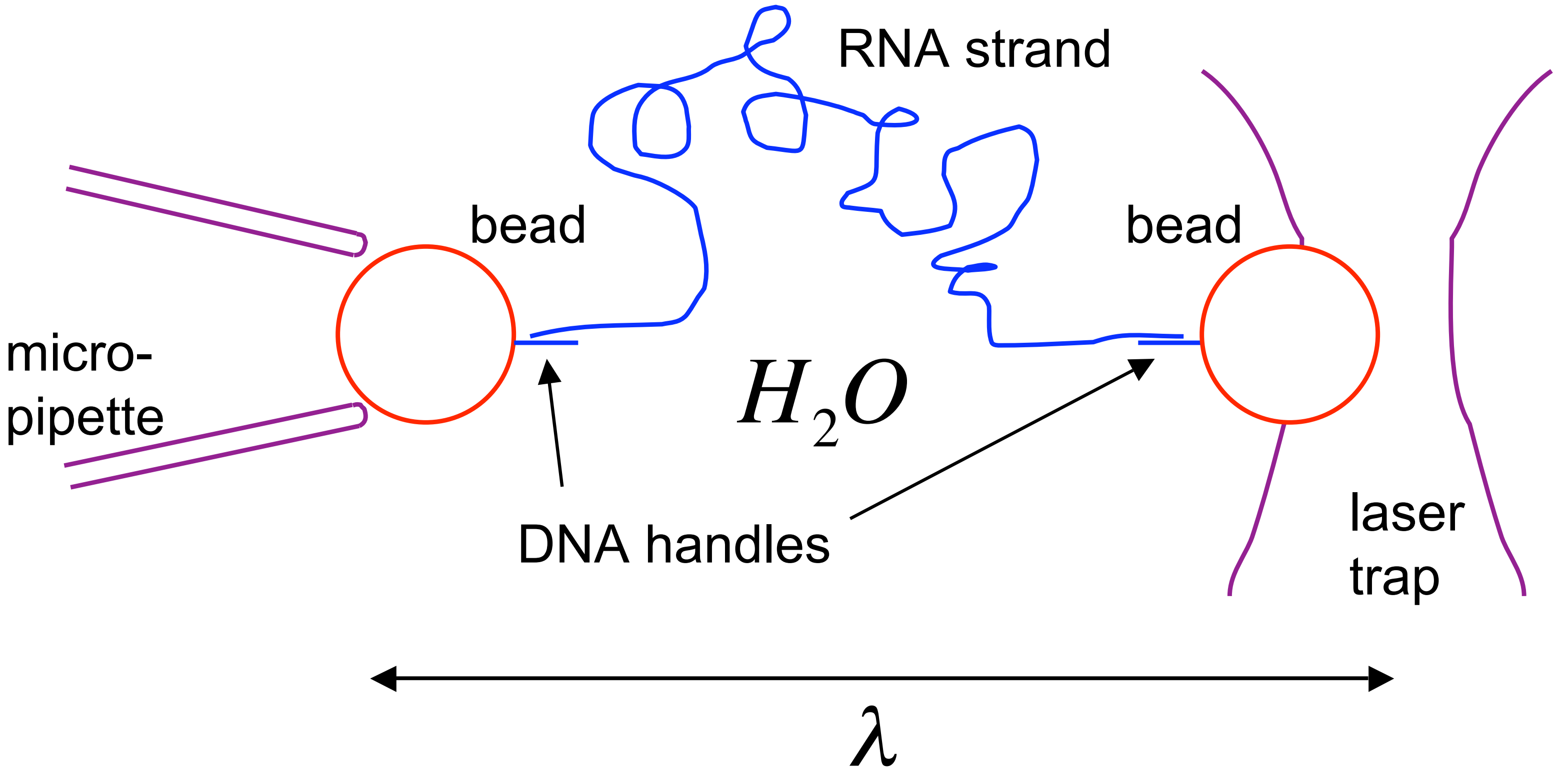




$$W = \int_A^B f \, d\lambda$$

$$\geq W_{rev}$$

$$= \Delta F = F_B - F_A$$



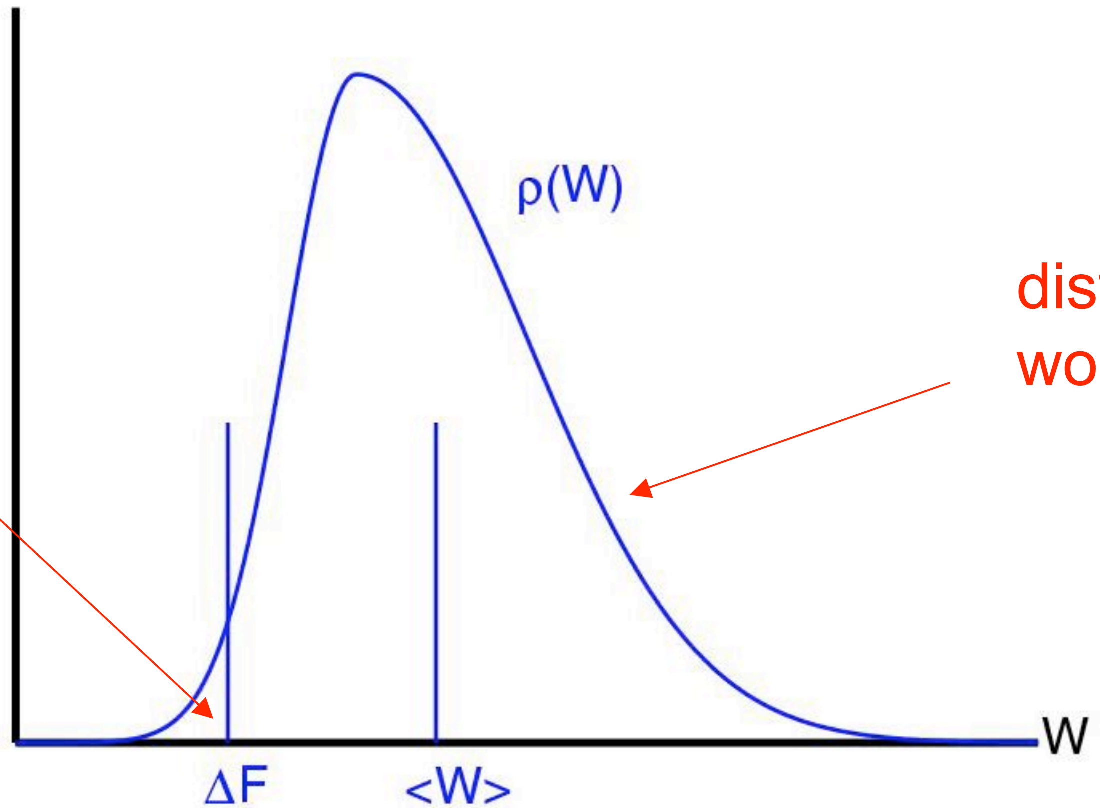
Irreversible process:

1. Begin in equilibrium $\lambda = A$
2. Stretch the molecule $\lambda : A \rightarrow B$

   W = work performed

3. End in equilibrium $\lambda = B$
4. Repeat

After infinitely many repetitions …



"violations" of 2ndLaw

distribution of work values

average work performed

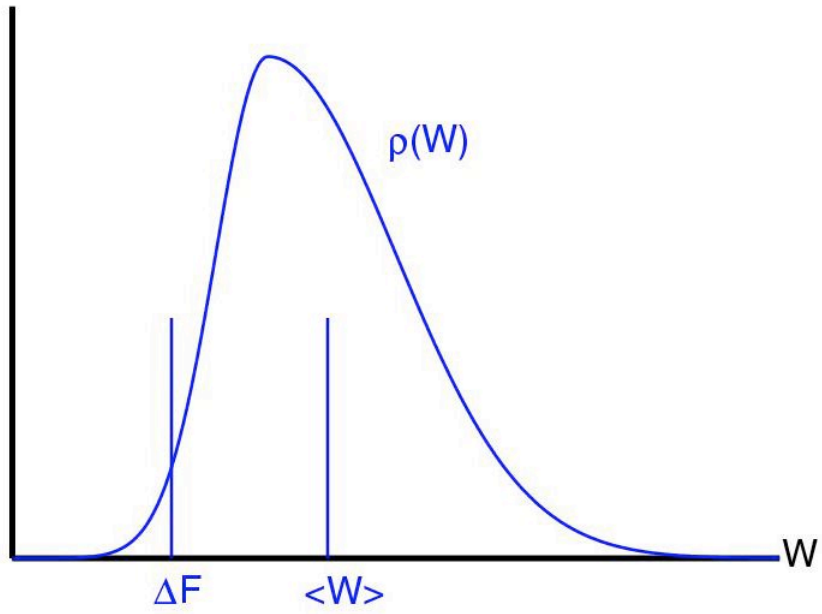
$$\Delta F = F_B - F_A$$

Nonequilibrium work theorem

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

$$\int dW\, \rho(W)\, e^{-\beta W}$$

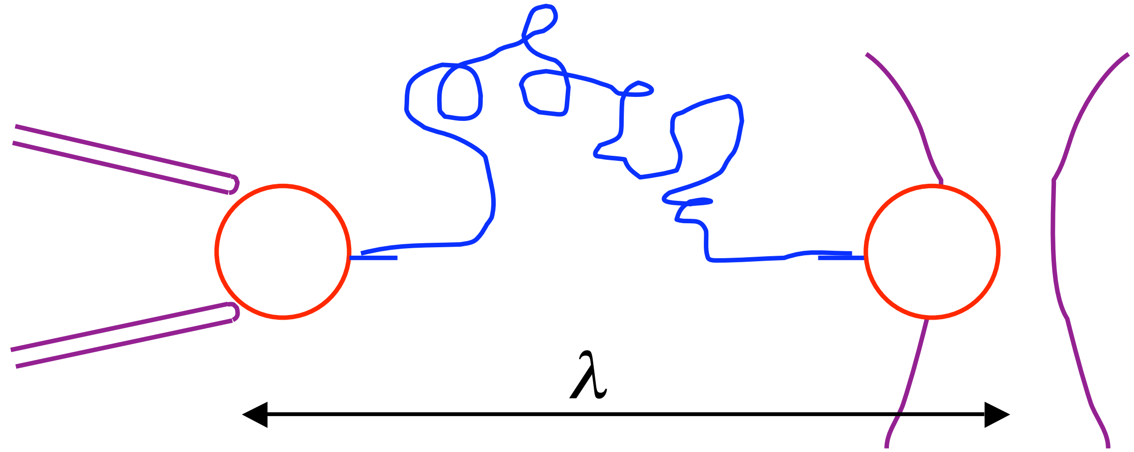
$$1/k_B T$$



- valid far from equilibrium
- fluctuations in W satisfy strong constraint
- nonequilibrium measurements reveal equilibrium properties

C.J., Phys Rev Lett (1997)
Crooks, J Stat Phys (1998)
Hummer & Szabo, PNAS (2001)
& others

Derivation (isolated system)



microstate	x	positions, momenta
Hamiltonian	$H(x;\lambda)$	internal energy

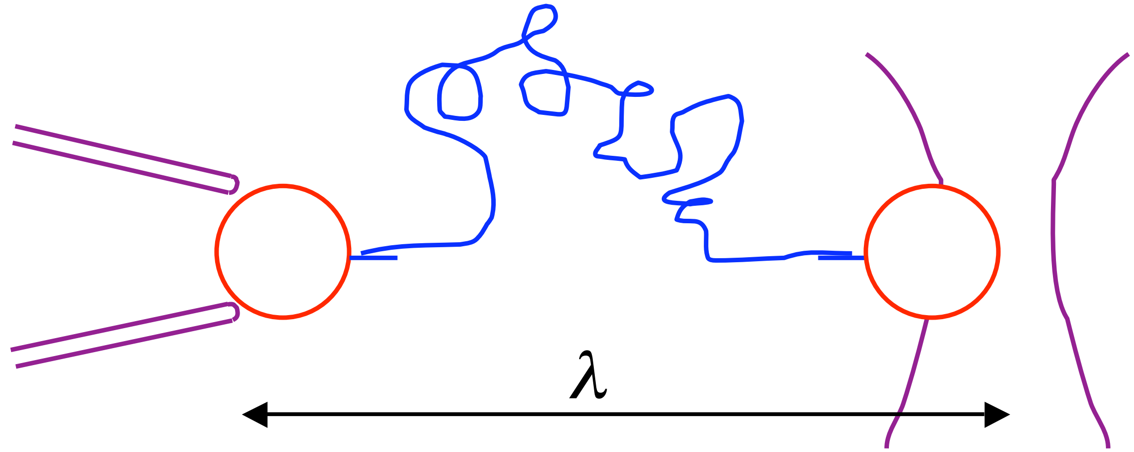
In equilibrium …

$$p^{eq}(x;\lambda) = \frac{1}{Z_\lambda} e^{-\beta H(x;\lambda)}$$ Boltzmann-Gibbs distribution

$$Z_\lambda = \int dx\, e^{-\beta H(x;\lambda)}$$ partition function

$$F_\lambda = -\beta^{-1} \ln Z_\lambda$$ free energy

Derivation
(isolated system)



One realization …

$$0 \le t \le \tau \begin{cases} \textit{protocol} & \lambda_t & \text{how we act on the system} \\ \textit{trajectory} & x_t & \text{how the system responds} \\ & & \\ \textit{work} & W = H(x_\tau;B) - H(x_0;A) & \end{cases}$$

1st law : ΔE = W + ~~Q~~

… now take average of $e^{-\beta W}$ over many realizations

$$x_\tau = x_\tau(x_0)$$

$$W(x_0) = H(x_\tau(x_0);B) - H(x_0;A)$$

$$\left\langle e^{-\beta W} \right\rangle = \int dx_0 \, \frac{1}{Z_A} e^{-\beta H(x_0;A)} \, e^{-\beta W(x_0)}$$

$$= \frac{1}{Z_A} \int dx_0 \, e^{-\beta H(x_\tau(x_0);B)}$$

=1 (Liouville's thm.)

$$= \frac{1}{Z_A} \int dx_\tau \left| \frac{\partial x_\tau}{\partial x_0} \right|^{-1} e^{-\beta H(x_\tau;B)}$$

$$= \frac{Z_B}{Z_A} \quad = e^{-\beta \Delta F}$$

QED

Various derivations

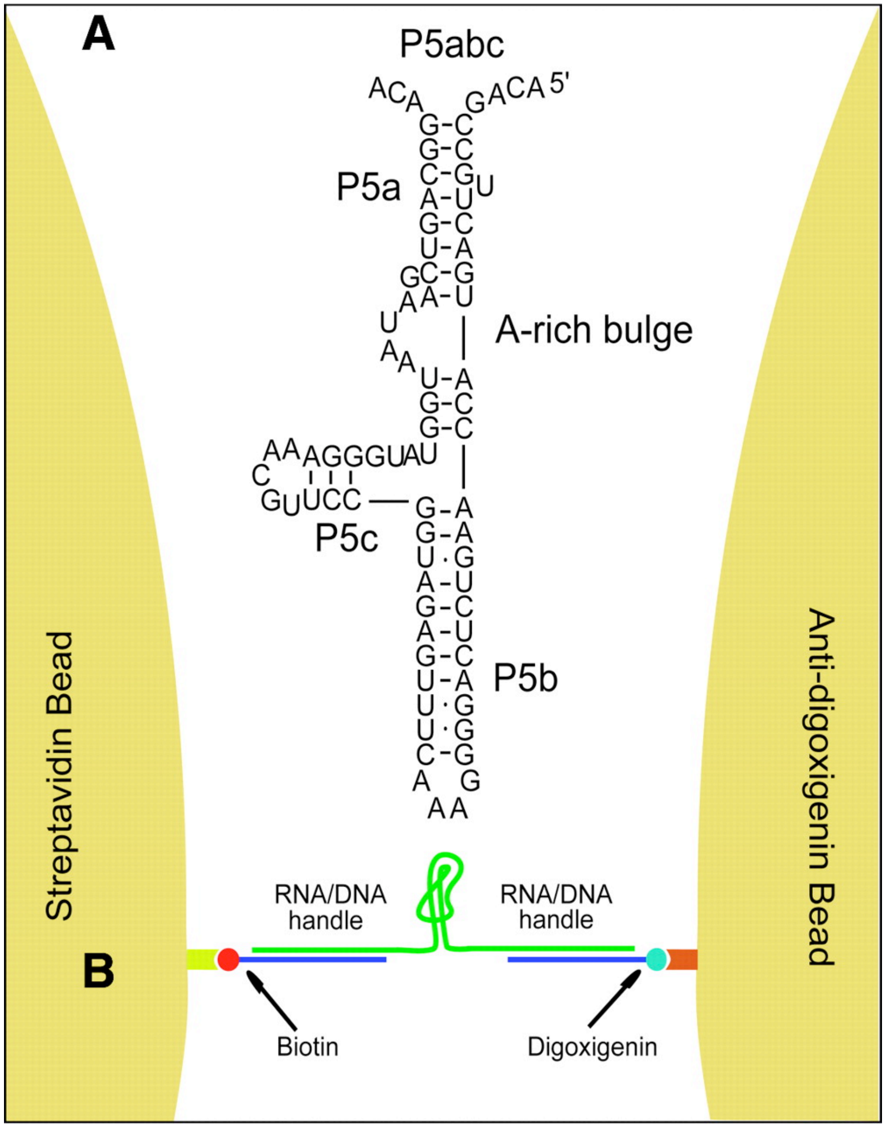
- C.J. PRL & PRE 1997, J.Stat.Mech. 2004
- G.E. Crooks J.Stat.Phys. 1998, PRE 1999, 2000
- G. Hummer & A. Szabo PNAS 2001
- S.X. Sun J.Chem.Phys. 2003
- D. J. Evans Mol.Phys. 2003
- S. Mukamel PRL 2003 … & others

Hamiltonian evolution, Markov processes,
Langevin dynamics, deterministic thermostats,
quantum dynamics … *robust*

see also S. Park & K. Schulten, J. Chem. Phys. 2004
R.C. Lua & A.Y. Grosberg, J. Phys. Chem. B 2005

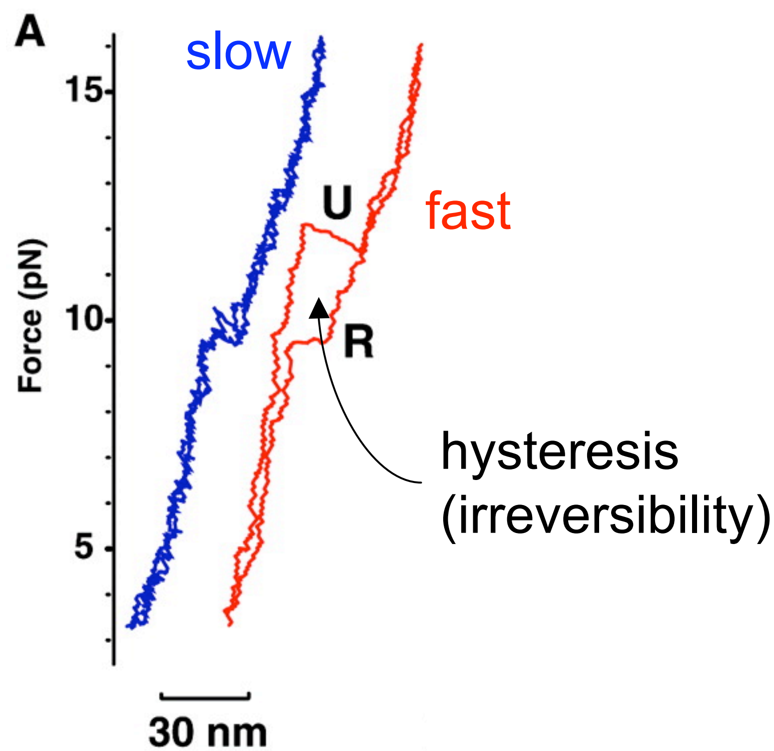
related result:
G.N. Bochkov & Y.E. Kuzovlev JETP 1977

Experimental verification: unfolding a single RNA molecule



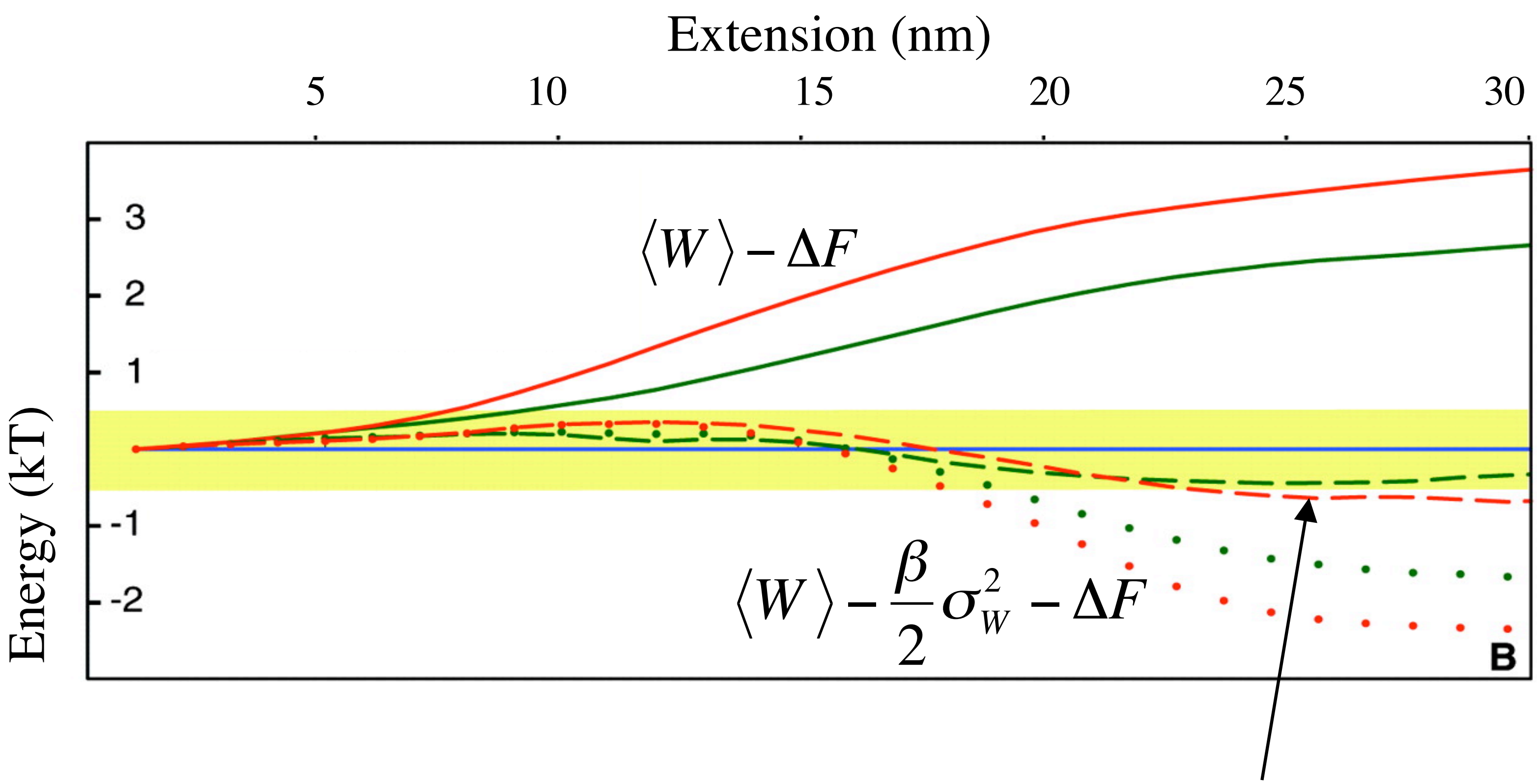
Liphardt *et al,* Science (2002)

unfolding / refolding cycles



Results: equilibrium ΔF from nonequilibrium work values

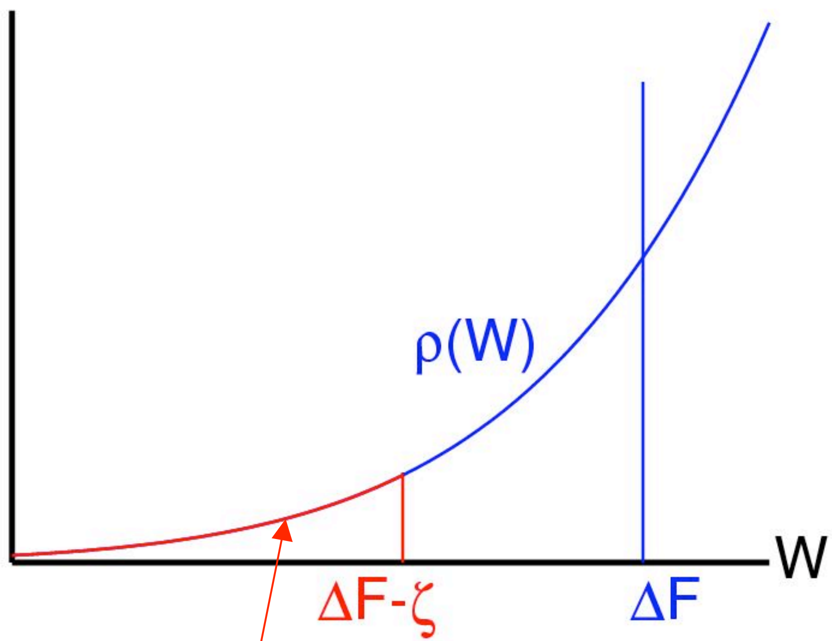
- three pulling rates: 2-5 pN/s , 34 pN/s , 52 pN/s
- ~ 300 cycles at each rate
- slow cycles (reversible) used to determine ΔF



J.Liphardt *et al*, Science (2002)

Relation to Second Law

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



What is the probability that the 2nd law will be "violated" by at least ζ units of energy?

exponentially rare

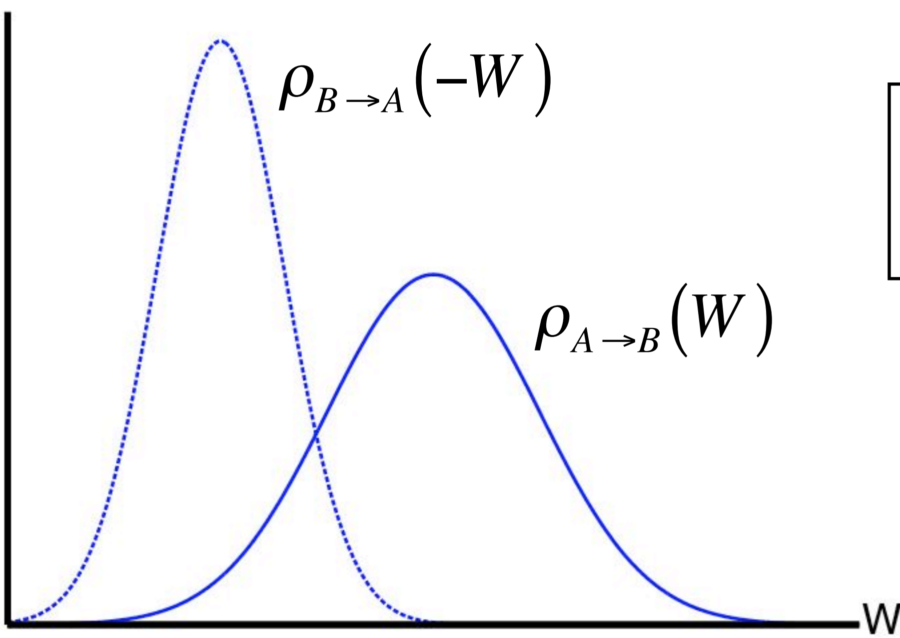
$$P[W < \Delta F - \zeta] = \int_{-\infty}^{\Delta F - \zeta} dW\ \rho(W)$$

$$\leq \int_{-\infty}^{\Delta F - \zeta} dW\ \rho(W)\, e^{\beta(\Delta F - \zeta - W)}$$

$$\leq e^{\beta(\Delta F - \zeta)} \int_{-\infty}^{+\infty} dW\ \rho(W)\, e^{-\beta W} = \exp(-\zeta / kT)$$

Crooks fluctuation theorem

Forward process …   λ : A -> B   (unfolding)
Reverse process …   λ : B -> A   (folding)



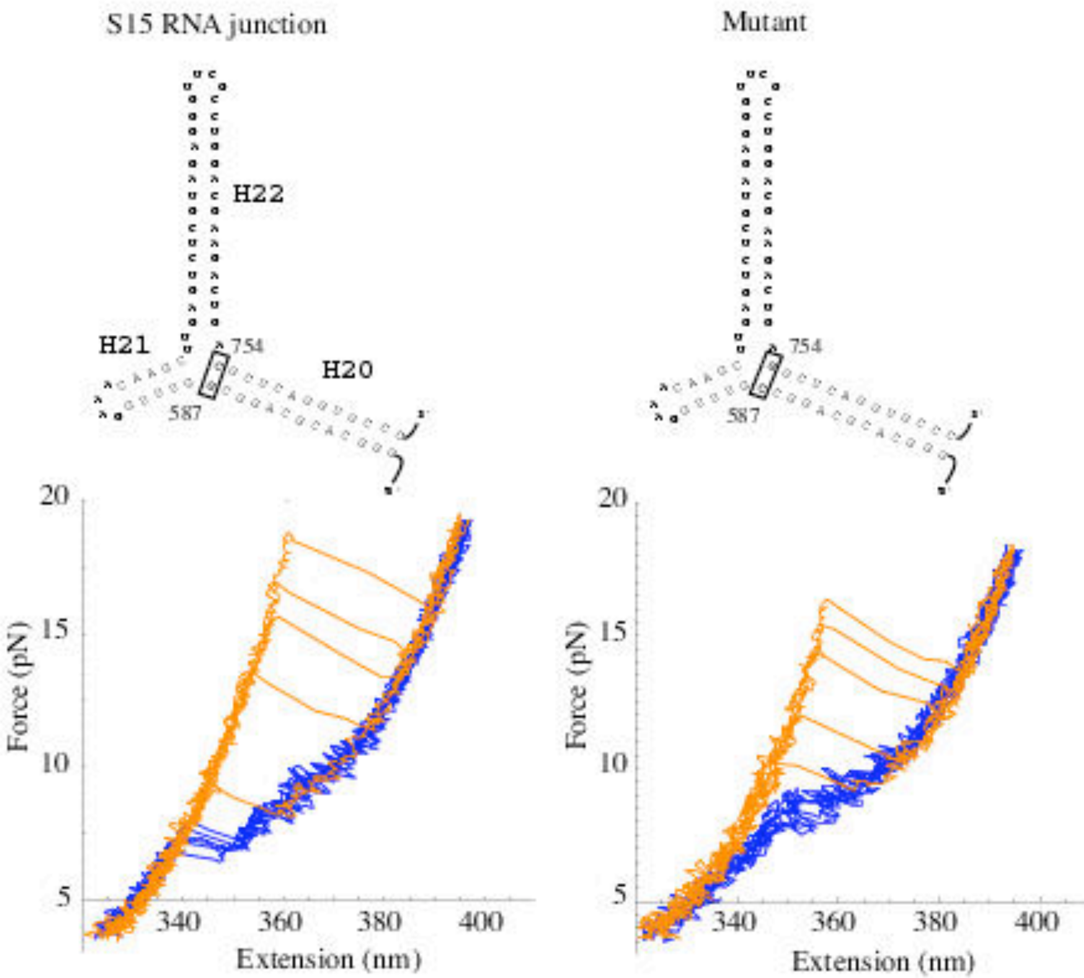
$$\frac{\rho_{A \to B}(+W)}{\rho_{B \to A}(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$$

Crooks, Phys Rev E (1999)

Experimental verification:
Collin *et al*, Nature (2005)

3-helix junction of ribosomal RNA of *E. coli*

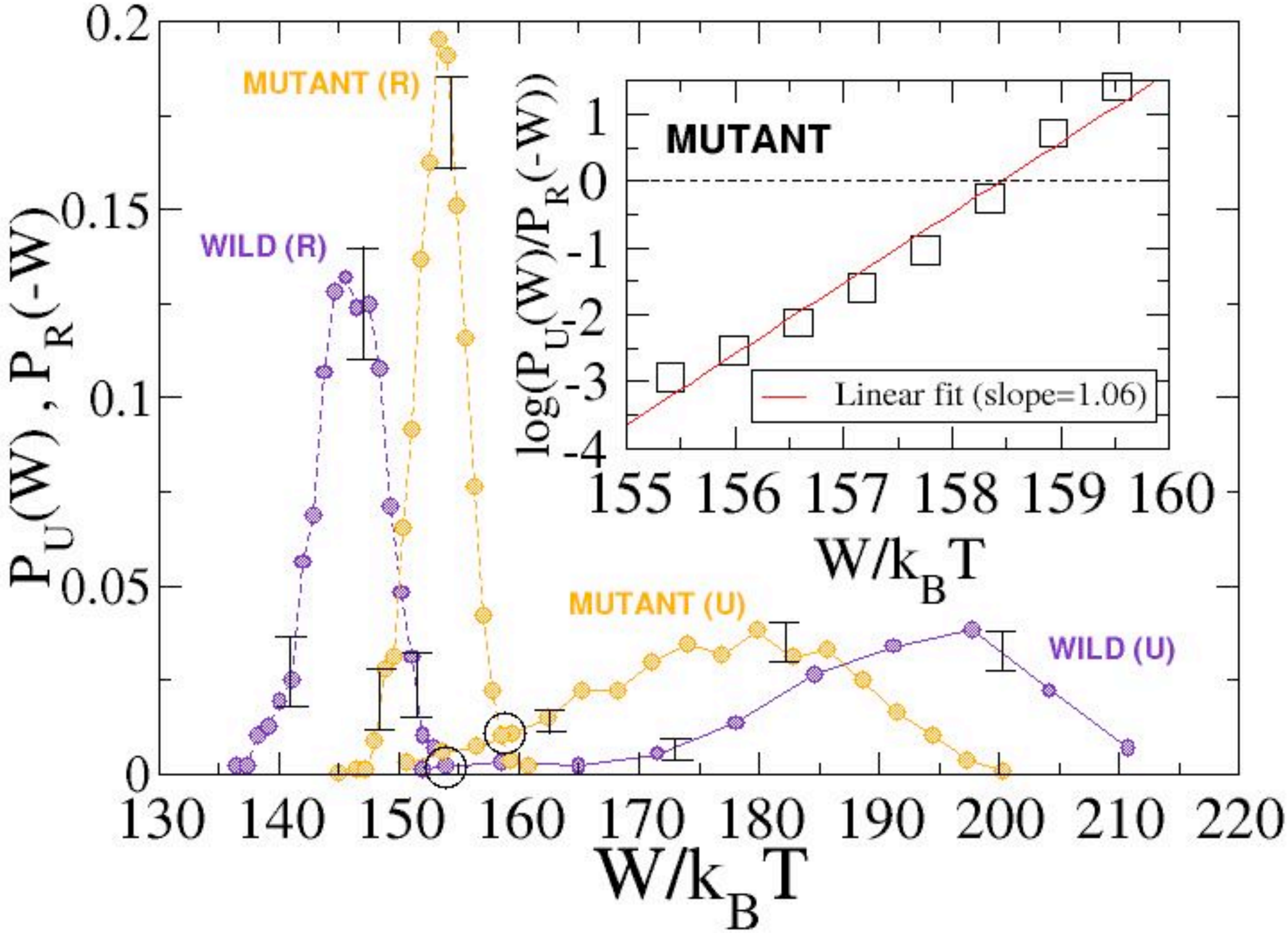
Collin *et al*, Nature 2005



wild type mutant

$$W_{diss} \approx 50\, k_B T$$

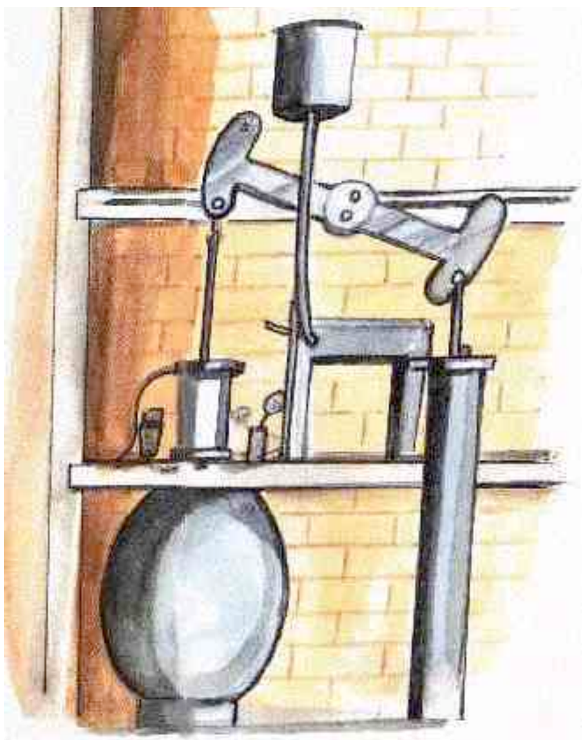
$$\frac{\rho_{A\to B}(+W)}{\rho_{B\to A}(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right] \quad \Rightarrow \quad \ln\frac{\rho_{A\to B}(+W)}{\rho_{B\to A}(-W)} = \beta(W - \Delta F)$$

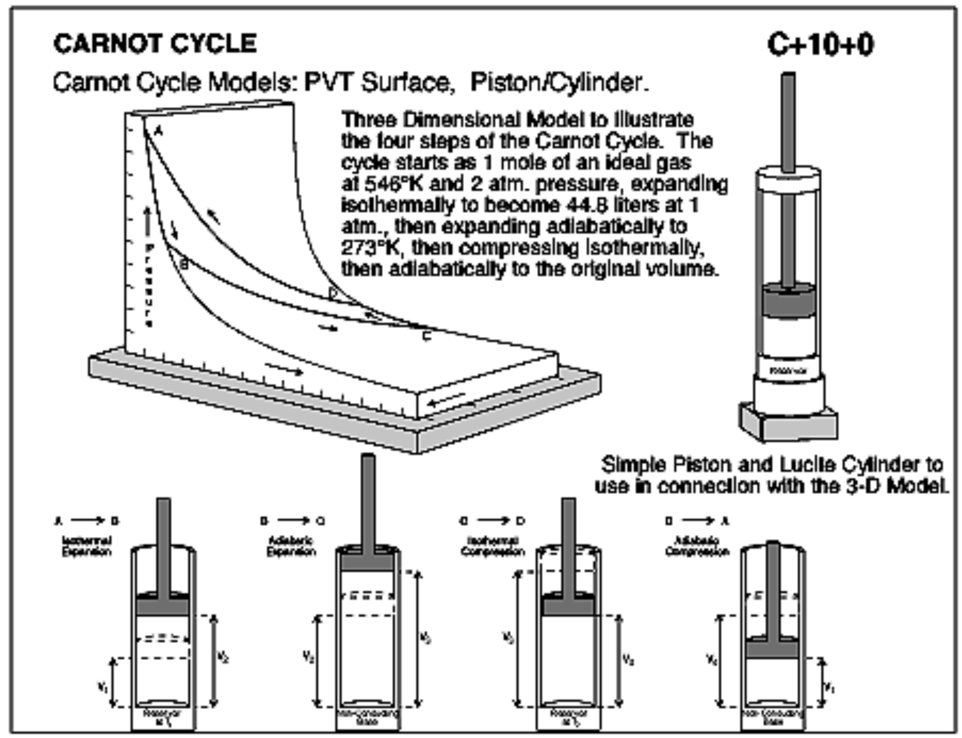


Macroscopic machines

steam engine

Carnot cycle

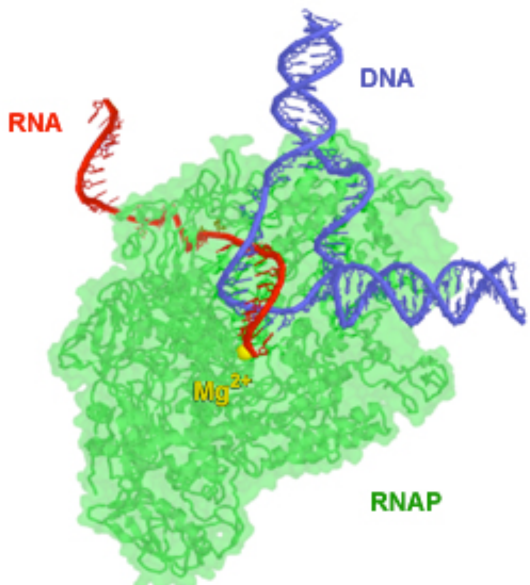


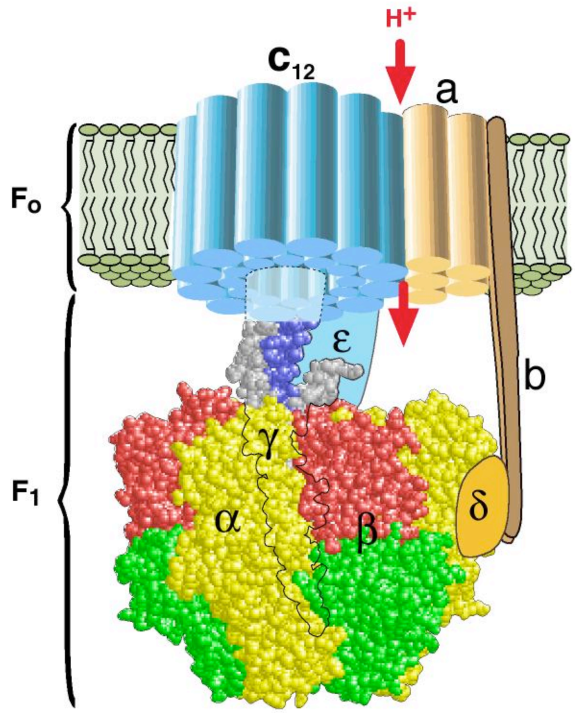


textbook thermodynamics

Molecular machines

RNA polymerase

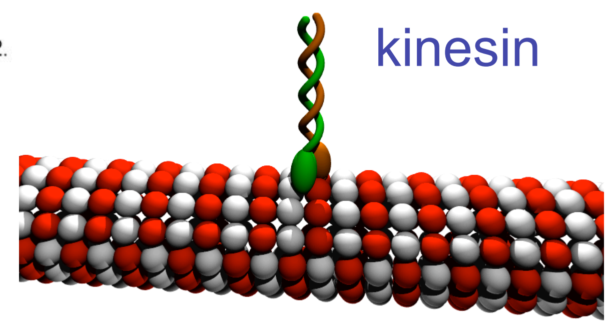




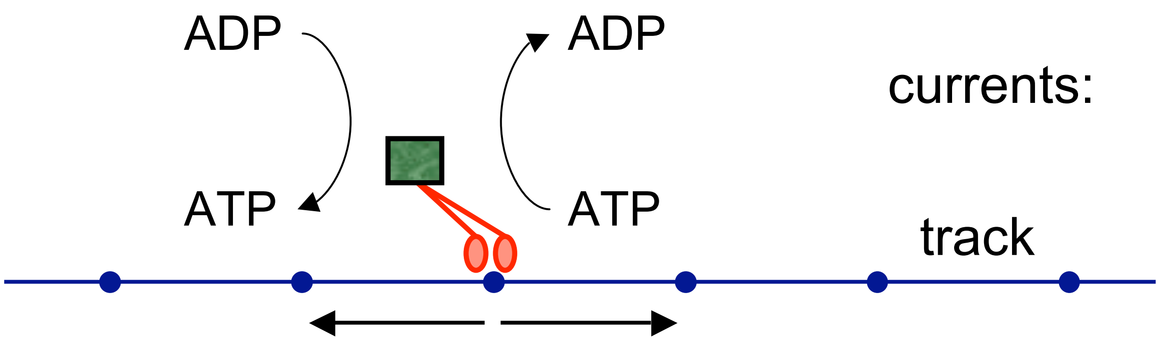
H. Wang and G. Oster (1998). Nature 396:279-282.

ATP synthase

kinesin



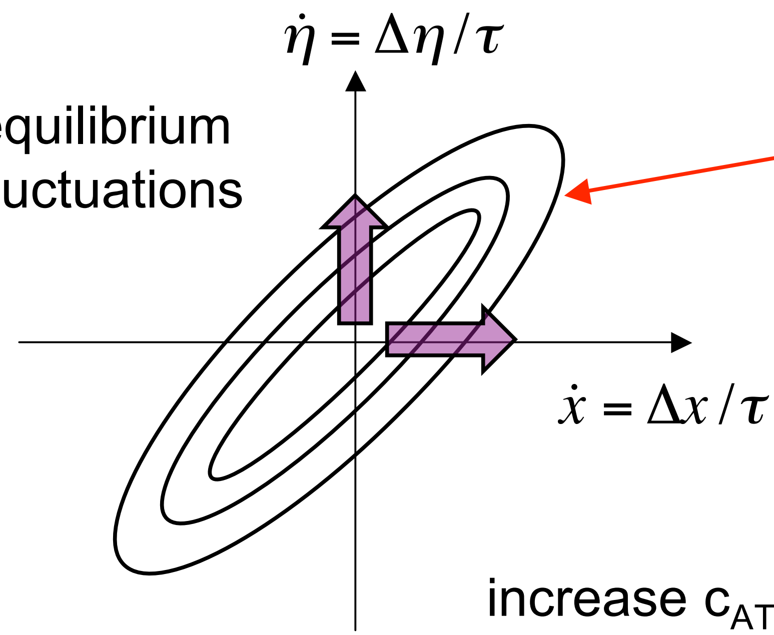
What are the underlying thermodynamics?
How is chemical energy converted to mechanical motion?



currents:

- $\dot{x}$ stepping velocity
- $\dot{\eta}$ ATP -> ADP conversion rate

equilibrium fluctuations



$$p_\tau^{eq}(+\Delta x, +\Delta\eta) = p_\tau^{eq}(-\Delta x, -\Delta\eta)$$

(detailed balance)

however …

$$\langle \Delta x \cdot \Delta\eta \rangle \neq 0 \qquad \text{(generically)}$$

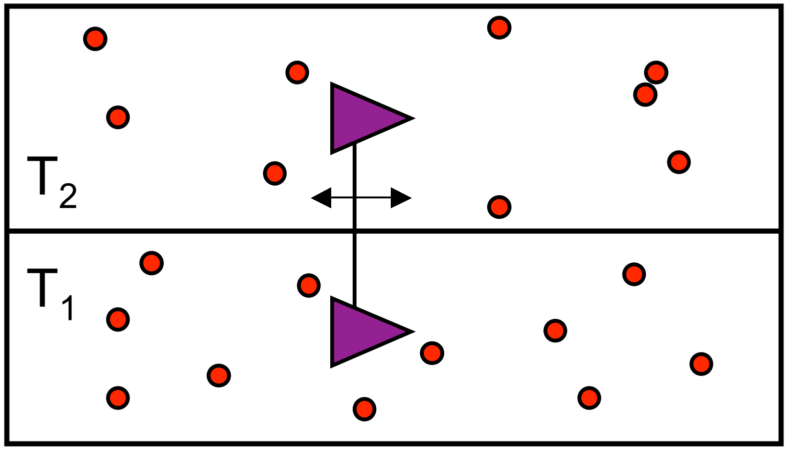
increase c_{ATP} $\Rightarrow + \dot{\eta}$ $\Rightarrow + \dot{x}$ motion!

A similar argument can be made far from equilibrium.

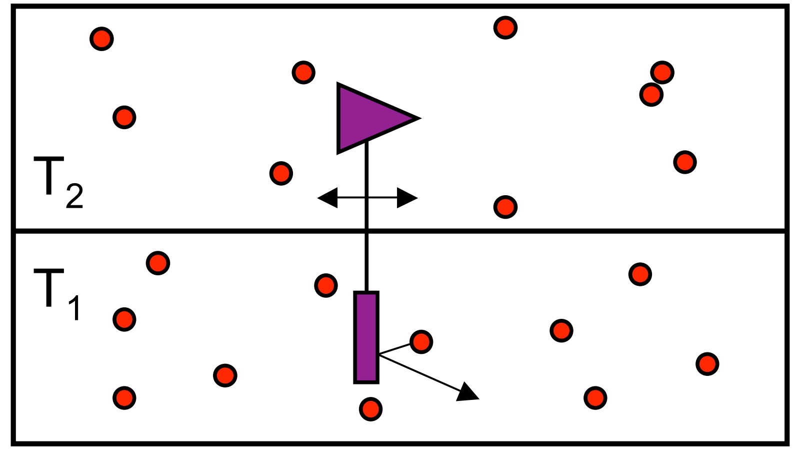
Minimal molecular motors

Van den Broeck, Meurs, Kawai
Phys Rev Lett (2004)

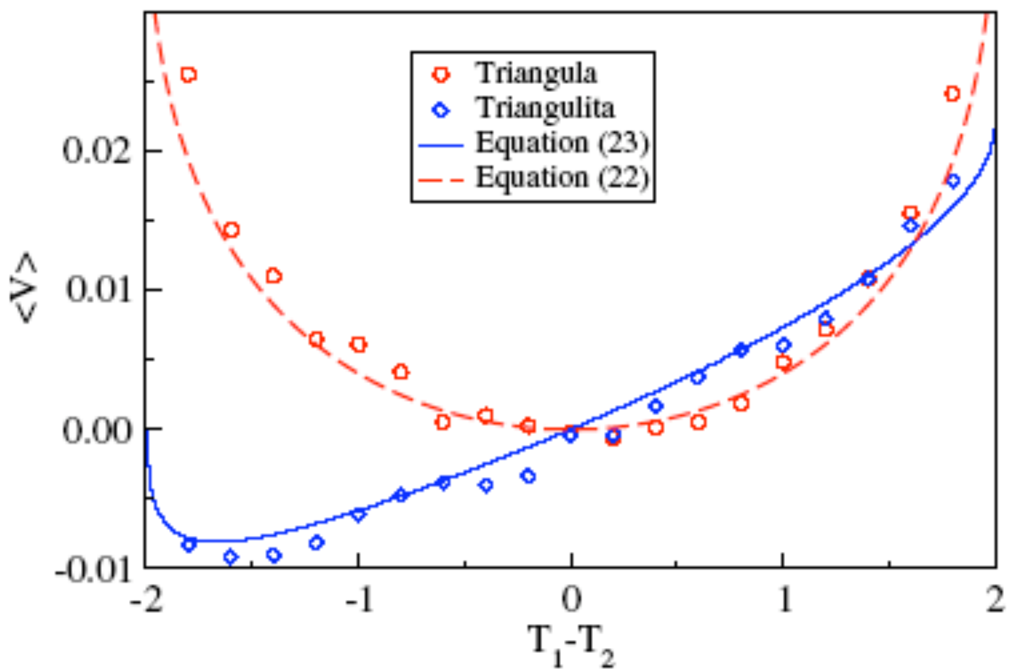
“Triangula”



“Triangulita”



Directed motion?



YES !

Summary

New & interesting thermodynamics at the microscale

- Fluctuation theorem $$\frac{\rho_\tau(+S)}{\rho_\tau(-S)} = \exp(S/k_B)$$

    symmetry between entropy generation & consumption

- Nonequilibrium work theorem $$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

    equilibrium thermodynamic information encoded in fluctuations far from equilibrium

- Molecular motors "generic"