Nonequilibrium thermodynamics at the microscale

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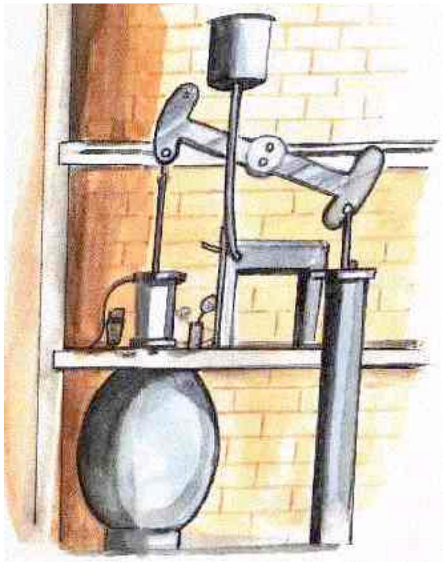
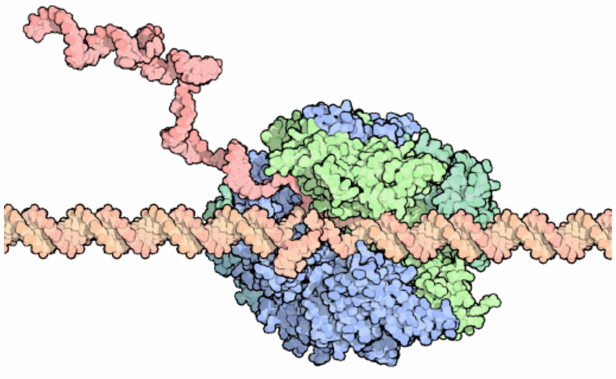
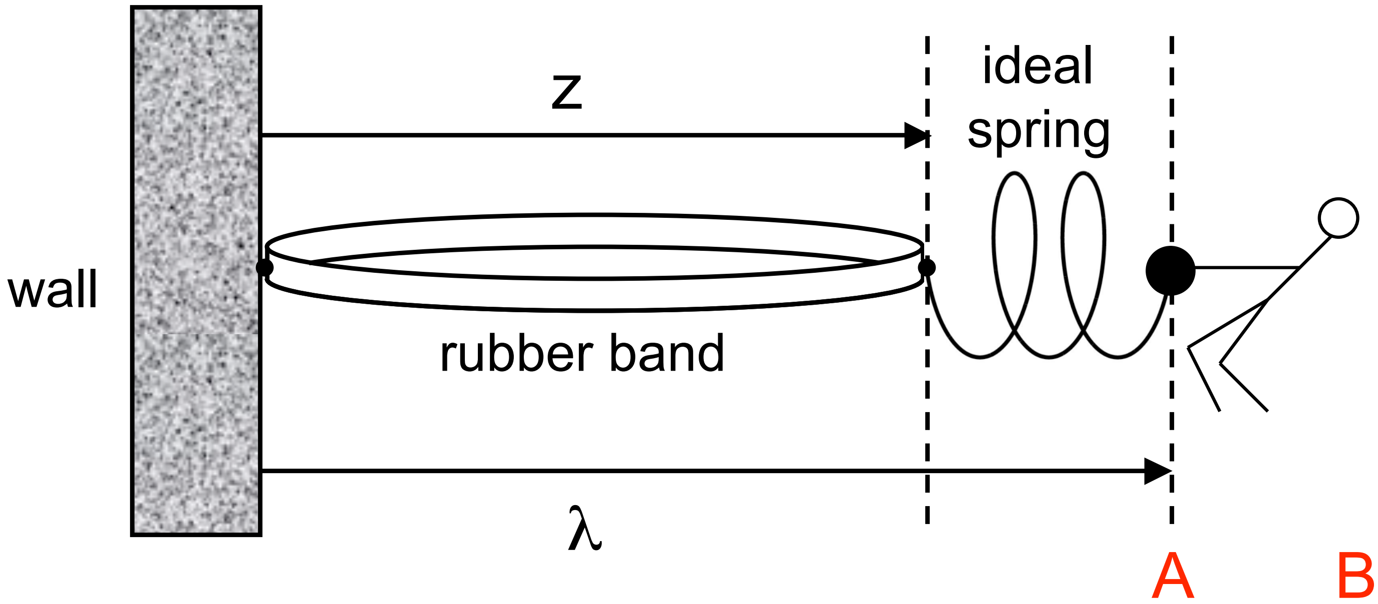
~1 m





~20 nm

Work and free energy: a macroscopic example …



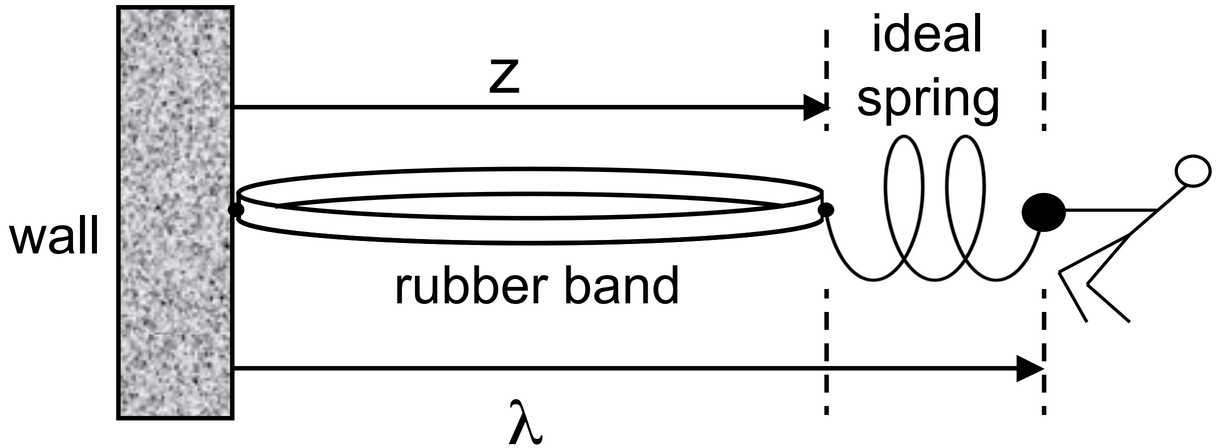
Irreversible process:

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

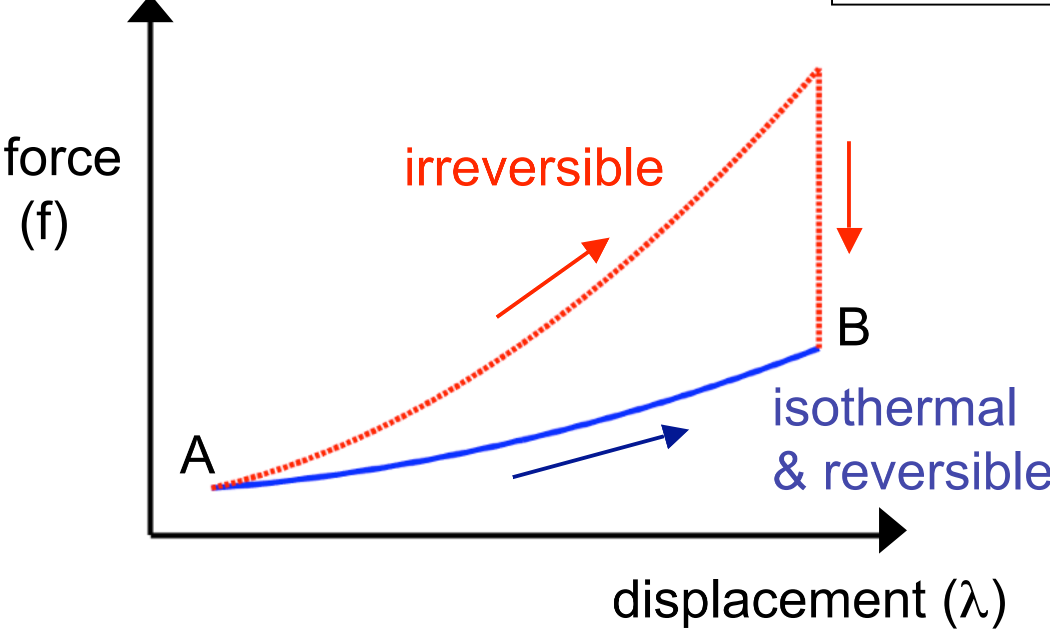
   W = work performed

3. End in equilibrium $\lambda = B$

Work and free energy: a macroscopic example …



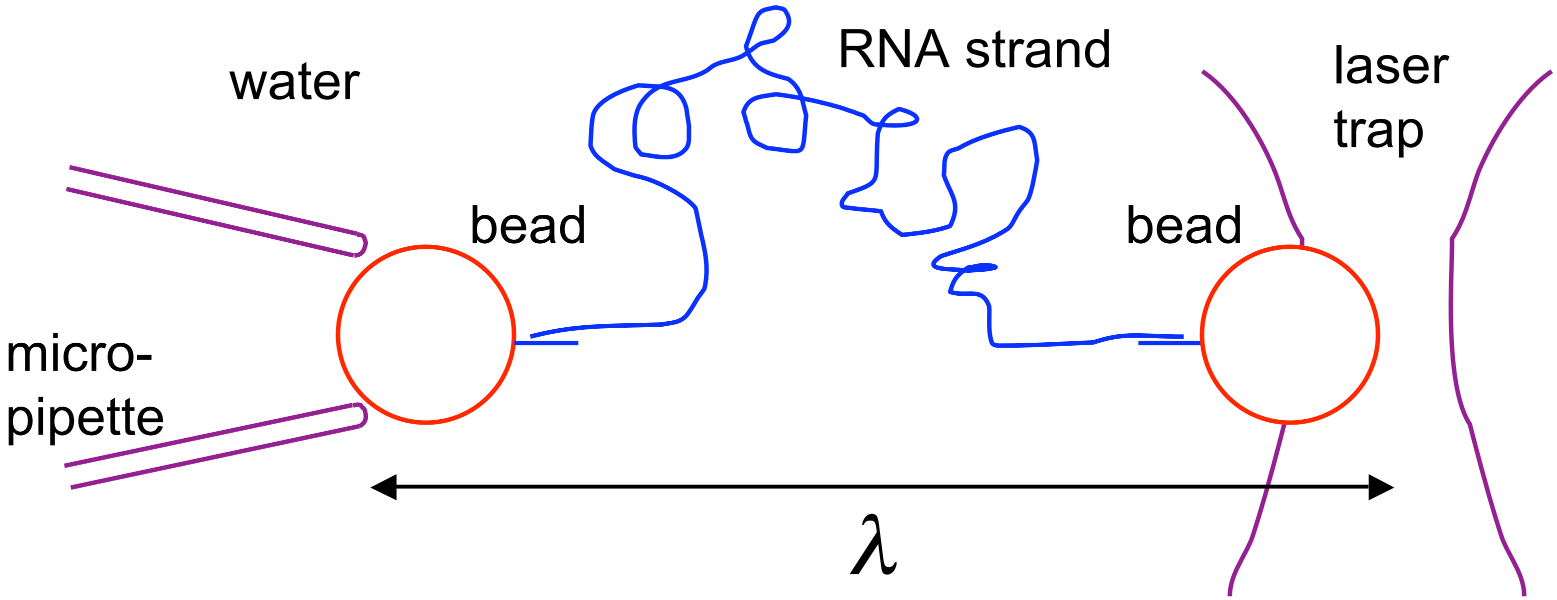
$$\boxed{W_{A\rightarrow B} \geq \Delta F}$$

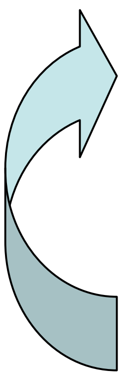


<u>Clausius inequality</u>

$$\int_A^B \frac{dQ}{T} \leq \Delta S$$

… and a microscopic analogue



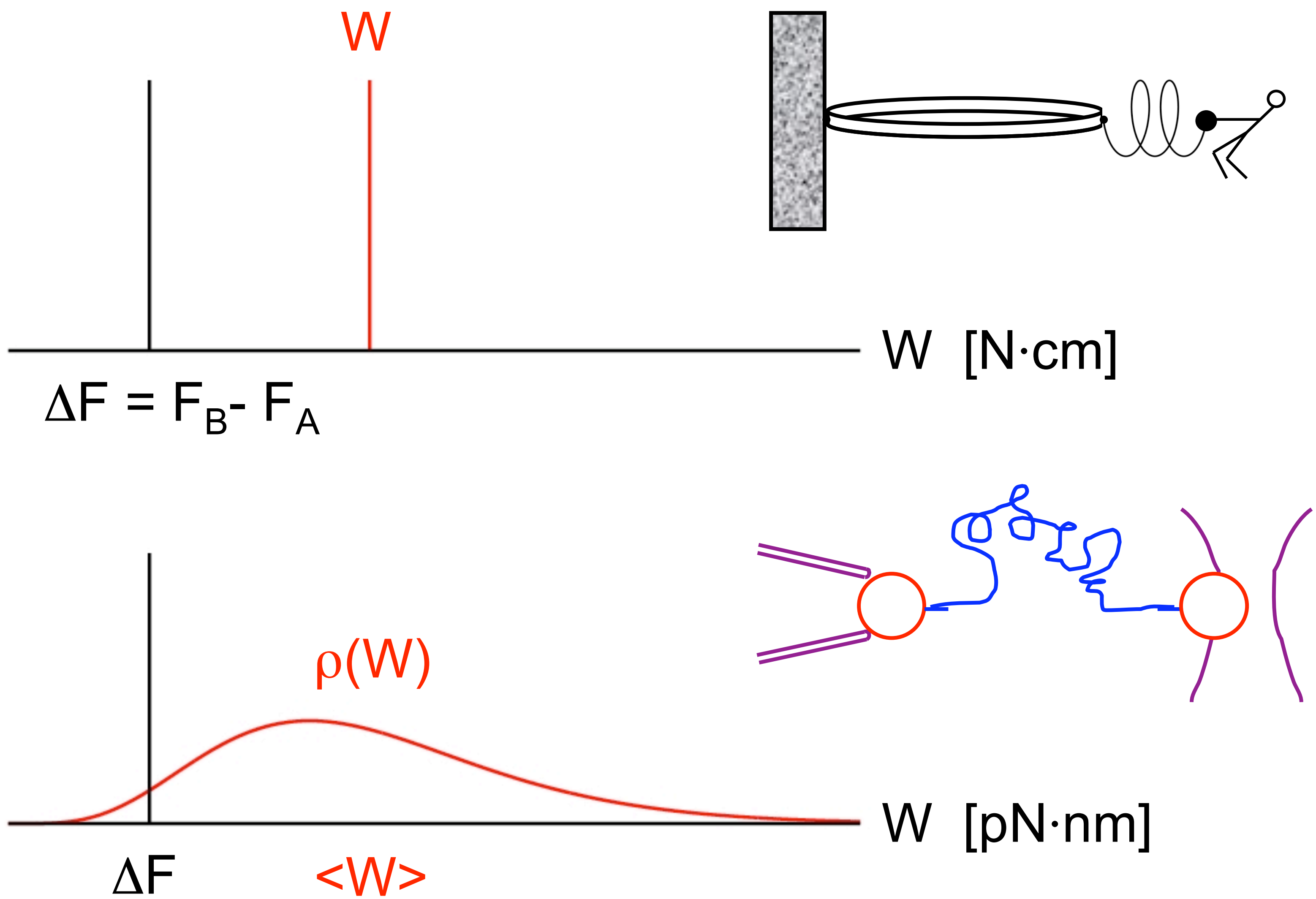


1. Begin in equilibrium $\lambda = A$
2. Stretch the molecule $\lambda : A \rightarrow B$

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

… *fluctuations* are now important !

Clausius inequality, *macro* & *micro*

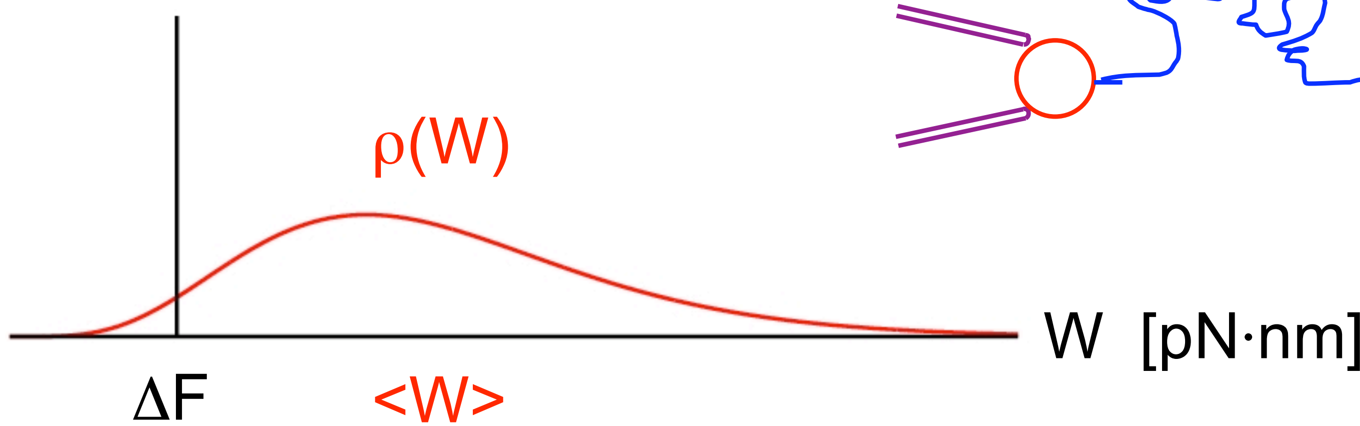


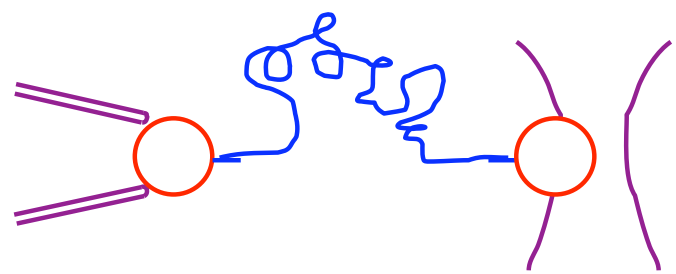
So what's new?

Fluctuations in W satisfy strong and unexpected laws.

e.g. $$\boxed{\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}}$$ C.J., PRL 1997

… places a strong constraint on the work distribution



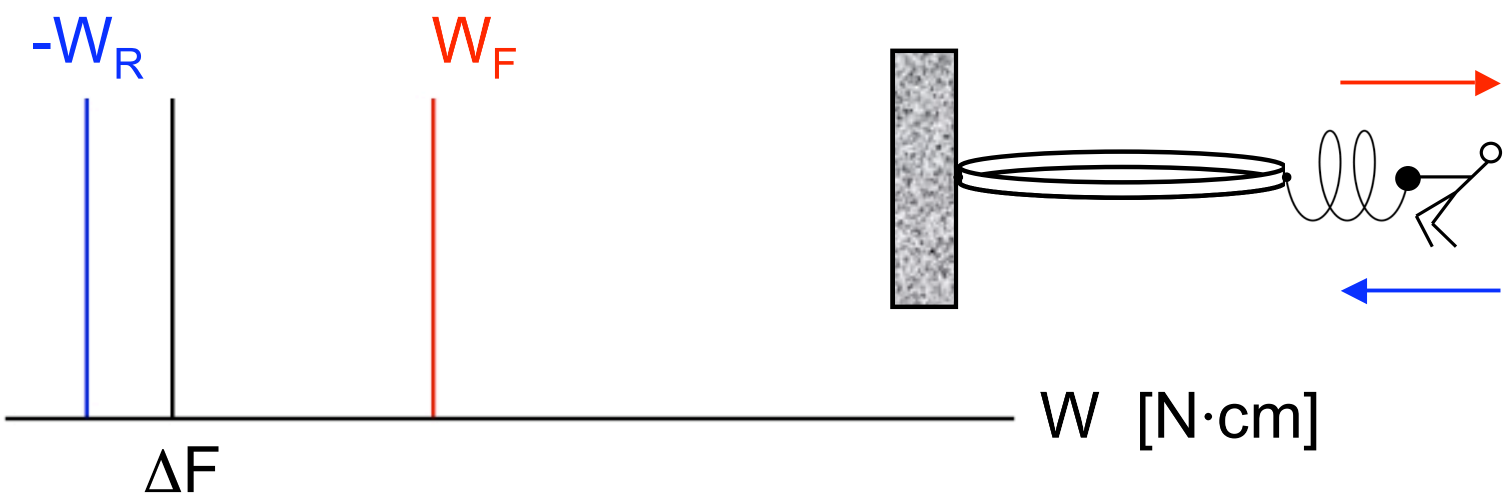


Thermodynamic cycles

forward process : A→B

reverse process : A←B

$W_R \geq -\Delta F$

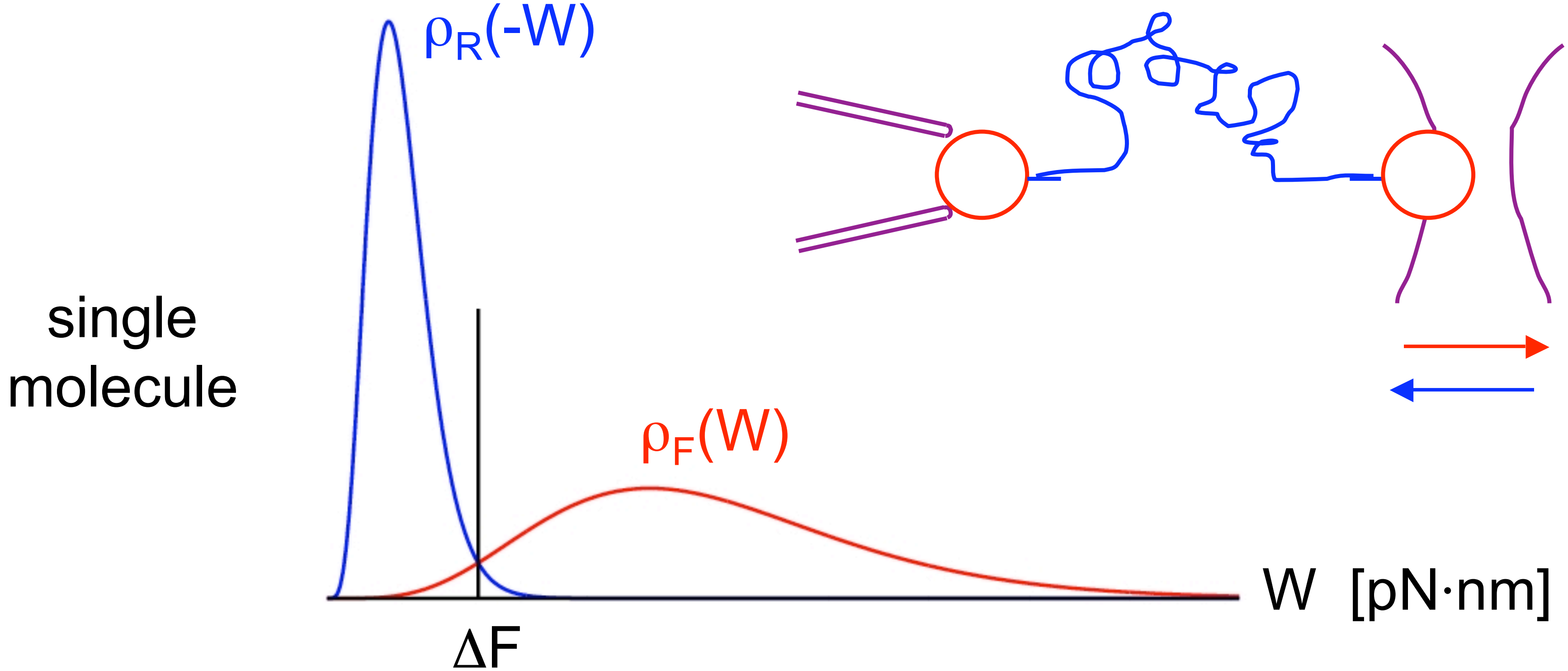


Kelvin-Planck statement of 2nd Law: $W_F + W_R \geq 0$

We perform more work during the forward half-cycle (A→B)
than we recover during the reverse half-cycle (A←B).

(no free lunch)

At the microscopic level :

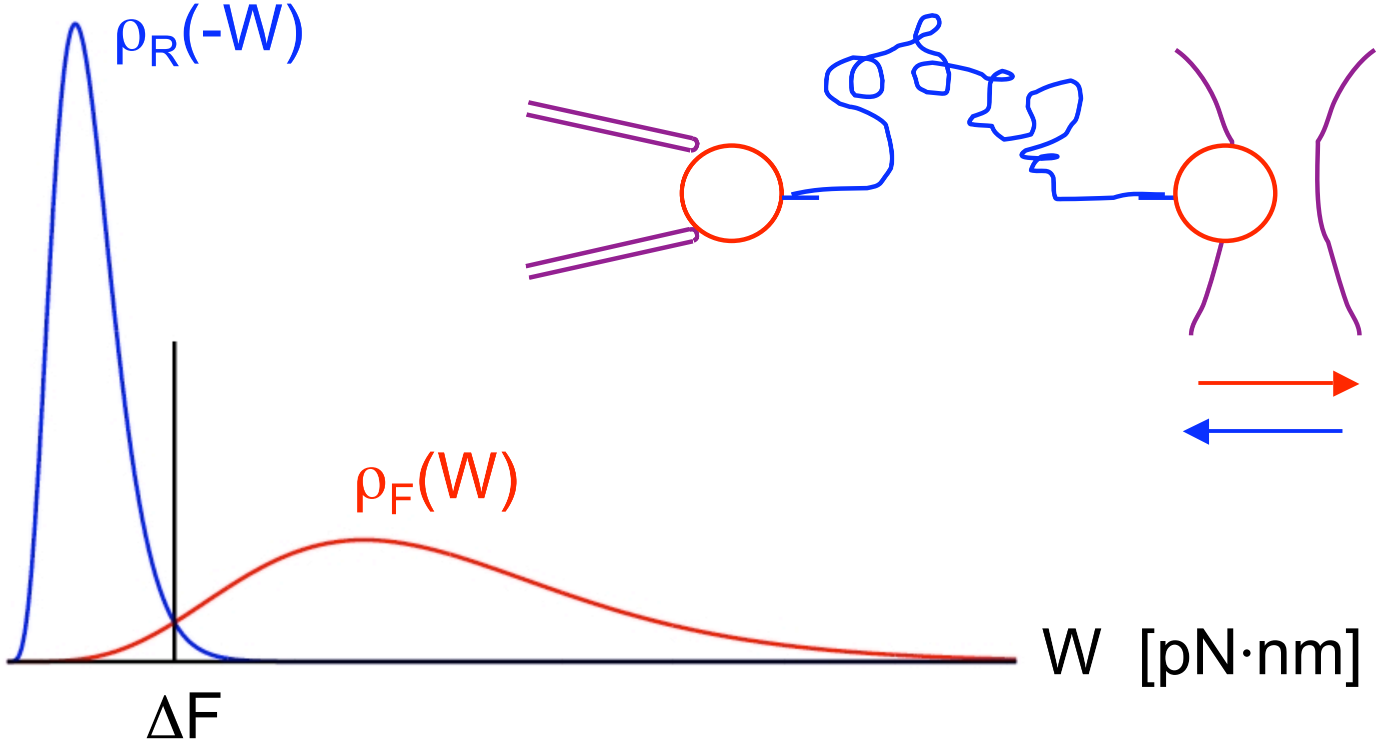


Kelvin-Planck statement of 2nd Law: $\langle W\rangle_F + \langle W\rangle_R \geq 0$

(no free lunch… *on average*)

At the microscopic level :

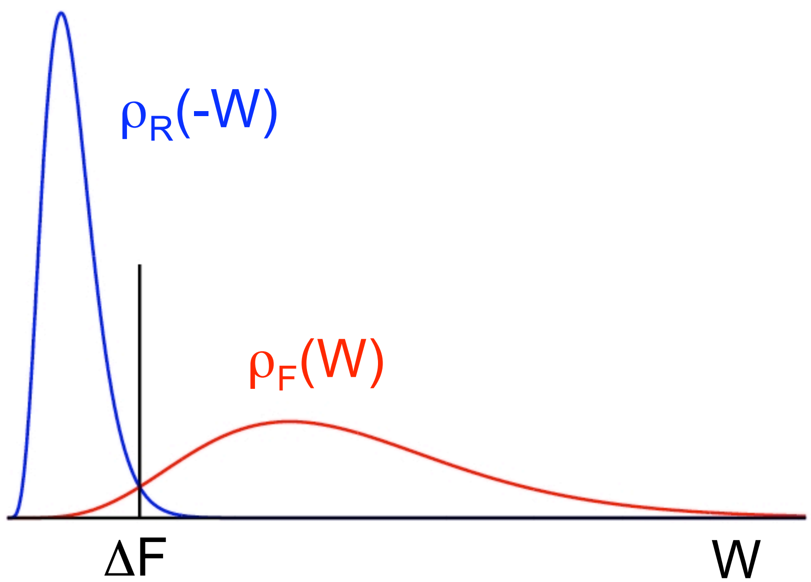
single molecule



$$\boxed{\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]}$$

G.E. Crooks, PRE 1999

Nonequilibrium work relations



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

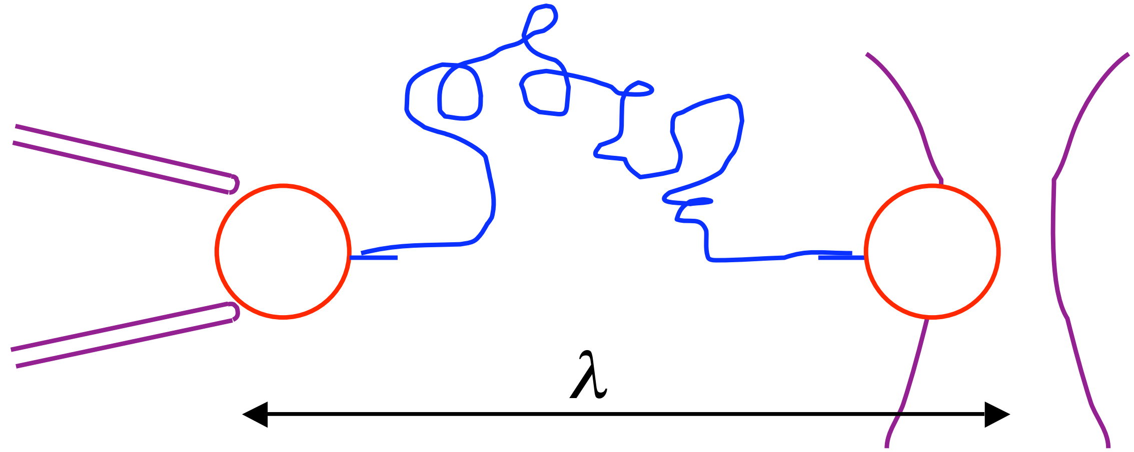
$$\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$$

& others …

Bustamante, Liphardt, & Ritort, *Physics Today*, 2005

- how they are derived
- what they are good for
- what they reveal about irreversibility

Derivation
(isolated system)



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

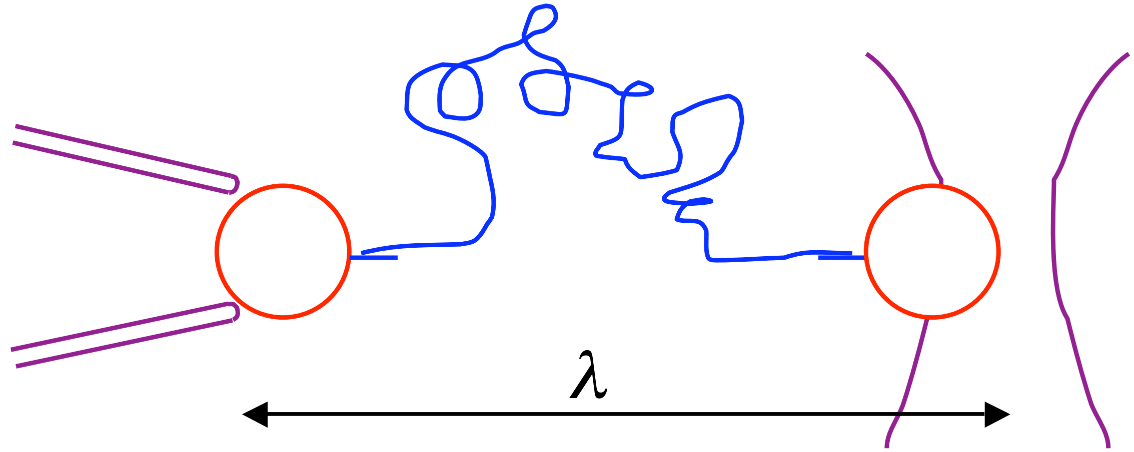
In equilibrium …

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

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

1st law : $\Delta E = W + \cancel{Q}$

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

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

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

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

=1 (Liouville's thm.)

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

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

QED

Various derivations

- C.J. PRL & PRE 1997, J Stat Mech 2004
- G.E. Crooks J Stat Phys 1998, PRE 1999, 2000
- J. Kurchan cond-mat 2000
- G. Hummer & A. Szabo PNAS 2001
- T. Hatano & S.I. Sasa PRL 2001
- S.X. Sun J Chem Phys 2003
- D. J. Evans Mol Phys 2003
- S. Mukamel PRL 2003
- H. Oberhofer, C. Dellago, P. Geissler J Phys Chem B 2005
- A. Imparato & L. Peliti Europhys Lett 2005
- U. Seifert PRL 2005 …

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

see also: G.N. Bochkov & Y.E. Kuzovlev JETP 1977

skepticism: E.G.D. Cohen & D. Mauzerall J Stat Mech 2004
J. Sung PRE 2005
J.M.G. Vilar & J.M Rubi PRL 2008

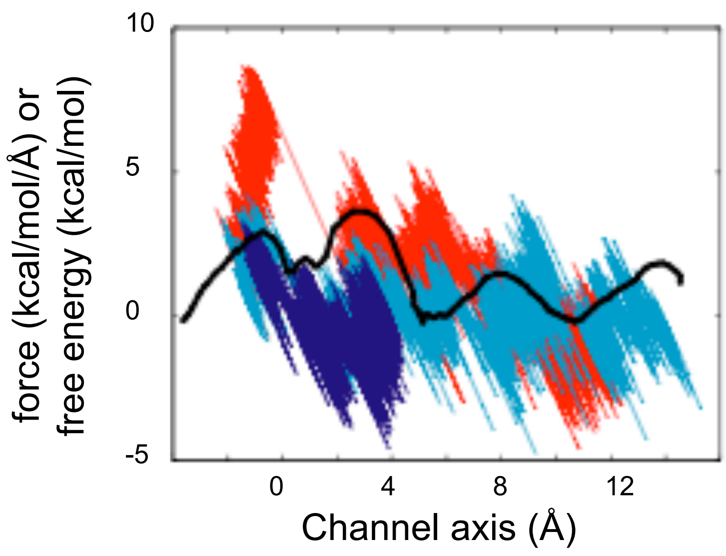
Free energy calculations

use nonequilibrium simulations to estimate equilibrium
free energy differences in complex systems

e.g. *potentials of mean force*

Hummer & Szabo, PNAS (2001)
Park & Schulten, J Chem Phys (2004)

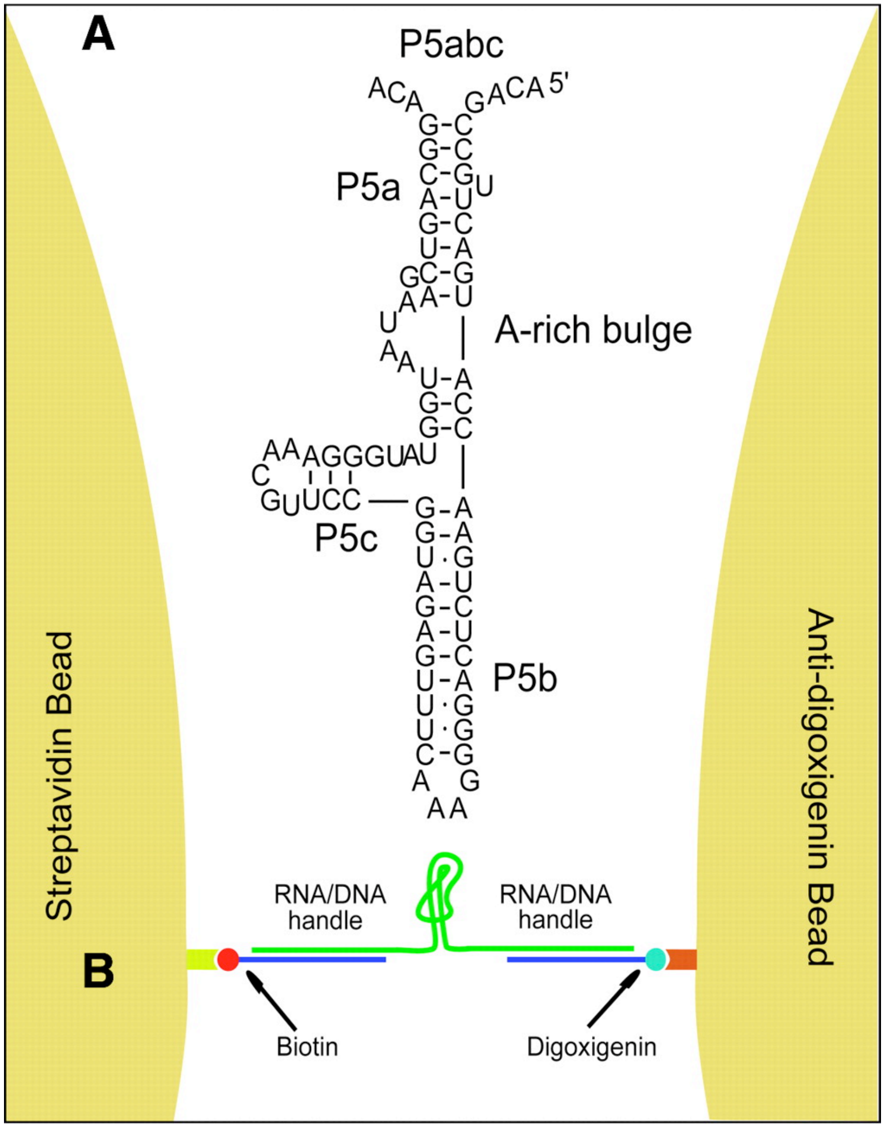
nonequilibrium trajectories + statistical weights exp(-βw)
=
equilibrium information



<u>example</u>: conduction of ammonia
through a barrel-like protein

R. Amaro & Z. Luthey-Schulten,
Chem Phys **307**, 147-155 (2004)

Single-molecule experiments



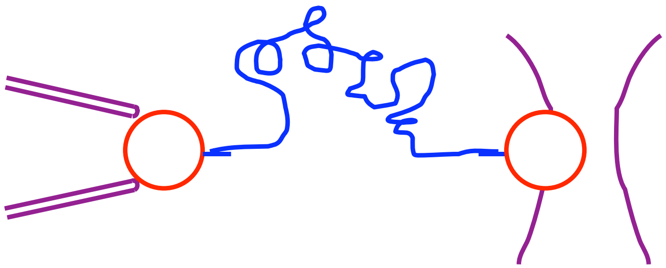
$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

Liphardt, Dumont, Smith, Tinoco, and Bustamante
Science **296**, 1832-1835 (2002)

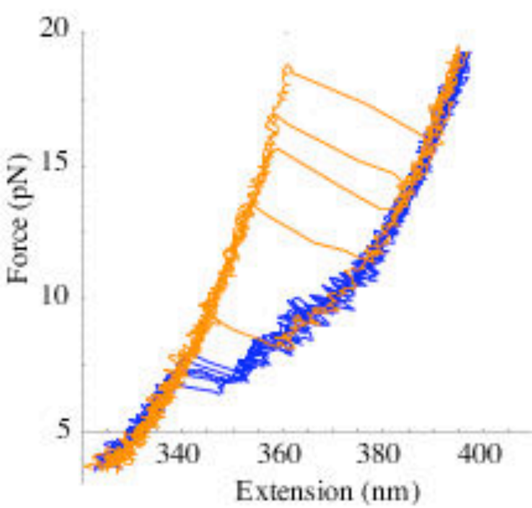
experimental confirmation that equilibrium free energy differences can be obtained from nonequilibrium work values

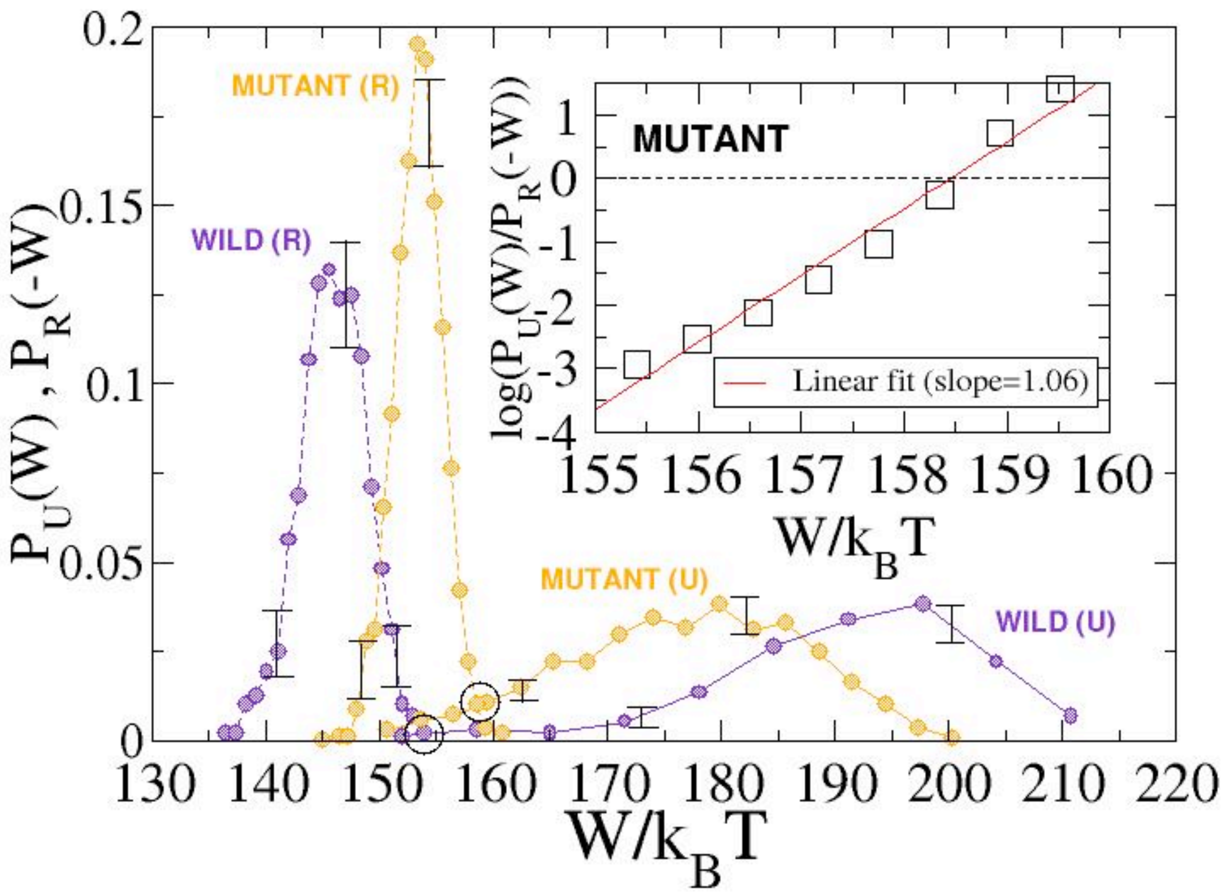
Unfolding & refolding of ribosomal RNA

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



Collin *et al*, *Nature* **437**, 231 (2005)





Further experimental tests

- optically trapped colloids

  Wang *et al*, *Phys Rev Lett* **89**, 050601 (2002)

  Blickle *et al*, *Phys Rev Lett* **96**, 070603 (2006)

- single-molecule unfolding of *titin*

  Harris, Song, and Kiang, *Phys Rev Lett* **99**, 068101 (2007)

- torsional pendulum

  Douarche *et al*, *Europhys Lett* **70**, 593 (2005)

  J Stat Mech P09011 (2005)

- other systems?

  magnetic nanoparticles?

  trapped cold ions?

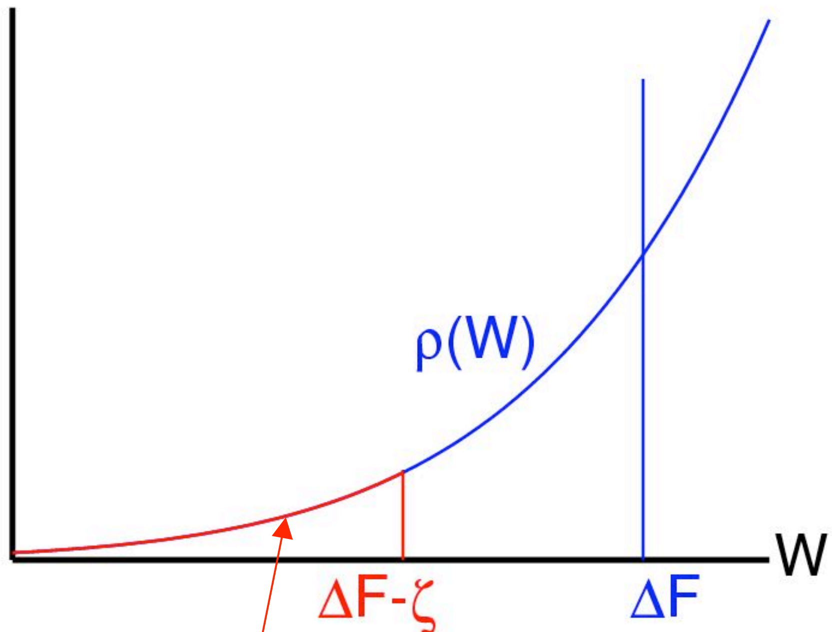
  quantum effects?

Irreversibility in microscopic systems

$$\left.\begin{aligned} \left\langle e^{-\beta W} \right\rangle &= e^{-\beta \Delta F} \\ \left\langle e^{x} \right\rangle &\geq e^{\langle x \rangle} \end{aligned}\right\} \longrightarrow \langle W \rangle \geq \Delta F$$

Jensen's inequality

(Clausius inequality)



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

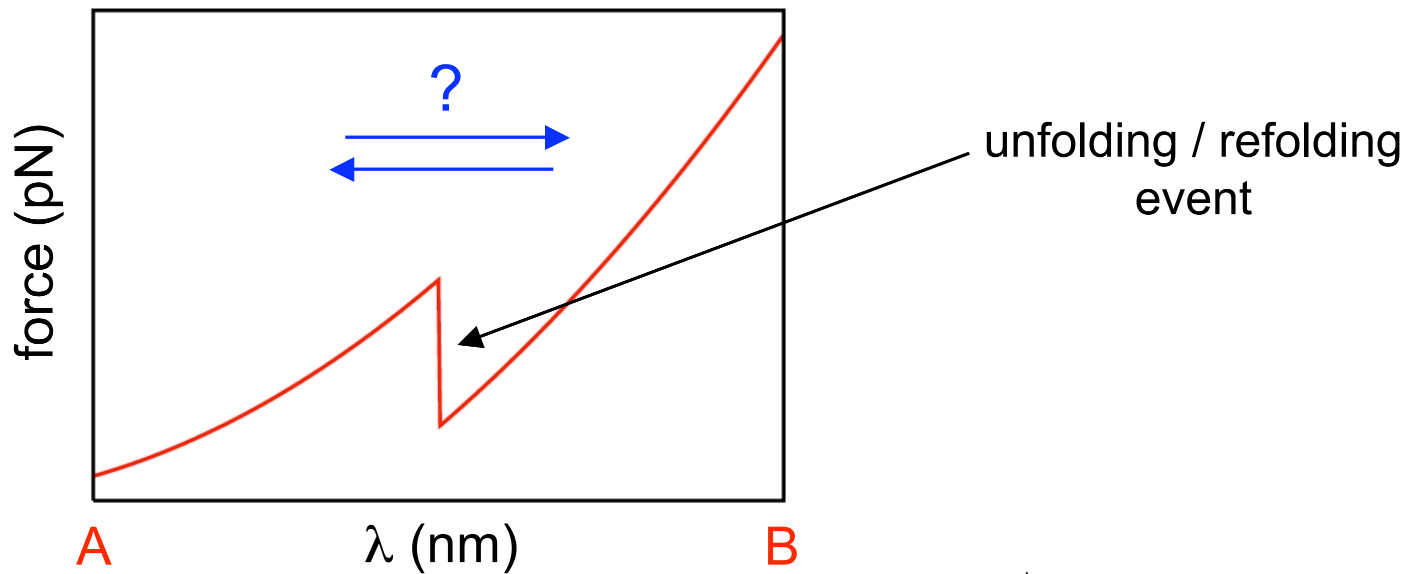
$$P[W < \Delta F - \zeta] = \int_{-\infty}^{\Delta F - \zeta} dW\, \rho(W) \leq \int_{-\infty}^{\Delta F - \zeta} dW\, \rho(W)\, e^{\beta(\Delta F - \zeta - W)}$$

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

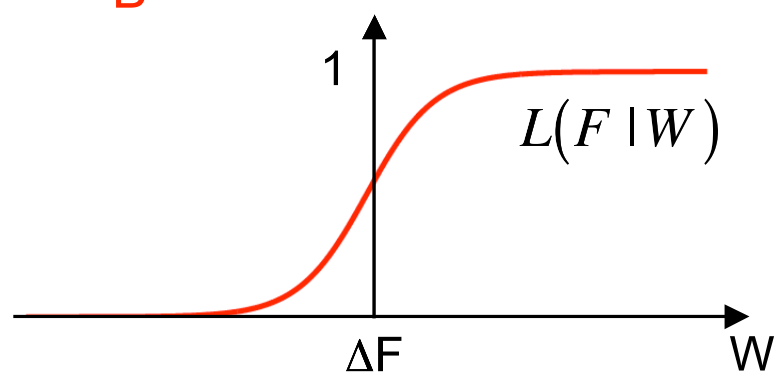
Guessing the direction of the arrow of time

You are shown a movie depicting a thermodynamic process, A→B.
Task: determine whether you are viewing the events in the order in which they actually occurred, or a movie run backward of the reverse process.

e.g.

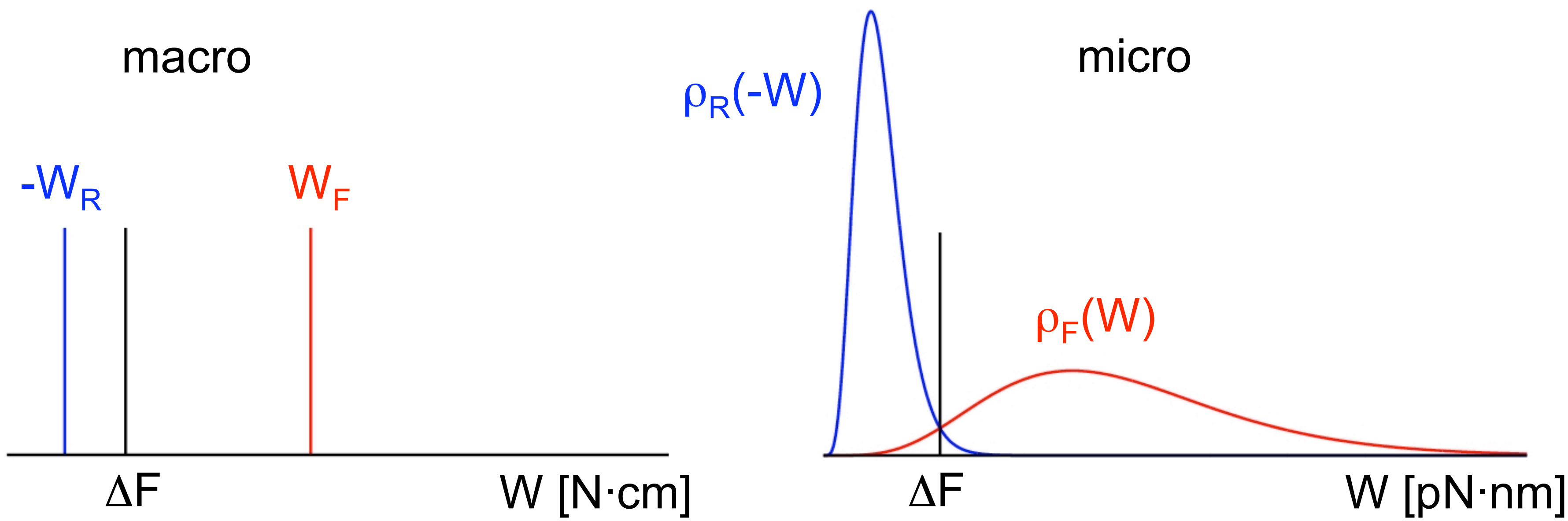


$$L(F \mid W) = \frac{1}{1 + \exp[-\beta(W - \Delta F)]}$$



~ Shirts *et al*, PRL 2003 ,
Maragakis *et al*, J Chem Phys 2008

Summary



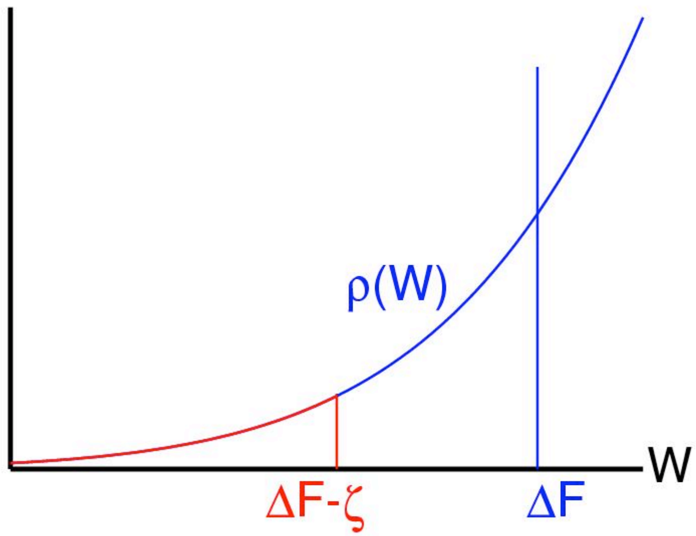
$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \quad , \quad \frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right] \quad , \quad \text{\& others}$$

Nonequilibrium work fluctuations:

- satisfy strong constraints
- encode equilibrium information
- irreversibility in microscopic systems

Irreversibility in microscopic systems

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \quad \text{implies} \quad \begin{cases} \langle W \rangle \geq \Delta F & \text{(Clausius inequality)} \\ P[W < \Delta F - \zeta] \leq \exp(-\zeta / kT) \end{cases}$$



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

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guessing the arrow of time

characteristic transition from
"almost certainly F" to "almost certainly R"

$$L(F|W) = \frac{1}{1 + \exp\left(-\dfrac{W - \Delta F}{kT}\right)}$$

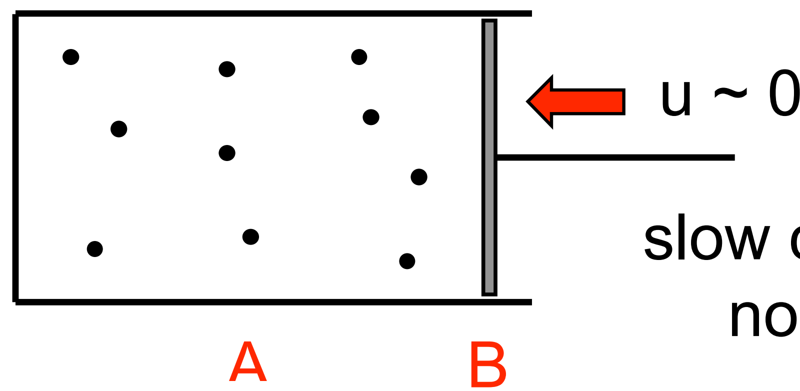
see also:
Kawai, Parrondo, van den Broeck PRL 2007

~ Shirts *et al*, PRL 2003

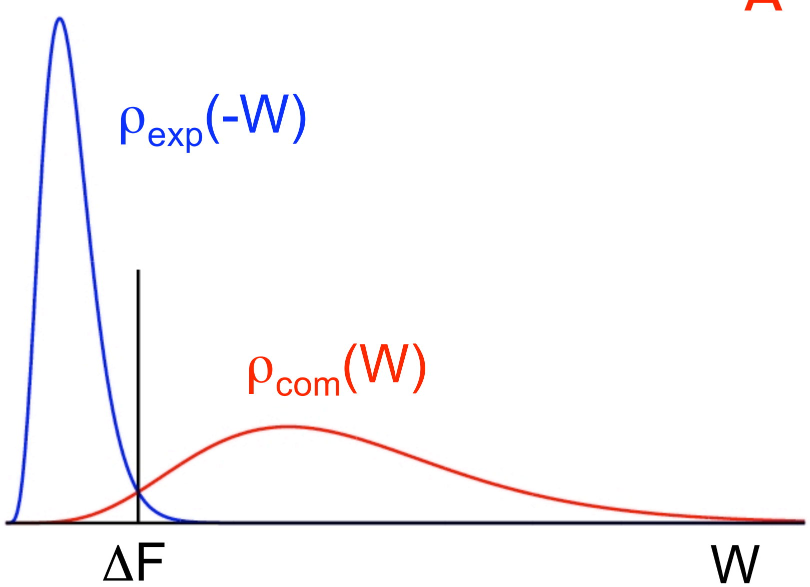
Exactly solvable model:
Compression /expansion of dilute classical gas

Crooks & Jarzynski, PRE 2007

n_p *interacting* particles,
initial temperature T



slow compression,
no heat bath



$$\boxed{\rho(W) = \frac{\beta}{\alpha\Gamma(k)}\left(\frac{\beta W}{\alpha}\right)^{k-1} \exp\left(-\frac{\beta W}{\alpha}\right)\theta(W)}$$

$$\alpha = \left(V_B / V_A\right)^{2/3} - 1$$

$$k = 3n_p / 2$$