Nonequilibrium work relations
III. Dissipation and the Arrow of Time

second law of thermodynamics (macroscopic) $\rightarrow$ $W \geq \Delta F$

nonequilibrium work relations (microscopic) $\rightarrow$ $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$, etc.

What is the precise relationship?
What does the 2nd law "look like" at the microscale?

Inequalities:

Jensen's inequality $\rightarrow$ $\left\langle e^{x} \right\rangle \geq e^{\langle x \rangle}$

holds for any real, convex function of a real variable

Simple derivation of Jensen's inequality:

convex function $\quad A(x) \quad , \quad A''(x) \geq 0 \;\; \forall x$

probability distribution

$$p(x) \quad , \quad 1 = \int dx\, p(x) \quad , \quad \bar{x} = \int dx\, x\; p(x)$$

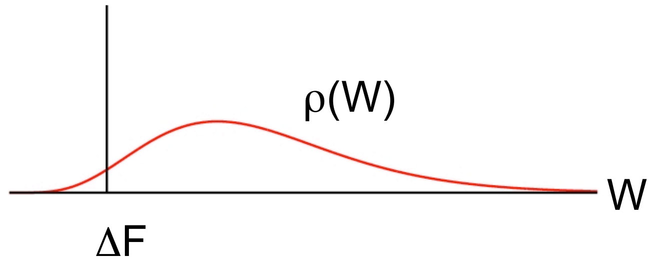
define a new function $\quad B(x) = A(\bar{x}) + (x - \bar{x}) A'(\bar{x})$

(tangent to A(x))

by construction: $\quad A(x) \geq B(x) \;\; \forall x$

$$\langle A(x) \rangle \geq \langle B(x) \rangle = \int dx\, p(x) \left[A(\bar{x}) + (x - \bar{x}) A'(\bar{x}) \right] = A(\bar{x})$$

$$e^{-\beta\Delta F} = \left\langle e^{-\beta W}\right\rangle \geq e^{-\beta\langle W\rangle} \quad \rightarrow \quad \langle W\rangle \geq \Delta F$$ (as expected)



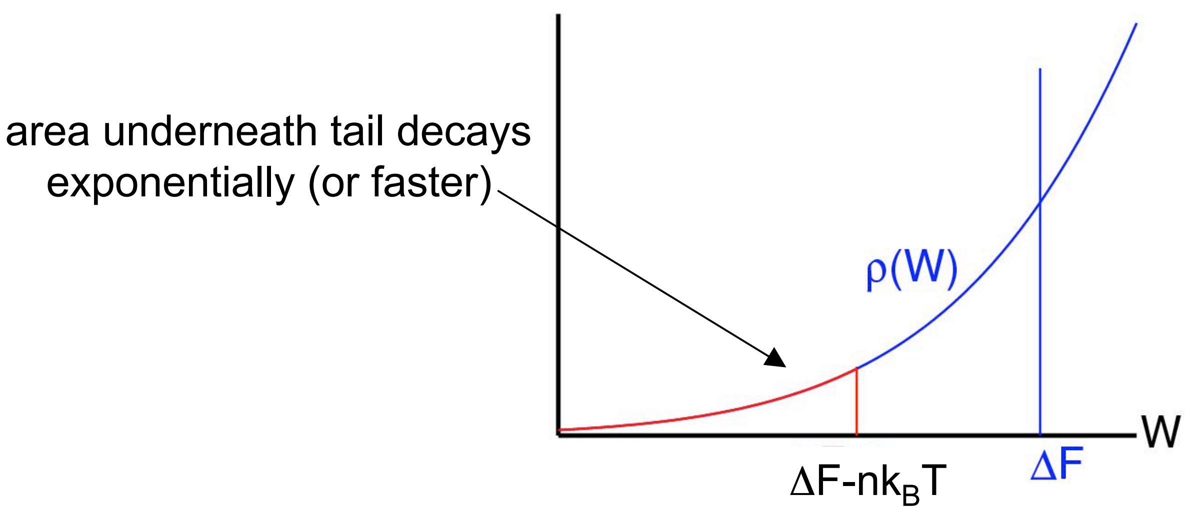
now let's obtain a somewhat stronger result …

$$P\left(W \leq \Delta F - n\beta^{-1}\right) =$$ probability that the 2nd law is "violated" by at least nk_BT

$$= \int_{-\infty}^{\Delta F - n\beta^{-1}} dW\, \rho(W)$$

$$\leq \int_{-\infty}^{\Delta F - n\beta^{-1}} dW\, \rho(W)\, e^{\beta\left(\Delta F - n\beta^{-1} - W\right)}$$

$$\leq e^{\beta\left(\Delta F - n\beta^{-1}\right)} \int_{-\infty}^{+\infty} dW\, \rho(W)\, e^{-\beta W} = \exp(-n)$$



Guessing the direction of Time's Arrrow:

In forward/reverse processes, trajectories come in conjugate pairs: if X denotes a possible realization of the forward process, then its conjugate twin X^+ is a possible realization of the reverse process.

Suppose you are shown a movie depicting the microscopic evolution of the system as $\lambda : A \to B$ (forward process). How can you tell whether you are viewing (1) the events in the order in which they actually occurred, or (2) a movie of the reverse process, run backward ?

exercise in statistical inference:

given the observed <u>data</u>, which <u>hypothesis</u> is more likely?

X F/R

Bayes' theorem *prior*

$$L(hyp \mid dat) \propto P(dat \mid hyp) \cdot P_0(hyp)$$

e.g.

$$L(F \mid X) \propto P^F(X) \cdot P_0(F)$$

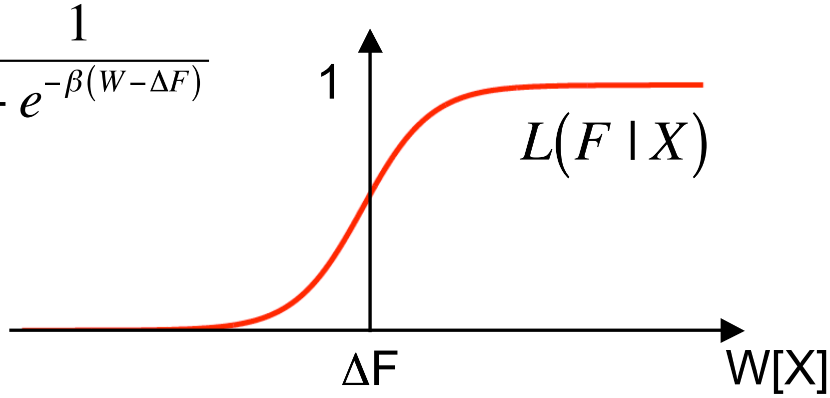
assume equal *priors* : $P_0(F) = P_0(R) = 1/2$

$$L(F \mid X) = \frac{P^F(X)}{P^F(X) + P^R(X^+)} = \frac{1}{1 + \left[P^R(X^+)/P^F(X)\right]}$$

$$= \frac{1}{1 + e^{-\beta(W - \Delta F)}}$$

[Shi03,Mar07]

$$L(F \mid X) = \frac{1}{1 + e^{-\beta(W - \Delta F)}}$$



- when W > ΔF , it is more likely that we are seeing the events in the correct order (“forward”), while for W < ΔF it is the other way around

- the transition from “almost certainly reverse” ($L \approx 0$) to “almost certainly forward” ($L \approx 1$) happens over a few $k_B T$ (consistent w/ earlier results: very low probability to see second law “violated” by more than a few $k_B T$)

Relative entropy and dissipation: [Mae99,Gas04,Jar06,Kaw07]

Given two normalized probability distributions p(x) & q(x), the *relative entropy* of p with respect to q is

$$D(p \mid q) = \int dx\, p(x) \ln \frac{p(x)}{q(x)} \geq 0$$

(aka *Kullback-Leibler divergence*)… provides a measure of the degree to which one distribution is distinguishable from the other

Let's use this to quantify thermodynamic irreversibility.

$P^F(X)$ = distribution of forward trajectories
$P^R(X^+)$ = distribution of reverse trajectories

The relative entropy between these two distributions measures *time-reversal asymmetry*. (How differently does the system respond in the two processes?)

$$\begin{aligned} D\left(P^F \mid P^R\right) &= \int dX\, P^F(X) \ln \frac{P^F(X)}{P^R(X^+)} \\ &= \int dX\, P^F(X)\, \beta\left[W^F(X) - \Delta F\right] \\ &= \beta\left(\langle W \rangle^F - \Delta F\right) \equiv \beta W_{diss}^F \end{aligned}$$

This result relates a *physical* measure of irreversibility (dissipated work) to an *information-theoretic* measure of time-reversal asymmetry (relative entropy).

Consistent w/ macroscopic experience:

$$W_{diss} >> k_B T \quad , \quad D >> 1$$

References

Below is a short list of papers cited in these lecture notes.
For a more comprehensive reference list, see the bibliography in my mini-review in *Eur. Phys. J. B* **64**, 331-340 (2008)

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