Scaling down the laws of thermodynamics

What do the laws of thermodynamics look like when applied to very small systems?

Chris Jarzynski
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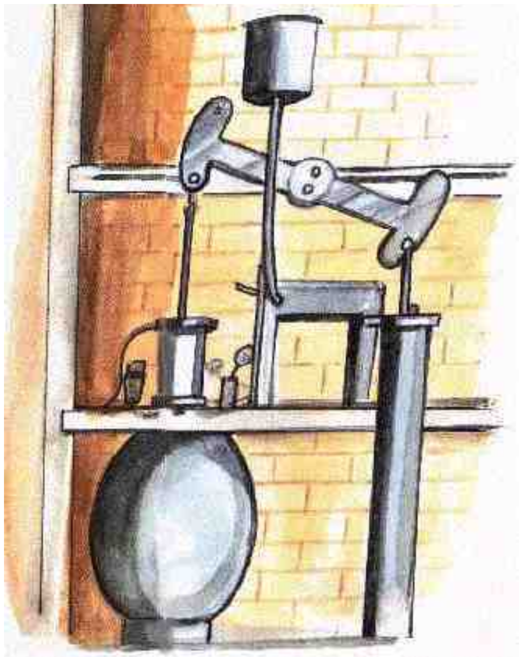
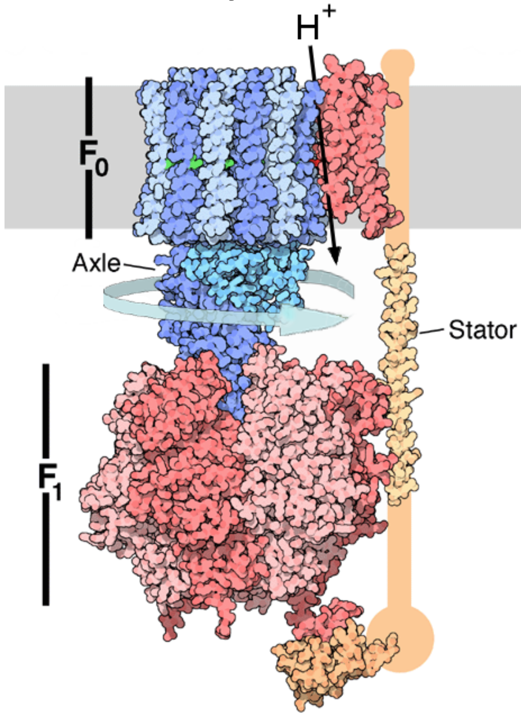
Department of Physics

Macroscopic and microscopic machines

steam engine



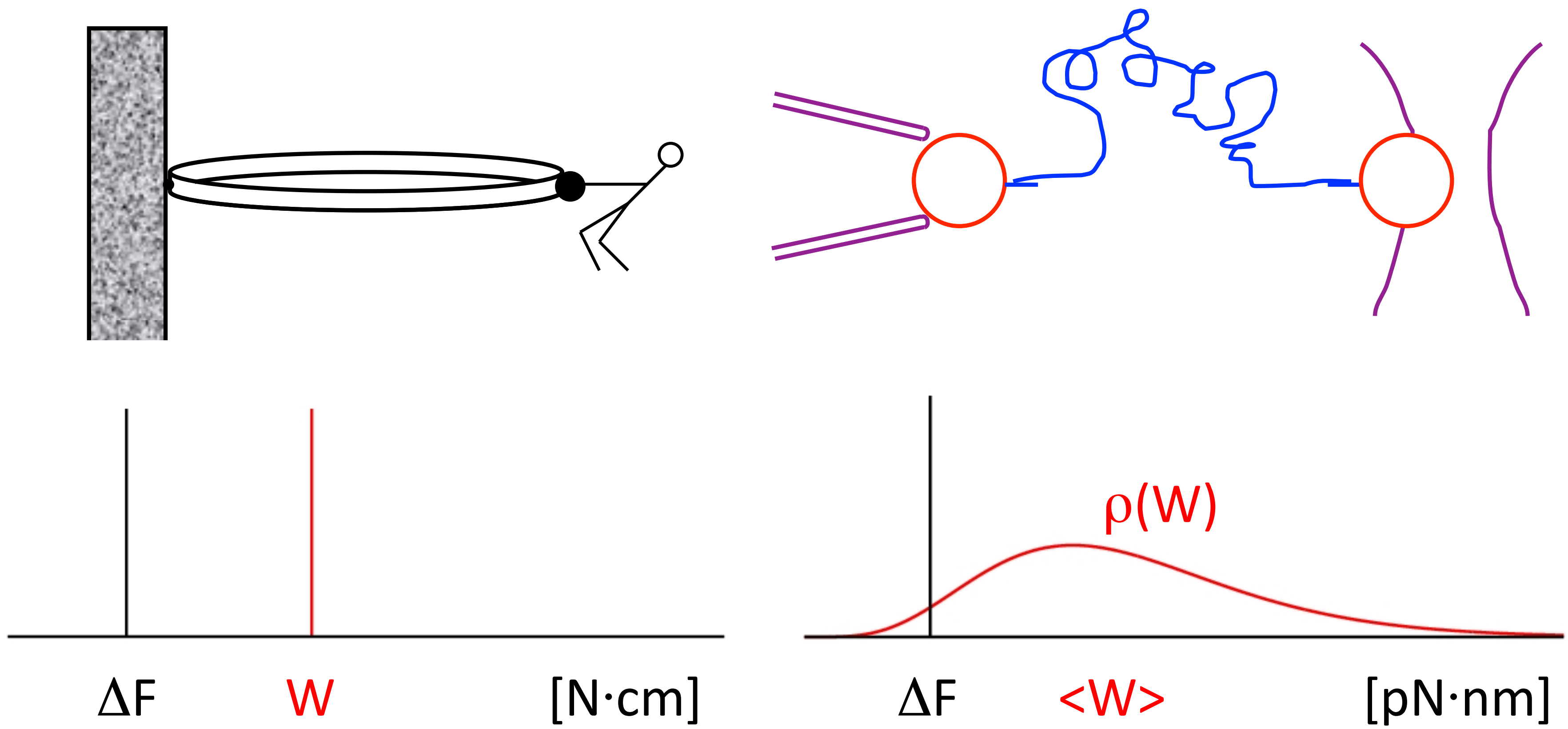
ATP synthase



RCSB Protein
Data Bank

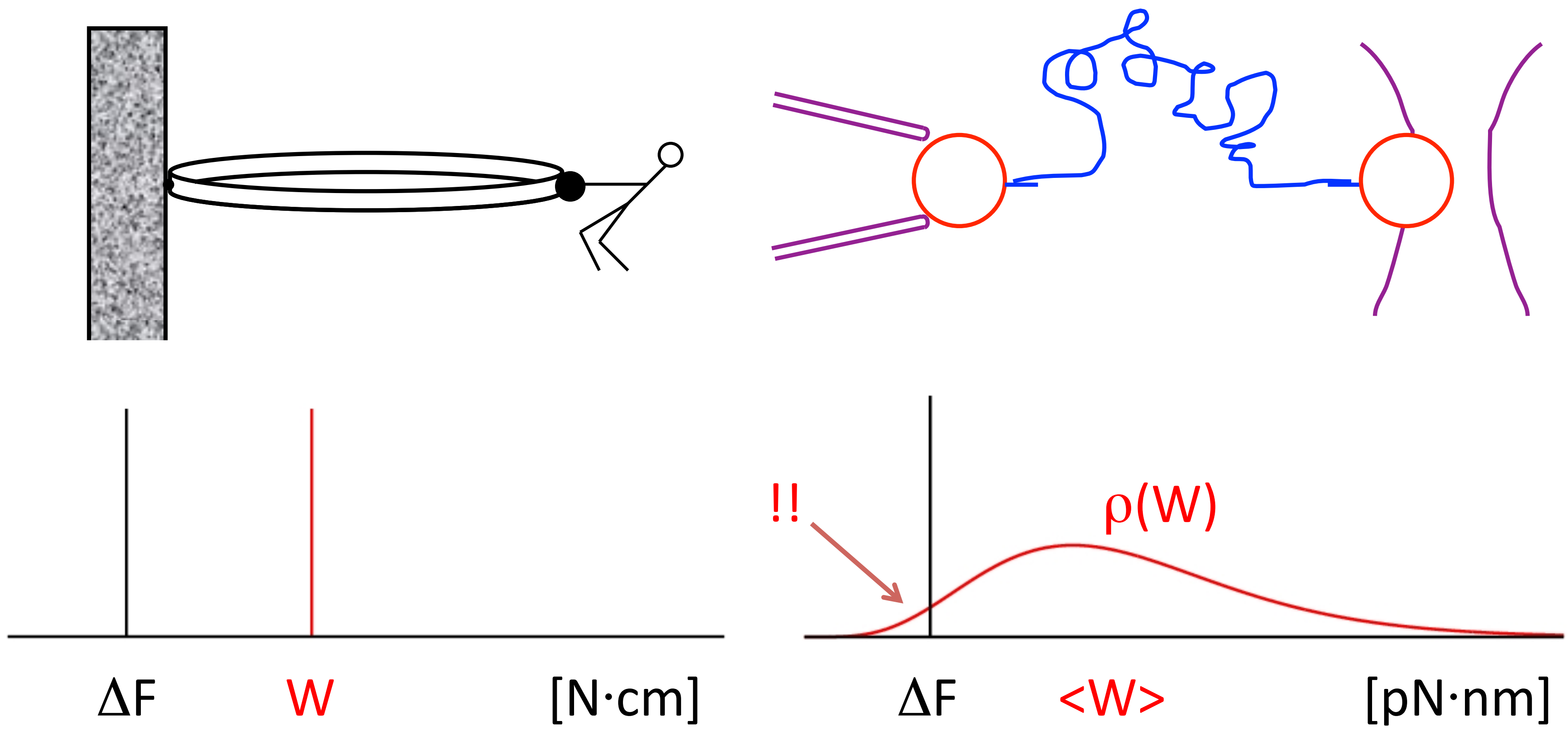
New features of thermodynamics at the nanoscale

- **Prominence of fluctuations**



New features of thermodynamics at the nanoscale

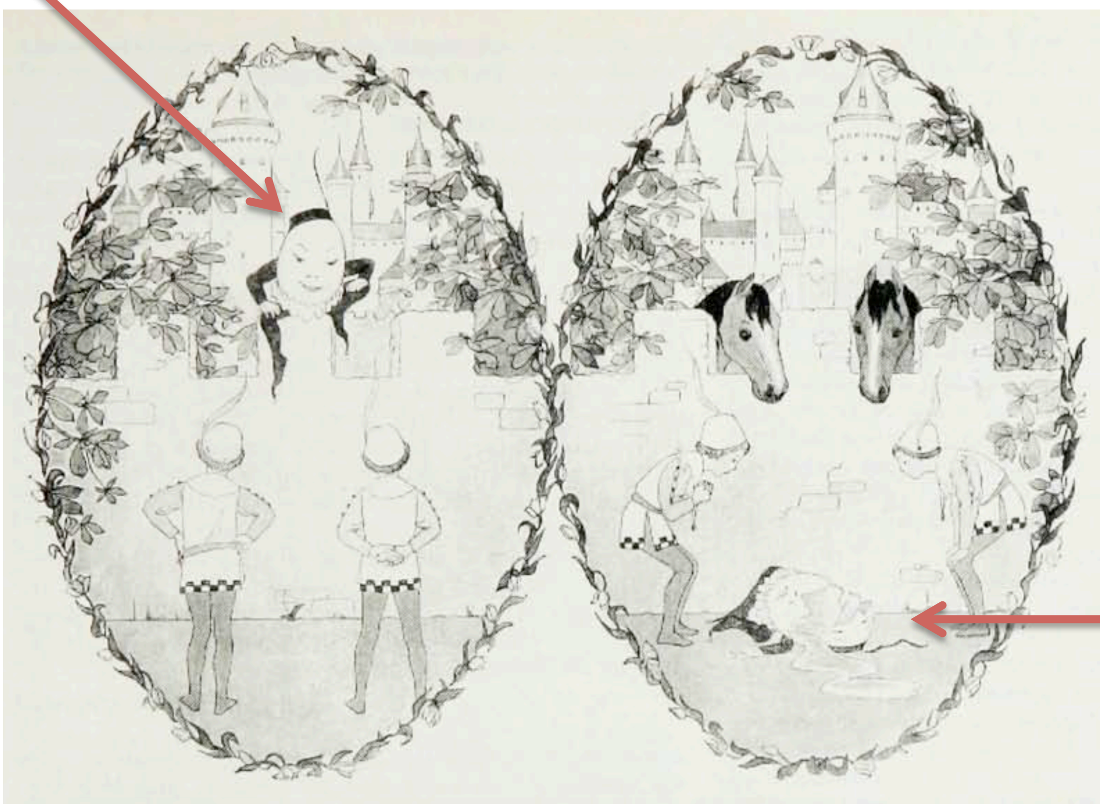
- Prominence of fluctuations
- **“Violations” of the second law**



New features of thermodynamics at the nanoscale

- Prominence of fluctuations
- “Violations” of the second law
- **Blurred arrow of time**

happy Humpty

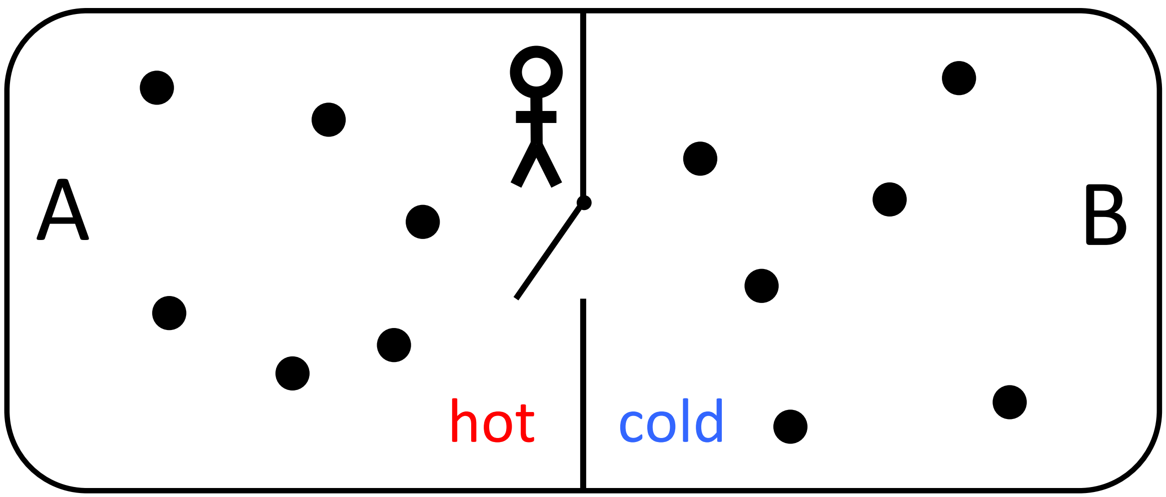


broken Humpty

J.L. Lebowitz, *Physics Today* (1993)

New features of thermodynamics at the nanoscale

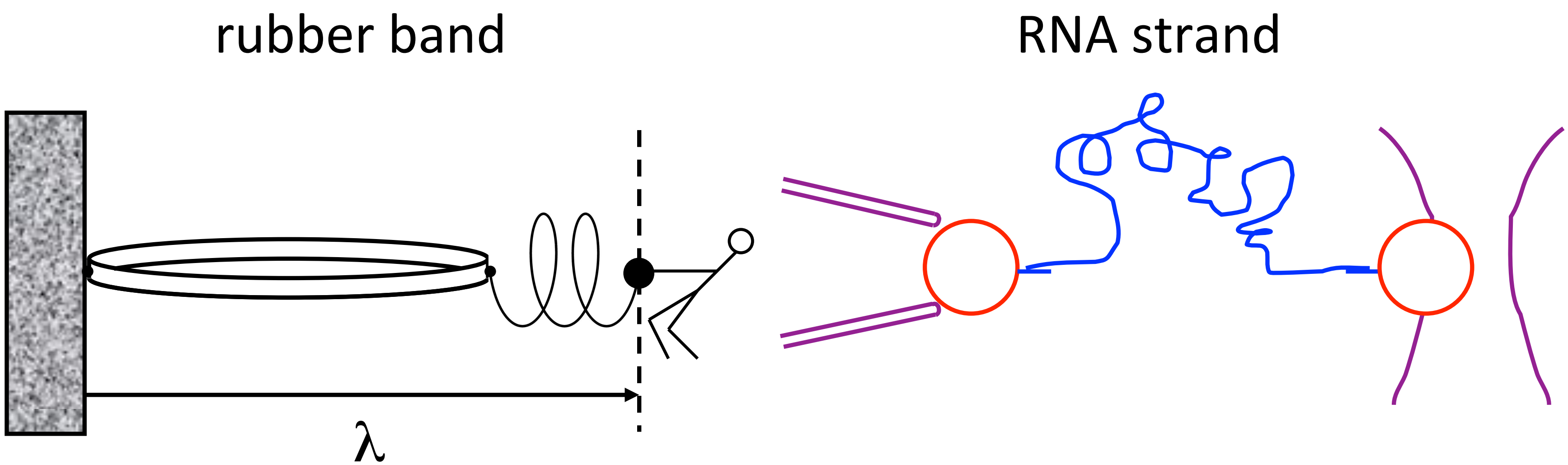
- Prominence of fluctuations
- “Violations” of the second law
- Blurred arrow of time
- **Feedback control & information processing**



New features of thermodynamics at the nanoscale

- Prominence of fluctuations
- “Violations” of the second law
- Blurred arrow of time
- Feedback control & information processing
- **Strong system-environment coupling**

Macro- and *nano*scale thermodynamic processes



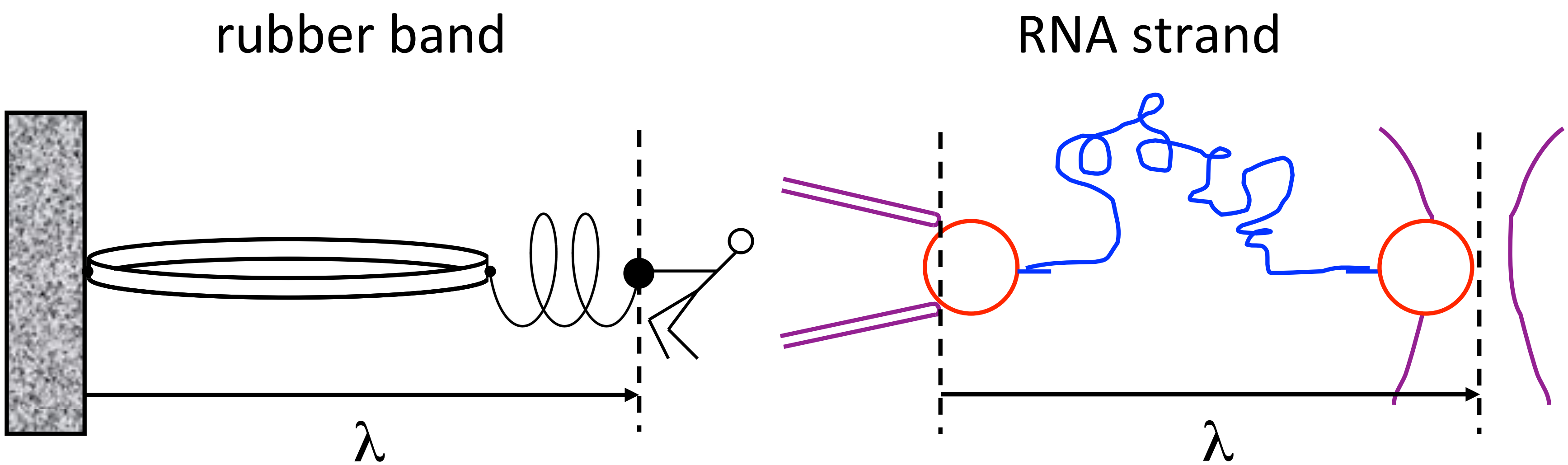
Irreversible process (rubber band):

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

   W = work performed $\geq \Delta F = F_B - F_A$

3. End in equilibrium $\lambda = B$

Macro- and *nano*scale thermodynamic processes



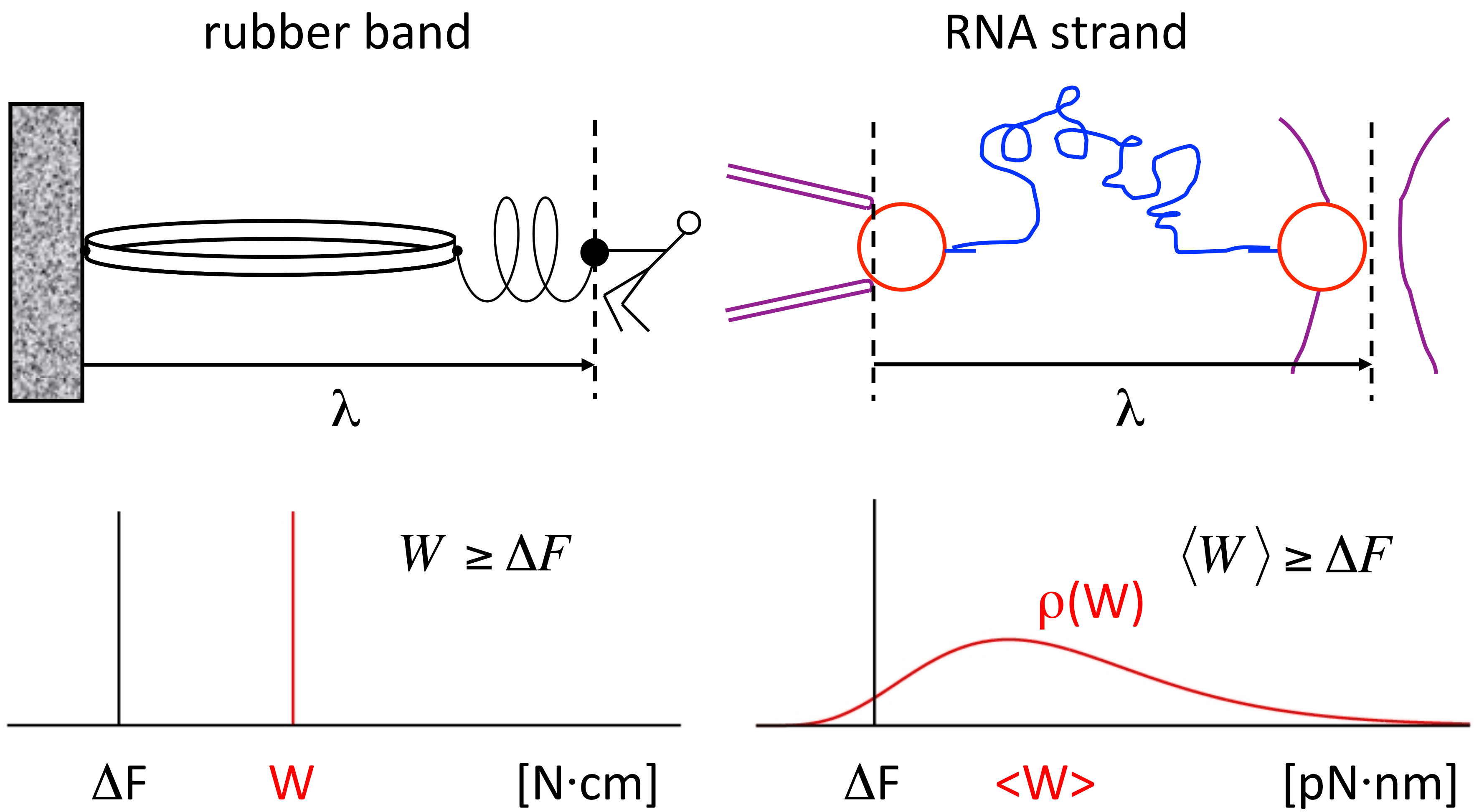
Irreversible process (RNA):

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

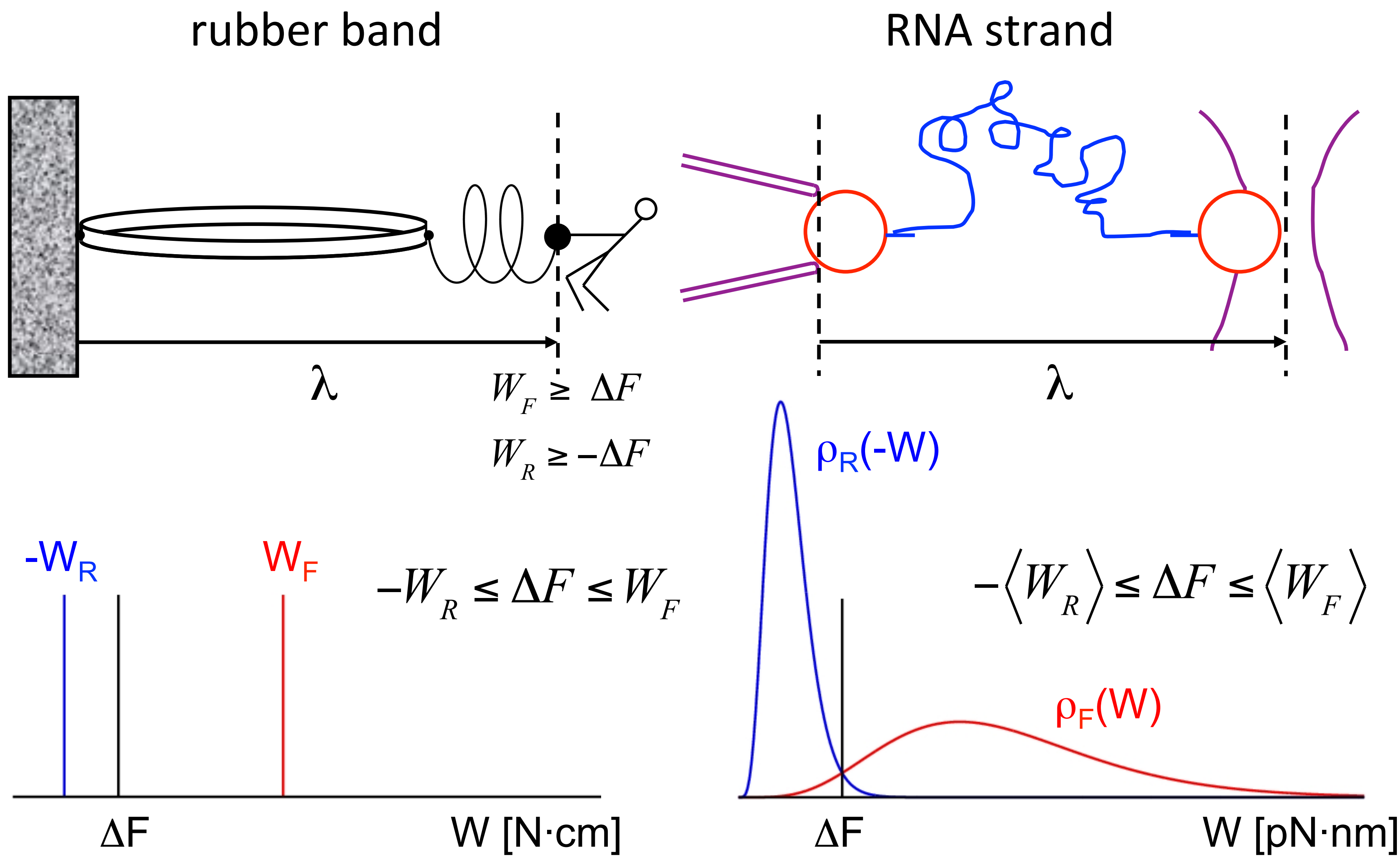
   $\langle W \rangle$ = *average* work $\geq \Delta F = F_B - F_A$

3. End in equilibrium $\lambda = B$

Macro- and *nano*scale thermodynamic processes



Macro- and *nano*scale thermodynamic processes

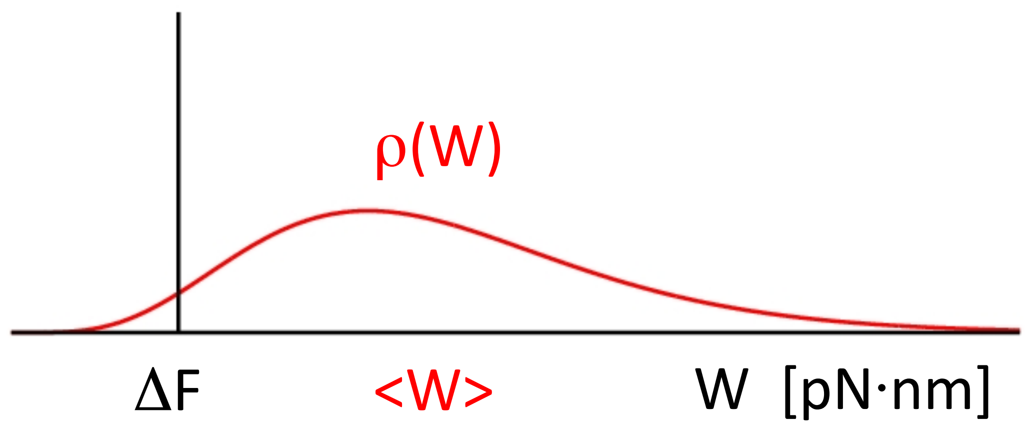


Fluctuations in W satisfy unexpected laws.

Fluctuation theorems / non-equilibrium work relations

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

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



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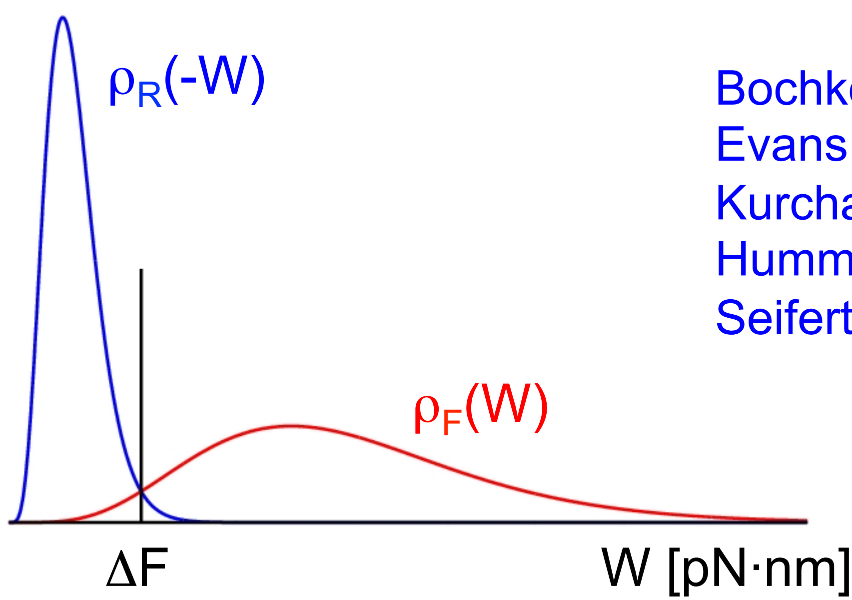
$$\frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta F\right)\right]$$

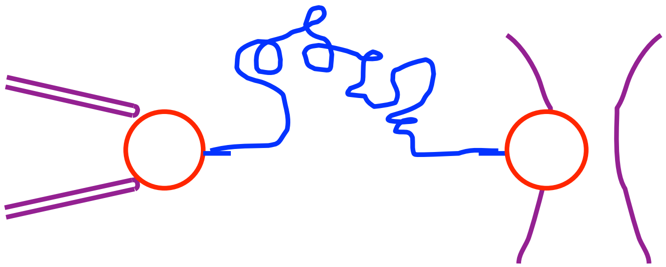
Crooks, *PRE* **60**, 2721 (1999)
[*J Stat Phys* **90**, 1481 (1998)]

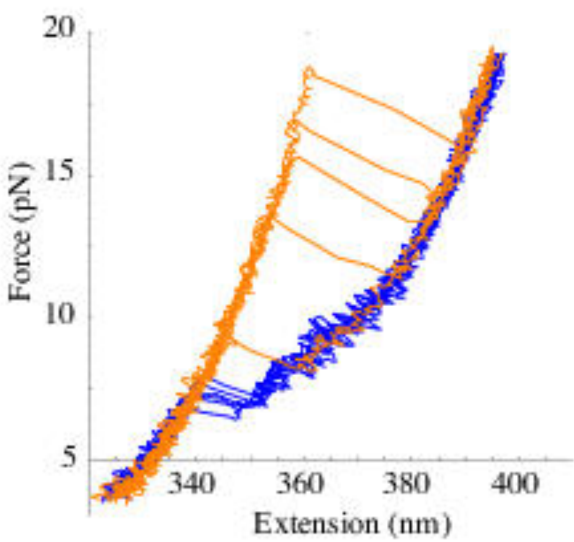


Bochkov & Kuzovlev
Evans, Cohen, Morriss, Searles, Gallavotti
Kurchan, Lebowitz, Spohn
Hummer & Szabo
Seifert …

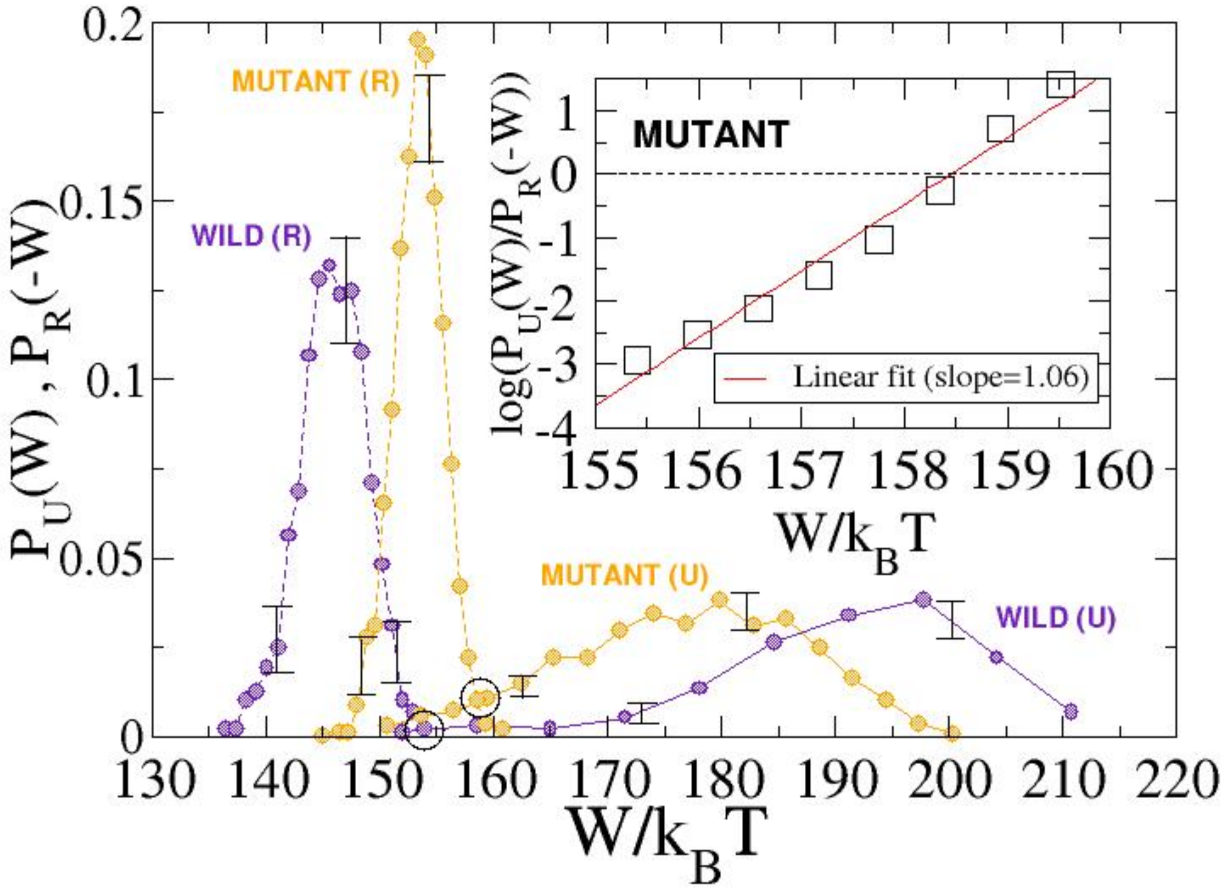
Unfolding & refolding of ribosomal RNA

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



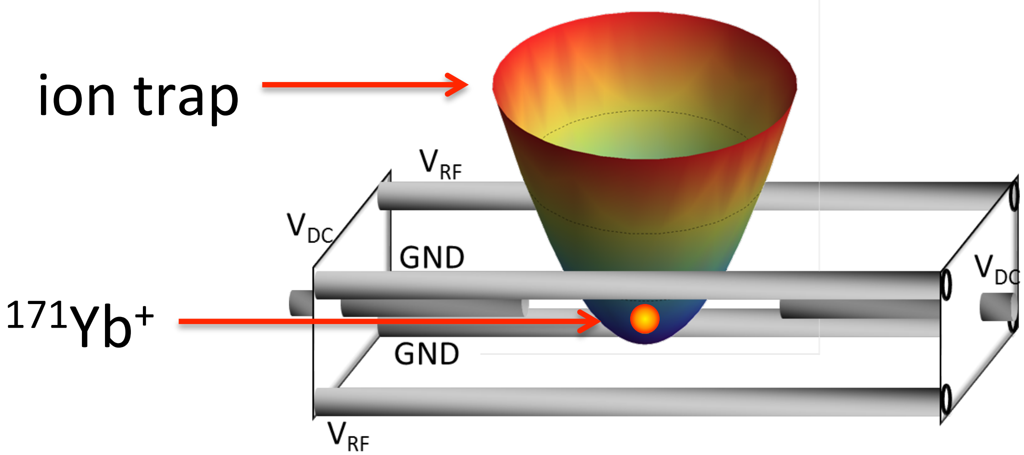


Collin *et al*, *Nature* **437**, 231 (2005)



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

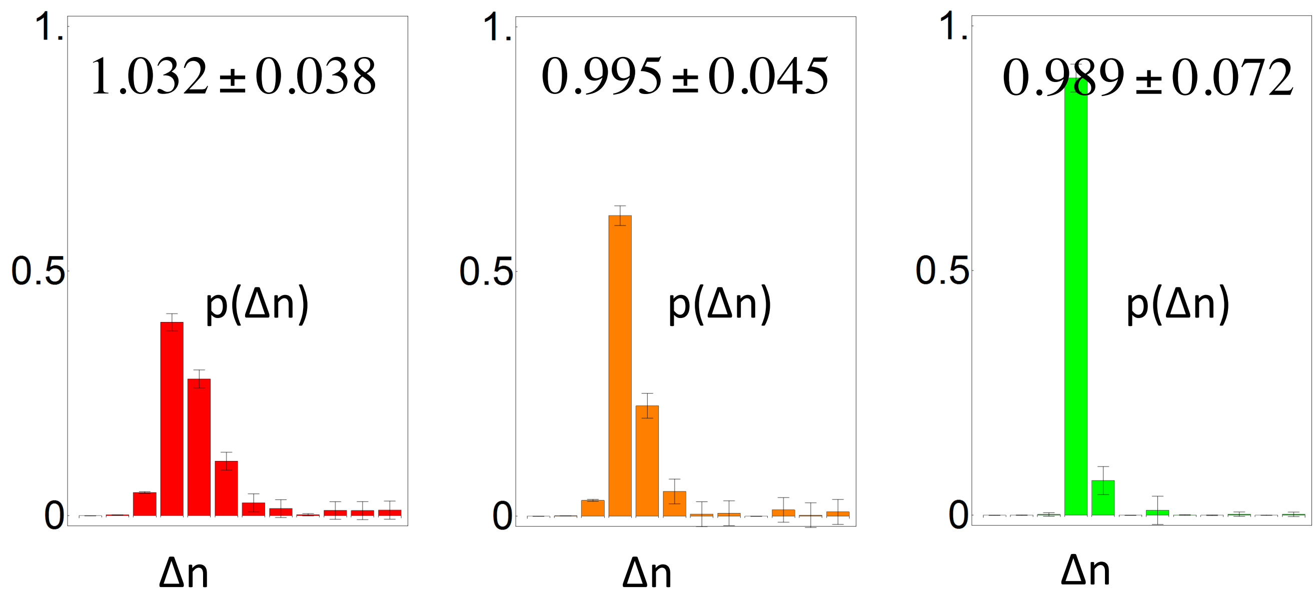
Mukamel, *PRL* **90**, 170604 (2003)
Kurchan, cond-mat/0007360 ; Tasaki, cond-mat/0009244



$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$W = \hbar\omega\left(n_f - n_i\right) = \hbar\omega\,\Delta n$$

An *et al*,
Nat. Phys. **11**, 193 (2015)



$$\Delta F = 0$$

$$\left\langle e^{-\beta W} \right\rangle \stackrel{?}{=} 1$$

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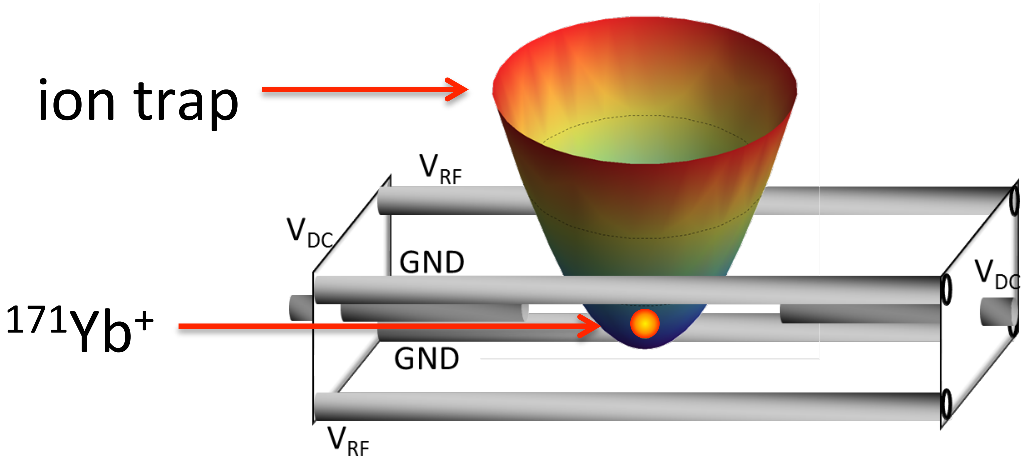

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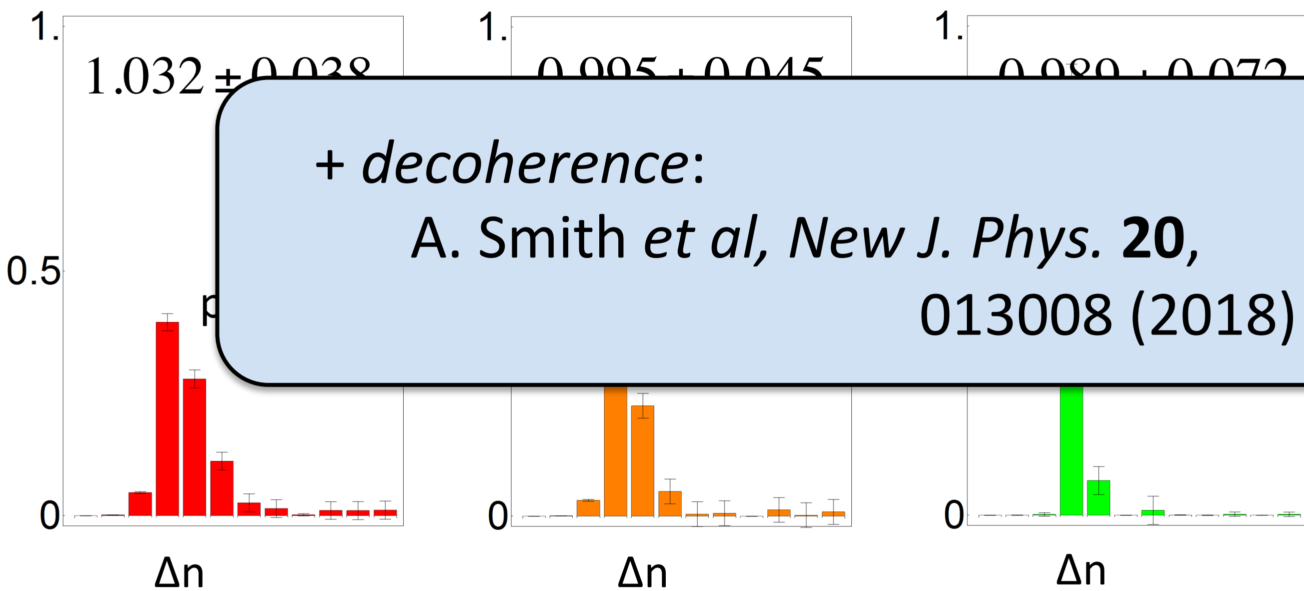
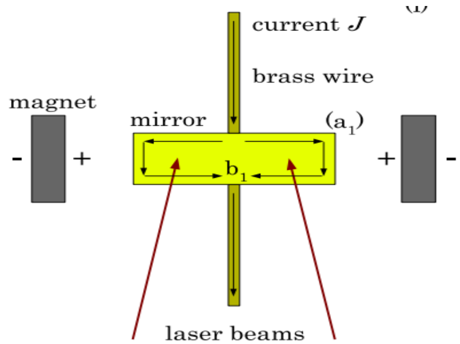


$$\Delta F = 0$$

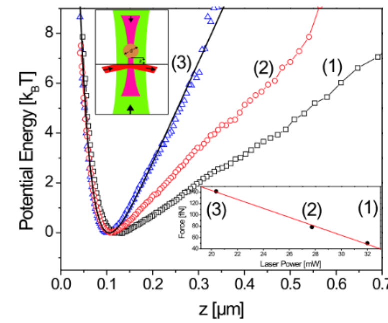
$$\left\langle e^{-\beta W} \right\rangle \stackrel{?}{=} 1$$

+ *decoherence*:
A. Smith *et al, New J. Phys.* **20**, 013008 (2018)

Further experimental verification



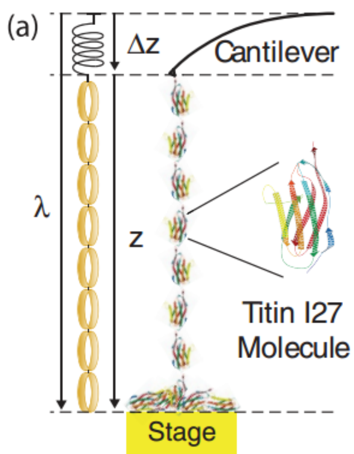
Mechanical oscillator
Douarche *et al, EPL* **70**, 593 (2005)



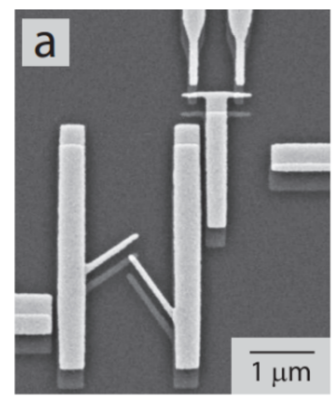
Trapped colloidal particle
Blickle *et al, PRL* **96**, 070603 (2006)

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

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



Protein unfolding
Harris, Song and Kiang,
PRL **99**, 068101 (2007)



Single electron box
Saira *et al, PRL* **109**, 180601 (2012)

& others …

Implications for the Second Law

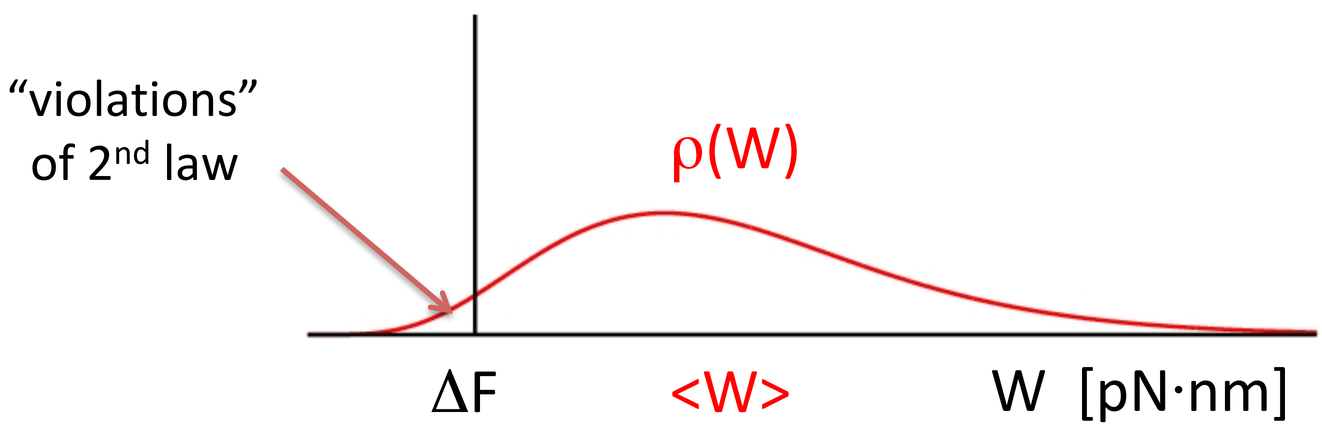
$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F}$$

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

implies

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

$$\Pr[W \leq \Delta F - \zeta] \leq \exp(-\zeta / k_B T)$$



Implications for the Second Law

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

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

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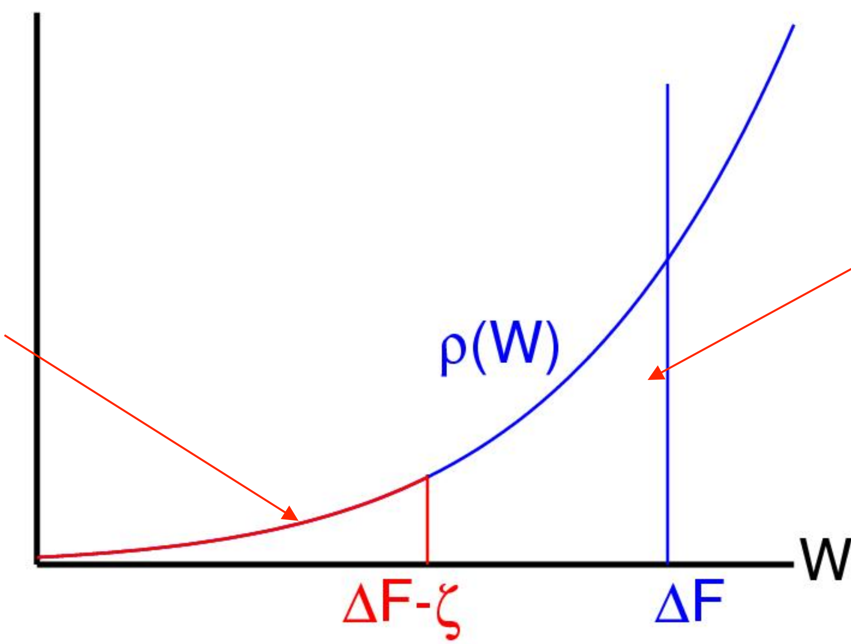
What is the probability that the 2nd law is "violated" by at least ζ ?

$$\Pr[W \leq \Delta F - \zeta]$$



$\zeta = 0^+$:

$$\Pr[W < \Delta F] < 1$$

weak bound

Implications for the Second Law

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

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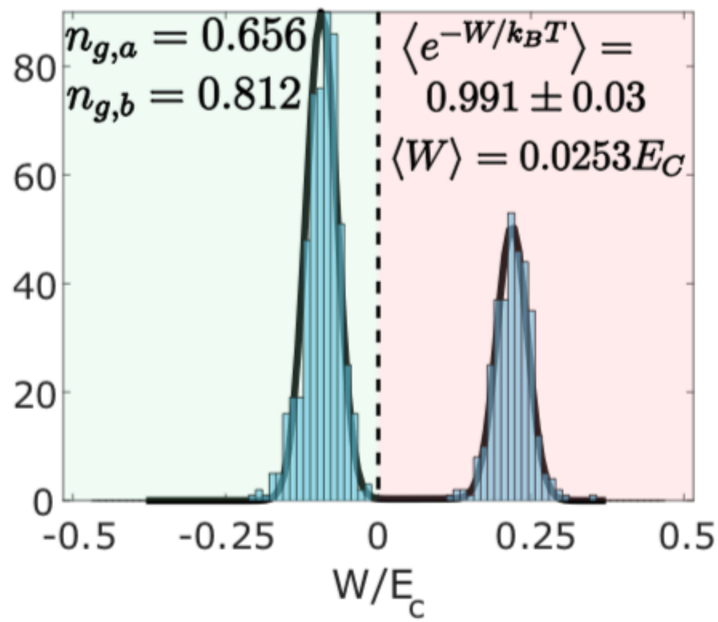


Single electron transistor
Maillet *et al,*
arXiv 1810:06274

$$\Pr[W < \Delta F] \approx 0.65$$

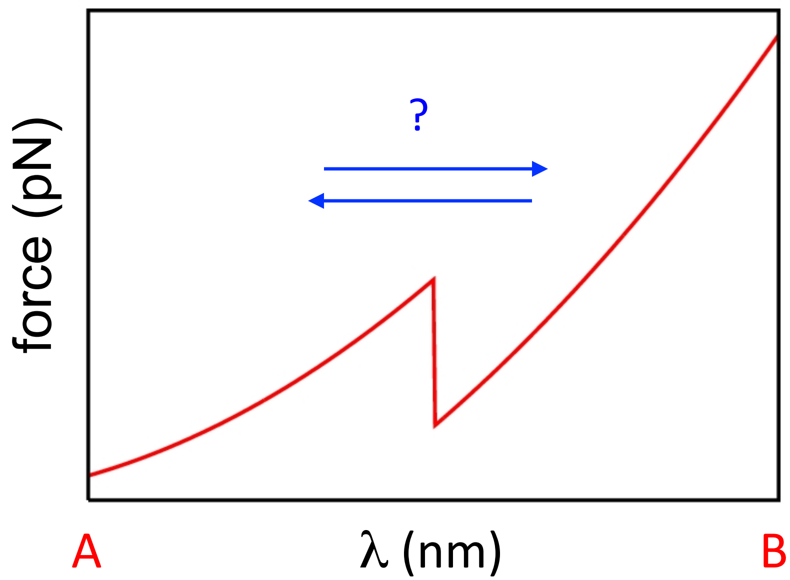
$$\left\langle W \right\rangle > \Delta F$$

Guessing the direction of the arrow of time

C.J., *Annu Rev Cond Matt Phys* **2**, 329 (2011)

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.

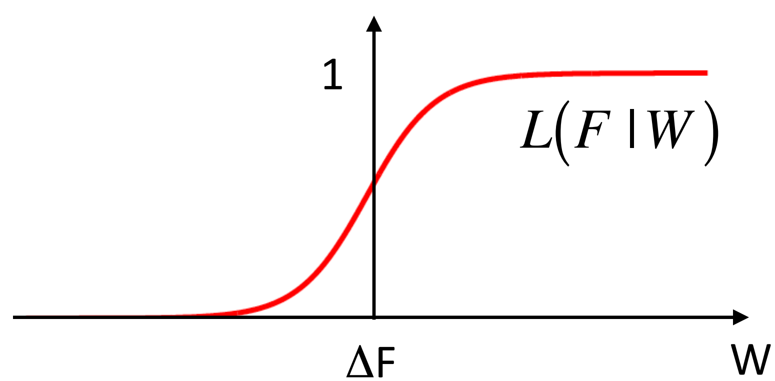
e.g.



Two hypotheses:

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

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



Shirts *et al*, *PRL* **91**, 140601 (2003) ,
Maragakis *et al*, *JCP* **129**, 024102 (2008)

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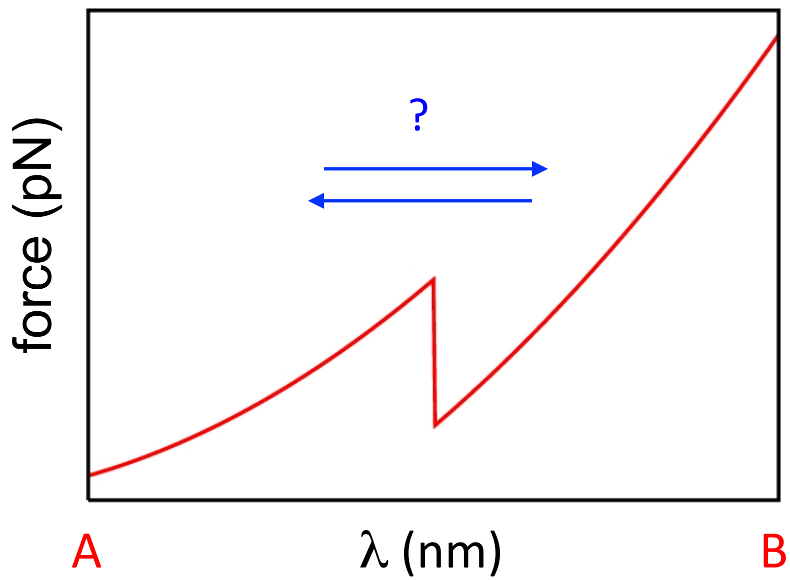

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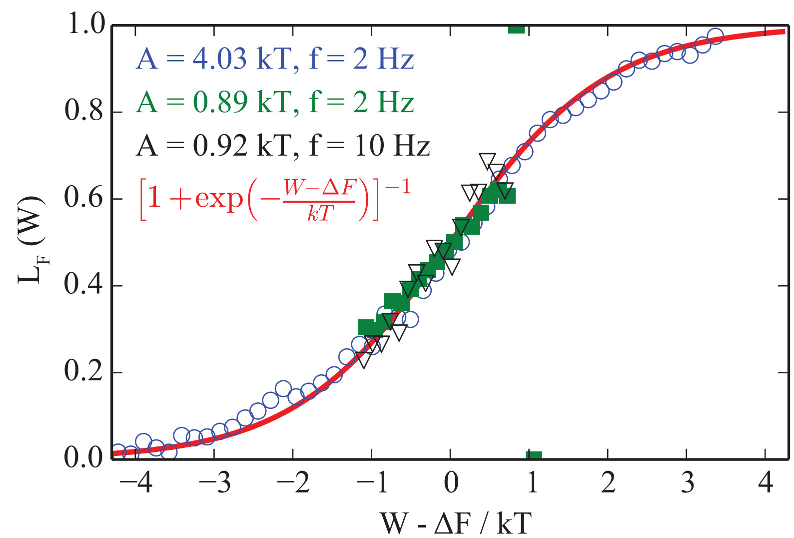
Hofmann *et al*, *Phys Status Solidi* **254**, 1600546 (2017)



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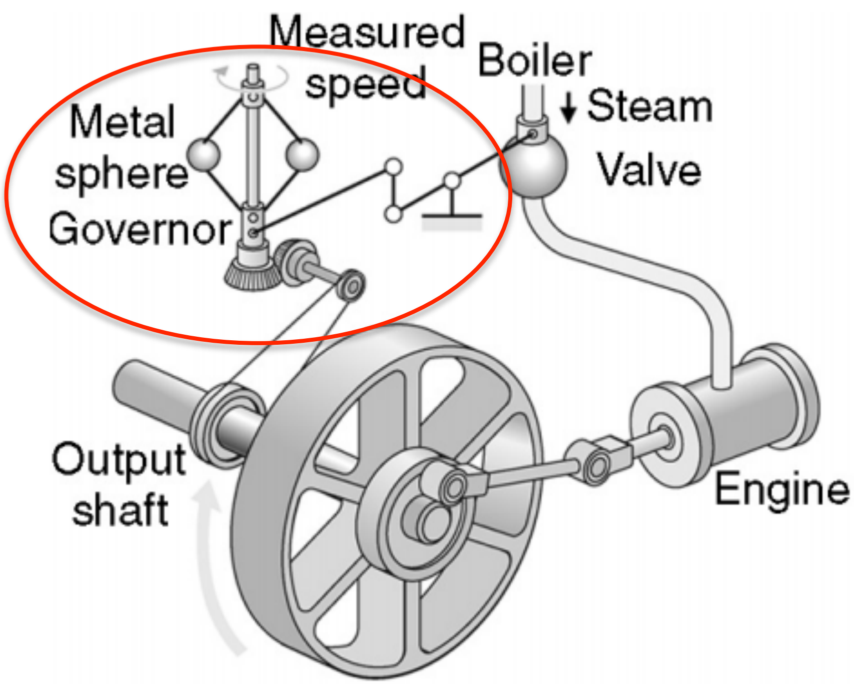
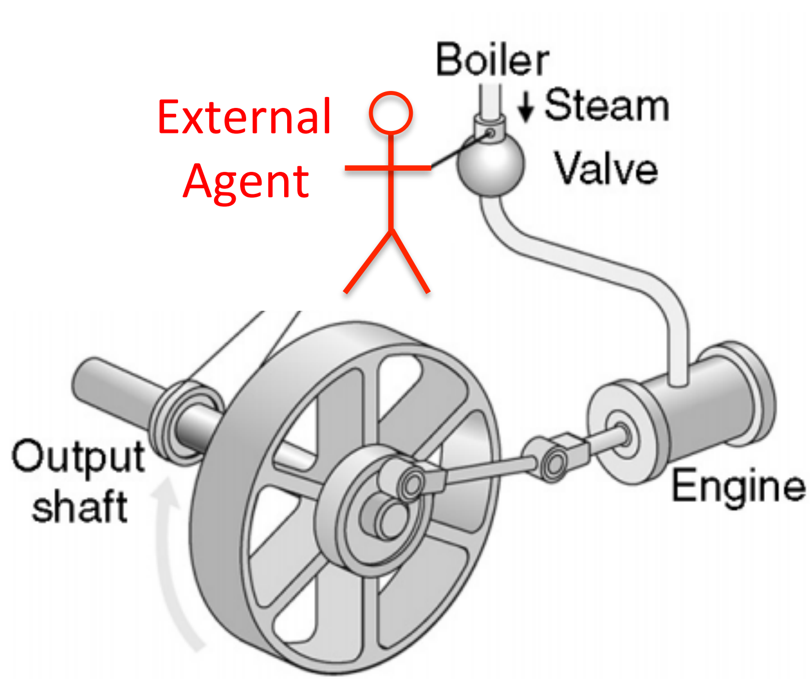
Shirts *et al*, *PRL* **91**, 140601 (2003) ,
Maragakis *et al*, *JCP* **129**, 024102 (2008)

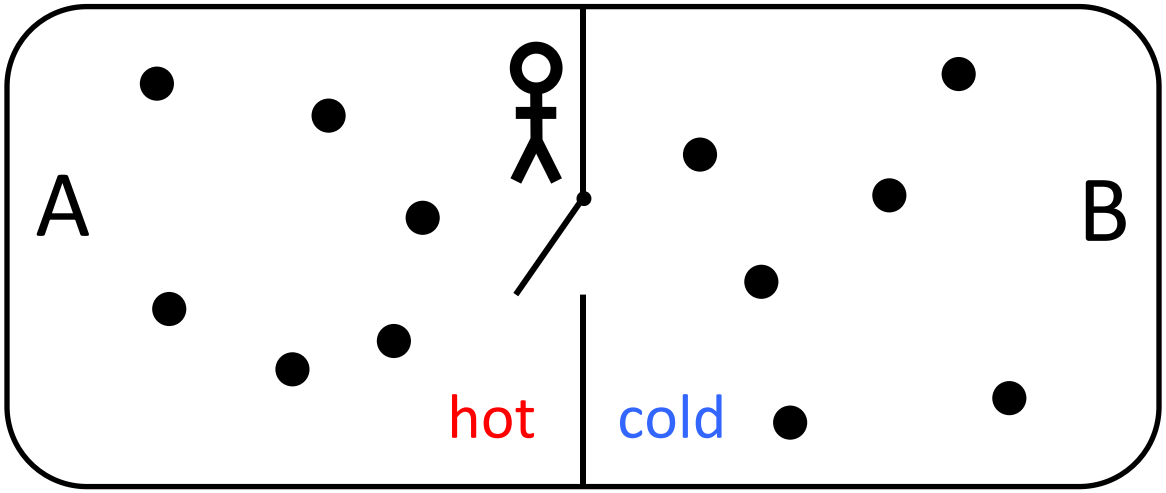
Feedback control

autonomous | *non-autonomous*





Maxwell's demon

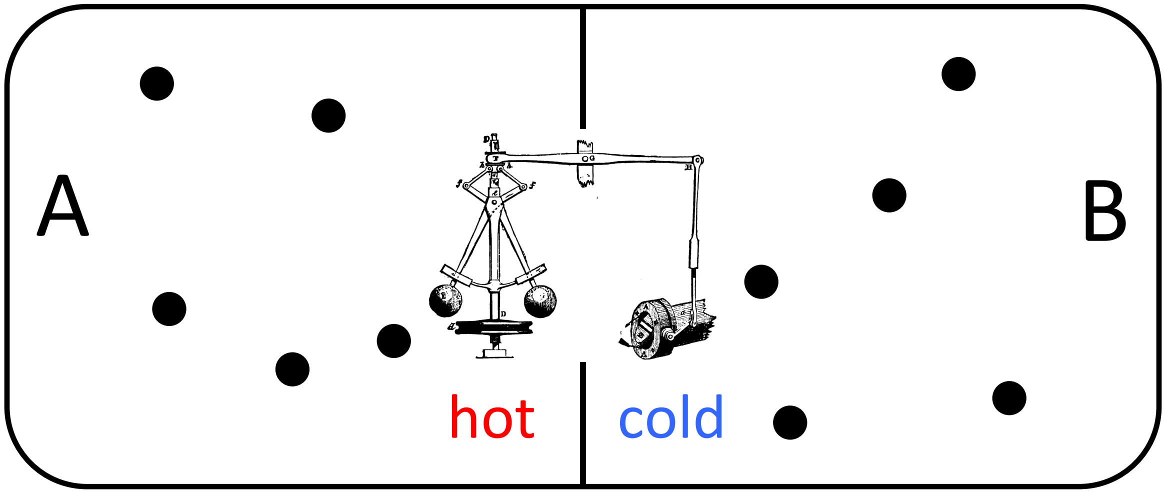


"… the energy in A is increased and that in B diminished; that is, the hot system has got hotter and the cold colder and yet no work has been done, only <u>the intelligence</u> of a very observant and neat-fingered being has been employed"

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

non-autonomous feedback control

Maxwell's demon



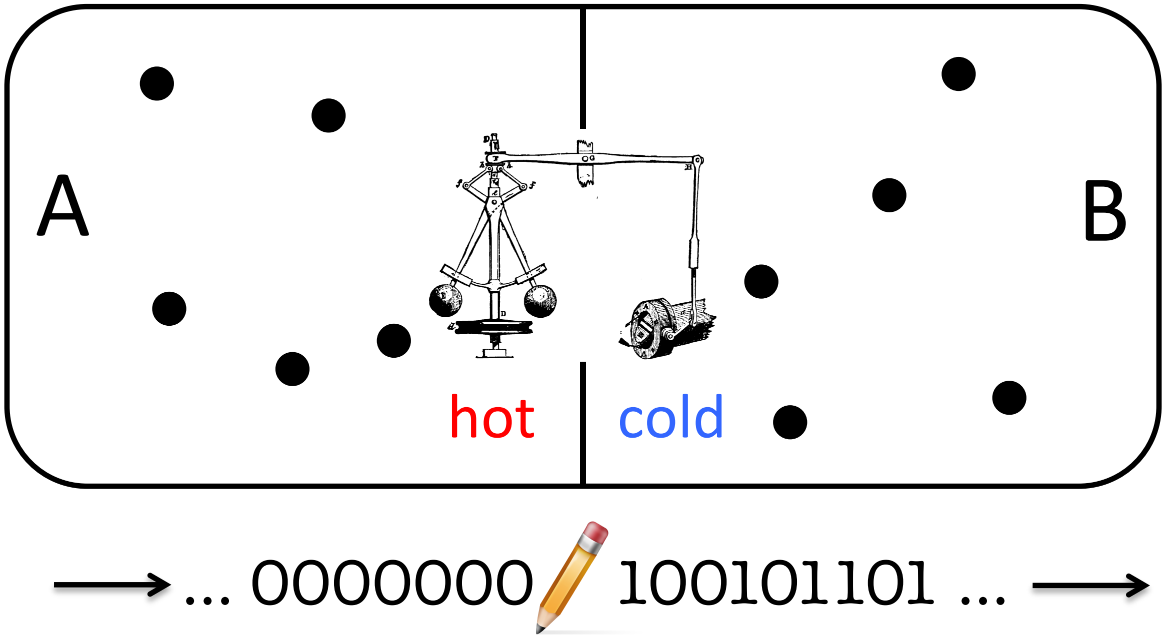
Is a "mechanical" Maxwell demon possible?

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

no!

autonomous feedback control

Maxwell’s demon



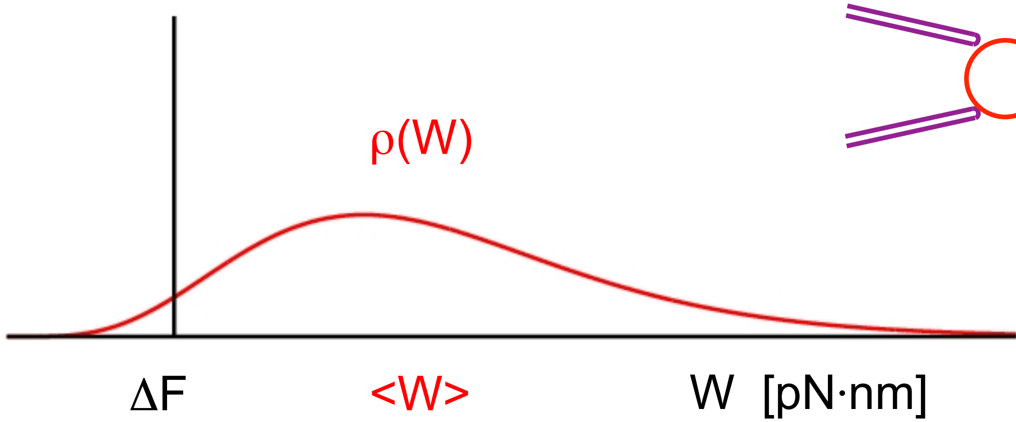
Is a “mechanical” Maxwell demon possible?

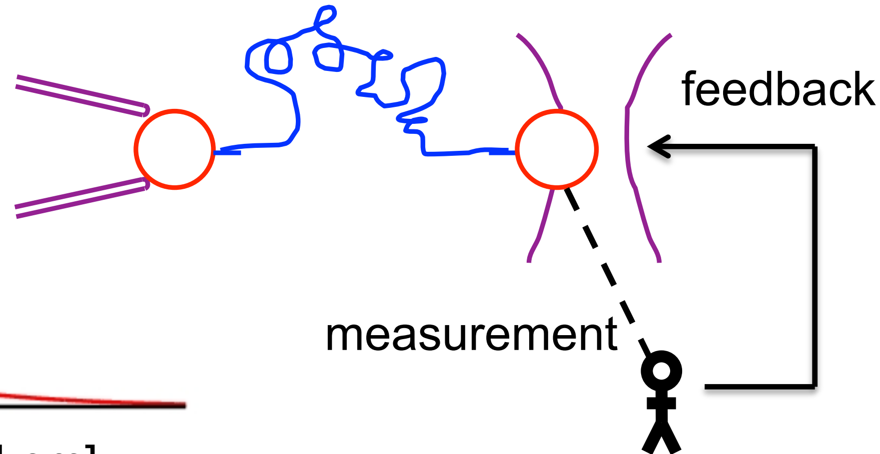
R. Landauer, *IBM J Res Dev* **5**, 183 (1961)
O. Penrose, *Foundations of Statistical Mechanics* (1970) ***yes, but …***
C.H. Bennett, *Int J Theor Physics* **21**, 905 (1982)

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)

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

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

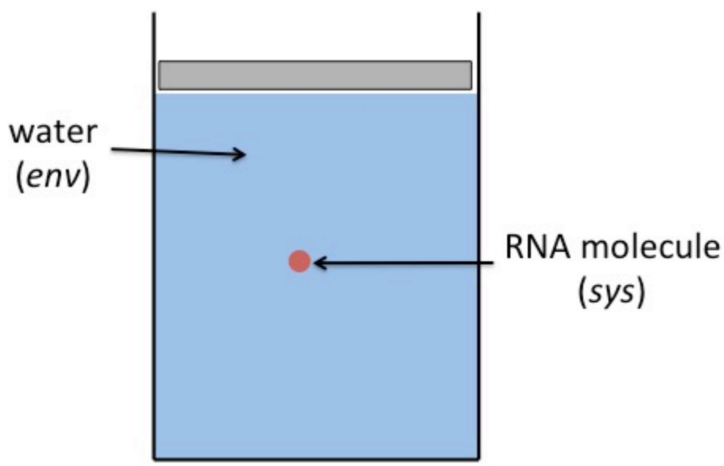
experiment:

Toyabe *et al, Nature Phys* ***6***, 988 (2010)

Strong system-environment coupling

$$W \geq \Delta F \qquad \left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \qquad \frac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta(W - \Delta F)\right]$$

- ΔF (Helmholtz) or ΔG (Gibbs) ? macro: G = F + PV
- How to define the volume of a single molecule ?
- How to define heat ? first law: ΔU = W - PΔV + Q



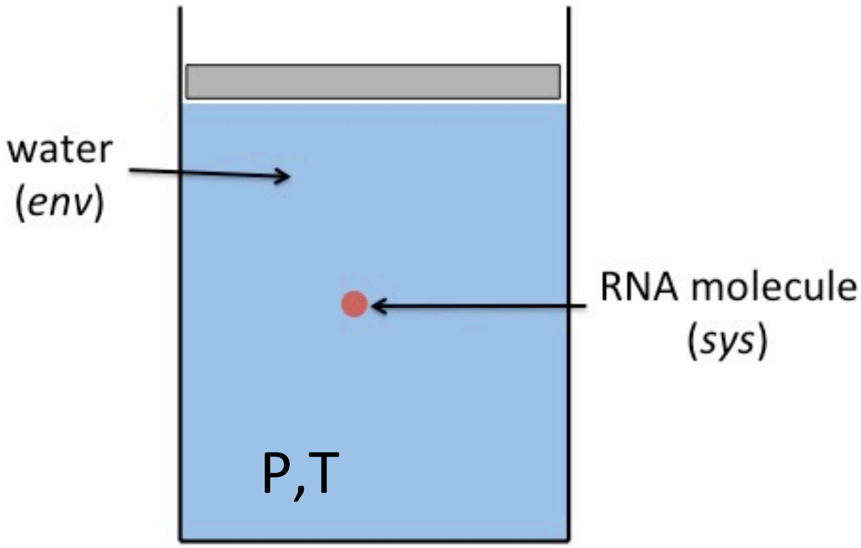
Total energy of *sys* + *env*:

$$U_{S+E} = U_{sys} + U_{env} + U_{\mathrm{int}}$$

non-negligible!

Strong system-environment coupling

C.J., *PRX* **7**, 011008 (2017)

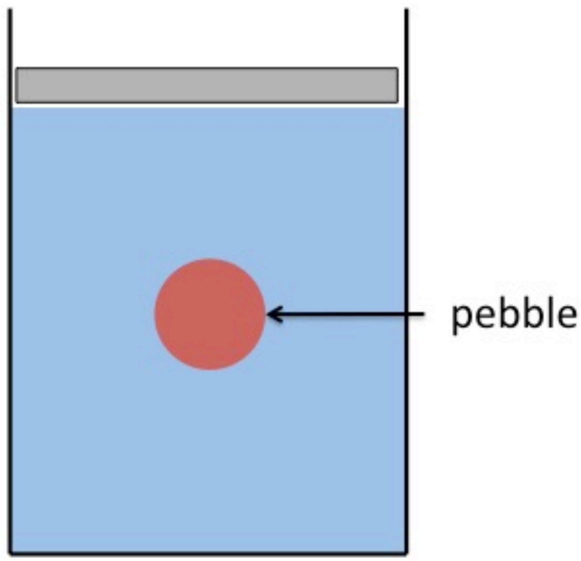


$$U_{S+E} = U_{sys} + U_{env} + U_{\text{int}}$$

$$p^{eq}(sys) = \frac{1}{Z}\exp\left[-\beta\left(U_{sys} + \phi\right)\right]$$

$\phi(q\,;P,T)$ = solvation potential of mean force

q ← microscopic configuration of molecule



$\phi(q\,;P,T)$ = reversible work required to insert pebble into water

$= P \times V_{\text{pebble}}$

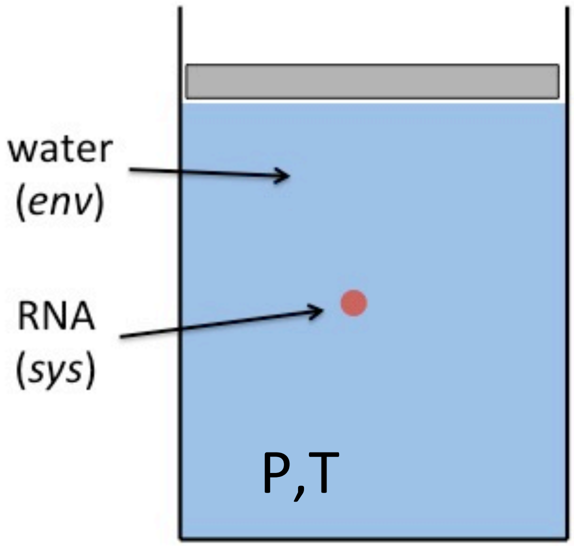
$$V_{pebble} = \phi / P$$

"thermodynamic volume"

Strong system-environment coupling

C.J., *PRX* **7**, 011008 (2017)

Seifert, *PRL* **116**, 020601 (2016)
Strasberg & Esposito, *PRE* **95**, 062101 (2017)



define volume of system: $v(q\,;P,T) \equiv \phi / P$

… leads to natural microscopic definitions of *internal energy, enthalpy, entropy, Helmholtz & Gibbs free energies, heat* and *work*

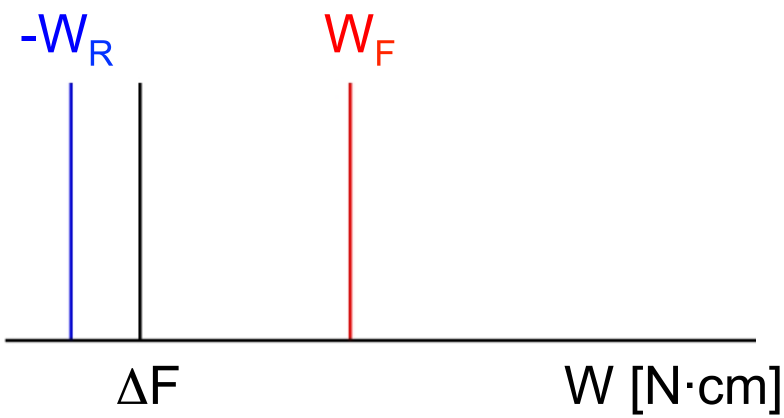
First law: $\Delta U_{sys} = Q + W - P\Delta v$

Second law: $\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta G}$, $\dfrac{\rho_F(+W)}{\rho_R(-W)} = \exp\left[\beta\left(W - \Delta G\right)\right]$

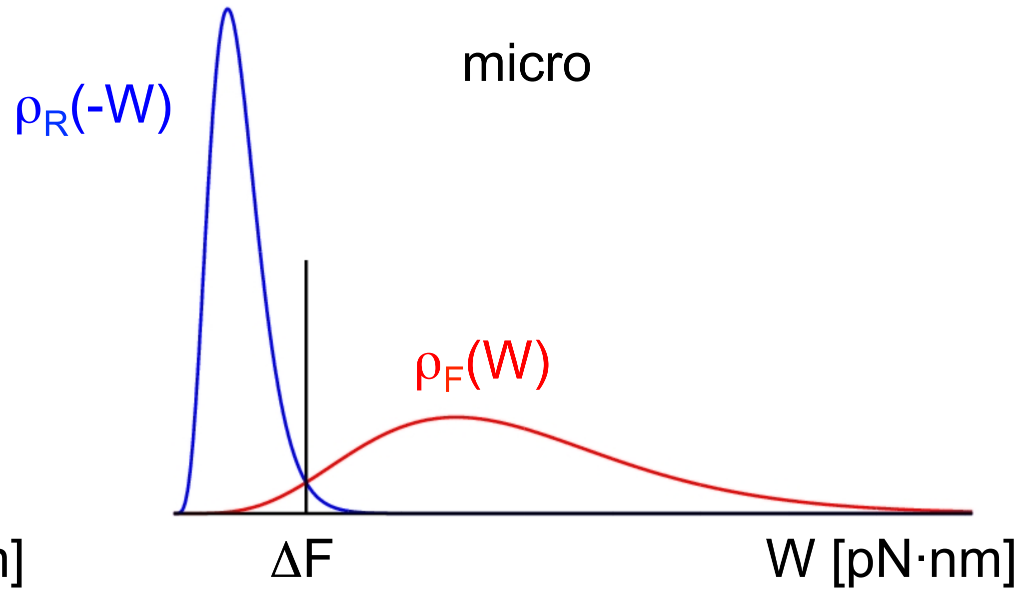
$$\langle W \rangle \geq \Delta G \quad , \quad \left\langle \int_A^B \frac{dQ}{T} \right\rangle \leq \Delta S$$

Summary

macro



micro



$$W \geq \Delta F$$

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

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

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

… & others !

C.J., Annu Rev Cond Matt Phys **2**, 329 (2011) (*classical*)
Campisi, Hänggi, & Talkner, Rev Mod Phys **83**, 771 (2011) (*quantum*)
Sagawa, Progress Theor Phys **127**, 1 (2012) (*information processing)*