UNIVERSITY OF MARYLAND

Time’s arrow at the nanoscale

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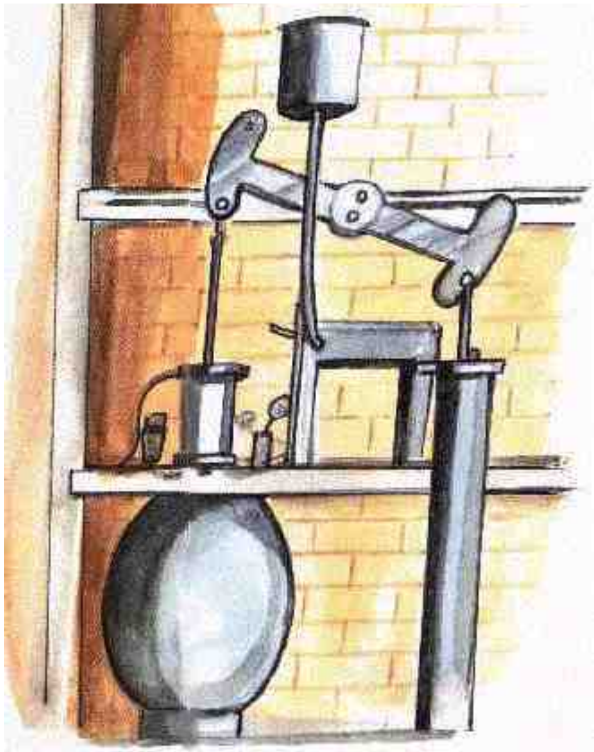
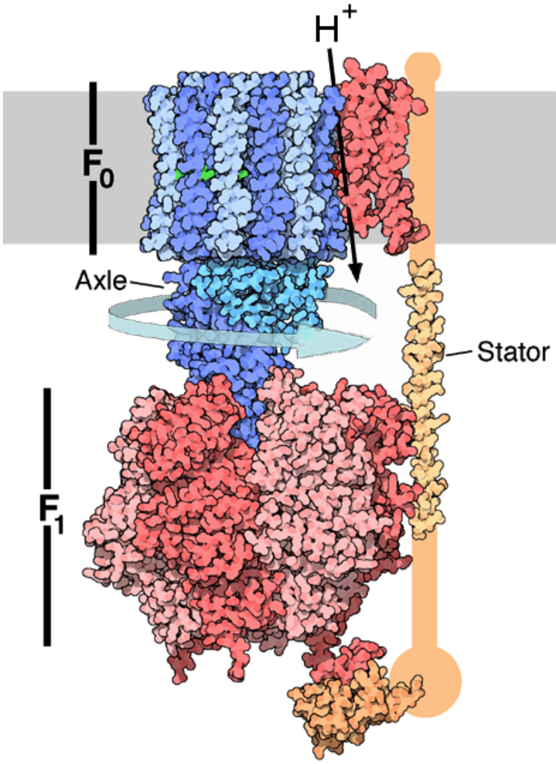
Macroscopic and microscopic machines

steam engine



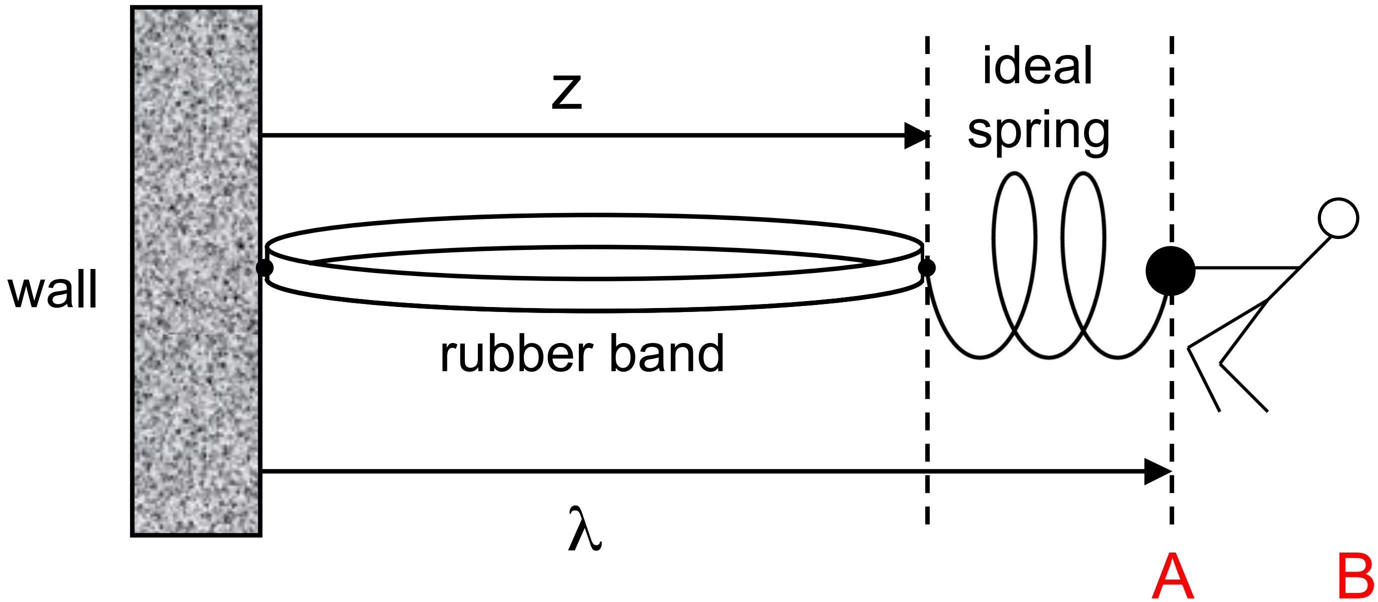
ATP synthase



RCSB Protein Data Bank

What do the laws of thermodynamics “look like” at the nanoscale?

Work and free energy: a macroscopic example …

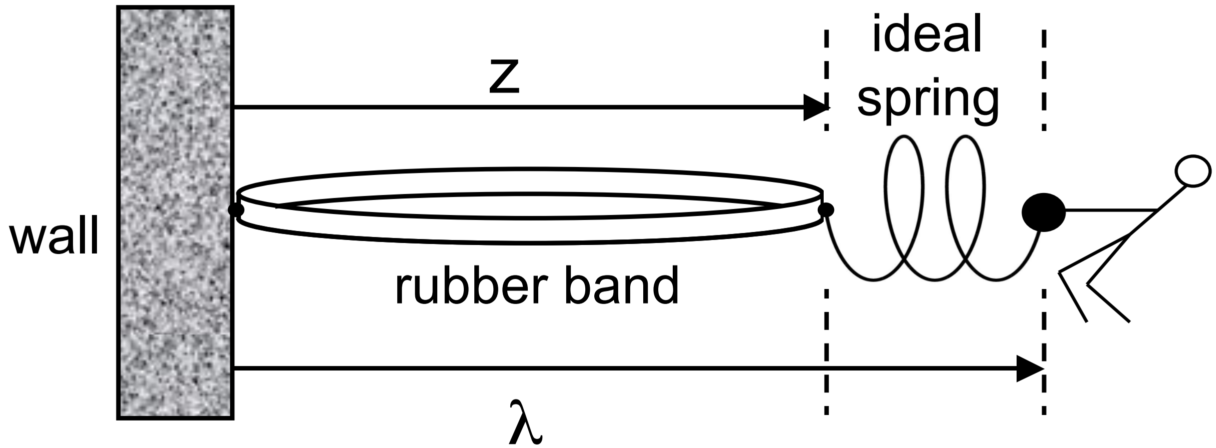


Irreversible process:

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 …

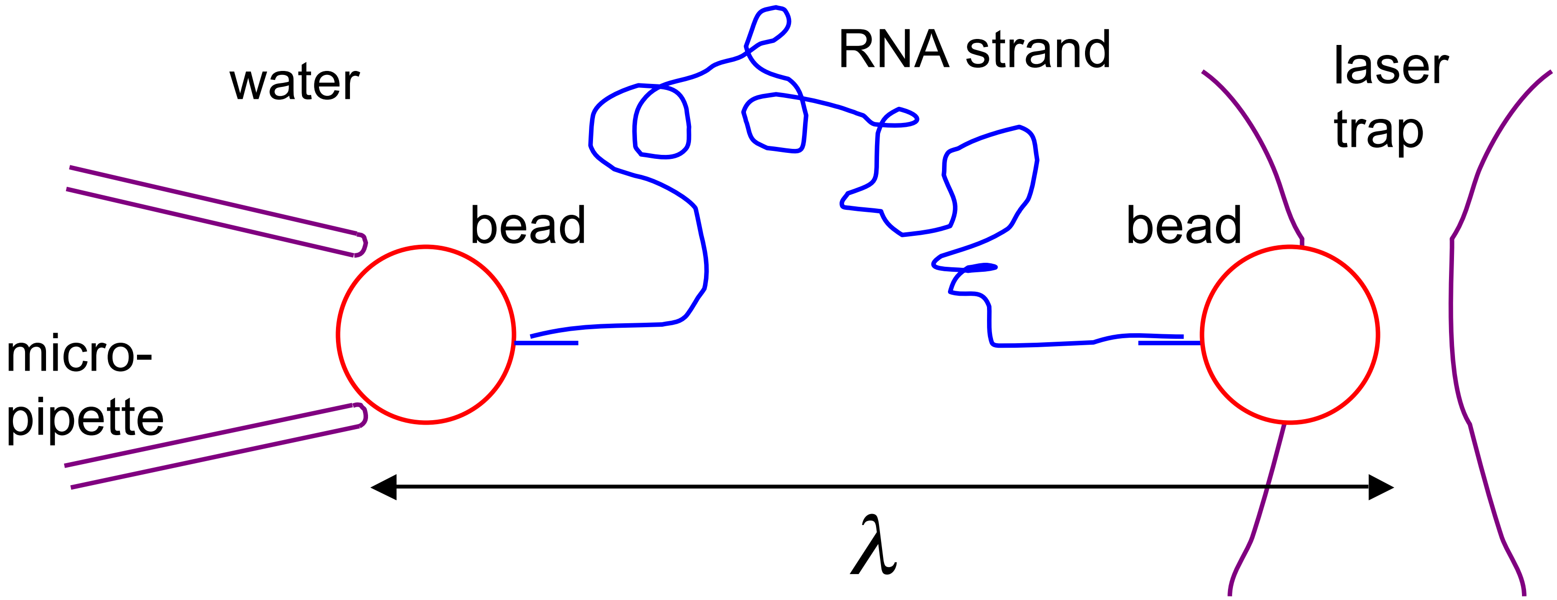


Clausius inequality :

$$\boxed{W_{A\rightarrow B} \geq \Delta F} \equiv F_B - F_A$$

$$\left(\int_A^B \frac{đQ}{T} \leq \Delta S \right)$$

… and a microscopic analogue

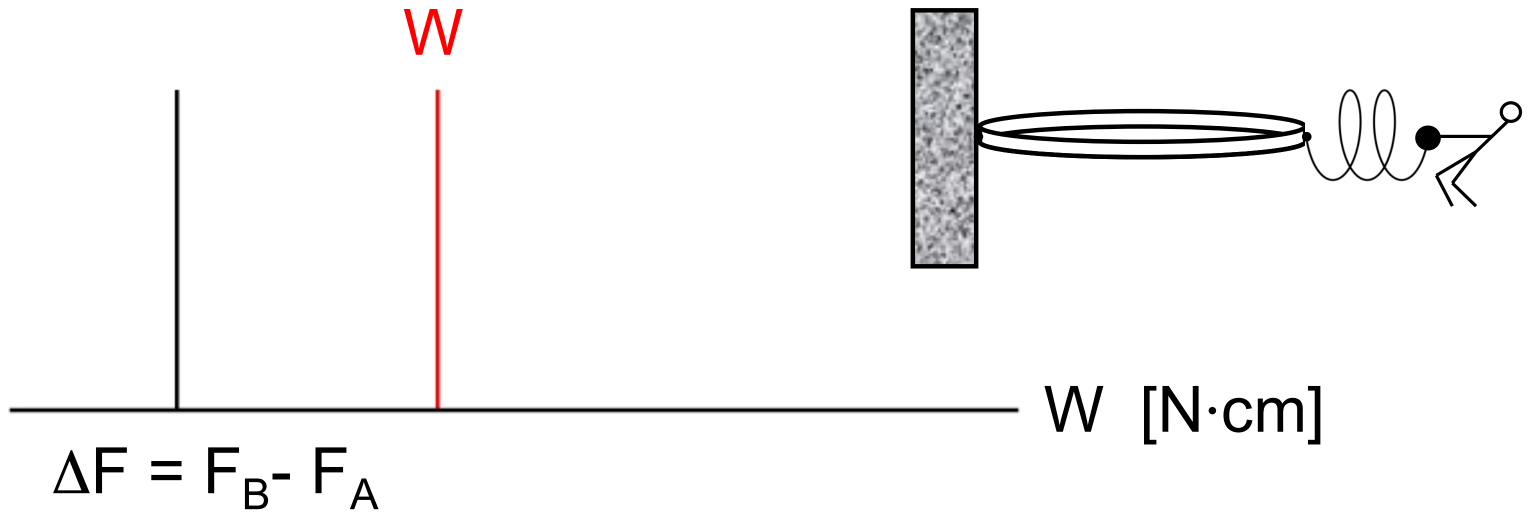


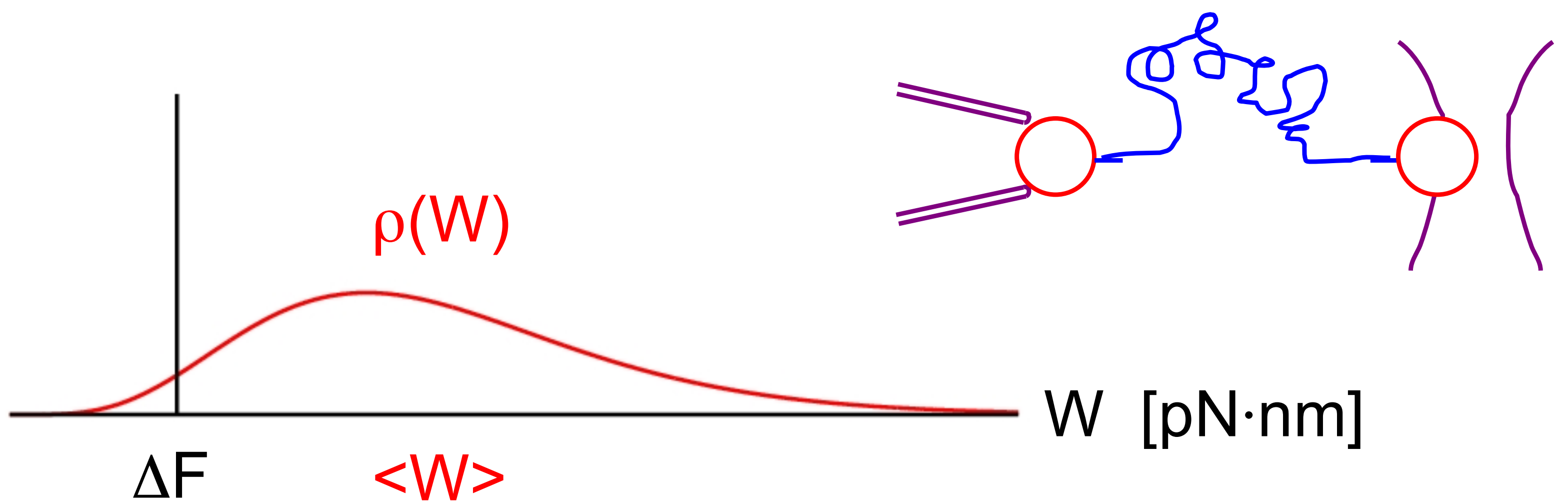
1. Begin in equilibrium $\lambda = A$
2. Stretch the molecule $\lambda : A \rightarrow B$

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

… *fluctuations* are now important !

Clausius inequality, *macro* & *micro*



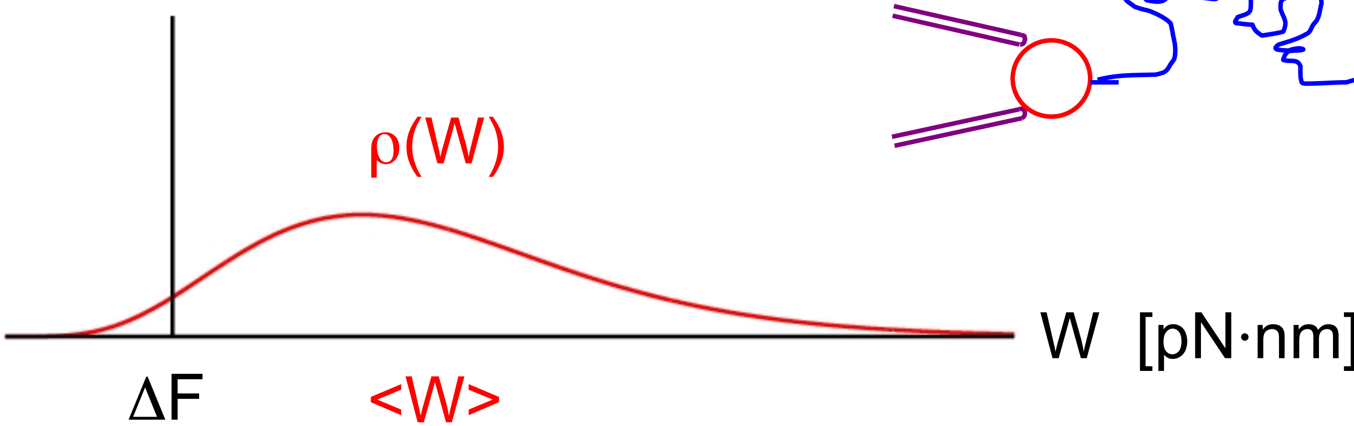


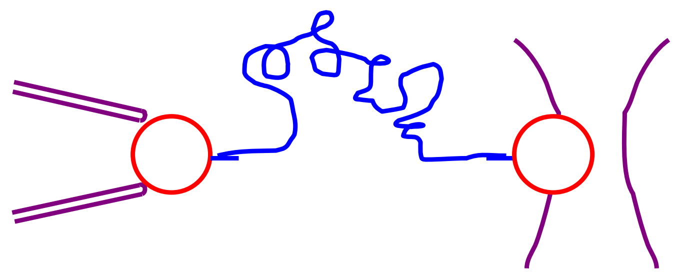
So what's new?

Fluctuations in W satisfy strong and unexpected laws.

e.g. $$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$ C.J., PRL 1997 $$\left(\beta = \frac{1}{k_B T} \right)$$

… places a strong constraint on the work distribution



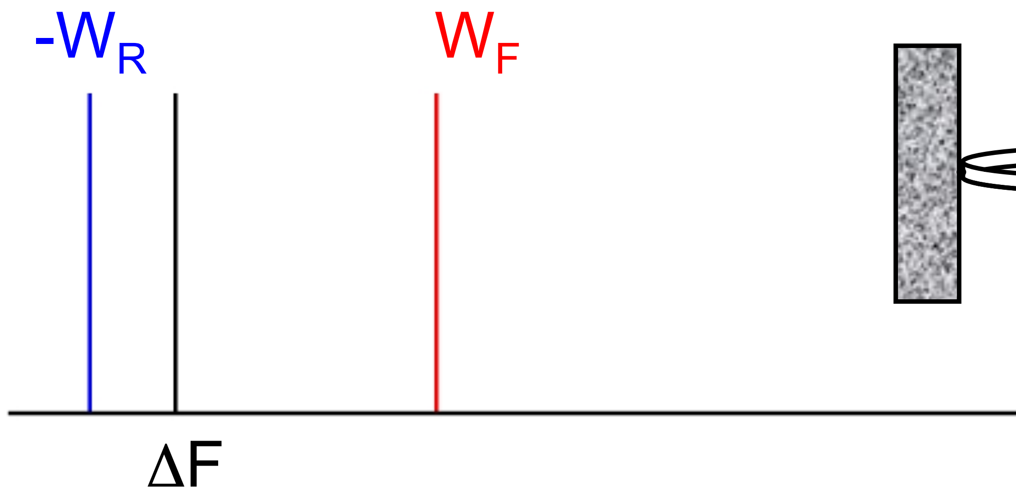


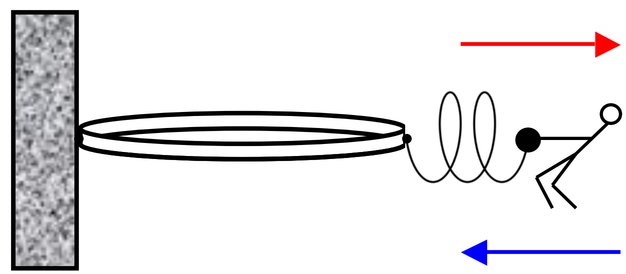
Thermodynamic cycles

forward process :   A→B

reverse process :   A←B

$W_R \geq -\Delta F$





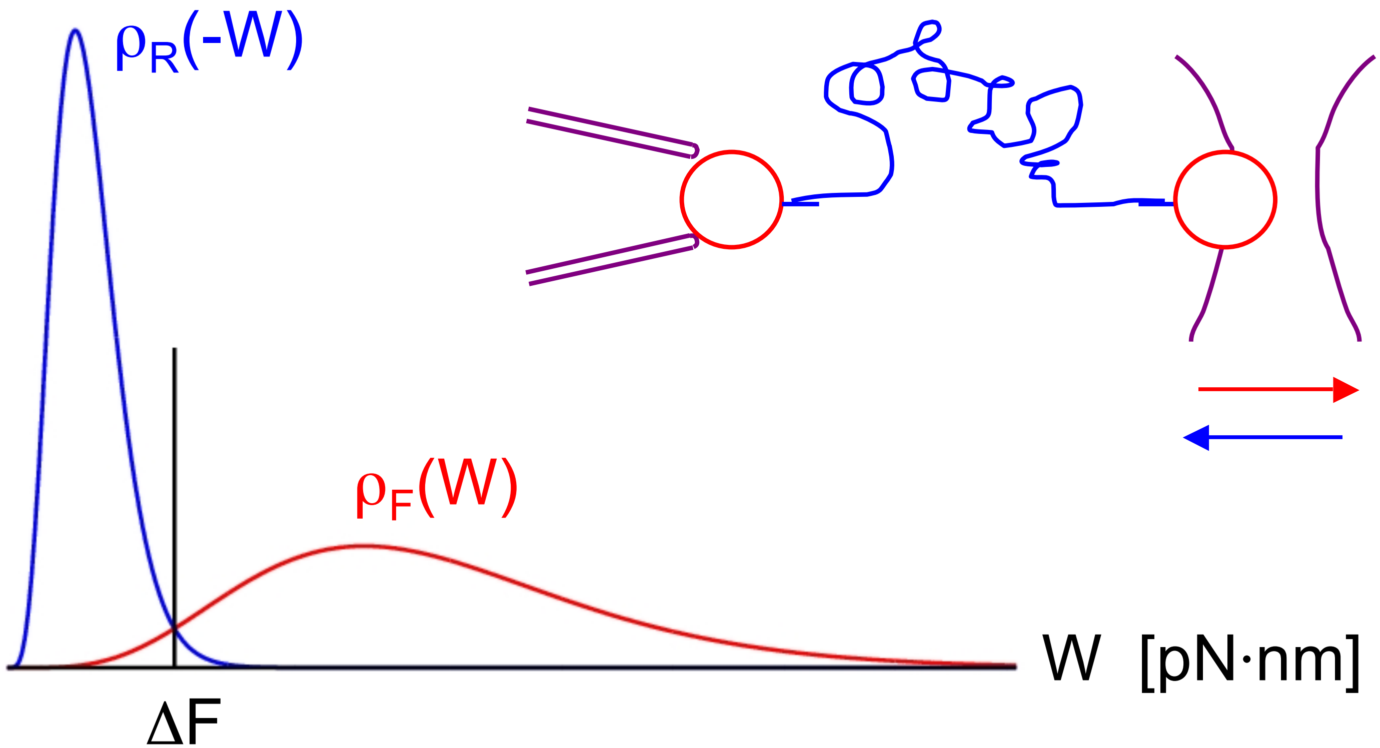
$$-W_R \leq \Delta F \leq W_F$$

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

(no free lunch)

At the microscopic level :

single molecule



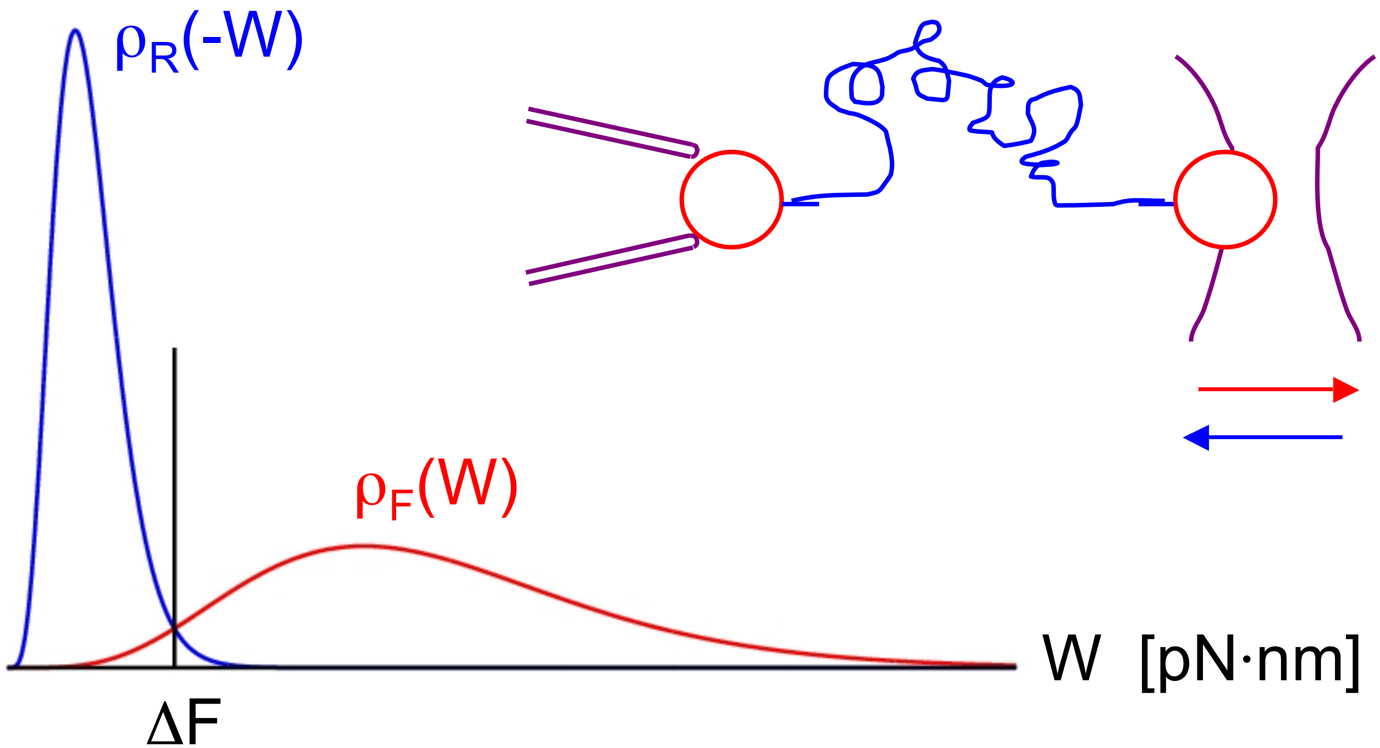
$$-\langle W\rangle_R \leq \Delta F \leq \langle W\rangle_F$$

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

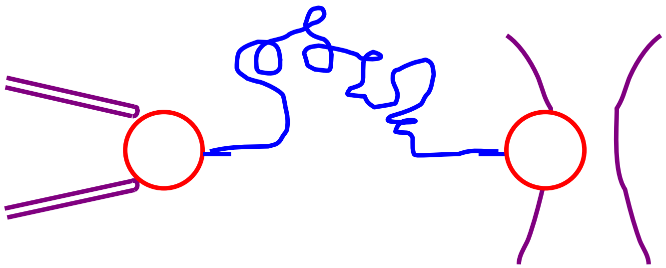


$$\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$$

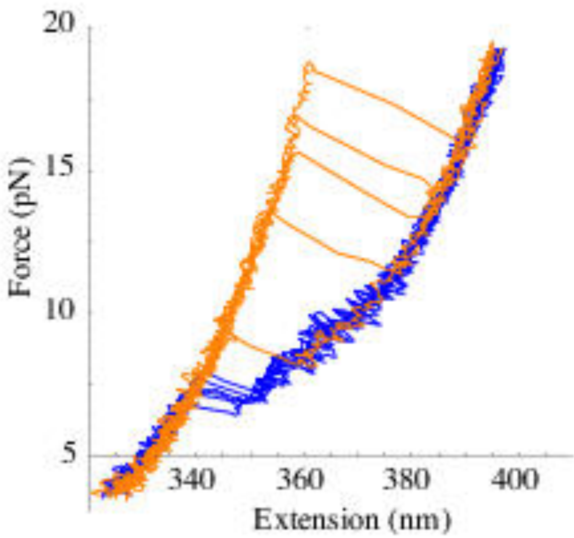
G.E. Crooks, PRE 1999

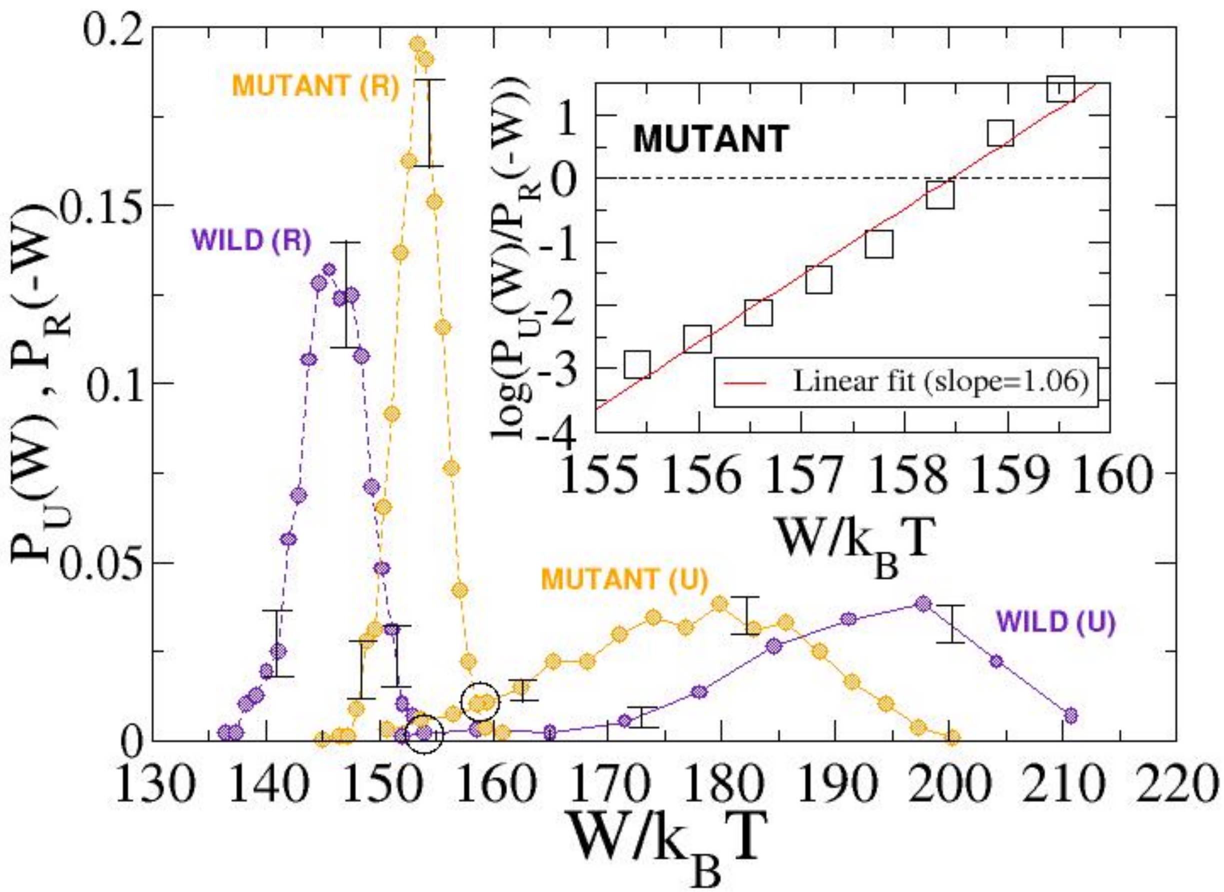
Unfolding & refolding of ribosomal RNA

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



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





Nonequilibrium work relations

macro	micro
$W \geq \Delta F$	$\langle W \rangle \geq \Delta F$
$-W_R \leq \Delta F \leq W_F$	$-\langle W \rangle_R \leq \Delta F \leq \langle W \rangle_F$

Nonequilibrium work relations

macro	micro
$W \geq \Delta F$	$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$
$-W_R \leq \Delta F \leq W_F$	$\dfrac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$
…	…

closely related to *Fluctuation Theorems* for entropy production*
and to early work by Bochkov & Kuzovlev†

* Evans, Cohen, Morriss, Gallavotti, Searles, Kurchan, Lebowitz, Spohn, Maes + many others

† JETP 1977, 1979

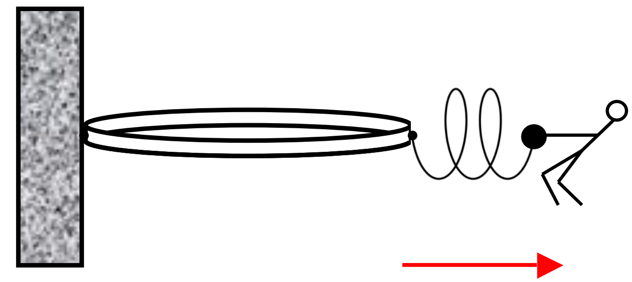
Nonequilibrium work relations

macro	micro
$W \geq \Delta F$	$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$
$-W_R \leq \Delta F \leq W_F$	$\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$
…	…

- apply far from equilibrium
- validated in experiments
- applications: analysis of single-molecule experiments
  & computational thermodynamics
- irreversibility and the arrow of time at the nanoscale

The thermodynamic arrow of time

Make a movie of a thermodynamic process (A→B)



Macroscopic system:

$W > \Delta F$ if the movie is run forward

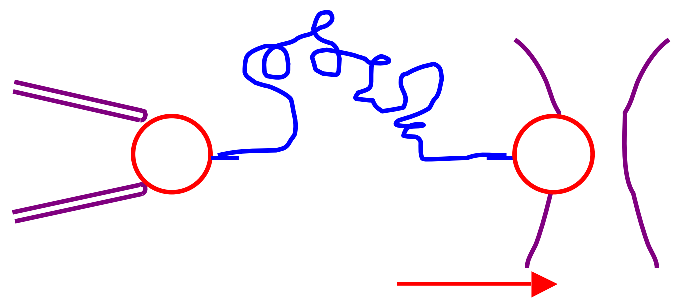
$W < \Delta F$ if the movie is run backward

… perfect correlation between sign($W-\Delta F$) and the chronological ordering of events.

The arrow of time is *sharp*.

The thermodynamic arrow of time

Make a movie of a thermodynamic process (A→B)



Microscopic system:

typically W > ΔF if the movie is run forward

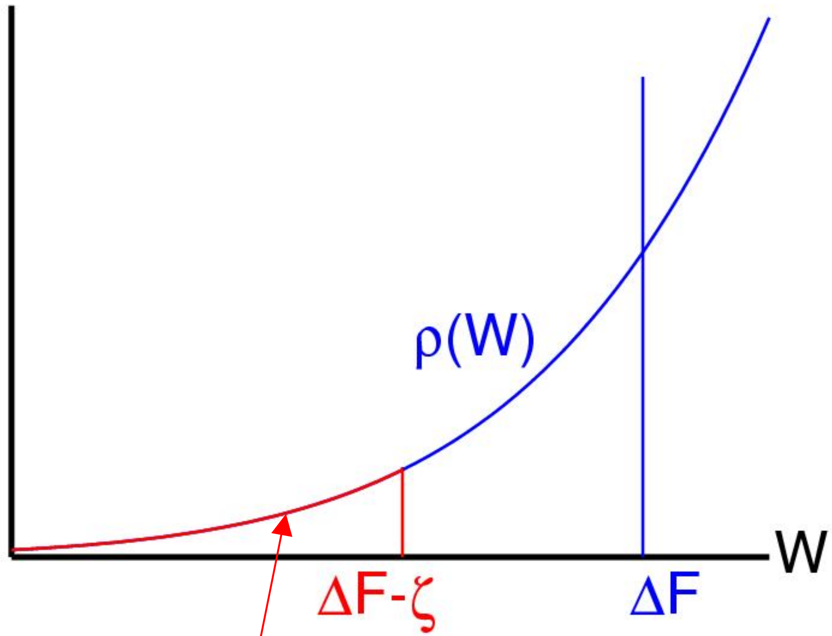
typically W < ΔF if the movie is run backward

… but there are exceptions (fluctuations).

The arrow of time is *blurred*.

How frequently do these exceptions occur?

Irreversibility in microscopic systems



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

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

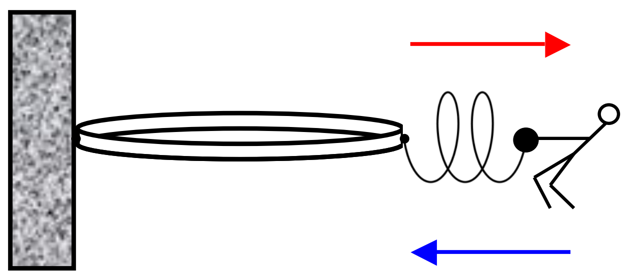
$$\leq e^{\beta(\Delta F - \zeta)} \int_{-\infty}^{+\infty} dW \; \rho(W)\, e^{-\beta W} = \exp(-\zeta / k_B T)$$

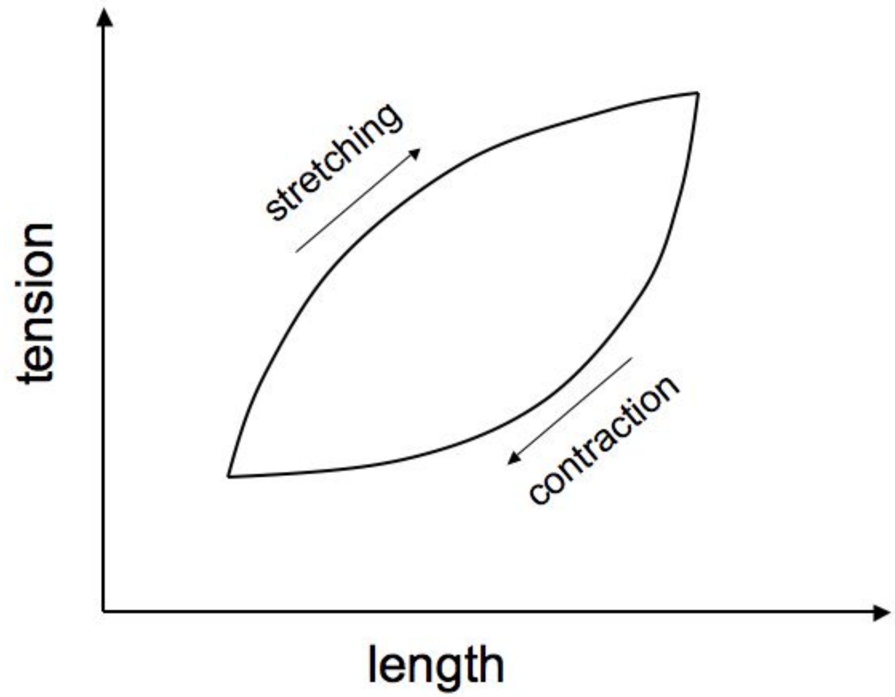
$$e^{-\beta \Delta F}$$

→ ρ(W) is *exponentially suppressed* in the thermodynamically forbidden region

Hysteresis and irreversibility

macroscopic systems



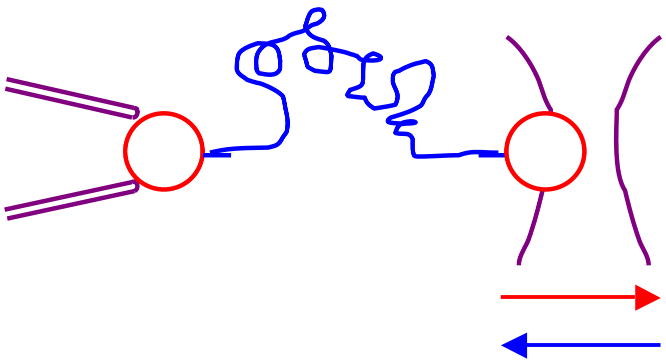


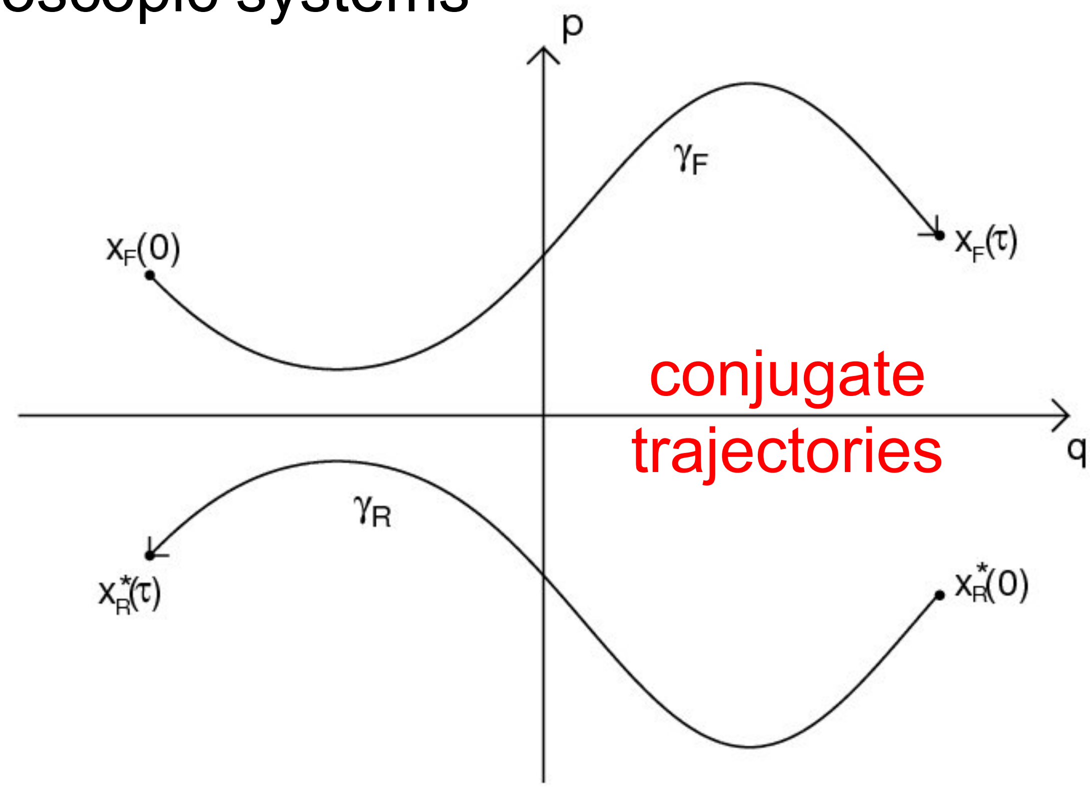
<u>Hysteresis</u>

The system evolves via one sequence of states during the forward process (stretching), but follows a different path during the reverse process (contraction).

Hysteresis and irreversibility

microscopic systems

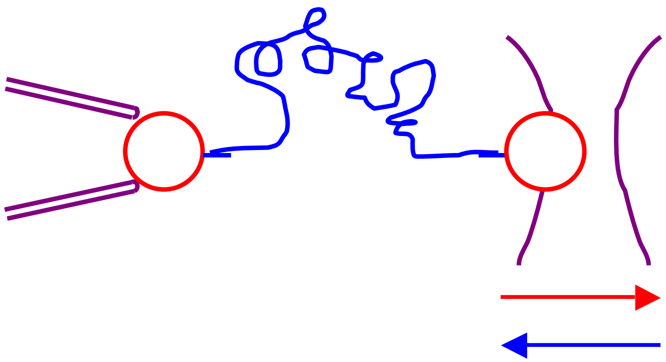


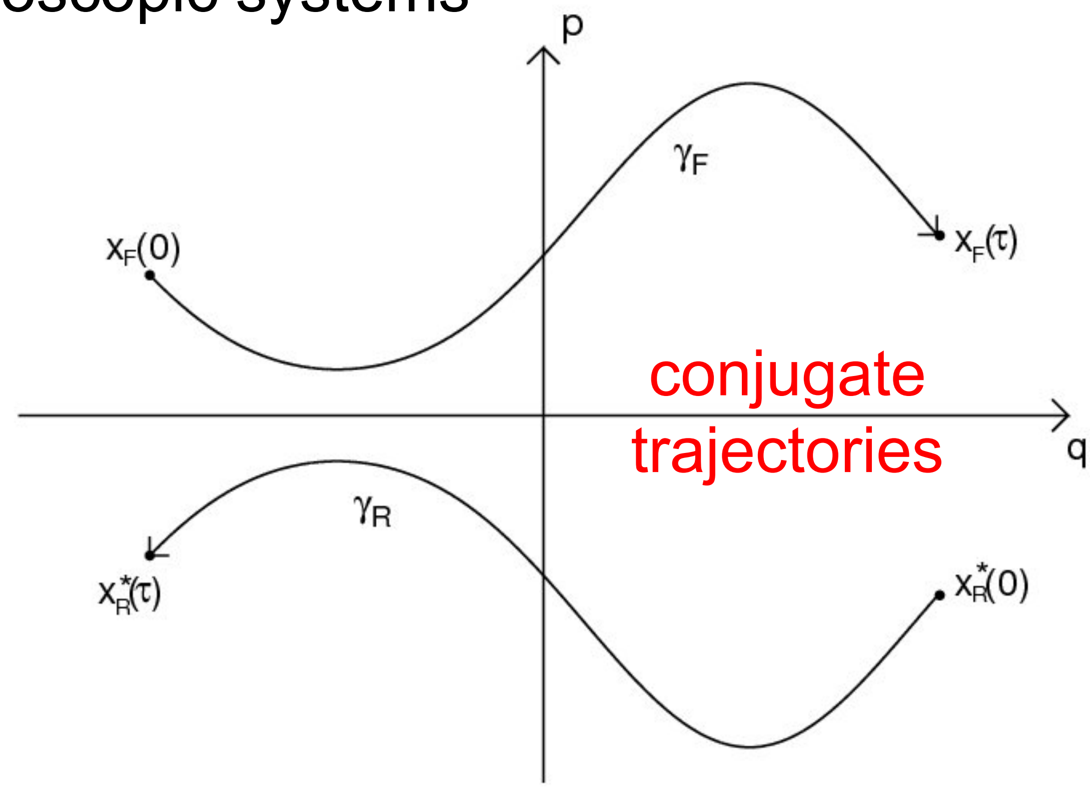


Hysteresis = ?

Hysteresis and irreversibility

microscopic systems





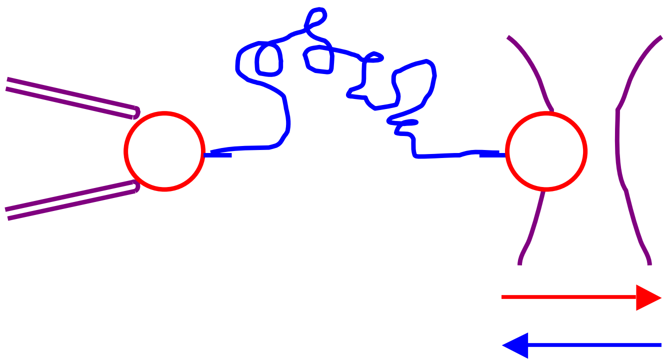
<u>Hysteresis</u>

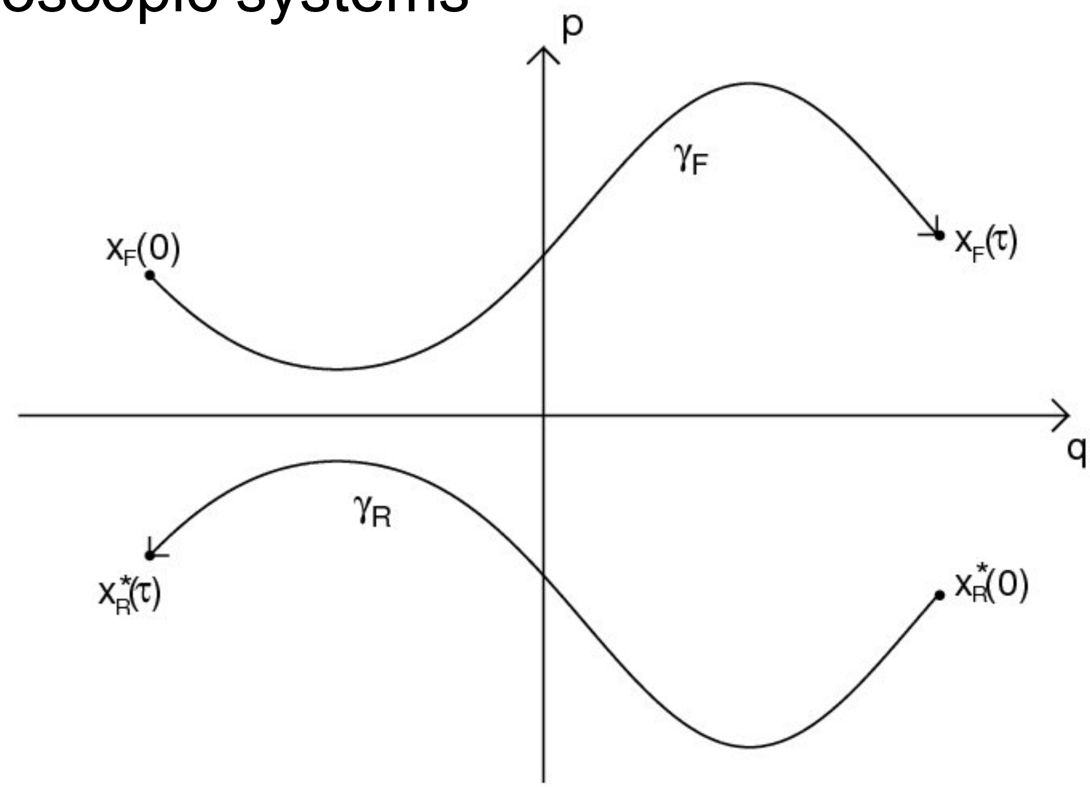
The probability to observe one sequence of events (γ_F) during the forward process is different from that of observing the conjugate sequence (γ_R) during the reverse process.

$$P_F\left[\gamma_F\right] \neq P_R\left[\gamma_R\right]$$

Hysteresis and irreversibility

microscopic systems



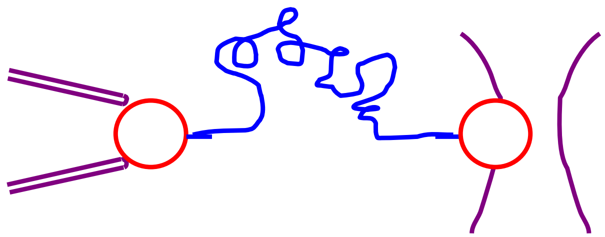


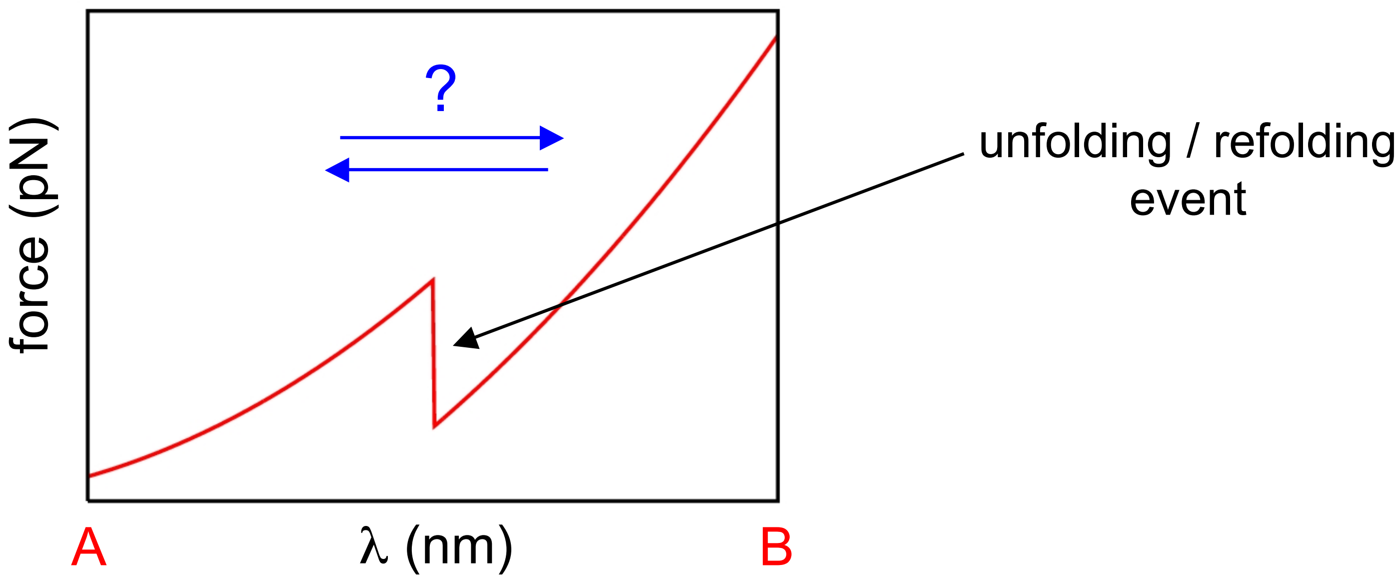
$$\frac{P_F\left[\gamma_F\right]}{P_R\left[\gamma_R\right]} = \exp\left[\beta\left(W_F - \Delta F\right)\right]$$

Guessing the direction of time's arrow

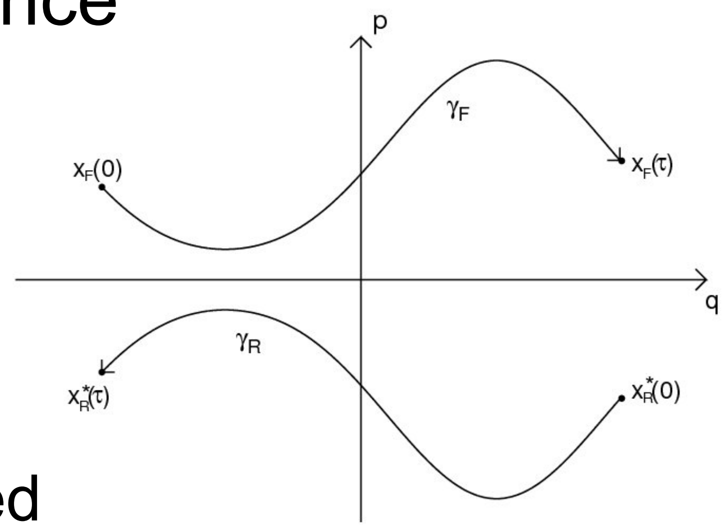
You are shown a movie depicting a thermodynamic process, A→B.
Task: determine whether you are viewing the events in the order in which they actually occurred, or a movie run backward of the reverse process.

e.g.





Statistical inference



outcome of experiment: γ

two hypotheses:

F = the molecule was stretched

R = the molecule was contracted

Bayes' rule
$$L(F\,|\,\gamma) = \frac{P(\gamma\,|\,F)\,P(F)}{P(\gamma)} \propto P(\gamma\,|\,F)\,P(F)$$

$P(F)$ ← 1/2

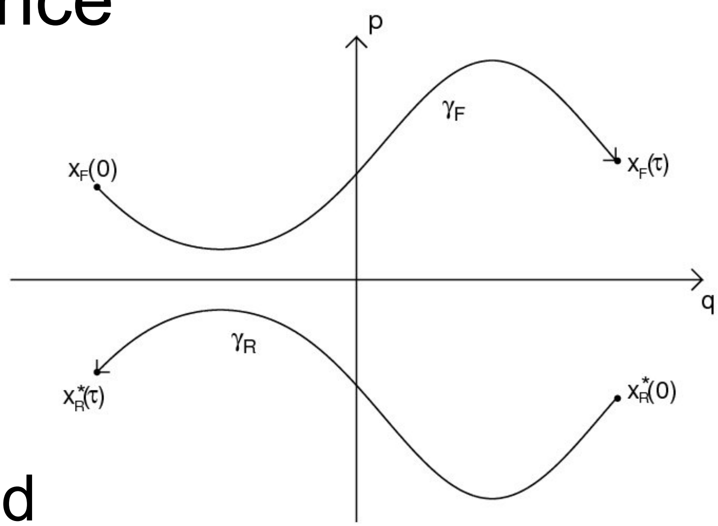
$P(\gamma\,|\,F)$ ← $P_F[\gamma_F]$

$$\frac{L(F\,|\,\gamma)}{L(R\,|\,\gamma)} = \frac{P_F[\gamma_F]}{P_R[\gamma_R]} = \exp\left[\beta\left(W - \Delta F\right)\right]$$

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

Statistical inference

outcome of experiment: γ



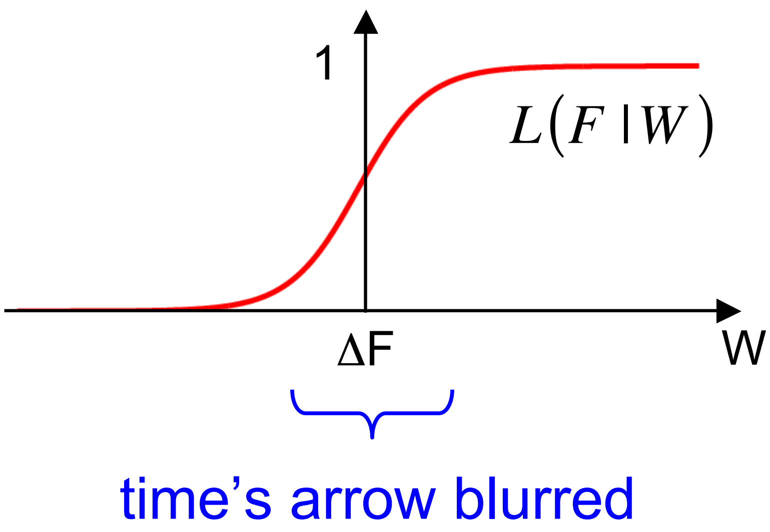
two hypotheses:

F = the molecule was stretched

R = the molecule was contracted

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

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



Relative entropy and time's arrow

Relative entropy D[f | g] provides a measure of the difference between two probability distributions f and g.

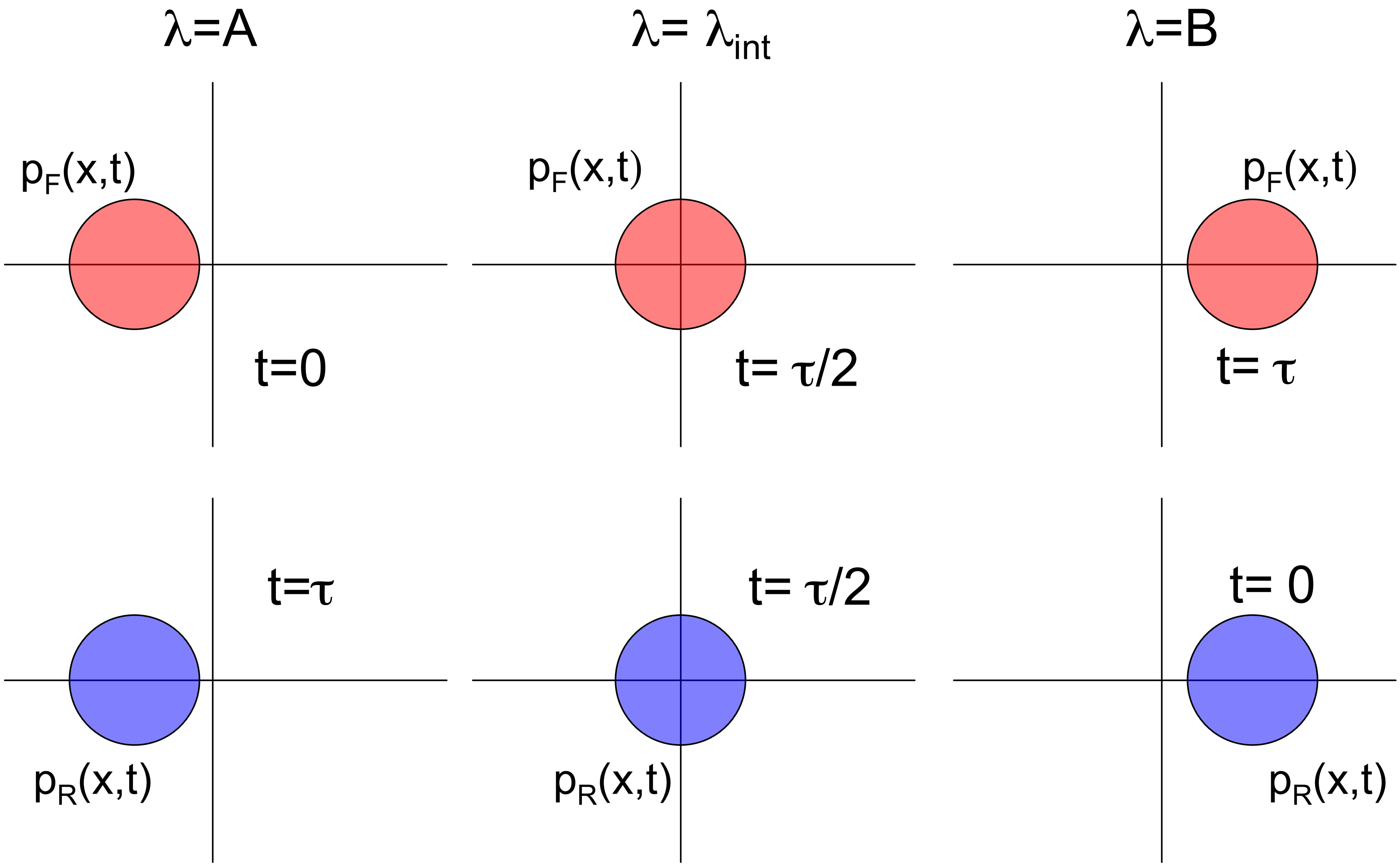
$$D[f \mid g] = \int f \ln \frac{f}{g} \quad \geq 0$$

forward process λ: A$\rightarrow$B $\quad$ $p_F(x,t)$
reverse process λ: A$\leftarrow$B $\quad$ $p_R(x,t)$

use relative entropy to quantify irreversibility, by comparing p_F with p_R

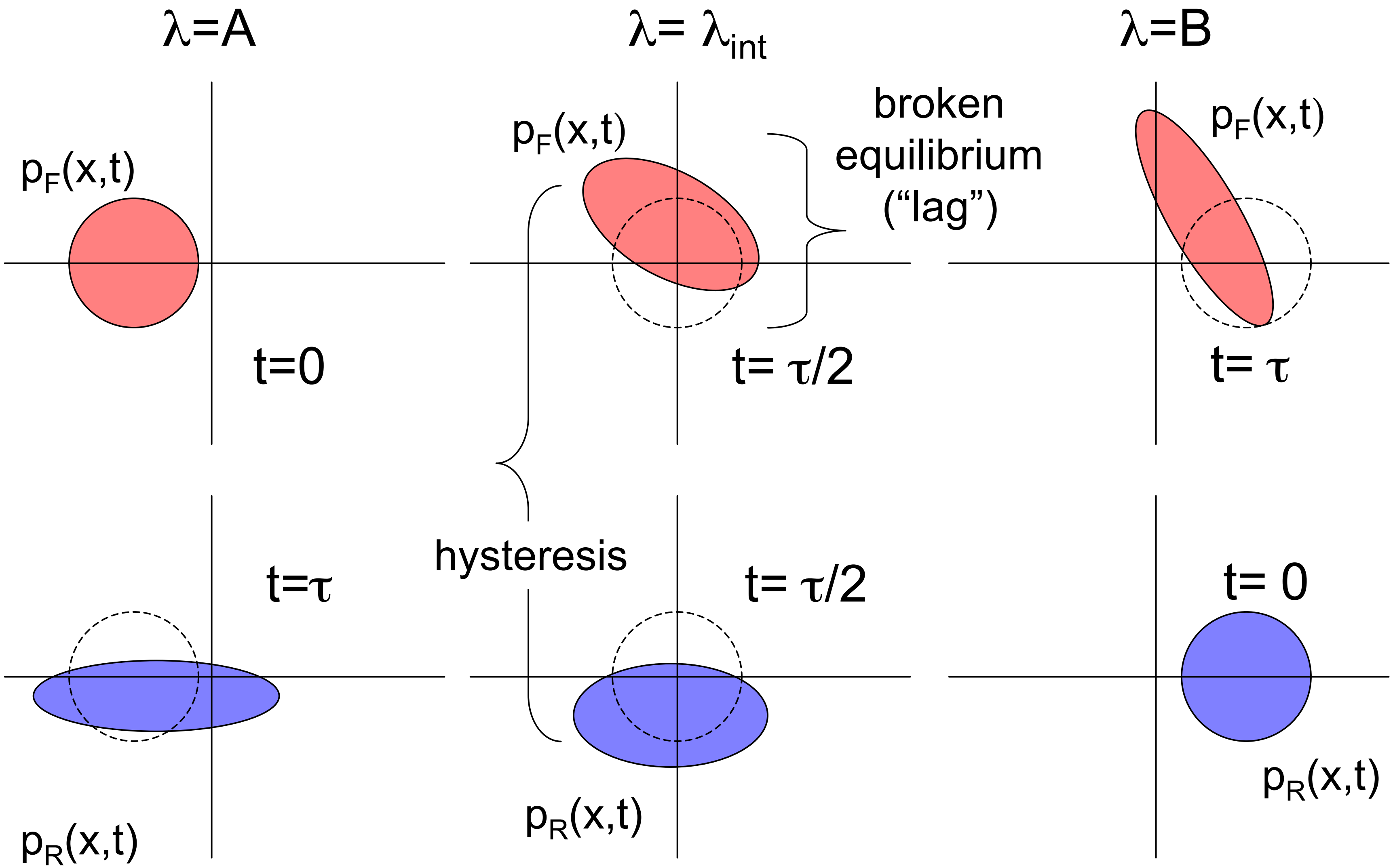
notation: $W_{diss} = W - \Delta F$, dissipated work

Reversible processes



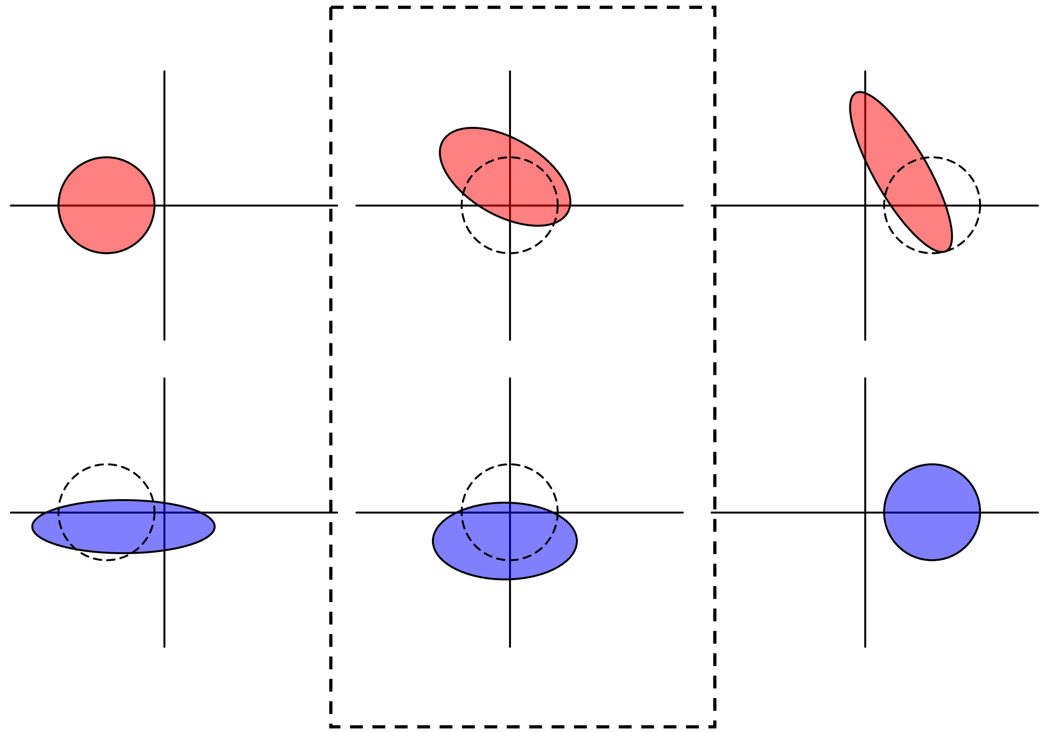
$$p_F(x,t) = p^{eq}(x;\ \lambda^F(t)) = p_R(x,\tau-t)$$

Irreversible processes



$$p_F(x,t) \neq p^{eq}(x;\, \lambda^F(t)) \neq p_R(x,\tau-t)$$

Relative entropy and time's arrow

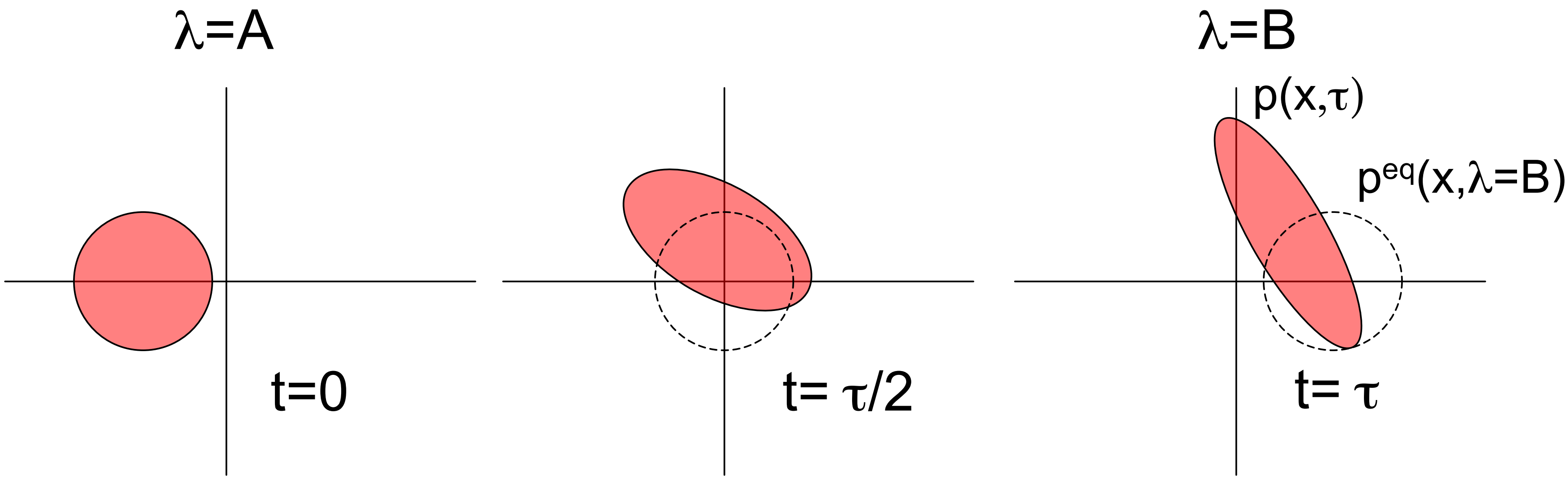


use relative entropy to quantify both hysteresis & lag:

$$D\left[p_F \mid p_R\right]_\lambda \le \beta\left\langle W_{diss}\right\rangle_F$$ Kawai, Parrondo, Van den Broeck, PRL 2007

$$D\left[p_F \mid p^{eq}\right]_t \le \beta\left\langle W_{diss}(t)\right\rangle_F$$ Vaikuntanathan & CJ, EPL 2009

Relative entropy and time's arrow



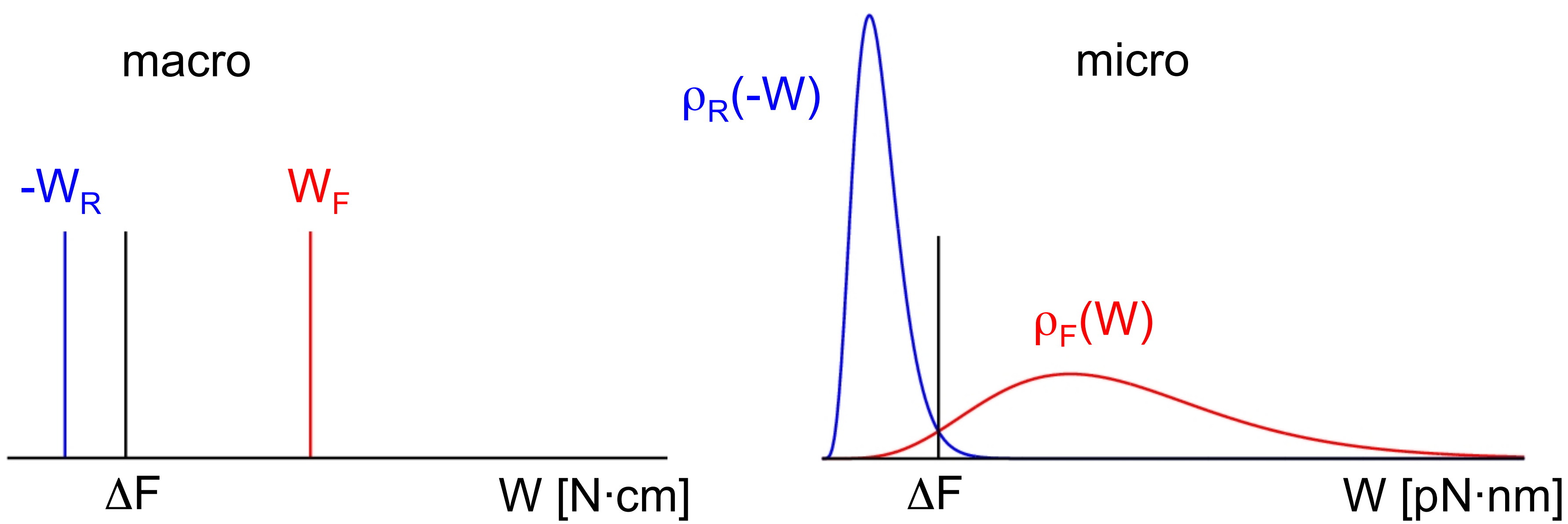
$$D\left[p \mid p^{eq}\right]_t \leq \beta\left\langle W_{diss}(t)\right\rangle$$

$$\rightarrow \quad D\left[p_\tau \mid p_B^{eq}\right] \leq \beta\left\langle W_{diss}\right\rangle$$

$$\rightarrow \langle W\rangle \geq \Delta F + k_B T\, D\left[p_\tau \mid p_B^{eq}\right]$$

2nd Law

Summary



At the nanoscale …

- the 2nd law can be represented by *equalities*

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

- the arrow of time is blurred, but can be quantified