Nonequilibrium thermodynamics at the microscale

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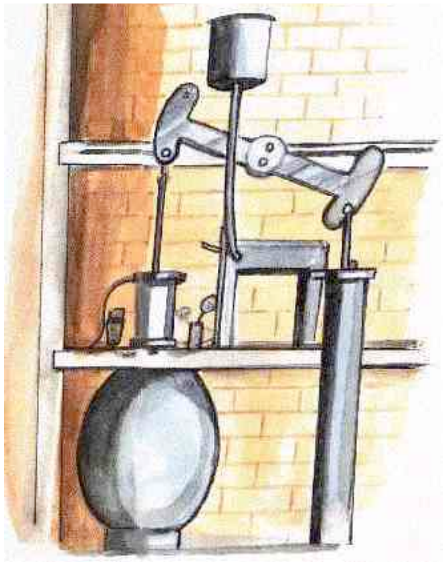
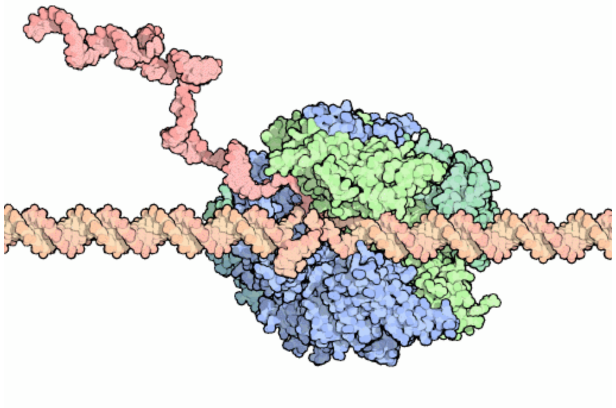
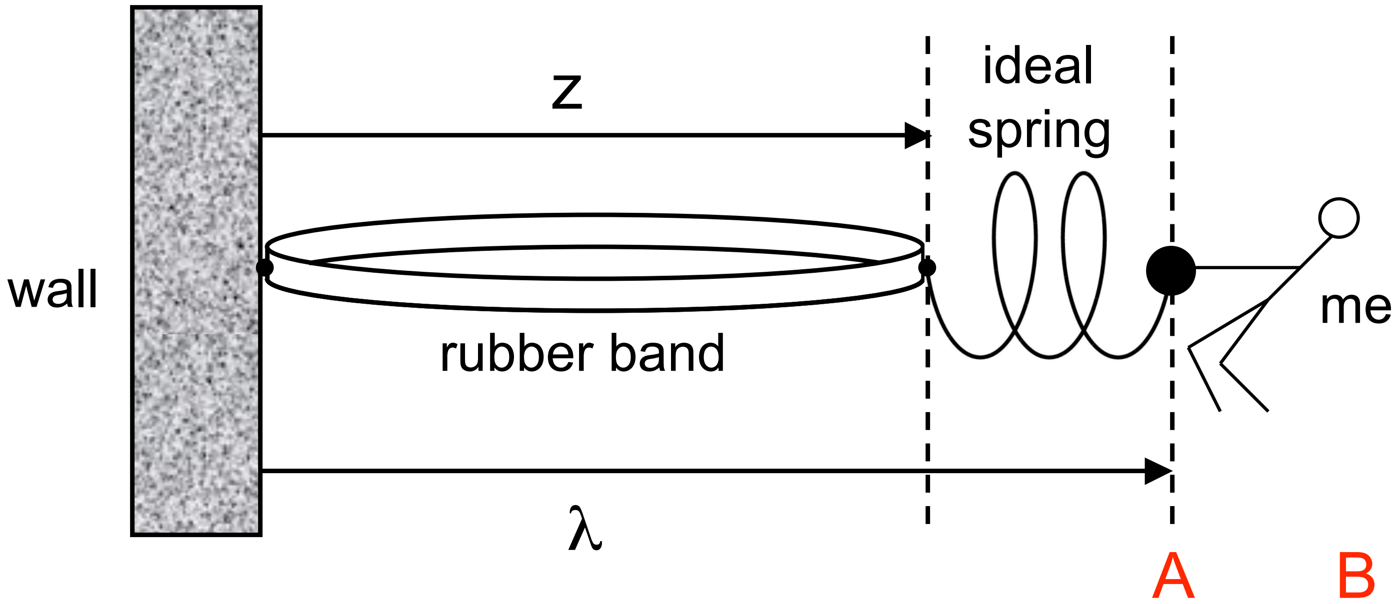
~1 m



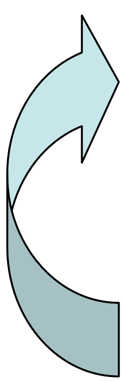


~20 nm

Work and free energy: a macroscopic example …



Irreversible process:

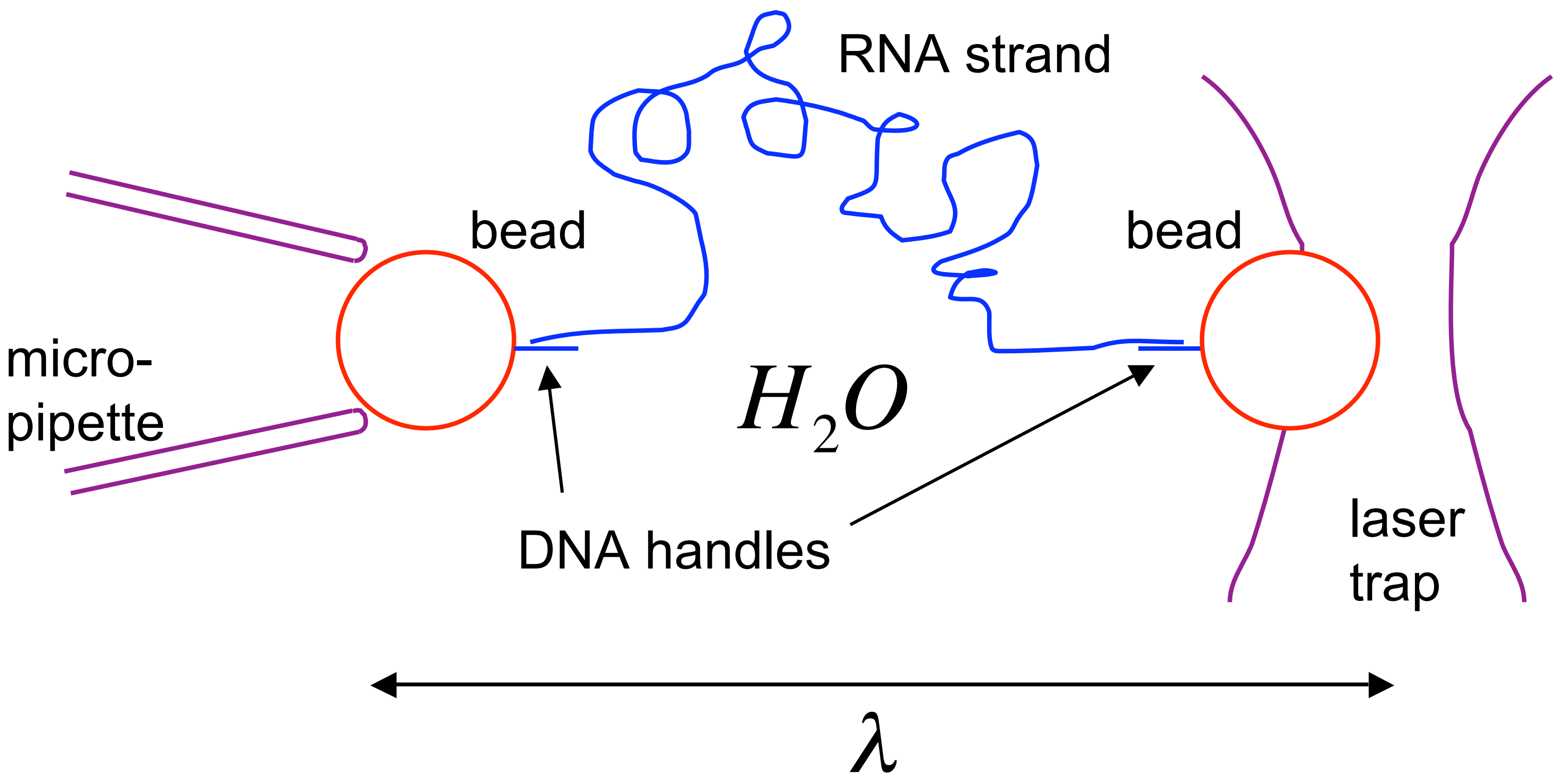


1. Begin in equilibrium — $\lambda = A$
2. Stretch the rubber band — $\lambda : A \rightarrow B$

   W = work performed

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

… and a microscopic analogue

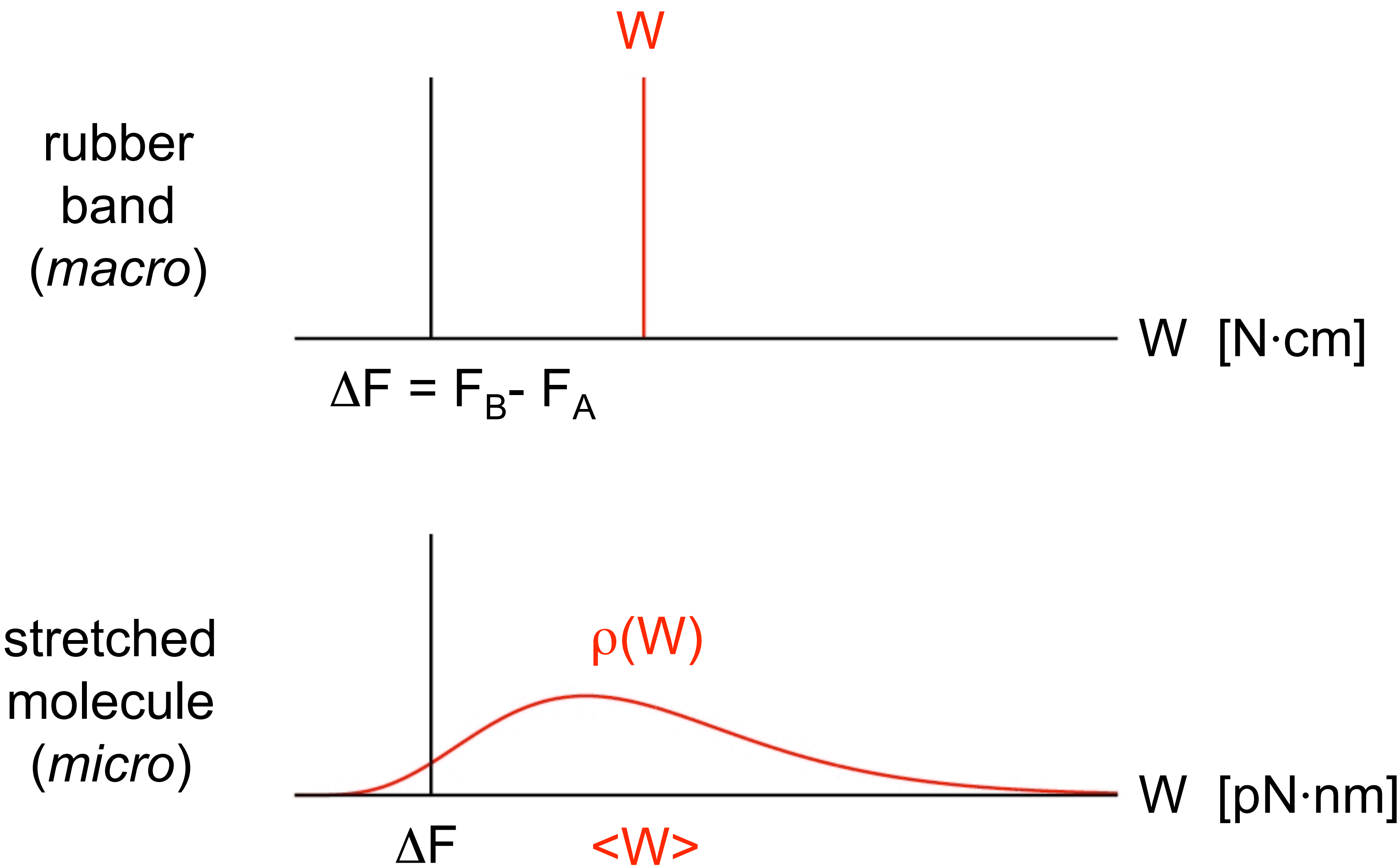


1. Begin in equilibrium $\lambda = A$
2. Stretch the molecule $\lambda : A \rightarrow B$

   W = work performed

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

Clausius inequality : $W \geq \Delta F$

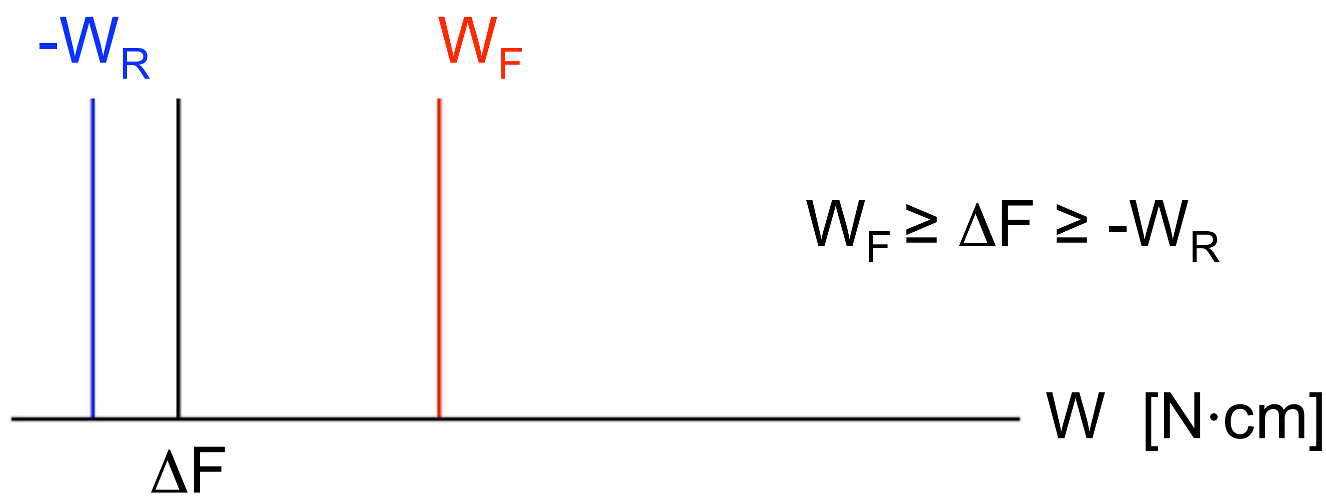


Thermodynamic cycles: stretching & *unstretching*

stretching (*forward*, F) : $A \rightarrow B$

unstretching (*reverse*, R) : $A \leftarrow B$ $W_R \geq -\Delta F$

rubber band (*macro*)



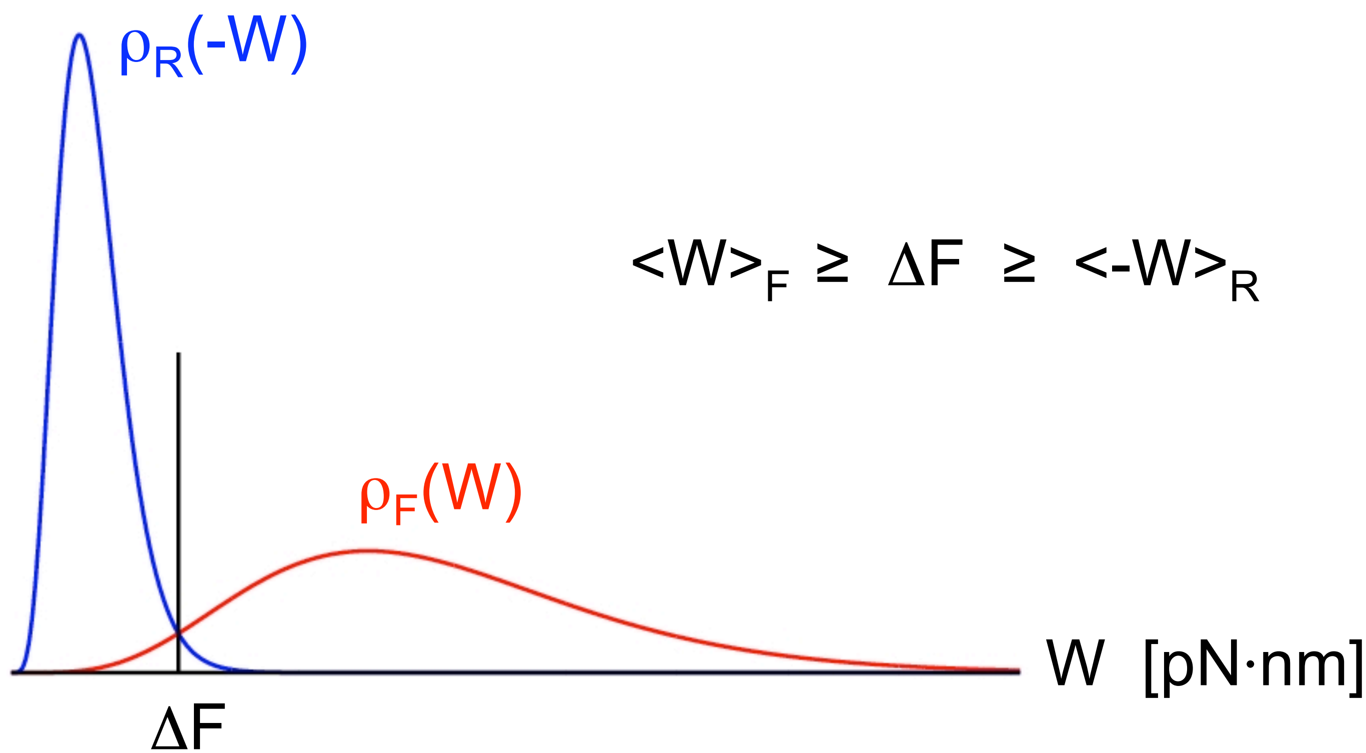
$W_F \geq \Delta F \geq -W_R$

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

We perform more work during the forward half-cycle ($A \rightarrow B$) than we recover during the reverse half-cycle ($A \leftarrow B$).

(no free lunch)

At the microscopic level :



single molecule (*micro*)

$\langle W \rangle_F \geq \Delta F \geq \langle -W \rangle_R$

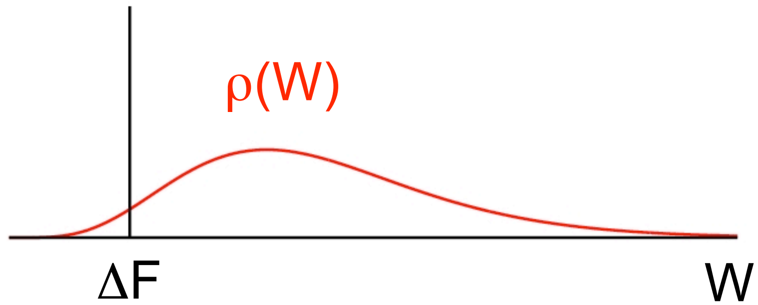
Kelvin-Planck statement of 2nd Law: $\langle W \rangle_F + \langle W \rangle_R \geq 0$

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

(no free lunch… in the long run)

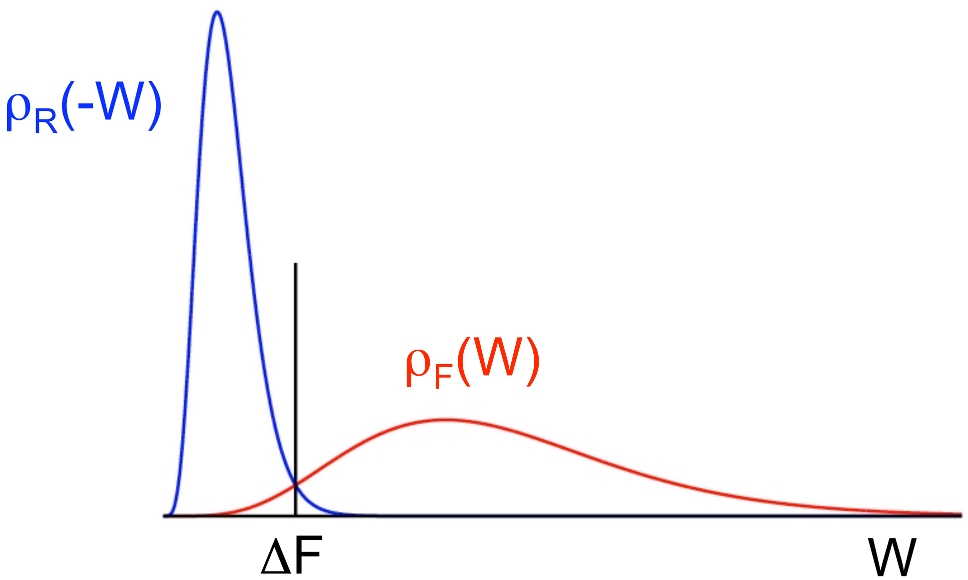
So what's new?

Fluctuations in W satisfy general and unexpected laws.



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

C.J., PRL 1997



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

G.E. Crooks, PRE 1999

So what?

Fluctuations in W satisfy general and unexpected laws.

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

& others … (Bustamante, Liphardt, & Ritort, Phys. Today, 2005)

- These results remain valid *far* from equilibrium.

  → also true of entropy fluctuation theorems

- They relate nonequilibrium observables to equilibrium properties.

  → free energy estimation (simulation & experiment)

✓ • They add to our understanding of the 2nd law of thermodynamics.

  → Clausius inequality
  → irreversibility, "arrow of time"

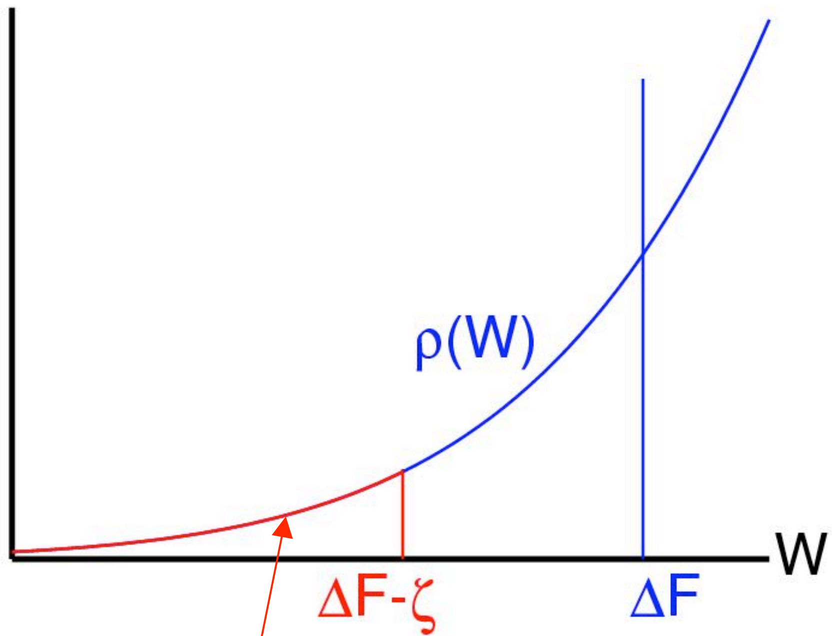
Clausius inequality : <W> ≥ ΔF

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

Jensen's inequality

$$\left\langle e^{x} \right\rangle \geq e^{\langle x \rangle}$$

$$\Longrightarrow \langle W \rangle \geq \Delta F$$



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

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

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

Irreversibility and the “arrow of time”

general observation:

Our everyday experience provides us with strong expectations regarding the order in which events ought to occur.

Macroscopic irreversibility

however:

Microscopic laws are time-reversal invariant.

Microscopic reversibility

Statistical resolution: a particular sequence of events might be **much** more likely than the reverse sequence.

(hence, arrow of time)

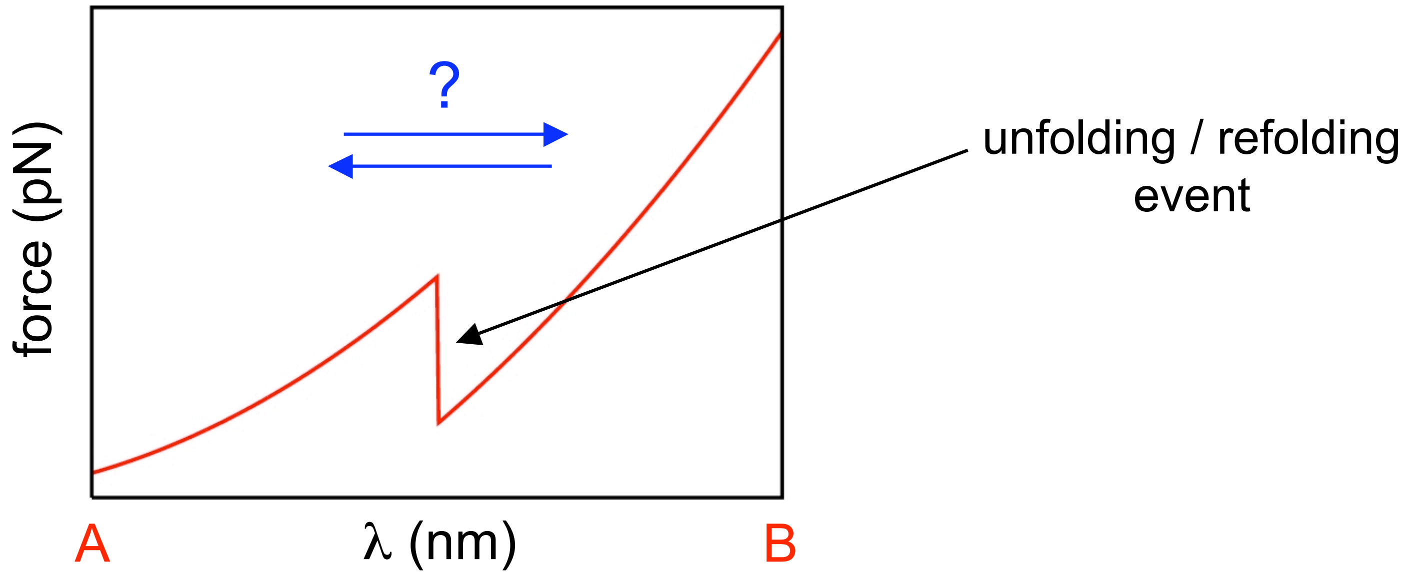
What about small systems?

A thought experiment / guessing game

Alice flips a coin.

Heads: She stretches a single molecule (A→B).
Tails: She unstretches the molecule (A←B).

Then she shows Bob the force-extension curve:



Bob's task: *guess the arrow of time !*

Maximum likelihood estimation

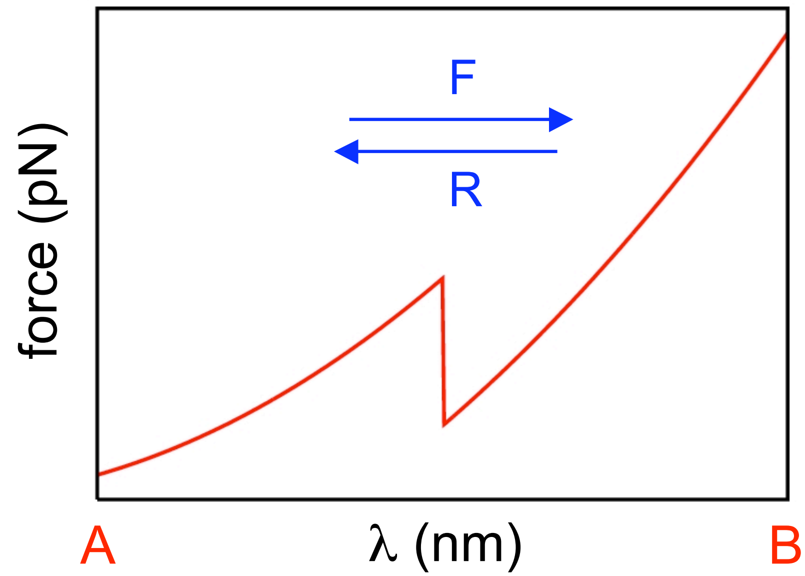
$$W = \int force \cdot d\lambda$$

$\Delta F = F_B - F_A$

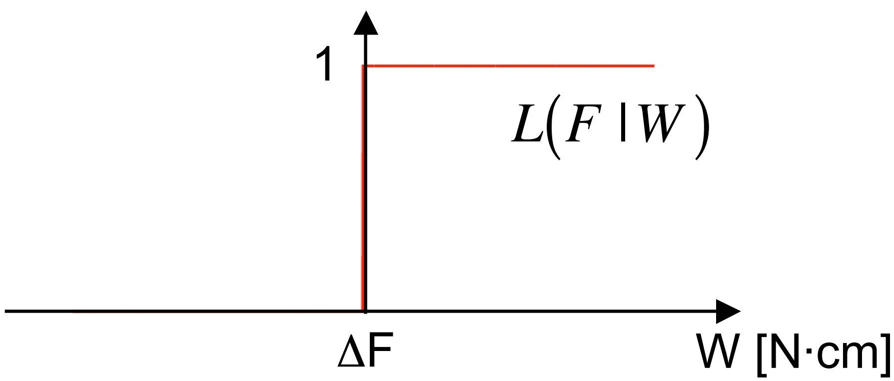
$L(F \mid W)$ = likelihood of A→B, given W

$L(R \mid W)$ = likelihood of A←B, given W

… which is greater ?



if this were a macroscopic system …



Analysis of likelihoods

Likelihood: degree to which an observation (W) supports a hypothesis (F/R).

law of likelihoods:

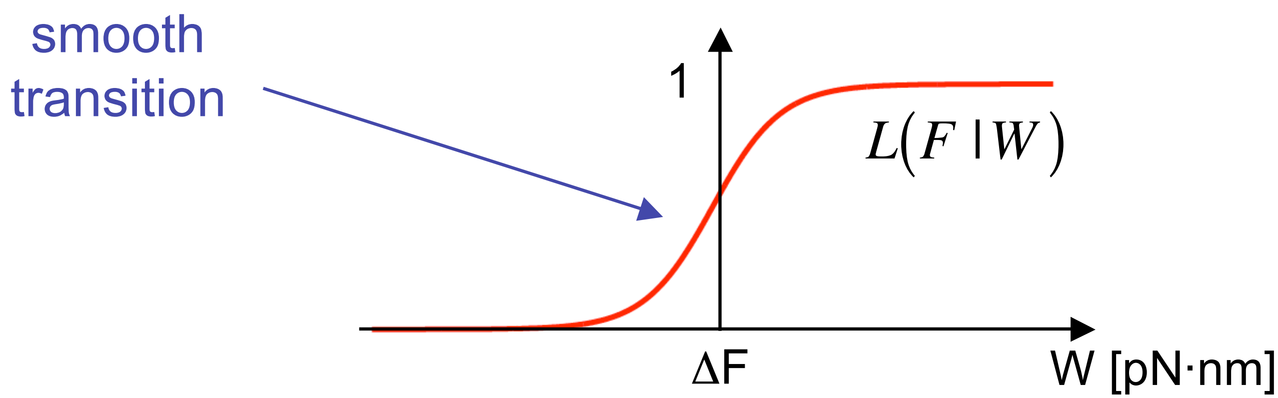
$$L(F \mid W) \propto P(W \mid F) \leftarrow \rho_F(W)$$

$$L(R \mid W) \propto P(W \mid R) \leftarrow \rho_R(-W)$$

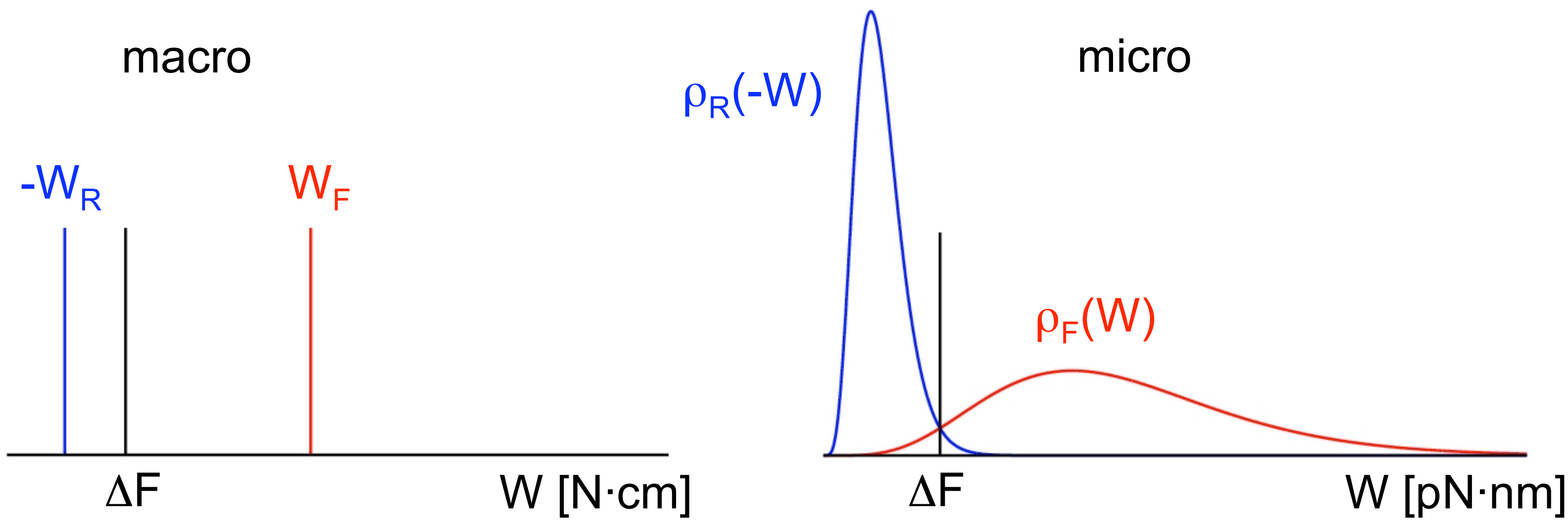
combine w/ Crooks's fluctuation theorem, normalization …

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

Shirts et al, PRL 2003
G.E. Crooks (personal comm.)



Summary



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

These & other results refine our understanding of the 2nd law, as it applies to microscopic systems:

- violations of the Clausius inequality
- irreversibility and the “arrow of time”

Experimental single-molecule data

Collin et al, Nature 2005