A brief introduction to the delights of ***non-equilibrium statistical physics***

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In the beginning …

- The energy of the universe is constant.
- The entropy of the universe tends toward a maximum.

Rudolf Clausius, 1865

Thermodynamics is organized logically around *equilibrium states*, in which "nothing happens".

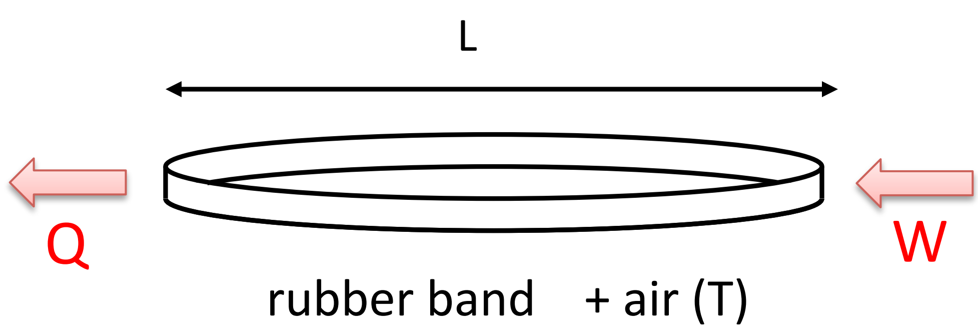
State function: an observable that has a well-defined value in any equilibrium state. E.g. U = U(state) = *internal energy*, S = S(state) = *entropy*.

Thermodynamic process: a sequence of events during which a system evolves from one equilibrium state (*A*) to another (*B*).

During a *reversible process*, the system and its surroundings remain in equilibrium at all times.

First Law of Thermodynamics: $\Delta U = W + Q$

$\Delta U = U_B - U_A$ = net change in system's internal energy
W = *work* performed on the system
(displacements dX against force F)
Q = *heat* absorbed by the system
(spontaneous flow of energy via thermal contact)



$$W = \int_A^B F\, dL$$

tension

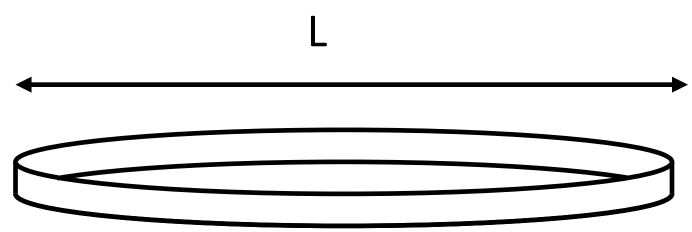
If we stretch the rubber band slowly: $W > 0$, $Q < 0$.

Second Law of Thermodynamics: $\int_A^B \frac{dQ}{T} \le \Delta S$

dQ = energy absorbed by system as heat

T = temperature of thermal surroundings

$\Delta S = S_B - S_A$ = net change in system's entropy



Isothermal processes:

$$\Delta S \ge \frac{Q}{T} = \frac{\Delta U - W}{T}$$

$$\boxed{W \ge \Delta F}$$

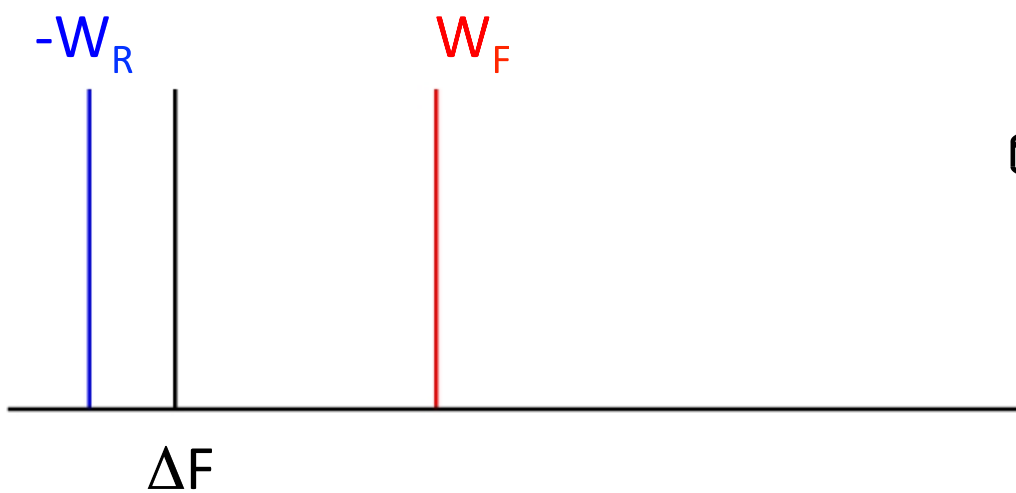
F = U-TS

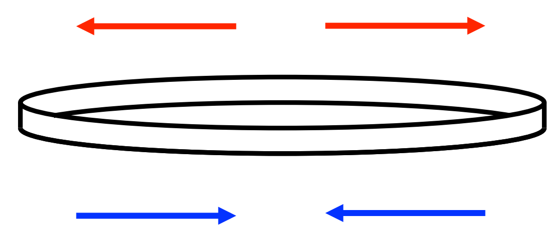
= *Helmholtz free energy*

Thermodynamic cycles

forward process : A⟶B $\quad W_F \geq \Delta F$

reverse process : A⟵B $\quad W_R \geq -\Delta F$

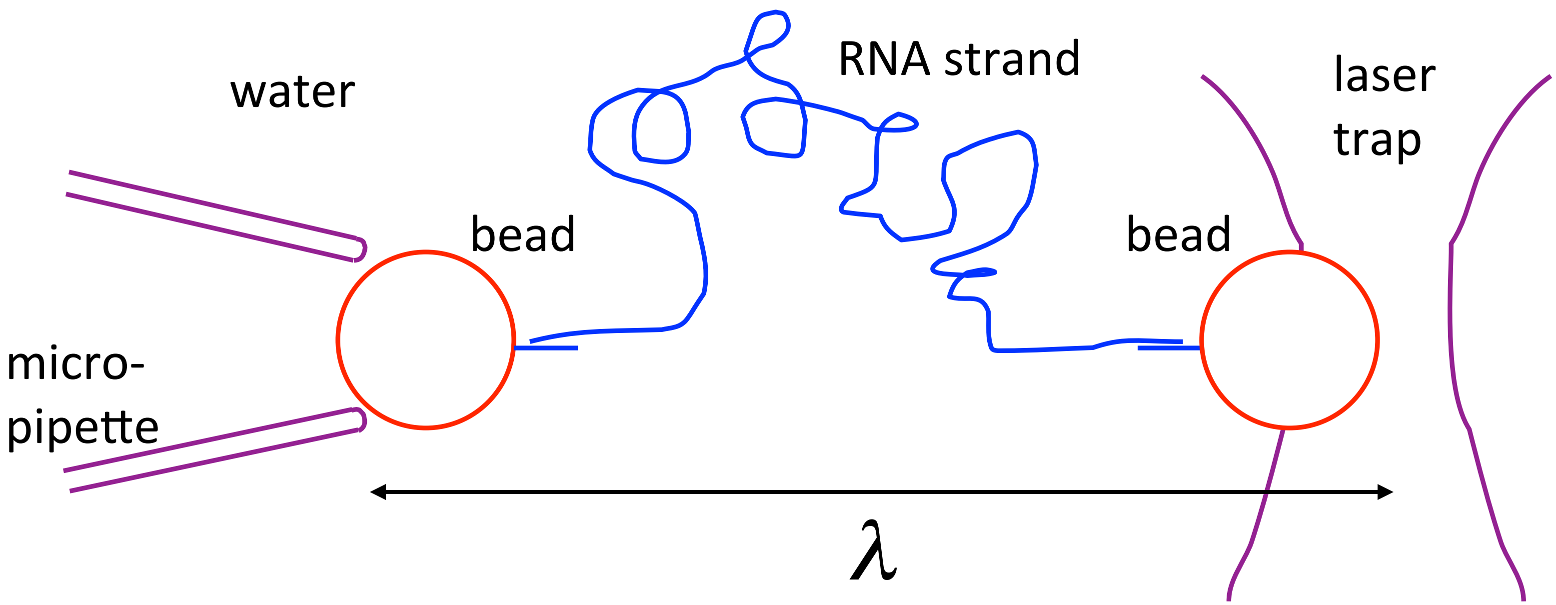




Kelvin-Planck statement of 2nd Law: $\quad W_F + W_R \geq 0$

We perform more work during the forward half-cycle (A⟶B) than we recover during the reverse half-cycle (A⟵B) … No free lunch !

Stretching a microscopic rubber band



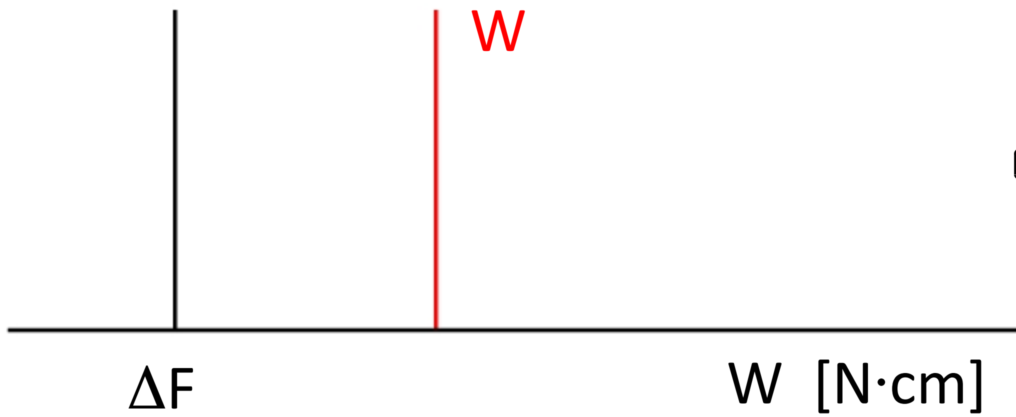
1. Begin in equilibrium $\lambda = A$
2. Stretch the molecule $\lambda : A \rightarrow B$

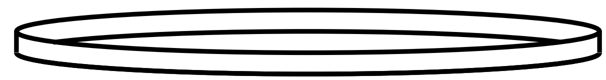
   W = work performed $\geq$ ΔF *on average*

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

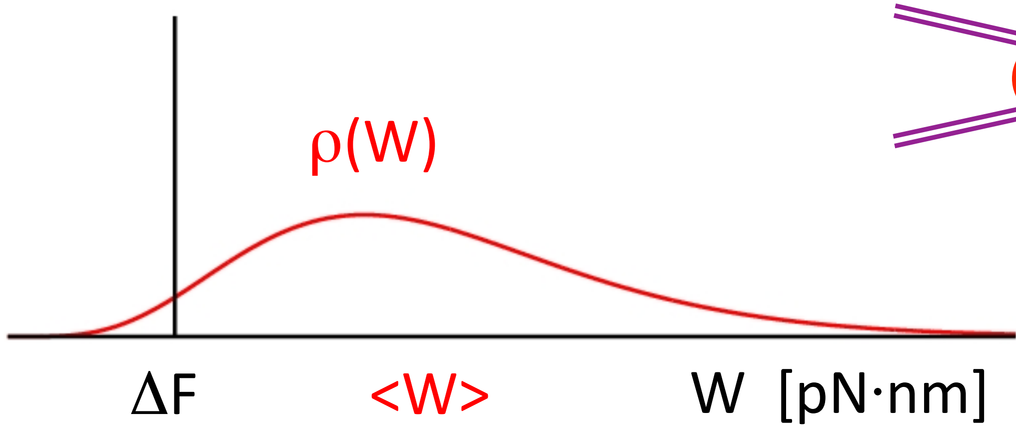
… *fluctuations* are important

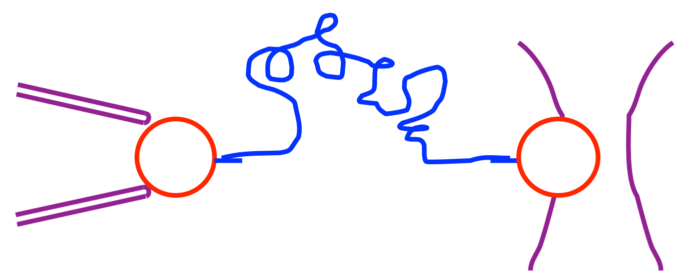
Second Law, macro *vs* micro





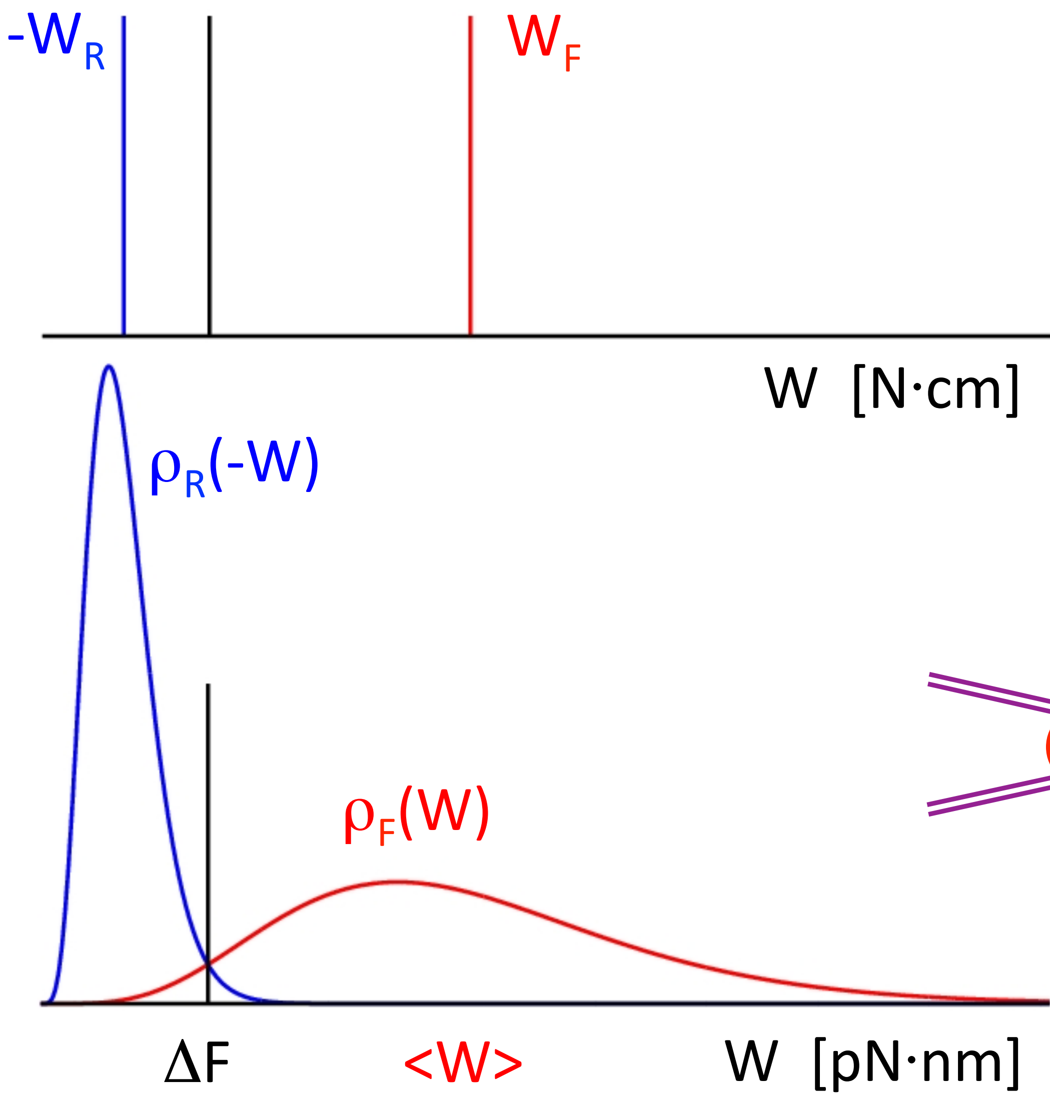
$$W \geq \Delta F$$

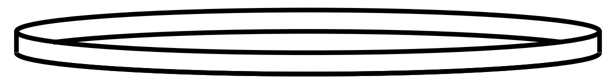




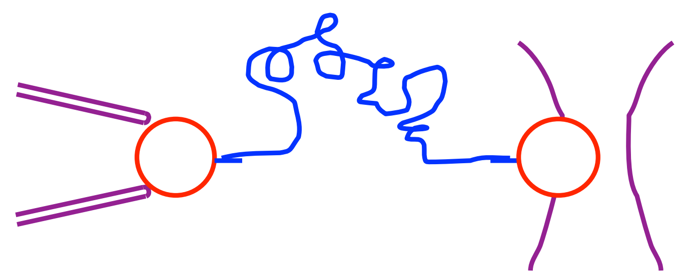
$$\langle W \rangle \geq \Delta F$$

Second Law, macro *vs* micro





$$-W_R \le \Delta F \le W_F$$



$$-\langle W_R \rangle \le \Delta F \le \langle W_F \rangle$$

Classical statistical mechanics

system: $x = (q, p) = (q_1, \cdots q_n, p_1, \cdots p_n)$

environment: $y = (Q, P)$

microscopic degrees of freedom

$$H(x, y; \lambda) = H_S(x; \lambda) + H_E(y) + \underbrace{h_{\text{int}}}_{\text{weak}}(x, y)$$

Equilibrium state: $p^{eq}(x; \lambda) = \frac{1}{Z} \exp\left[-\underbrace{\beta}_{1/k_B T} H_S(x; \lambda)\right]$

State functions: $U = H_S(x; \lambda)$ or $\int dx\, p^{eq} H_S$

$$S = -k_B \int p^{eq} \ln p^{eq}$$

$$F = -k_B T \ln Z$$

Classical statistical mechanics

system: $x = (q, p) = (q_1, \cdots q_n, p_1, \cdots p_n)$

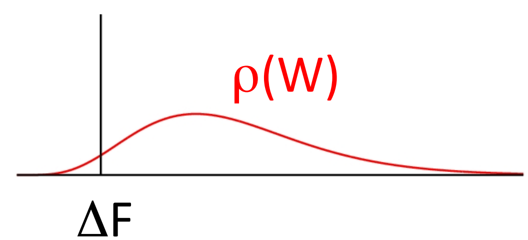
environment: $y = (Q, P)$

$$H(x, y; \lambda) = H_S(x; \lambda) \; + \; H_E(y) \; + \; h_{\text{int}}(x, y)$$

First law of thermodynamics: $\Delta U = W + Q$

$$\underbrace{\frac{dH_S}{dt} = \frac{\partial H_S}{\partial x} \cdot \frac{dx}{dt}}_{\text{heat}} + \underbrace{\frac{\partial H_S}{\partial \lambda} \frac{d\lambda}{dt}}_{\text{work}} \quad \left\{ \begin{aligned} W &= \int dt \frac{d\lambda}{dt} \frac{\partial H_S}{\partial \lambda}\big(x(t); \lambda(t)\big) \\ Q &= \int dt \frac{dx}{dt} \cdot \frac{\partial H_S}{\partial x}\big(x(t); \lambda(t)\big) \end{aligned} \right.$$

Second law (isothermal): $\langle W \rangle \geq \Delta F$



Classical statistical mechanics

system: $x = (q, p) = (q_1, \cdots q_n, p_1, \cdots p_n)$

environment: $y = (Q, P)$

$$H(x, y; \lambda) = H_S(x; \lambda) \; + \; H_E(y) \; + \; h_{\text{int}}(x, y)$$

$$\boxed{\begin{array}{l} U = H_S(x;\lambda) \quad or \quad \int p^{eq} H_S \\ S = -k_B \int p^{eq} \ln p^{eq} \quad , \quad F = -k_B T \ln Z \\ W = \int dt \dfrac{d\lambda}{dt} \dfrac{\partial H_S}{\partial \lambda} \quad , \quad Q = \int dt \dfrac{dx}{dt} \cdot \dfrac{\partial H_S}{\partial x} \end{array}}$$

$\Delta U = W + Q$

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

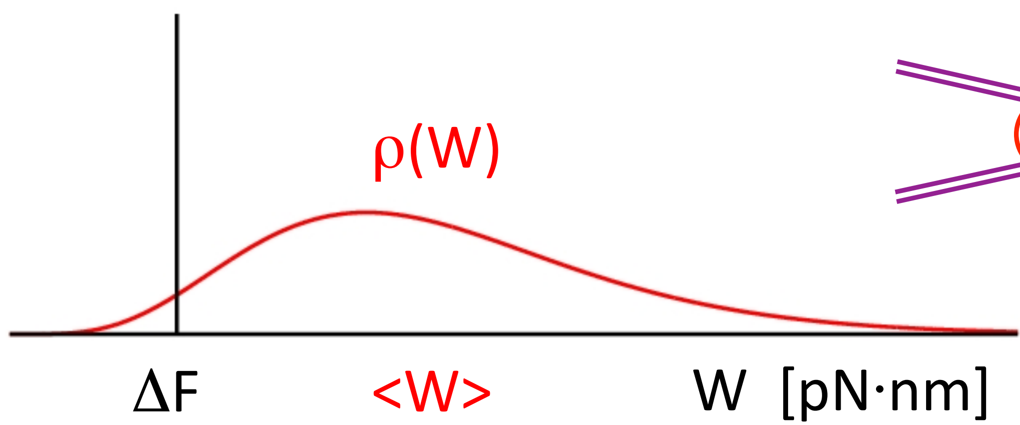
- Some modifications required if h_{int} is not weak
- Same definitions apply if system's evolution is modeled stochastically (e.g. Brownian dynamics)

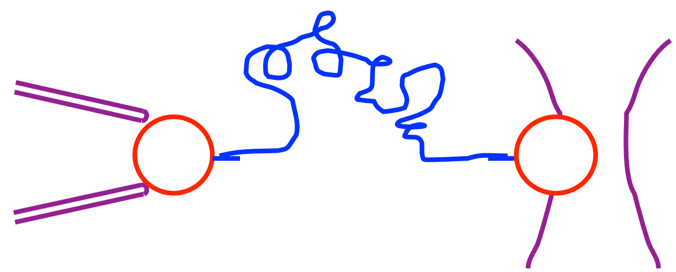
Beyond classical thermodynamics:
Fluctuation Theorems

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

C.J., *PRL* **78**, 2690 (1997)

… places a strong constraint on ρ(W).





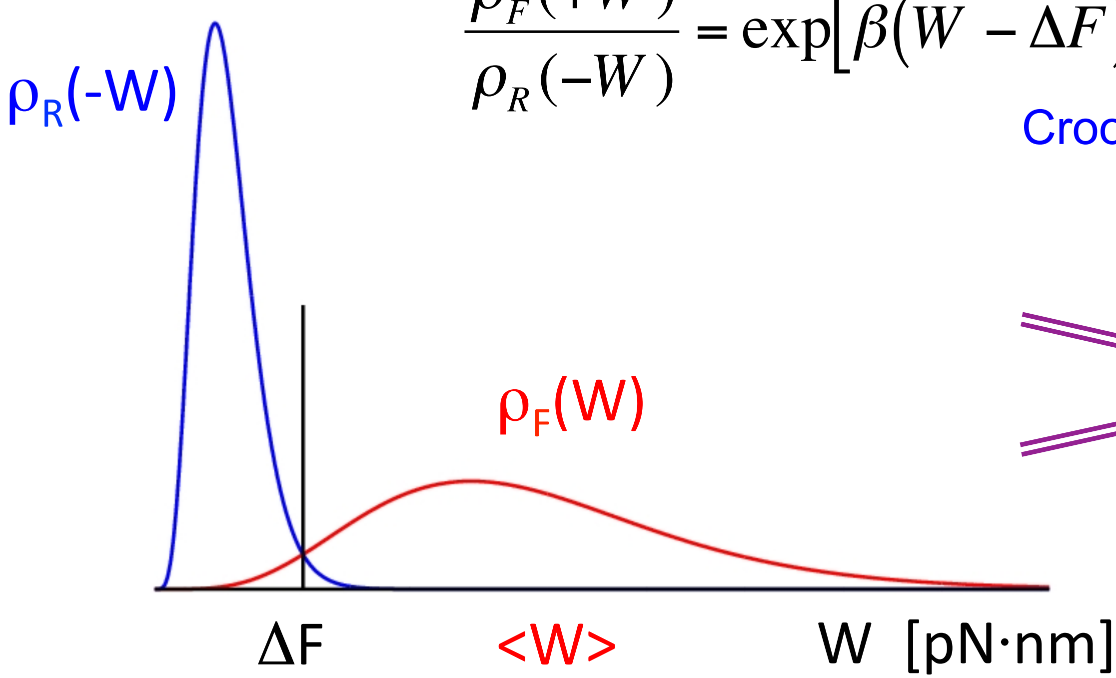
Beyond classical thermodynamics:
Fluctuation Theorems

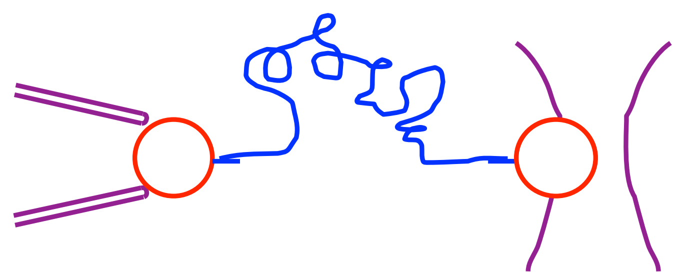
$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

C.J., *PRL* **78**, 2690 (1997)

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

Crooks, *PRE* **60**, 2721 (1999)

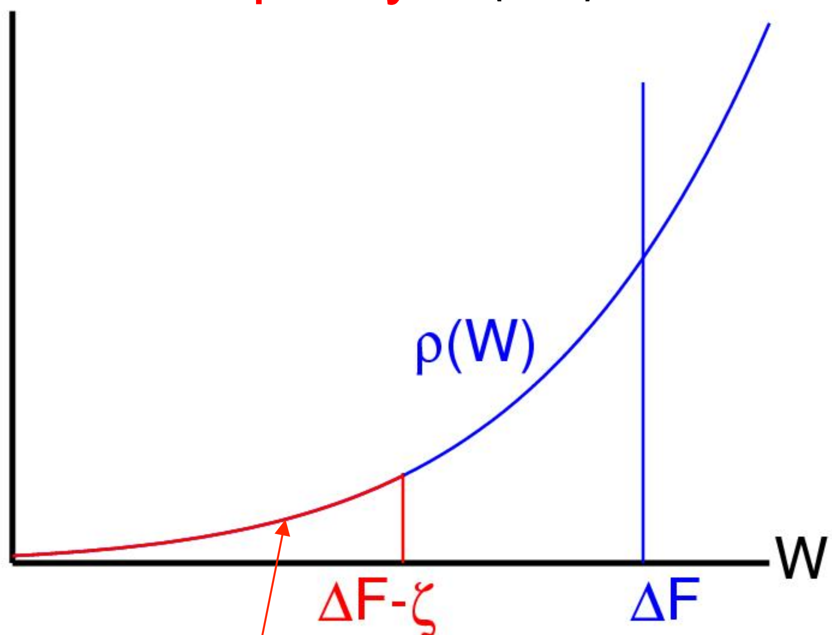




Relation to Second Law

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

Jensen's inequality



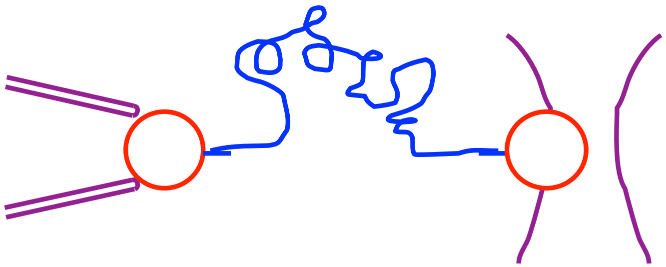
What is the probability that the 2nd law will be "violated" by at least ζ ?

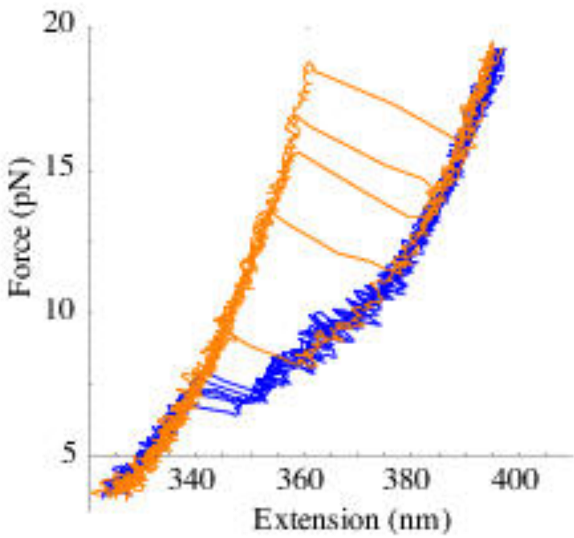
$$P[W < \Delta F - \zeta] = \int_{-\infty}^{\Delta F-\zeta} dW\ \rho(W) \quad \leq \int_{-\infty}^{\Delta F-\zeta} dW\ \rho(W)\, e^{\beta(\Delta F-\zeta-W)}$$

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

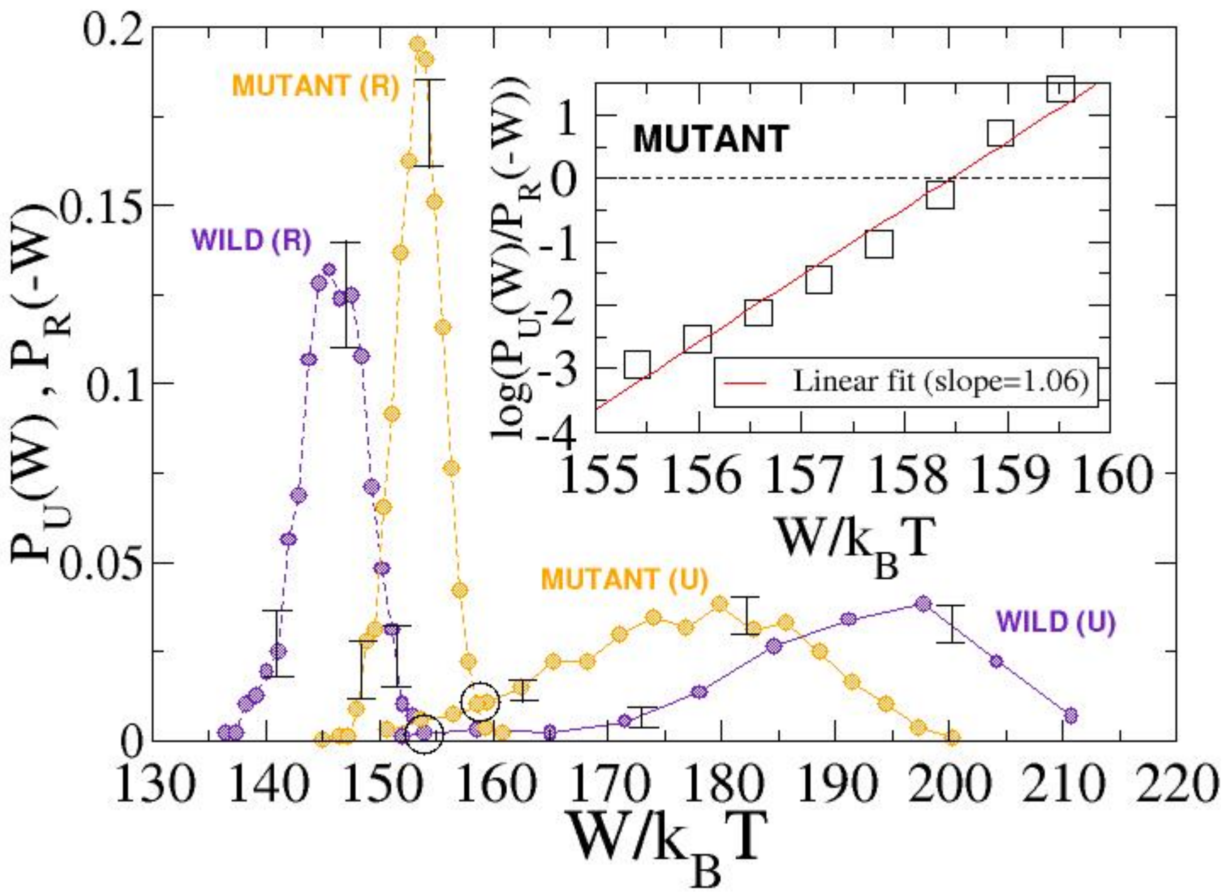
Folding and unfolding of ribosomal RNA

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

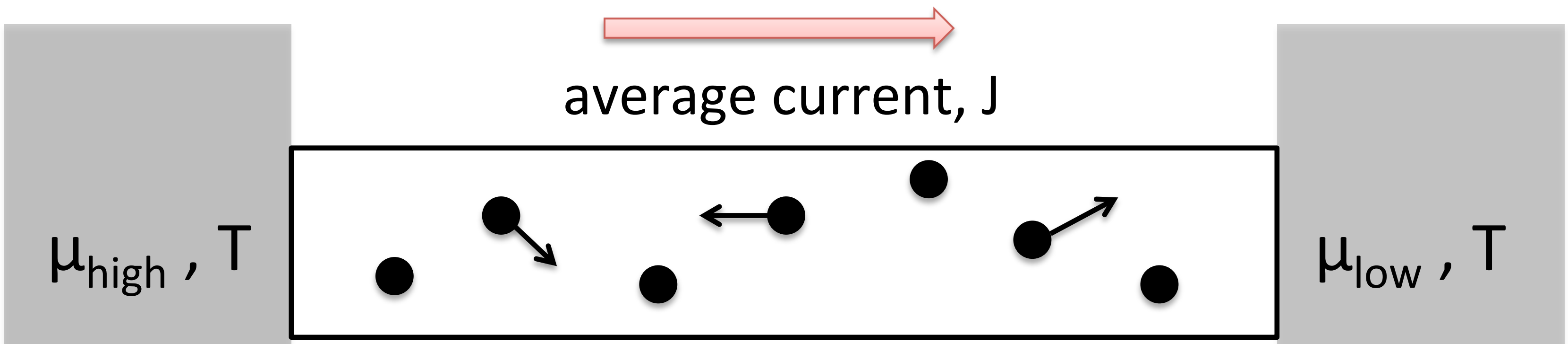




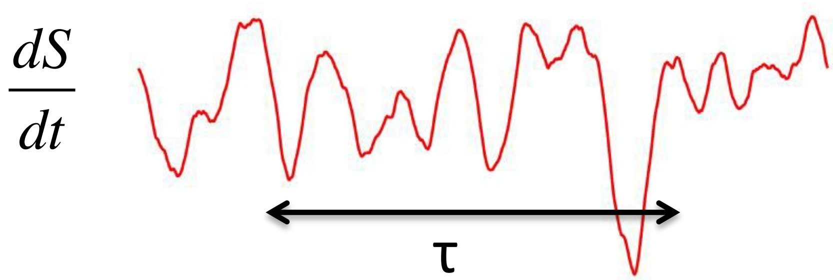
Collin *et al*, *Nature* **437**, 231 (2005)



Nonequilibrium Steady States



entropy production: $\left\langle \dfrac{dS}{dt} \right\rangle = \dfrac{J\,\Delta\mu}{T}$

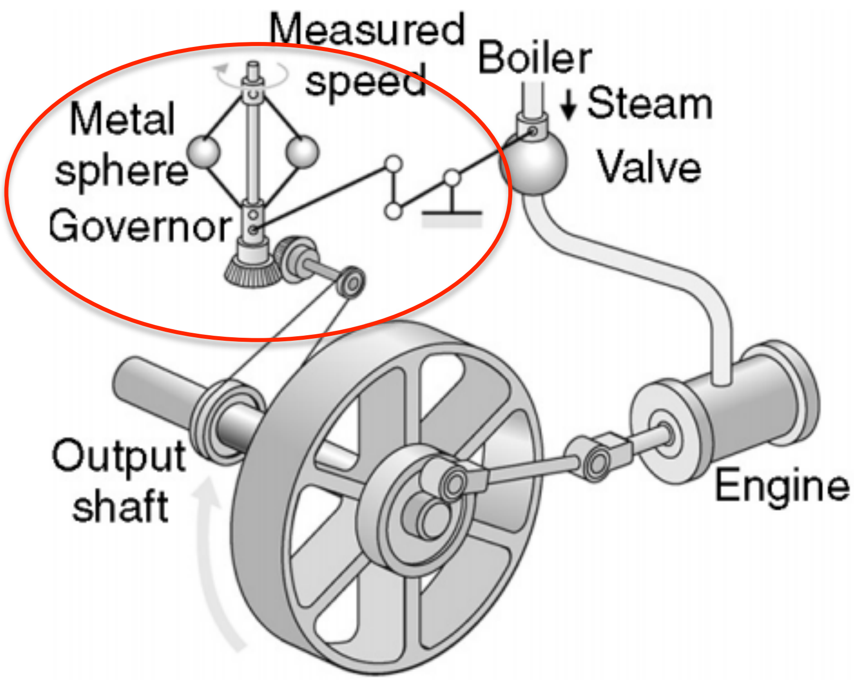


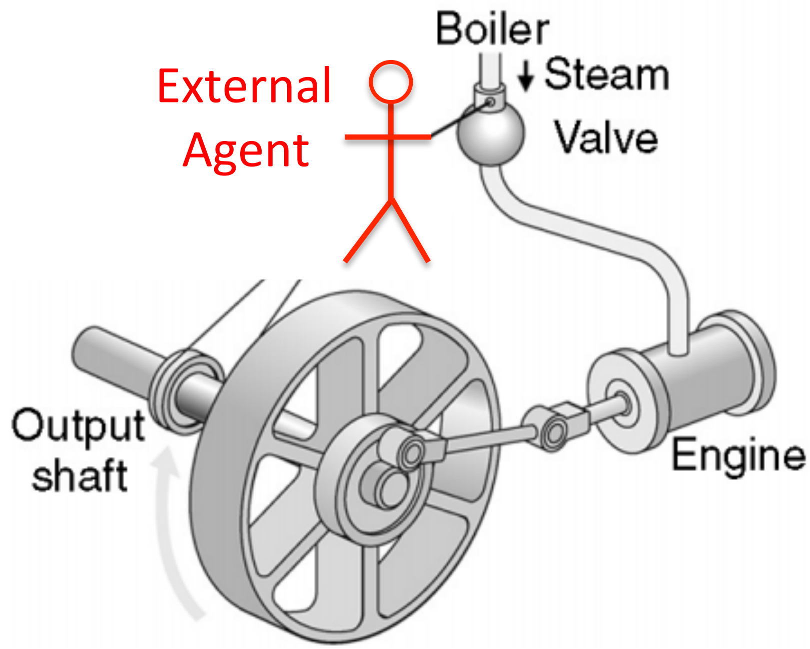
$$\sigma = \frac{1}{\tau}\int_t^{t+\tau} dt\,\frac{dS}{dt} = \frac{\Delta S}{\tau}$$

$$\frac{p_\tau(+\Delta S)}{p_\tau(-\Delta S)} \approx \exp(\Delta S) \qquad \lim_{\tau\to\infty} \frac{1}{\tau} \ln \frac{p_\tau(+\sigma)}{p_\tau(-\sigma)} = \sigma$$

(Gallavotti, Cohen, Evans, Searles, Kurchan, Lebowitz, Spohn … 1990’s)

Autonomous and *non-autonomous* feedback control

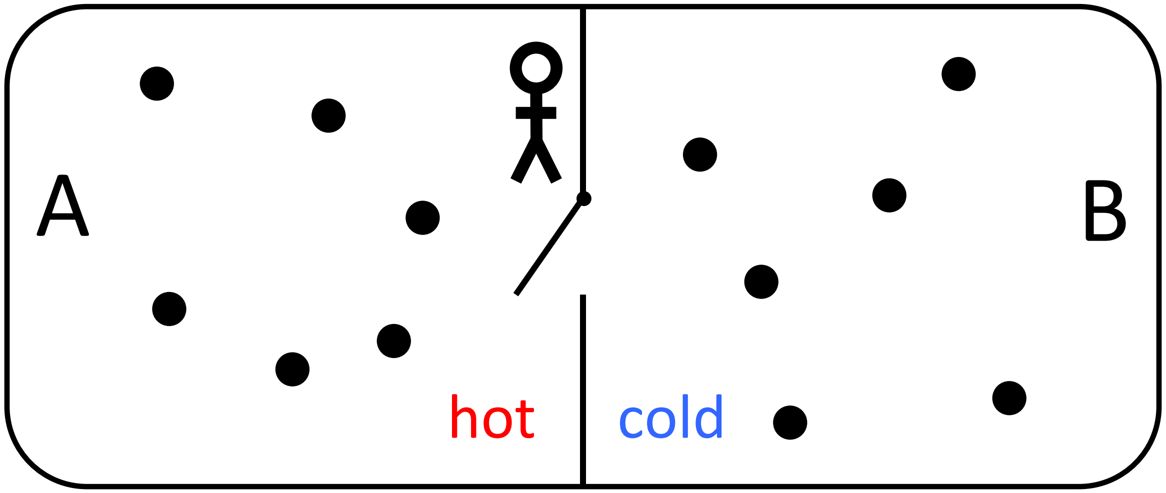




How to design a device with the desired specifications?

What can be achieved by an agent with given abilities of measurement and feedback?

Maxwell's Demon

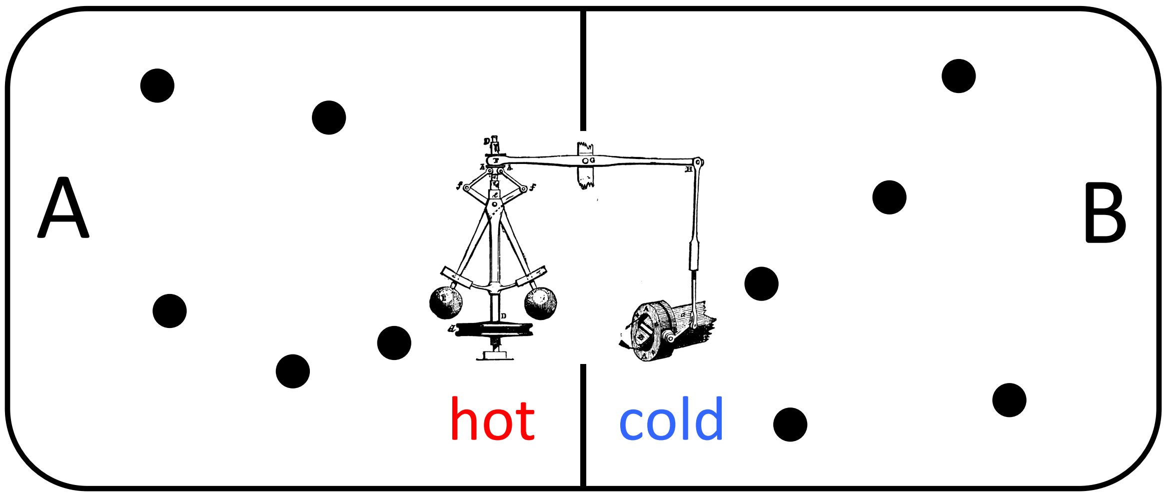


"… the energy in A is increased and that in B diminished; that is, the hot system has got hotter and the cold colder and yet no work has been done, only <u>the intelligence</u> of a very observant and neat-fingered being has been employed"

J.C. Maxwell, letter to P.G. Tait, Dec. 11, 1867

non-autonomous feedback control

Maxwell's Demon



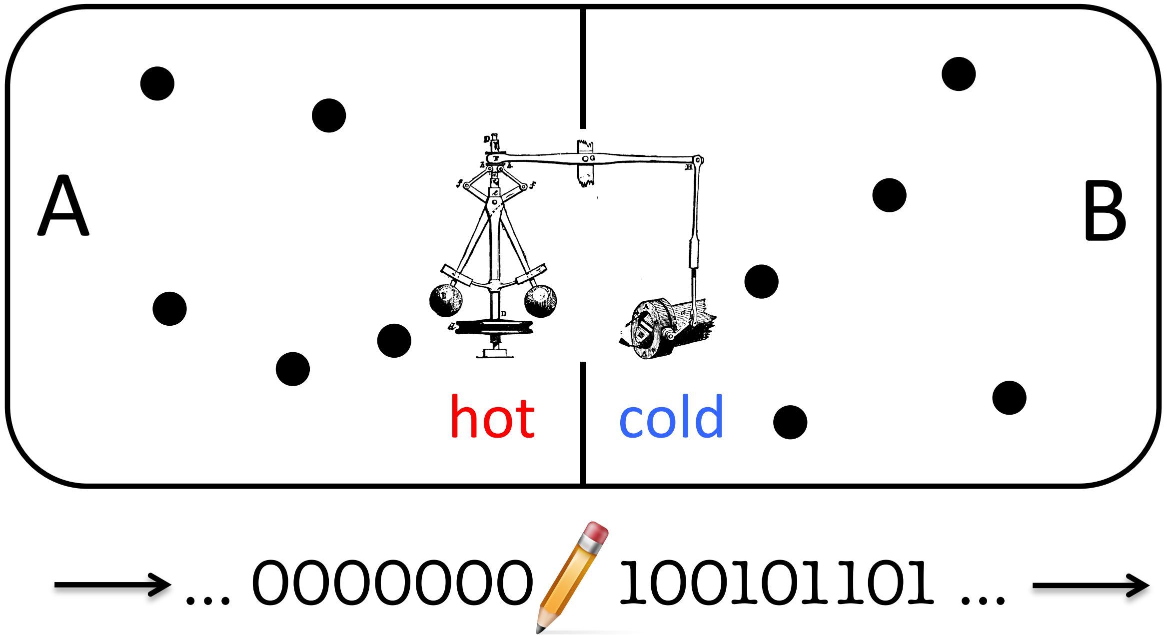
Is a "mechanical" Maxwell demon possible?

M. Smoluchowski, *Phys Z* **13**, 1069 (1912)
R.P. Feynman, *Lectures*

no!

autonomous feedback control

Maxwell's Demon



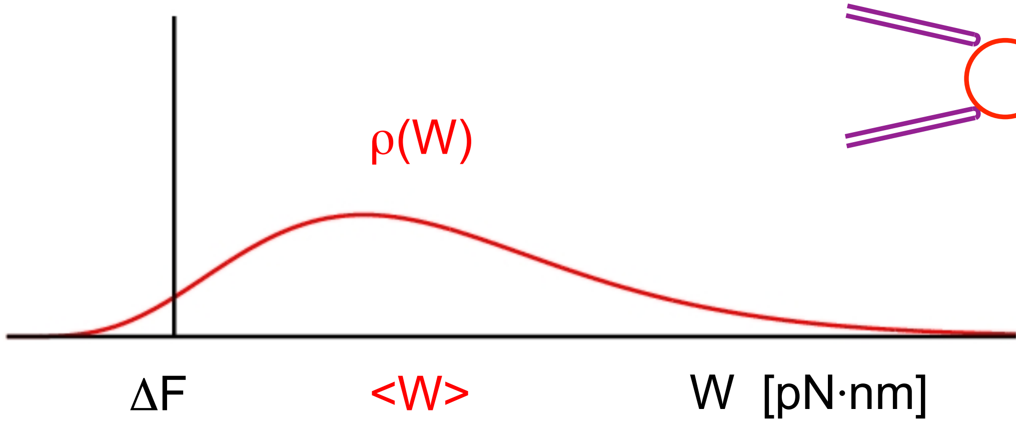
Is a "mechanical" Maxwell demon possible?

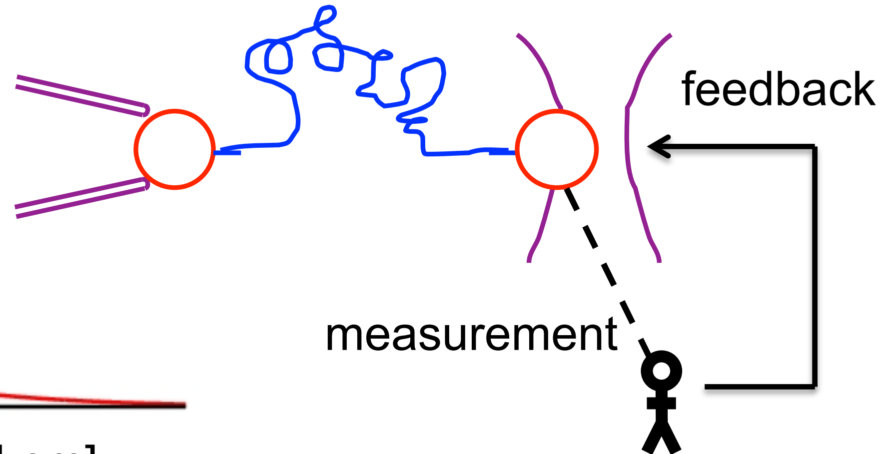
R. Landauer, *IBM J Res Dev* **5**, 183 (1961)
O. Penrose, *Foundations of Statistical Mechanics* (1970) ***yes, but …***
C.H. Bennett, *Int J Theor Physics* **21**, 905 (1982)

autonomous feedback control

Second Law of Thermodynamics

… with measurement and feedback





I = information gained by measurement

$$\langle W \rangle \geq \Delta F - k_B T \langle I \rangle$$

Sagawa & Ueda, *PRL* **100**, 080403 (2008)

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

Sagawa & Ueda, *PRL* **104**, 090602 (2010)

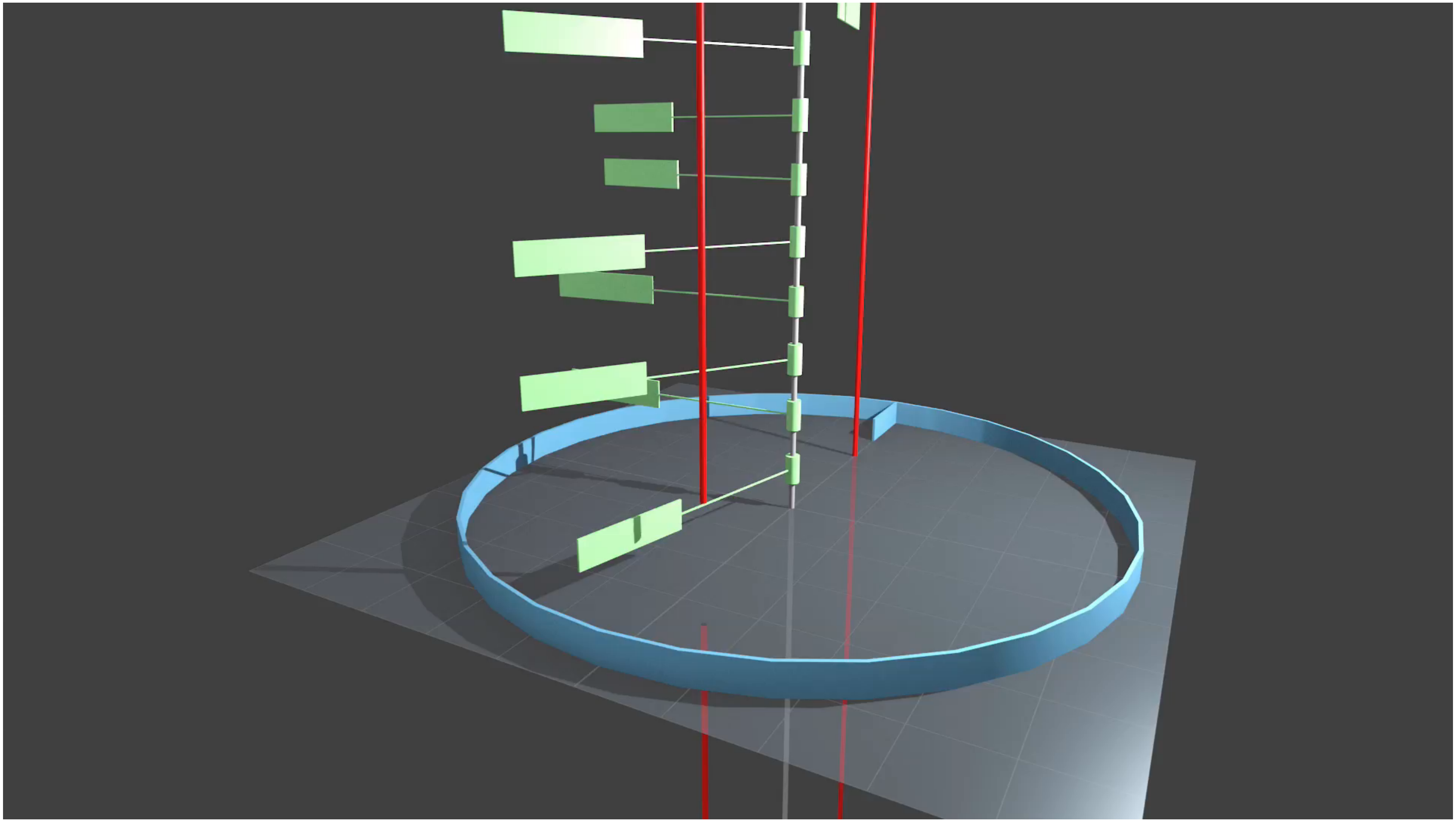
Autonomous demons

H.T. Quan *et al*, *PRL* **97**, 180402 (2006)
D. Mandal and C. Jarzynski, *PNAS* **109**, 11641 (2012)
T. Sagawa and M. Ueda, *PRL* **109**, 180602 (2012)
P. Strasberg *et al*, *PRL* **110**, 040601 (2012)
J.M. Horowitz, T. Sagawa and J.M.R. Parrondo *PRL* **111**, 010602 (2013)
A.C. Barato and U. Seifert, *EPL* **101**, 60001 (2013)
D. Mandal, H.T. Quan and C. Jarzynski, *PRL* **111**, 030602 (2013)
S. Deffner, *PRE* **88**, 062128 (2013)
Z. Lu, D. Mandal and C. Jarzynski, *Phys Today* **67**, 60 (Aug 2014)

<u>Gedankenengineering</u>:

Design a mechanical gadget that …

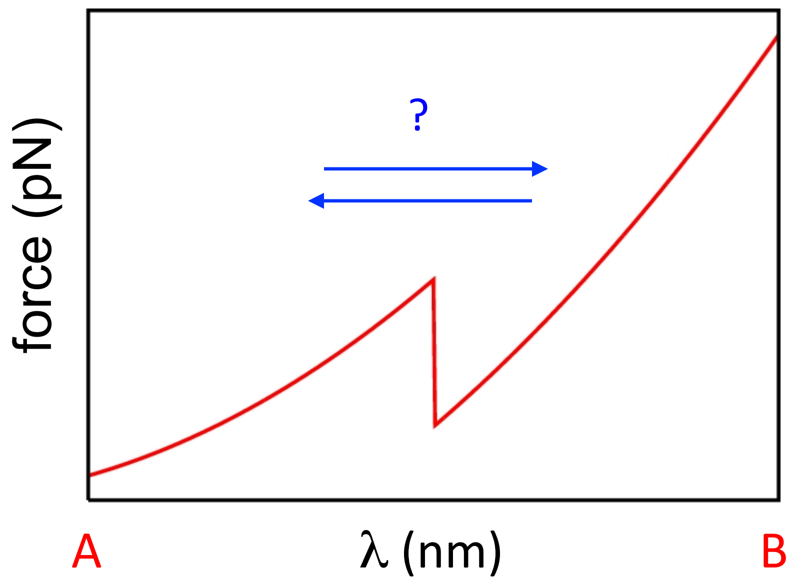
(1) systematically withdraws energy from a single thermal reservoir,
(2) delivers that energy to raise a mass against gravity, and
(3) records information in a memory register.



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.

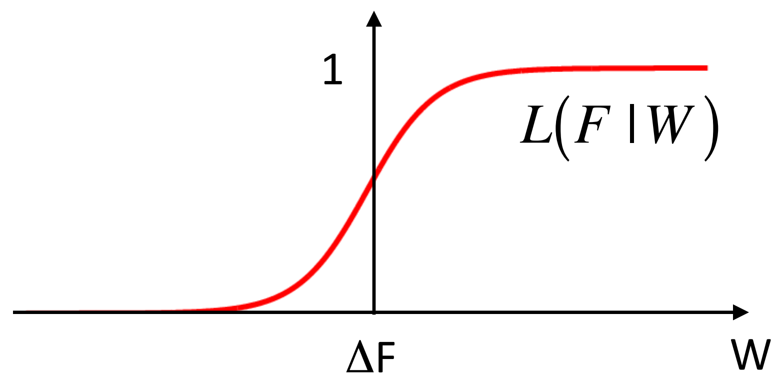
e.g.



Two hypotheses:

The molecule was stretched (F)
The molecule was contracted (R)

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



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

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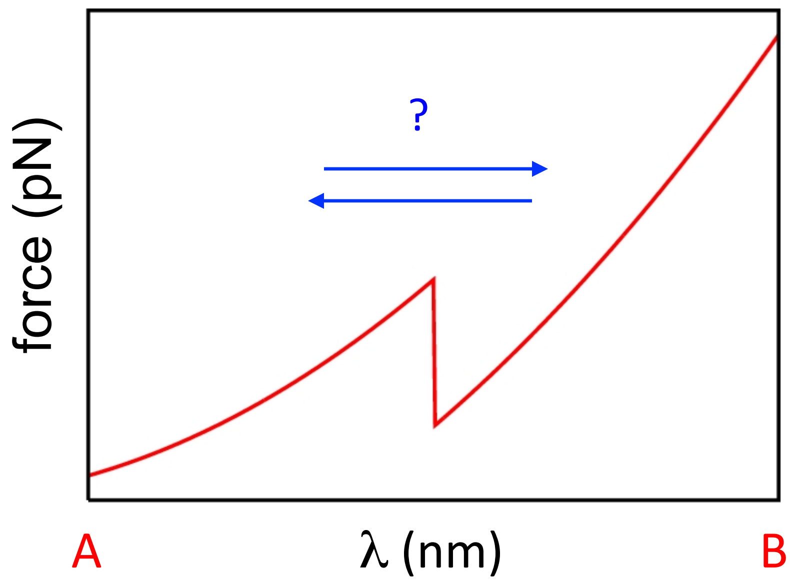

Two hypotheses:

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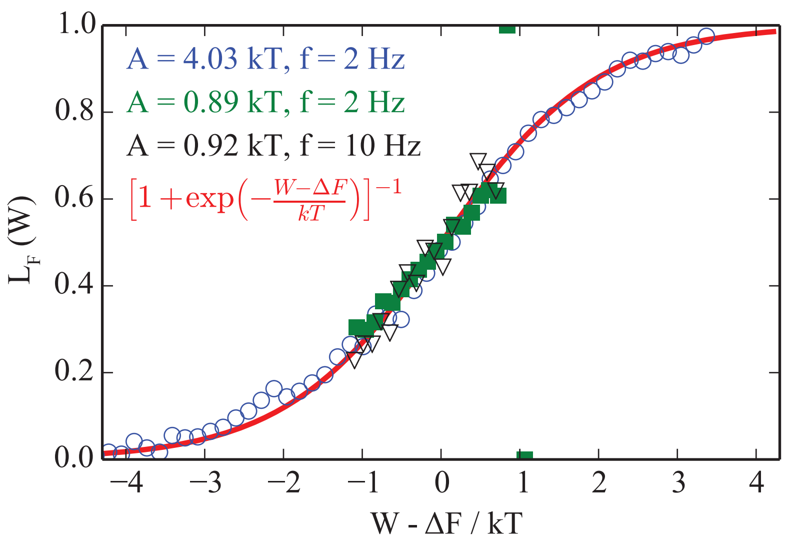
Hofmann *et al*,
Phys Status Solidi (2016)



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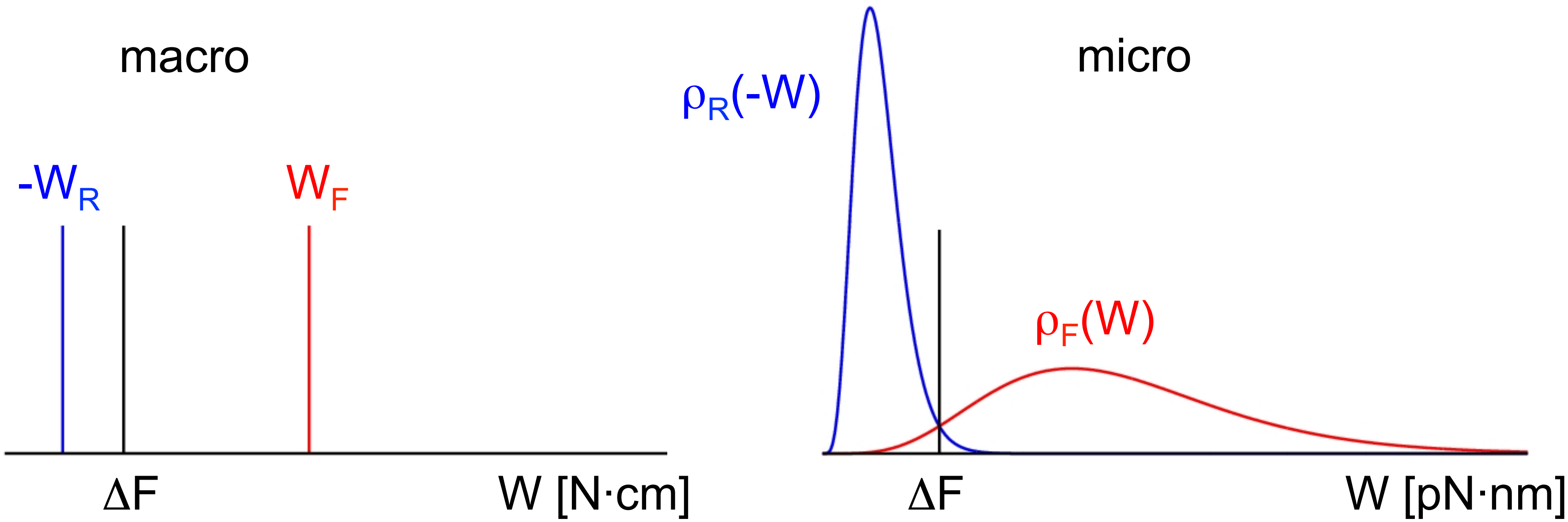
References



C.J., Annu Rev Cond Matt Phys **2**, 329 (2011)
fluctuation theorems for work

Seifert, Rep Prog Phys **75**, 126001 (2012)
stochastic thermodynamics

Sagawa, Progress Theor Phys **127**, 1 (2012)
information processing – non-autonomous

Deffner & C.J., Phys Rev X **3**, 041003 (2013)
information processing – autonomous