Let's look @ some consequences of non-equilibrium work relations for the 2nd Law.

First: Jensen's inequality:

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

To show this, first note that

$$e^{y} \geq y+1$$

← draw both sides!

Then

$$\langle e^{x} \rangle = \langle e^{x-\langle x \rangle} \rangle e^{\langle x \rangle}$$

$$\geq \langle x - \langle x \rangle + 1 \rangle e^{\langle x \rangle} = e^{\langle x \rangle}$$

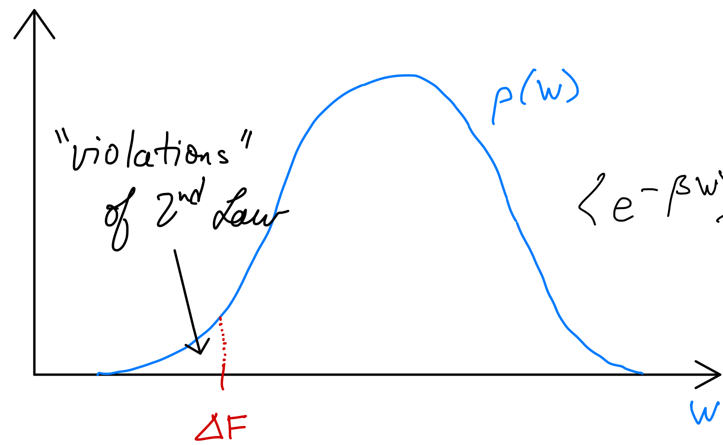
We then get:

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

$$\Delta F \leq \langle W \rangle \quad \checkmark$$

We already expected this result from the 2nd Law, & we have derived it using different eqns. of motion.

Now let's obtain a stronger result ...



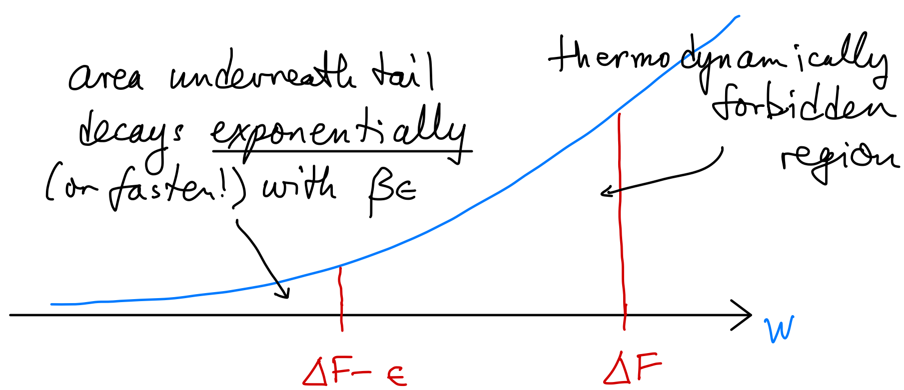
$$\langle e^{-\beta W}\rangle = e^{-\beta \Delta F}$$

$P(W \leqslant \Delta F - \epsilon)$ = probability that the 2nd Law is violated by at least ϵ.

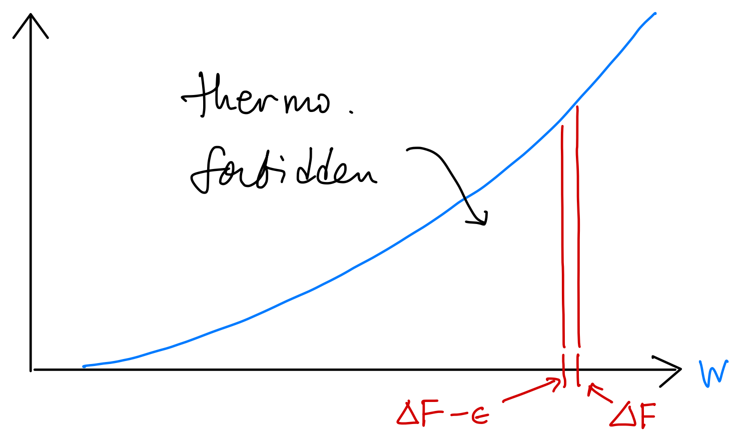
$$= \int_{-\infty}^{\Delta F - \epsilon} dW \, p(W)$$

$$\leqslant \int_{-\infty}^{\Delta F - \epsilon} dW \, p(W) \, e^{\beta \overbrace{(\Delta F - \epsilon - W)}^{>0 \text{ over range of integration}}}$$

$$\leqslant e^{\beta(\Delta F - \epsilon)} \int_{-\infty}^{+\infty} p(W) \, e^{-\beta W} = e^{-\beta\epsilon}$$



Can we say anything about the net probability of seeing a "violation" of the 2^{nd} Law?



$$P(W \leq \Delta F - \epsilon) \leq e^{-\beta\epsilon}$$

As $\epsilon \to 0^+$, this result becomes $P(W < \Delta F) < 1$, which seems <u>weak</u>.

Can we derive a tighter bound, i.e. is there some number $p_0 < 1$ s.t. $P(W < \Delta F) < p_0$ for all systems? No!

Editors' Suggestion

Optimal Probabilistic Work Extraction beyond the Free Energy Difference with a Single-Electron Device

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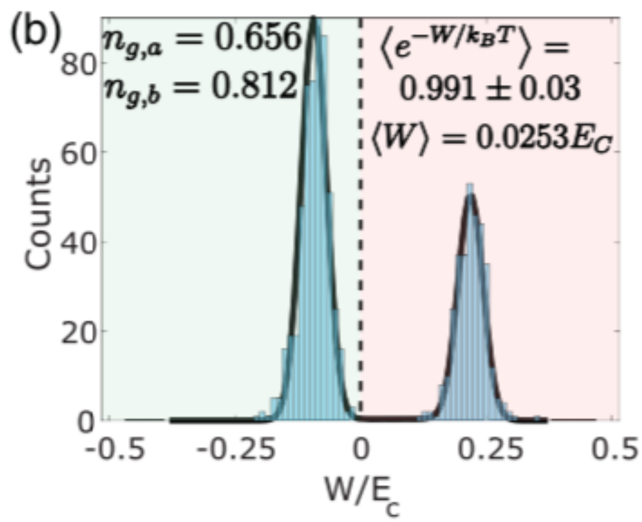


This is one histogram, not two!
It is bimodal, and the left peak
corresponds to “violations”
of the Second Law.

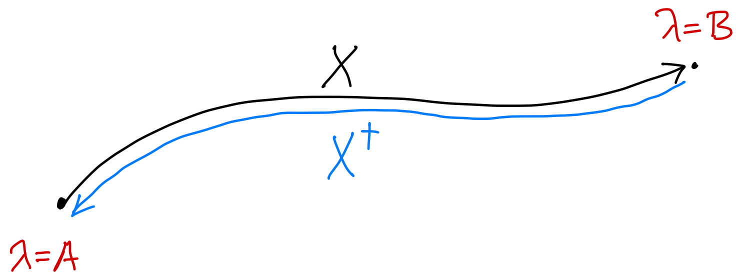
P(W<∆F) = 0.65

Guessing the direction of Time's Arrow

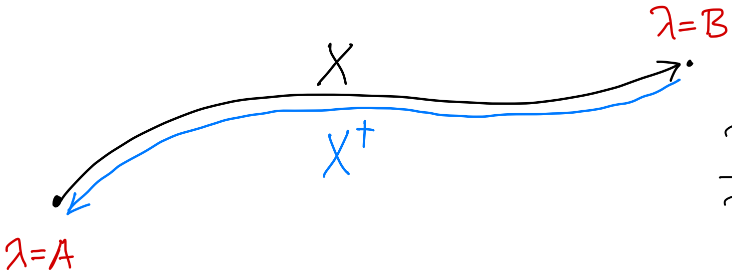
Sir Arthur Eddington, 1927

Recall from Apr. 30 lecture:

$$\boxed{\frac{P_F[X]}{P_R[X^\dagger]} = e^{\beta(W-\Delta F)}}$$



Suppose I show you a movie of the trajectory X, as $\lambda: A \to B$. You must guess whether you are observing the events in the order in which they actually occurred, or whether I performed & filmed the reverse process, & am running the movie backward in an attempt to deceive you.



$$\frac{P_F[X]}{P_R[X^\dagger]} = e^{\beta(W-\Delta F)}$$

I.e. you must guess which process was actually performed: F or R ?

→ Combined statistical inference with

<u>Bayes' rule</u> : $p(a|b)\,p(b) = \underbrace{p(b|a)\,p(a)}_{=\,p(a,b)}$, joint prob. dist'n.

$p(a|b)$: conditional prob. dist'n

$p(b)$: marginal prob. dist'n.

... kind of obvious, but extremely useful!

Apply to our guessing game ⟶

Two hypotheses: F & R

observation: X (trajectory, w/ $\lambda: A \to B$)

$p(F|X)$ = <u>likelihood</u> of F, given X

hypothesis data

$$\begin{cases} p(X|F) = P_F[X] \\ p(X|R) = P_R[X^+] \end{cases}$$

If process R is performed & the result is X^+, you will see X in the movie.

Bayes' Rule $\longrightarrow$ $p(F|X) = \dfrac{p(X|F)\,p(F)}{p(X)}$

& similar result for $p(R|X)$

$$\therefore \quad \frac{p(F|X)}{p(R|X)} = \frac{p(X|F)}{p(X|R)}\,\frac{p(F)}{p(R)}$$

<u>prior</u> probabilities, assume equal

$$= \frac{P_F[X]}{P_R[X^+]} = e^{\beta(W - \Delta F)}$$

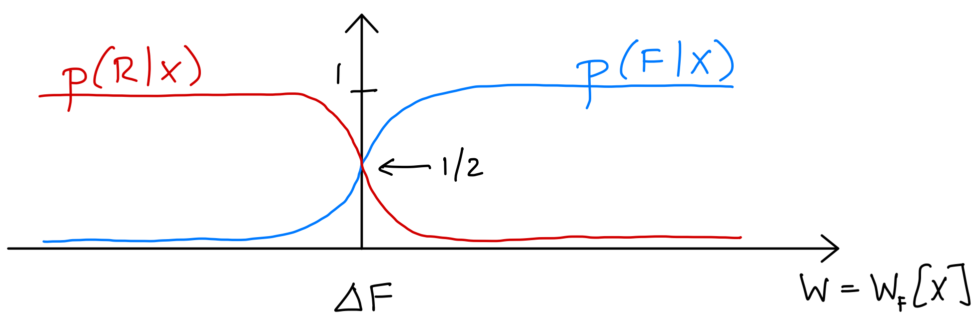
$(W = W_F[X])$

$$\frac{p(F|X)}{p(R|X)} = e^{\beta(W-\Delta F)}$$

Normalization: $p(F|X) + p(R|X) = 1$

These combine to give

$$\boxed{p(F|X) = \frac{1}{1+e^{-\beta(W-\Delta F)}}} = 1 - p(R|X)$$

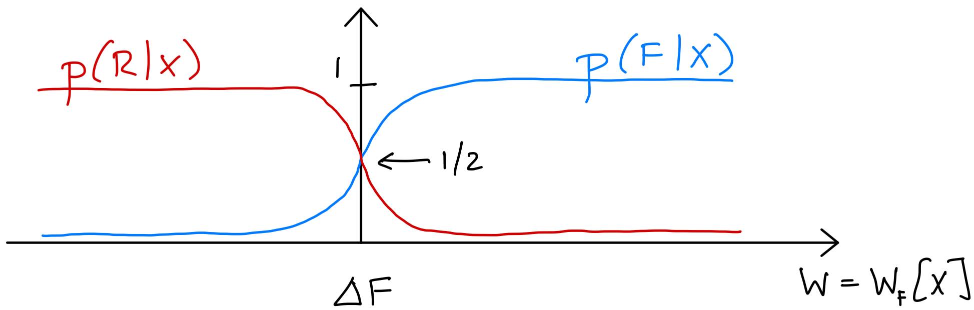


This is consistent w/ 2^{nd} Law:

if $W - \Delta F \gg k_B T$, then with near certainty you're watching the events in the order in which they occurred: $P(F|X) \simeq 1$.

If $W - \Delta F \ll -k_B T$, then $P(R|X) \simeq 1$

as the movie depicts a large violation of the 2^{nd} Law.

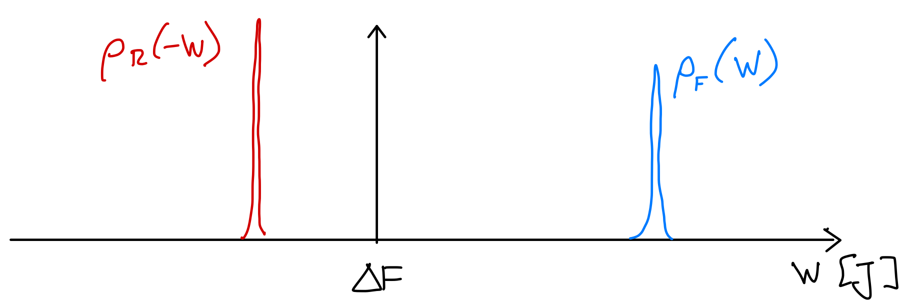


$$\boxed{p(F|x) = \frac{1}{1+e^{-\beta(W-\Delta F)}}}$$

This result quantifies your ability to determine the direction of Time's Arrow, even when $W \sim \Delta F$.

Independent of system size or degree of irreversibility!

If we plot $p(F|x)$ on a W-axis with macroscopic units, e.g. Joules, then it looks like a step function : $p(F|x) \cong \Theta(W - \Delta F)$



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Single-Electron Control in Solid-State Devices

Heat dissipation and fluctuations in a driven quantum dot

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