UNIVERSITY OF MARYLAND

IPST

A brief introduction to ***non-equilibrium statistical physics***

Chris Jarzynski
Institute for Physical Science and Technology
Department of Chemistry & Biochemistry
Department of Physics
University of Maryland, College Park

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.

<u>First Law</u> of Thermodynamics: $\Delta U = W + Q$

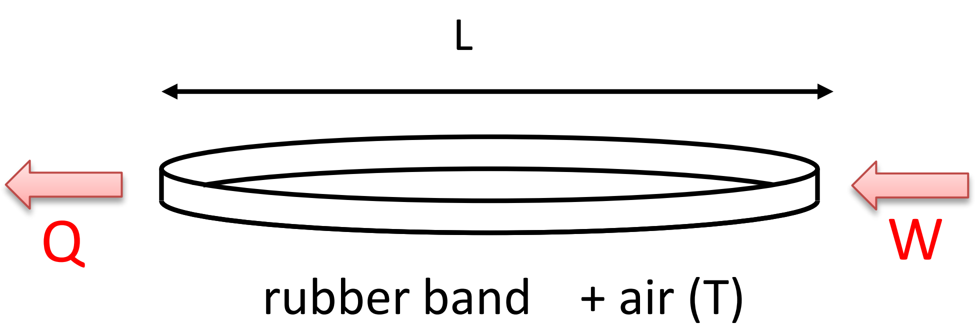
$\Delta U = U_B - U_A$ = net change in system's internal energy

W = *work* performed on the system

(displacements dX against force F)

Q = *heat* absorbed by the system

(spontaneous flow of energy via thermal contact)



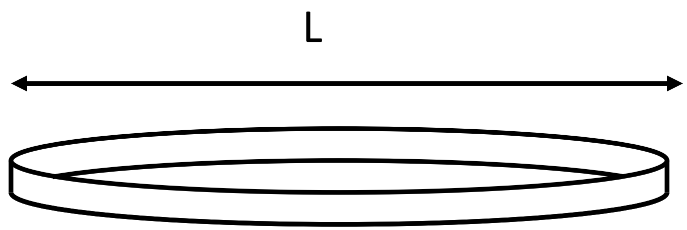
$$W = \int_A^B F\, dL$$

tension

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

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

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:

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

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

F = U-TS
= *Helmholtz free energy*

Thermodynamic cycles

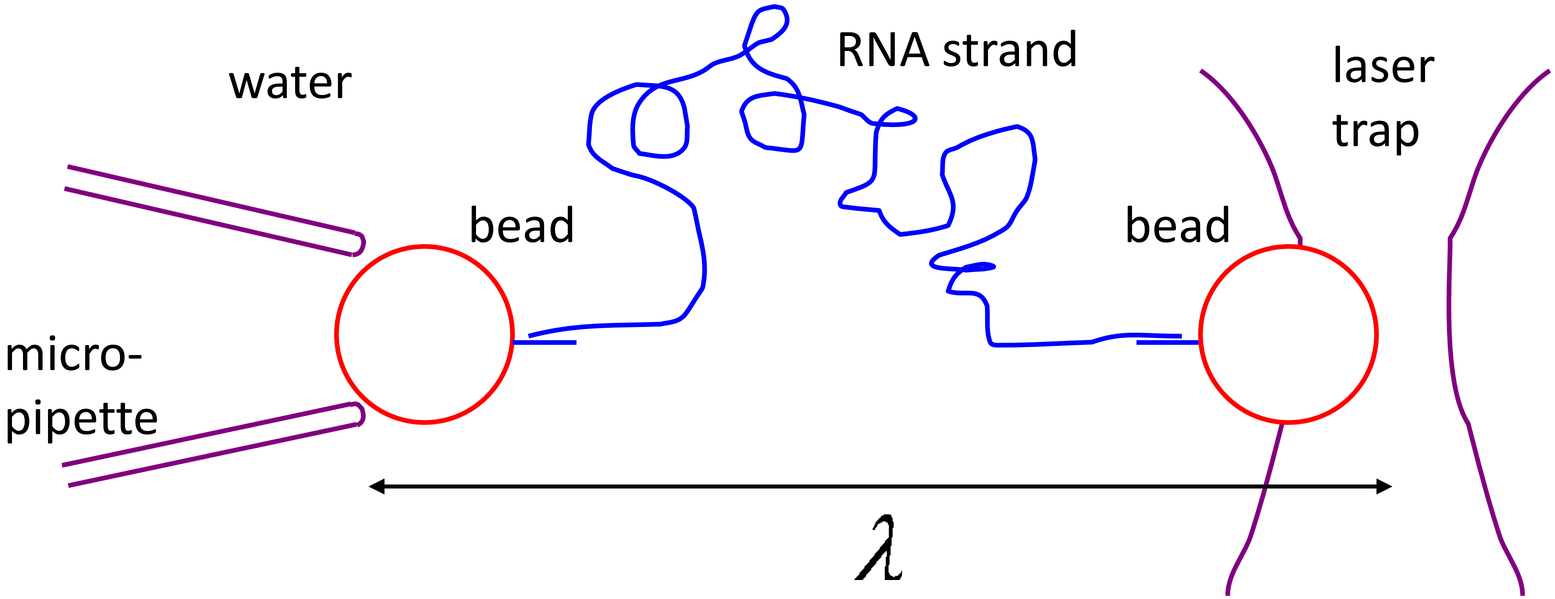
forward process : A→B $W_F \geq \Delta F$

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

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

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



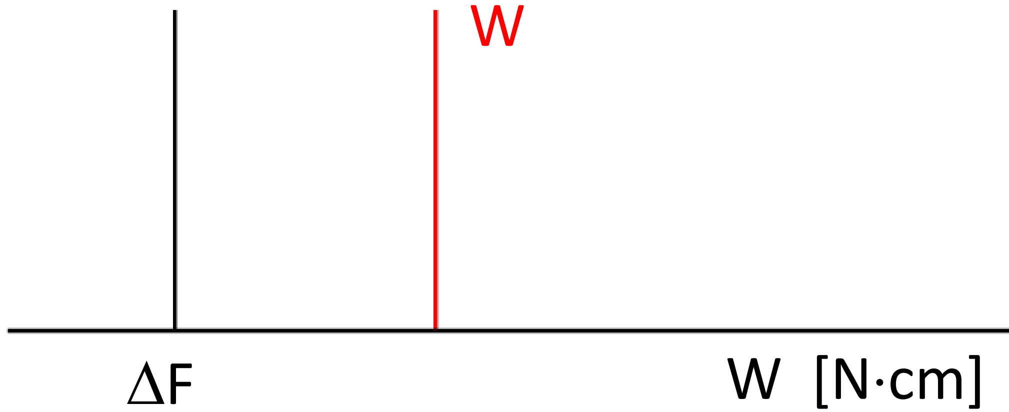
1. Begin in equilibrium $\lambda = A$
2. Stretch the molecule $\lambda : A \rightarrow B$

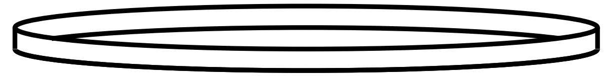
W = work performed ≥ ΔF *on average*

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

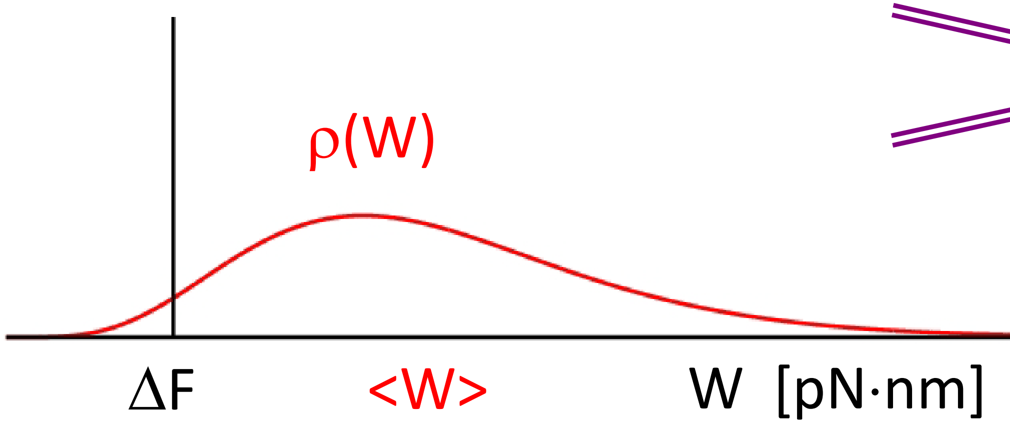
… *fluctuations* are important

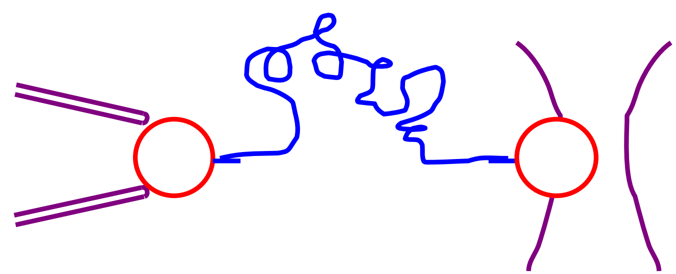
Second Law, macro *vs* micro





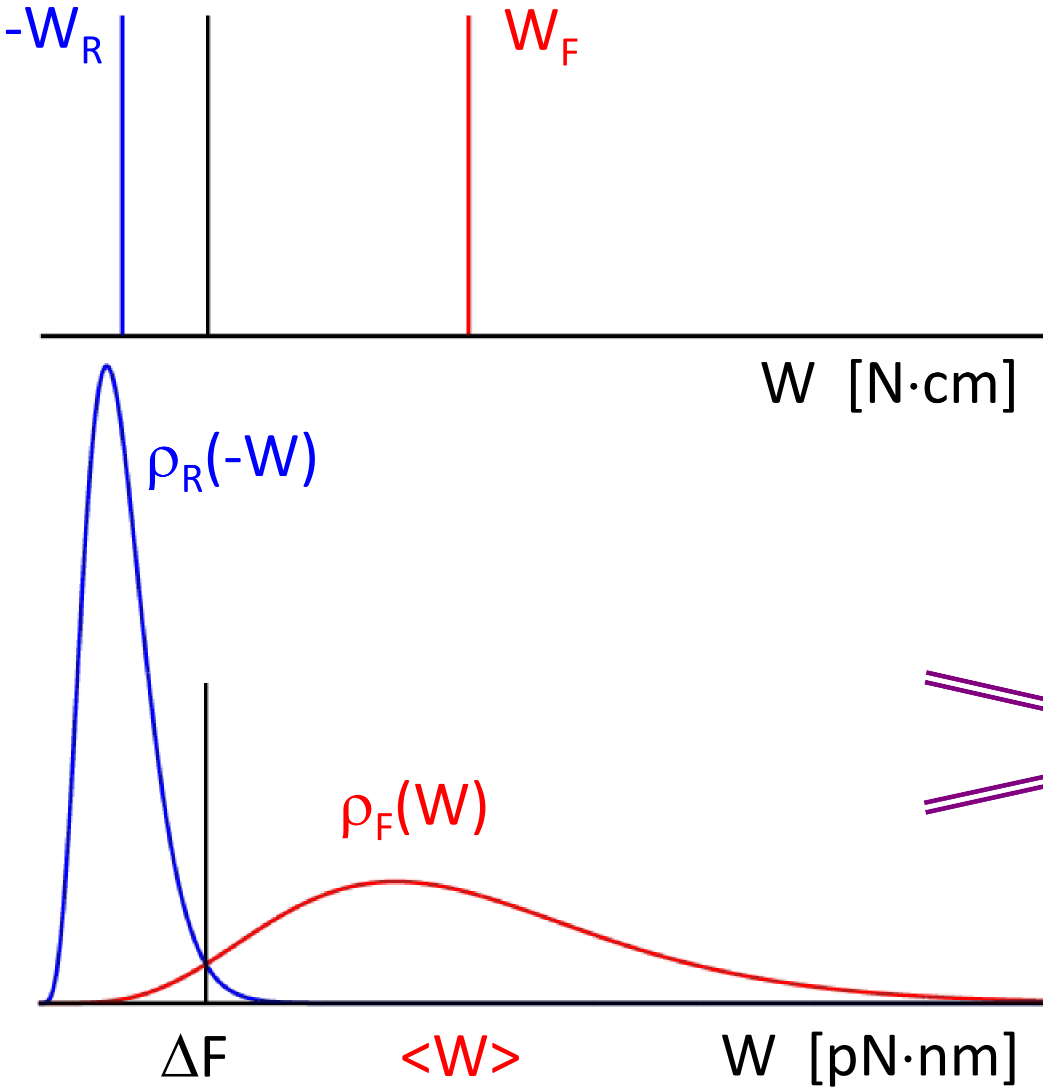
$$W \geq \Delta F$$

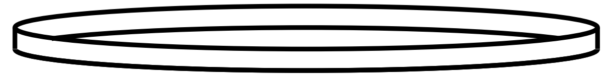




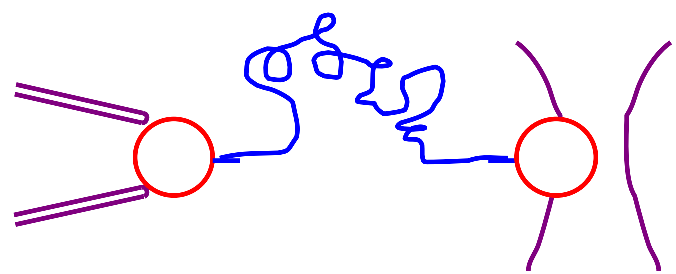
$$\langle W \rangle \geq \Delta F$$

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

weak

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

$1/k_B T$

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

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

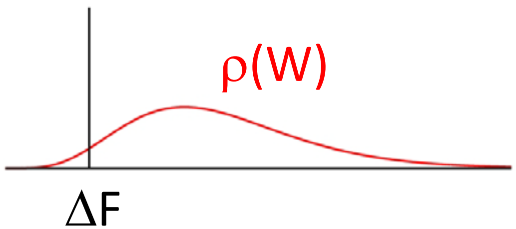
environment: $y = (Q, P)$

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

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

$$\frac{dH_S}{dt} = \underbrace{\frac{\partial H_S}{\partial x} \cdot \frac{dx}{dt}}_{\text{heat}} + \underbrace{\frac{\partial H_S}{\partial \lambda} \frac{d\lambda}{dt}}_{\text{work}} \qquad \begin{cases} W = \int dt \, \frac{d\lambda}{dt} \frac{\partial H_S}{\partial \lambda}\big(x(t); \lambda(t)\big) \\ Q = \int dt \, \frac{dx}{dt} \cdot \frac{\partial H_S}{\partial x}\big(x(t); \lambda(t)\big) \end{cases}$$

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: $y = (Q, P)$

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

$$U = H_S(x; \lambda) \quad or \quad \int p^{eq} H_S$$

$$S = -k_B \int p^{eq} \ln p^{eq} \quad , \quad F = -k_B T \ln Z$$

$$W = \int dt \frac{d\lambda}{dt} \frac{\partial H_S}{\partial \lambda} \quad , \quad Q = \int dt \frac{dx}{dt} \cdot \frac{\partial H_S}{\partial x}$$

$\Delta U = W + Q$

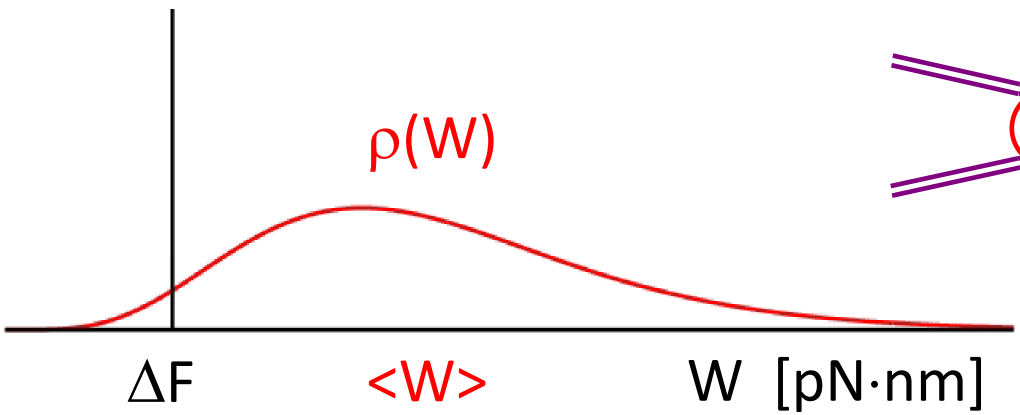
$\langle W \rangle \geq \Delta F$

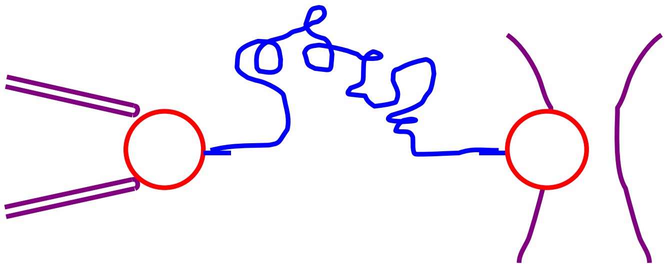
Beyond classical thermodynamics:
Fluctuation Theorems

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

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

… places a strong constraint on ρ(W).





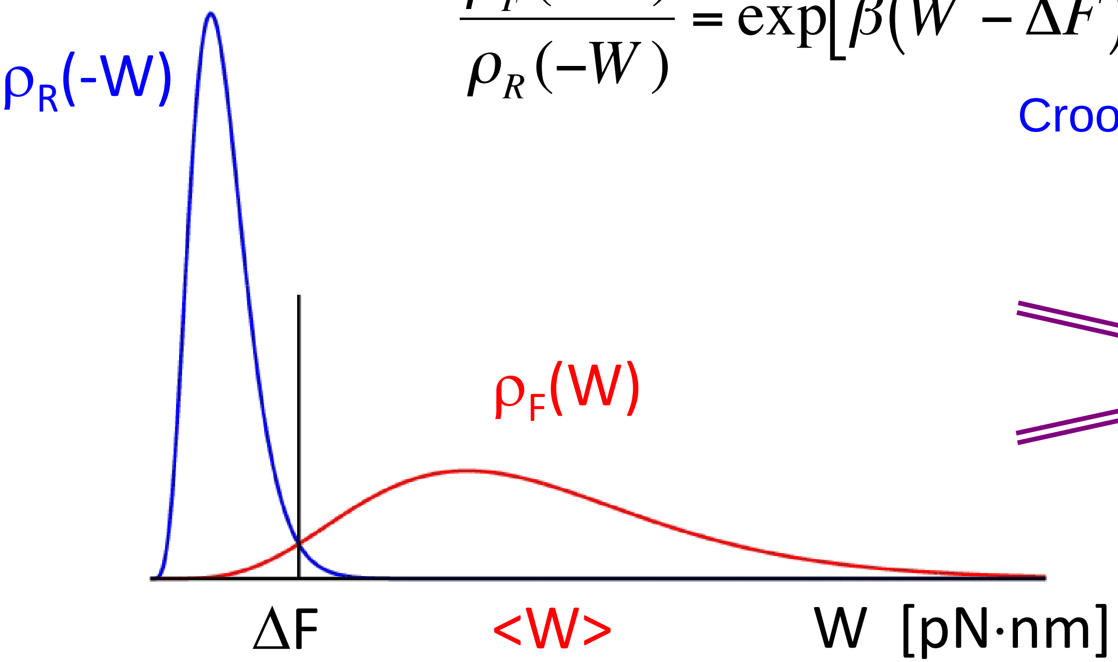
Beyond classical thermodynamics: *Fluctuation Theorems*

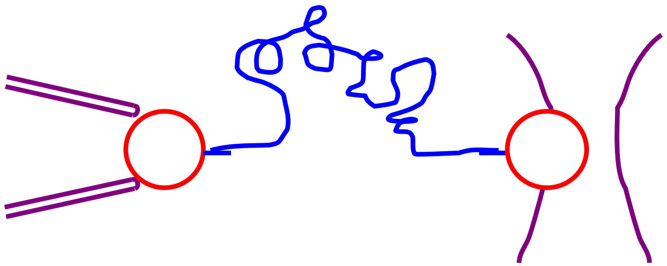
$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

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

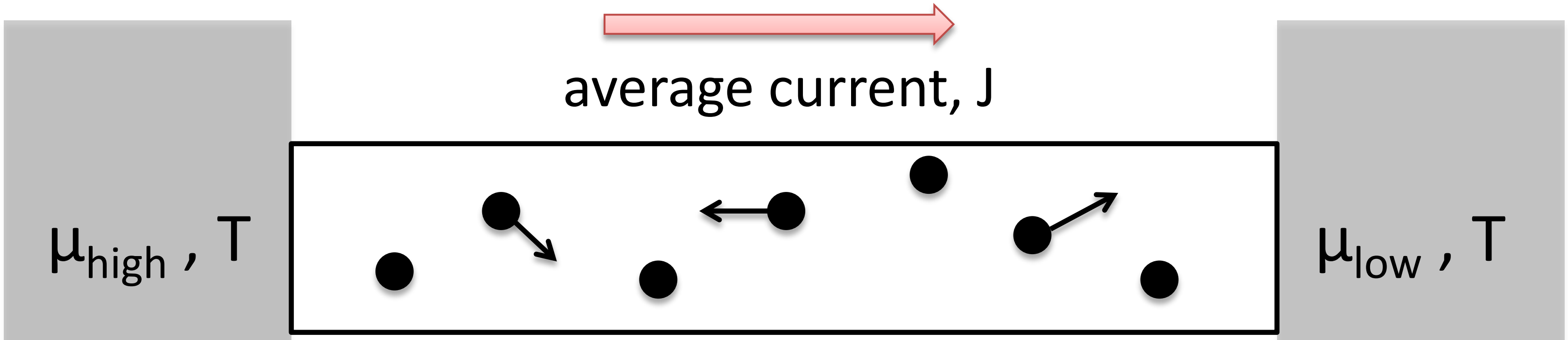
$$\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$$

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

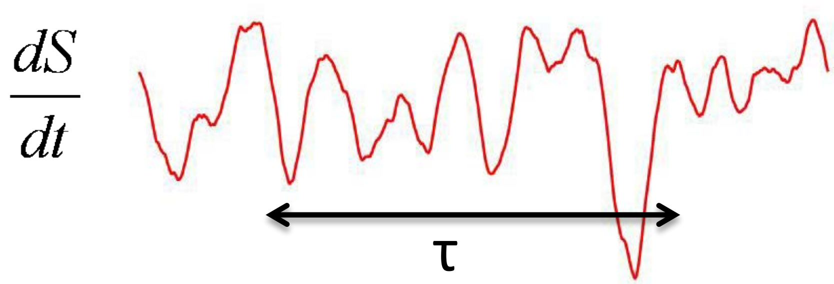




Nonequilibrium Steady States



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

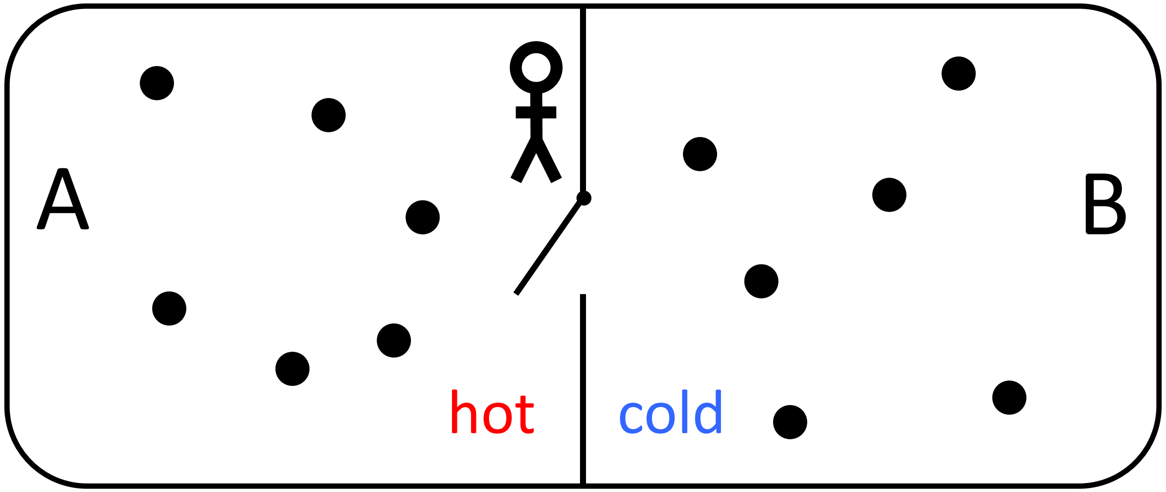


$$\sigma = \frac{1}{\tau}\int_t^{t+\tau} dt\,\frac{dS}{dt} = \frac{\Delta S}{\tau}$$

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

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

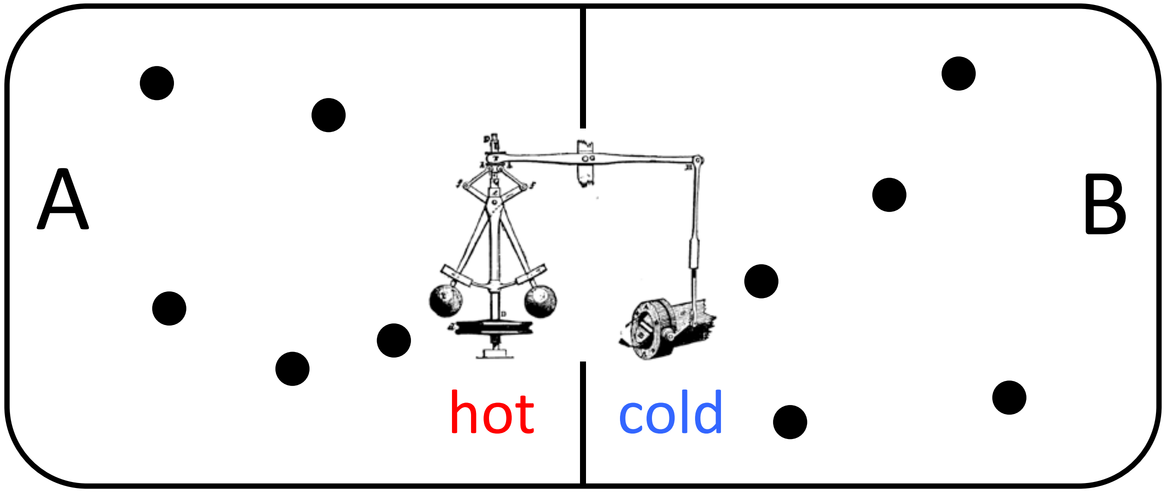
Maxwell's Demon



"… 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 the intelligence of a very observant and neat-fingered being has been employed"

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

Maxwell's Demon

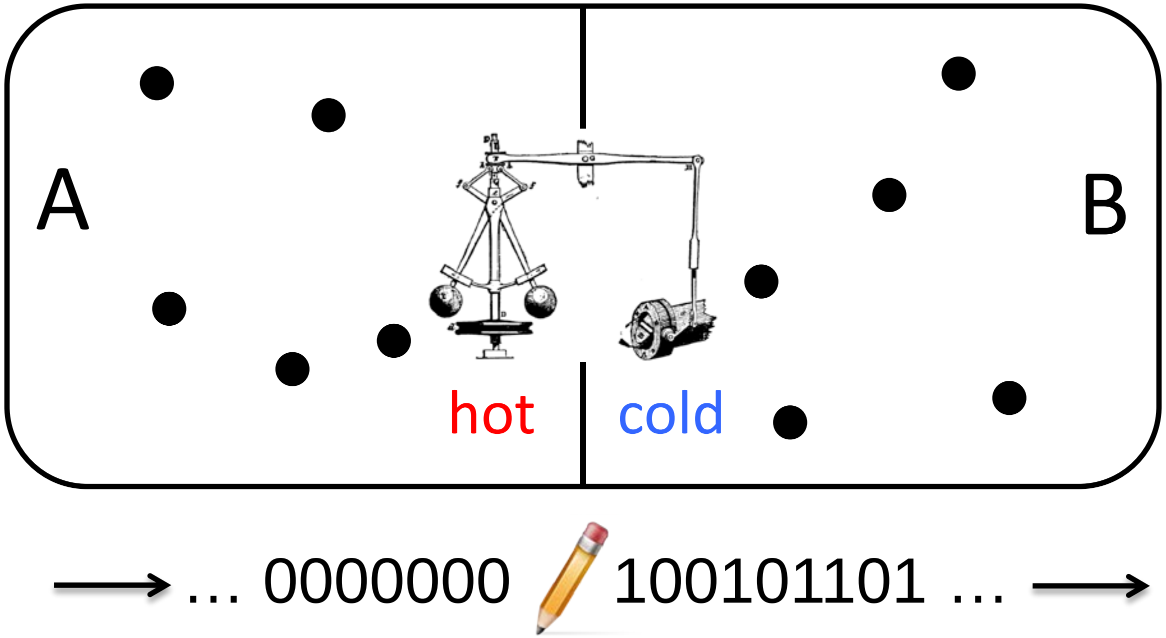


Is a "mechanical" Maxwell demon possible?

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

no!

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)
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yes, but …

Autonomous demons

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T. Sagawa and M. Ueda, *PRL* **109**, 180602 (2012)
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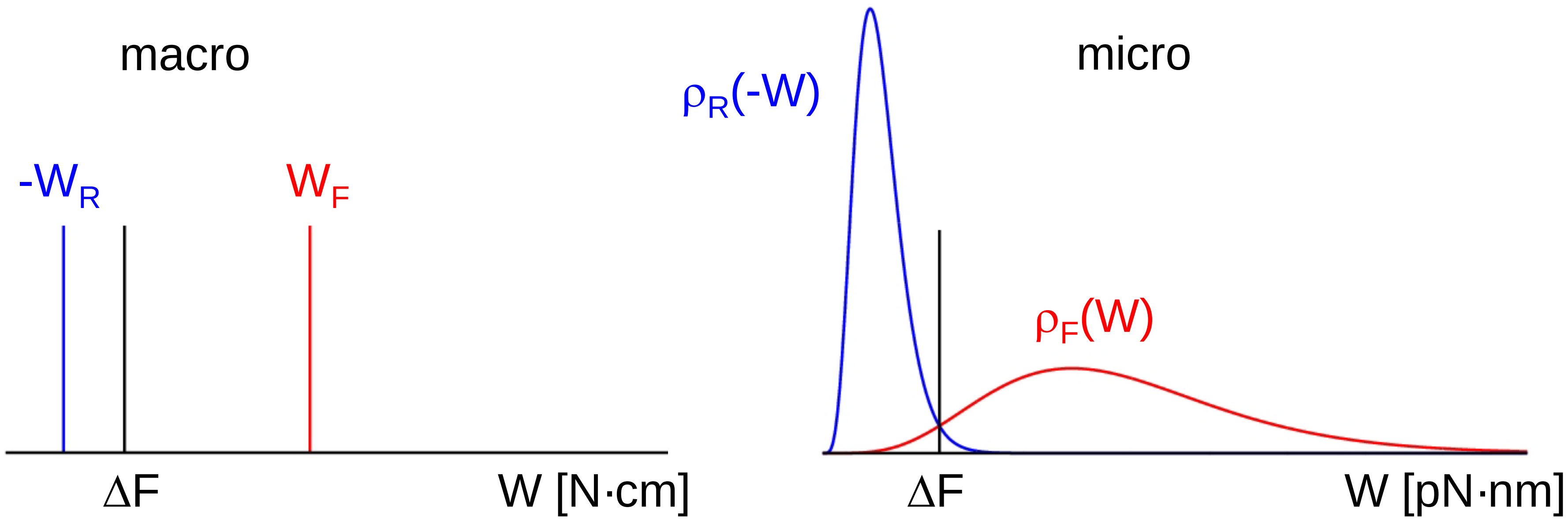
<u>Gedankenengineering</u>:

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.

References



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stochastic thermodynamics

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information processing – non-autonomous

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