Scaling down the laws of thermodynamics

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

Chris Jarzynski

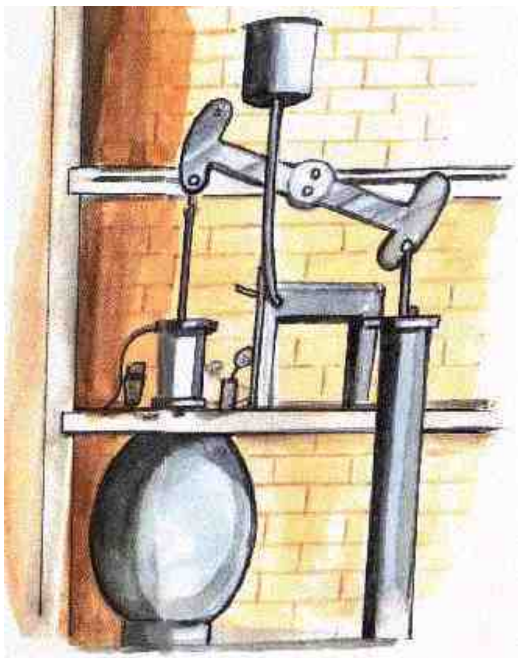
Institute for Physical Science and Technology

Department of Chemistry & Biochemistry

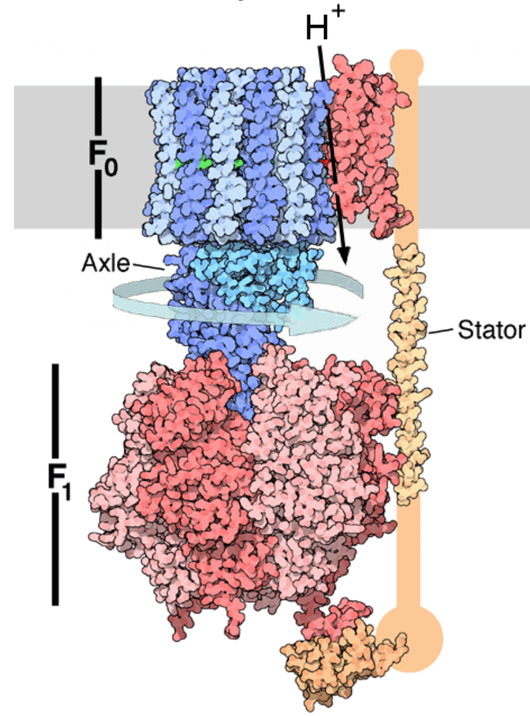
Department of Physics

Macroscopic and microscopic machines

steam engine



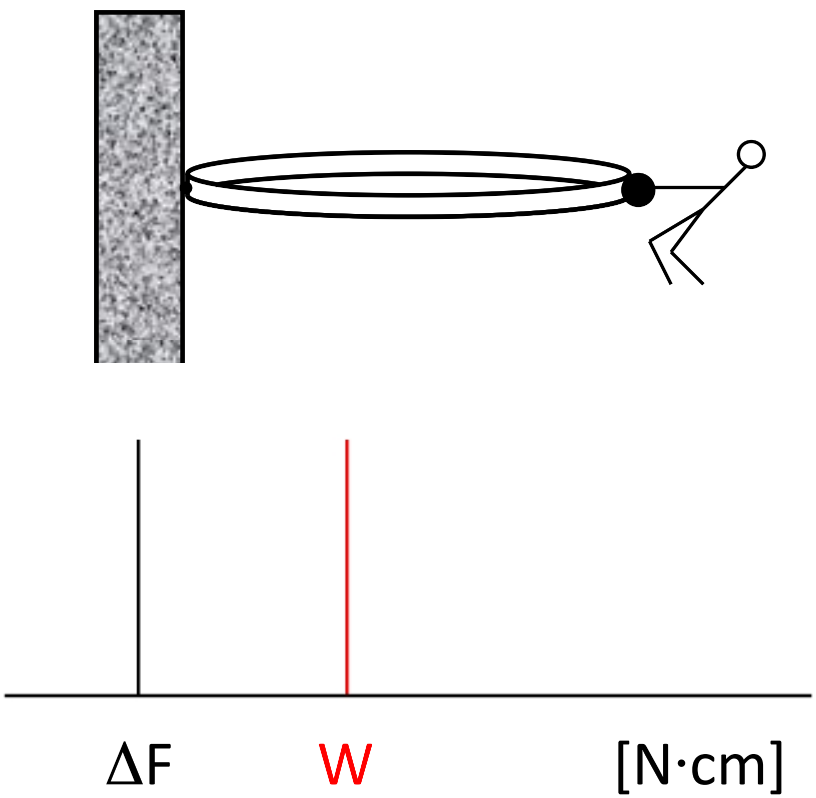
ATP synthase

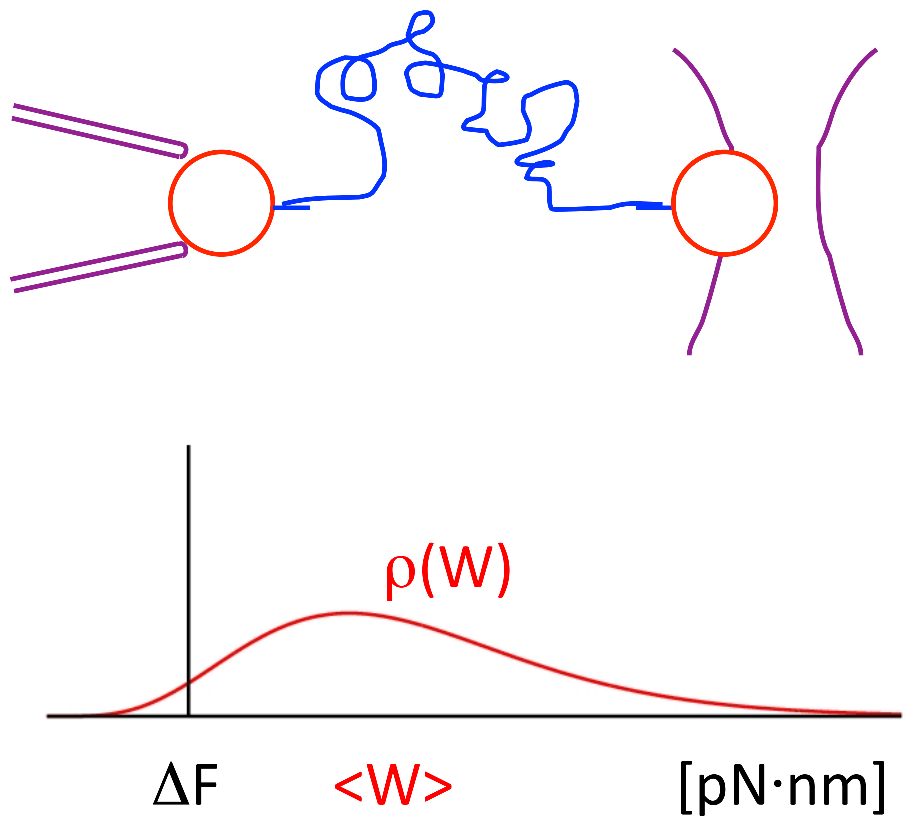


RCSB Protein Data Bank

New features of thermodynamics at the nanoscale

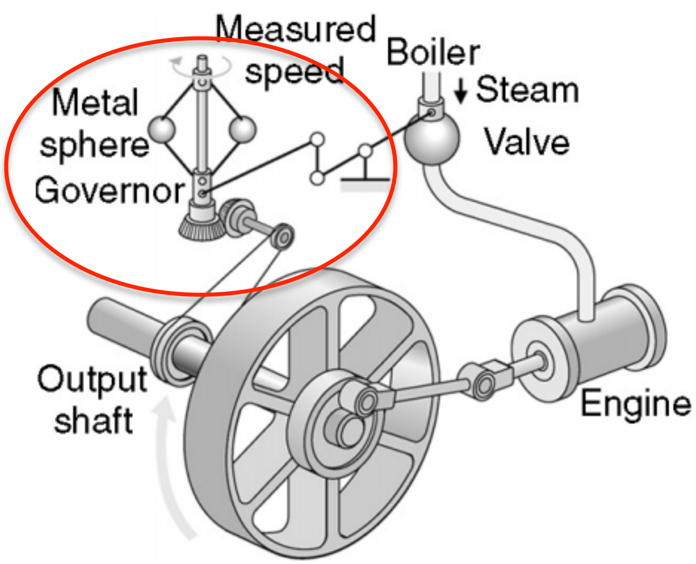
- **Prominence of fluctuations**



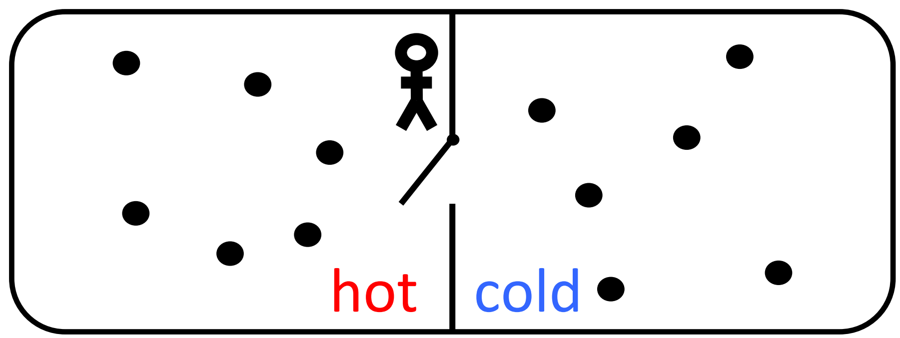


New features of thermodynamics at the nanoscale

- Prominence of fluctuations
- **Implications of feedback control**



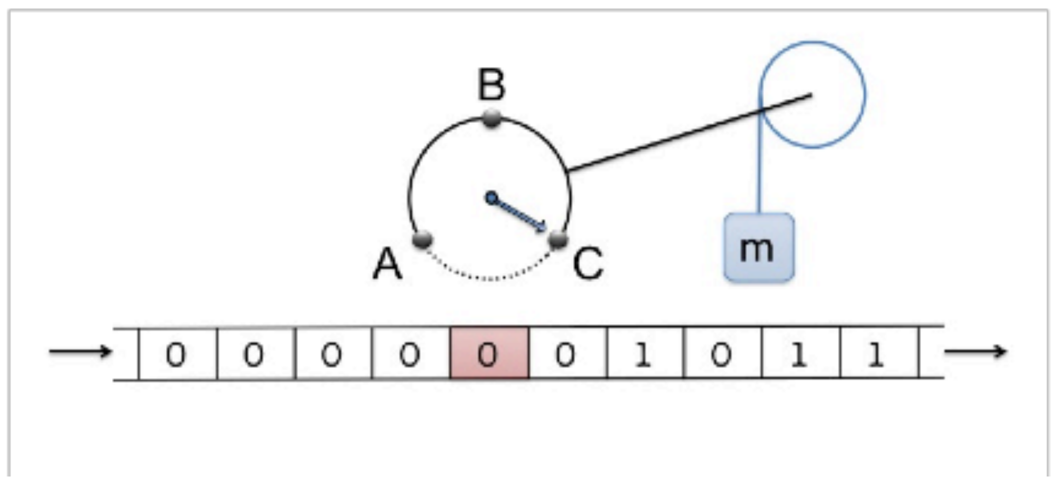
James Watt (1788)



James Maxwell (1867)

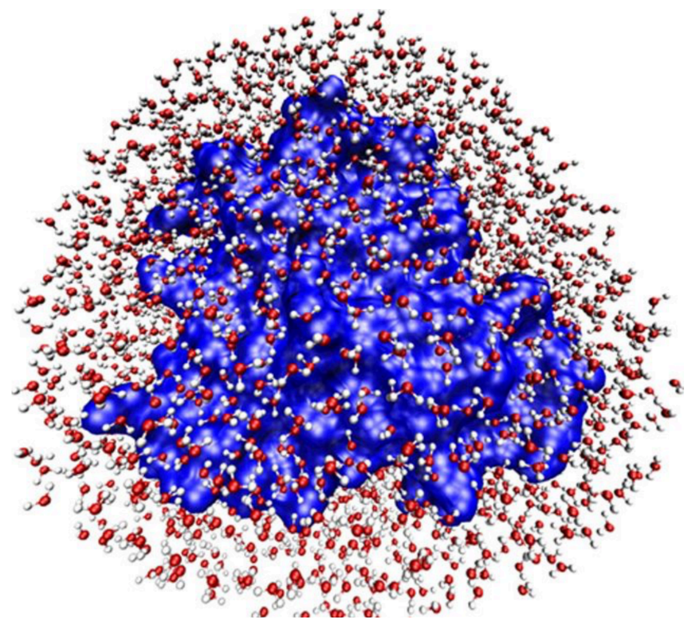
New features of thermodynamics at the nanoscale

- Prominence of fluctuations
- Implications of feedback control
- **Thermodynamics of information processing**

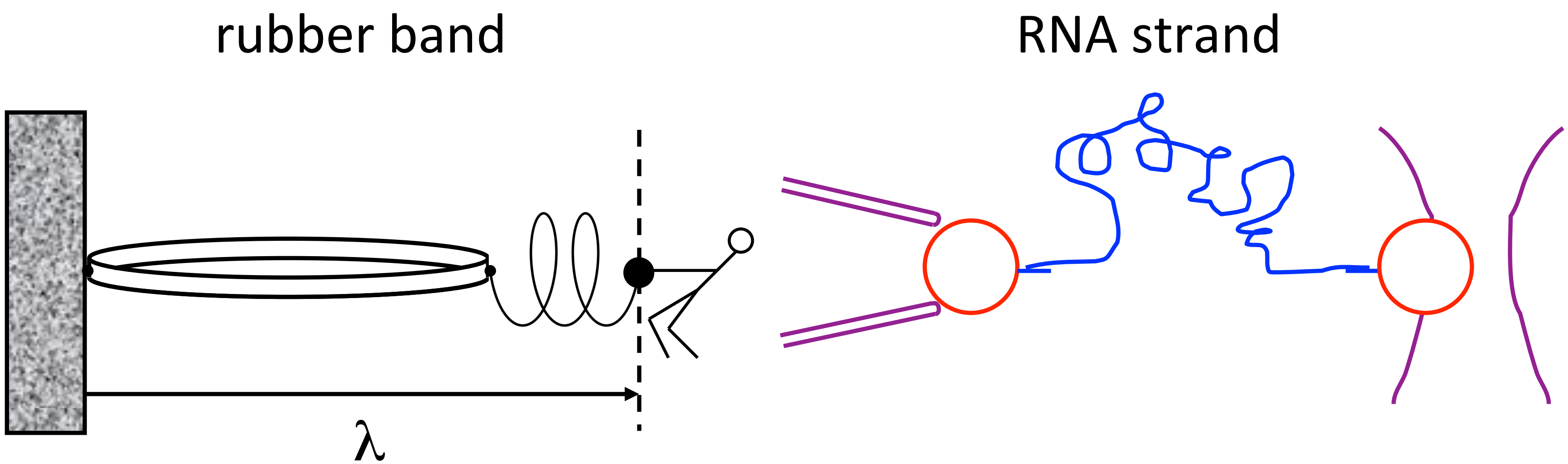


New features of thermodynamics at the nanoscale

- Prominence of fluctuations
- Implications of feedback control
- Thermodynamics of information processing
- **Strong system-environment coupling**



Macro- and *nano*scale thermodynamic processes

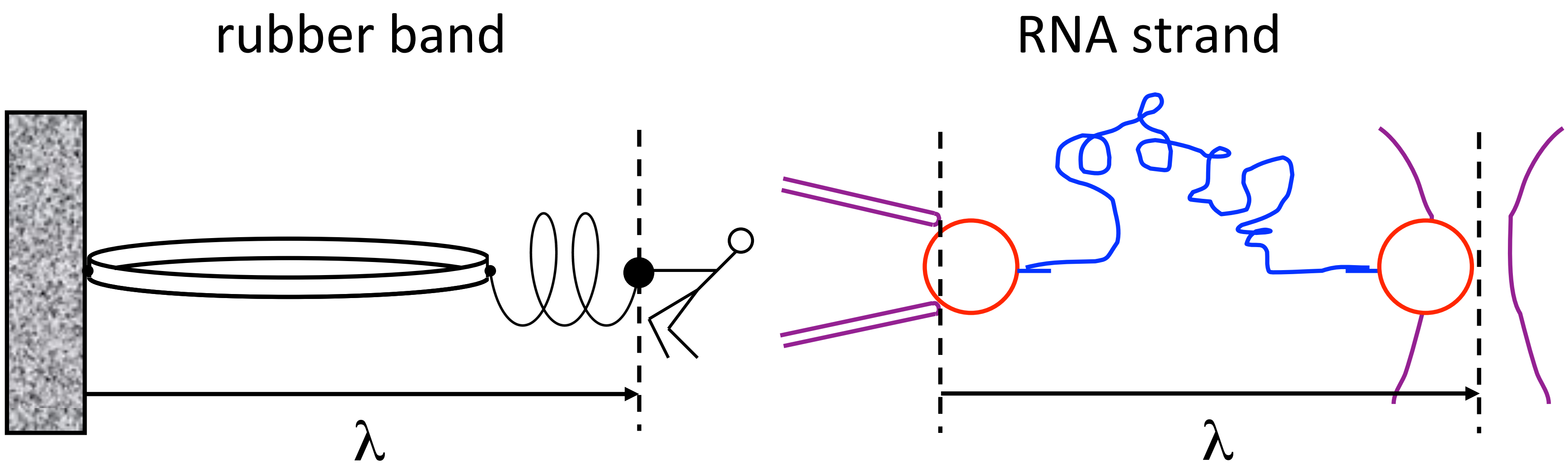


Irreversible process (rubber band):

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



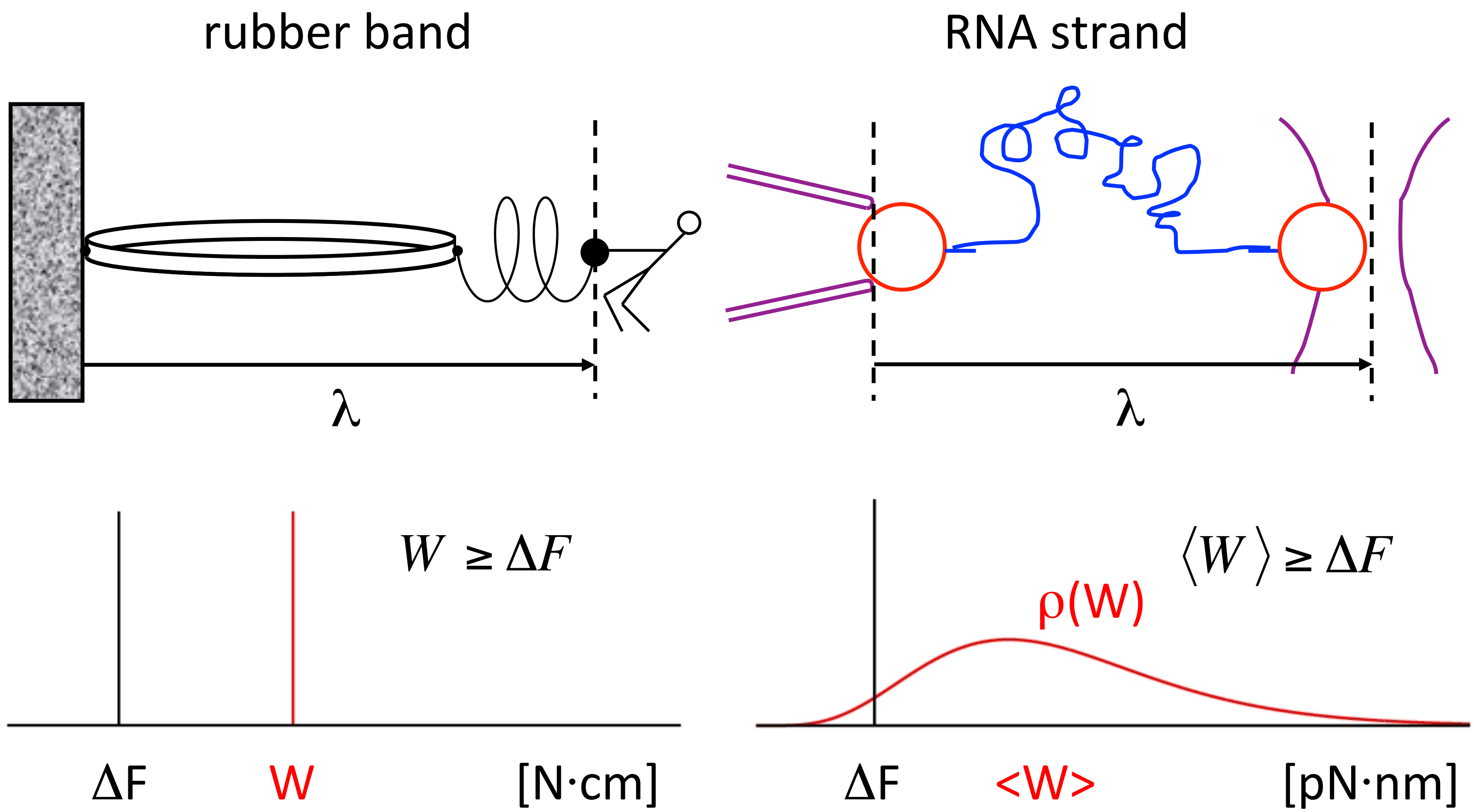
Irreversible process (RNA):

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

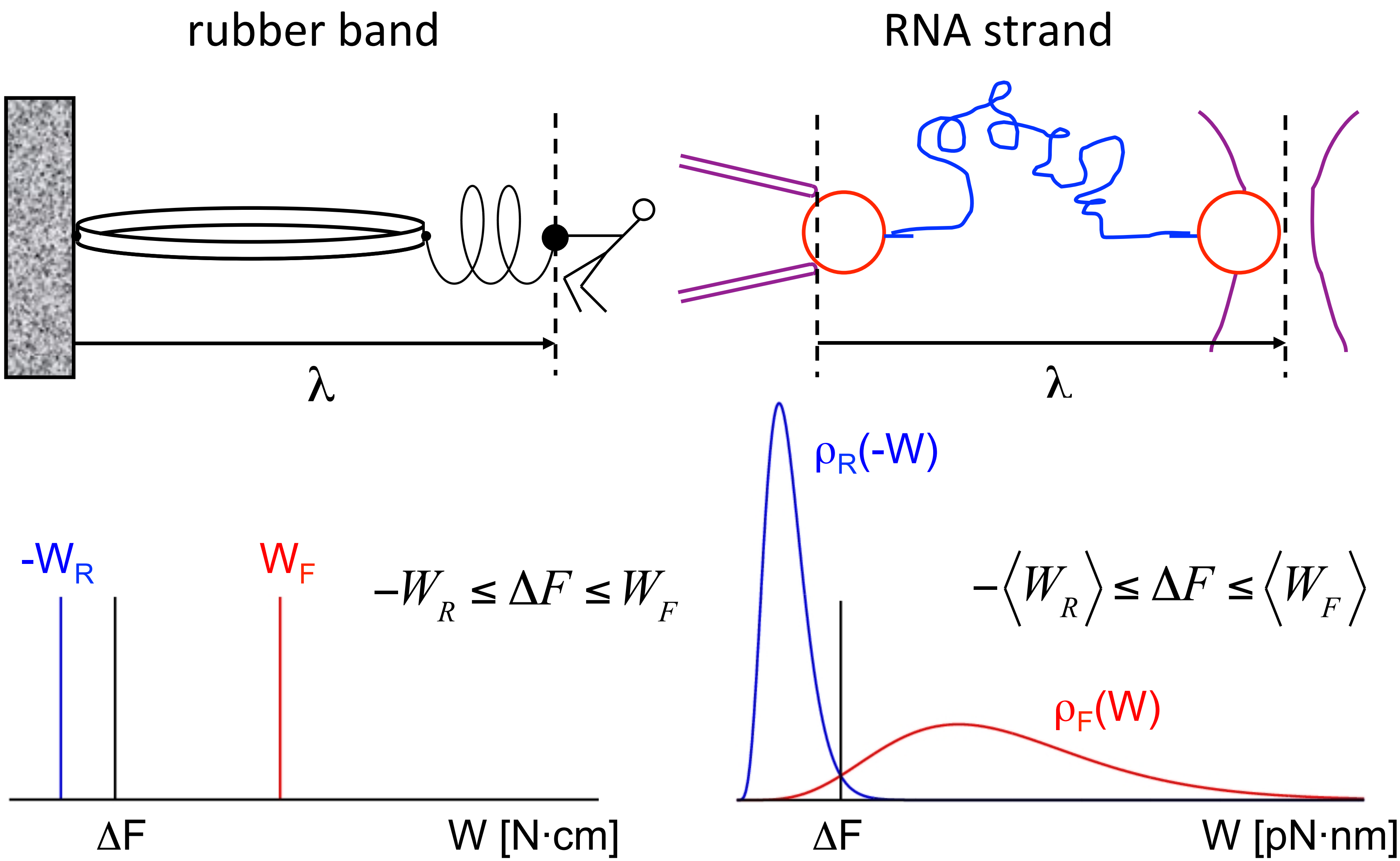
   $\langle W \rangle$ = *average* work $\geq \Delta F = F_B - F_A$

3. End in equilibrium $\lambda = B$

Macro- and *nano*scale thermodynamic processes



Macro- and *nano*scale thermodynamic processes



Fluctuations in W satisfy unexpected laws.

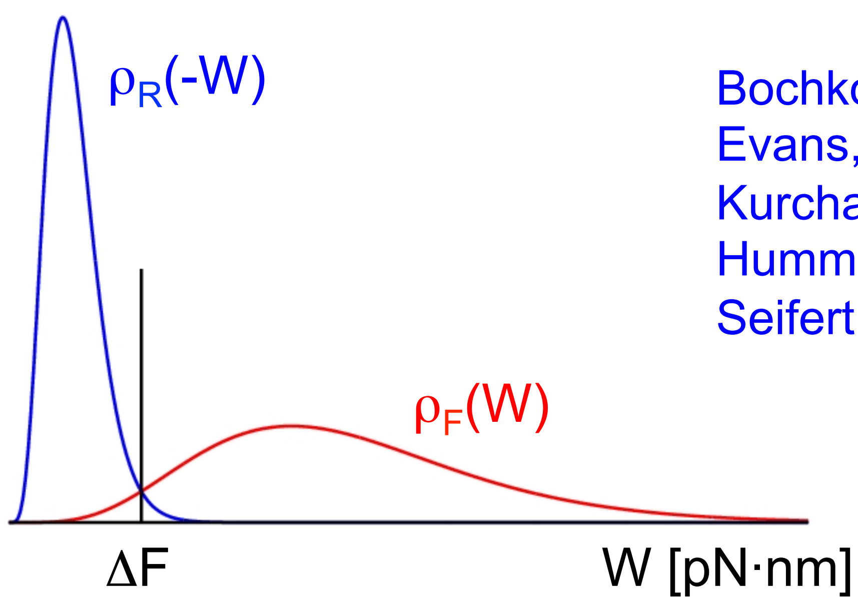
Fluctuation theorems / non-equilibrium work relations

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

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

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

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



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

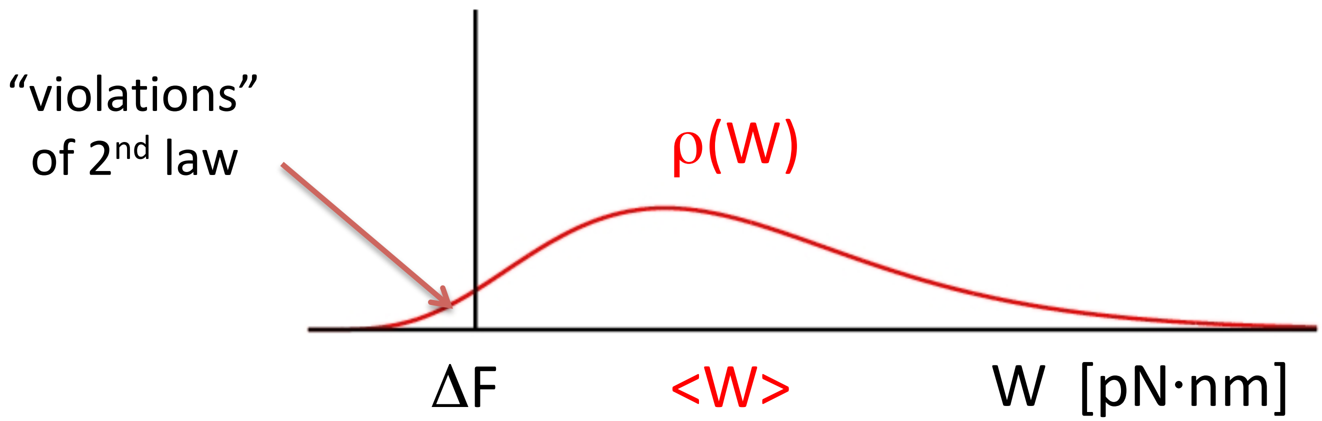
Irreversibility in microscopic systems

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

implies

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

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

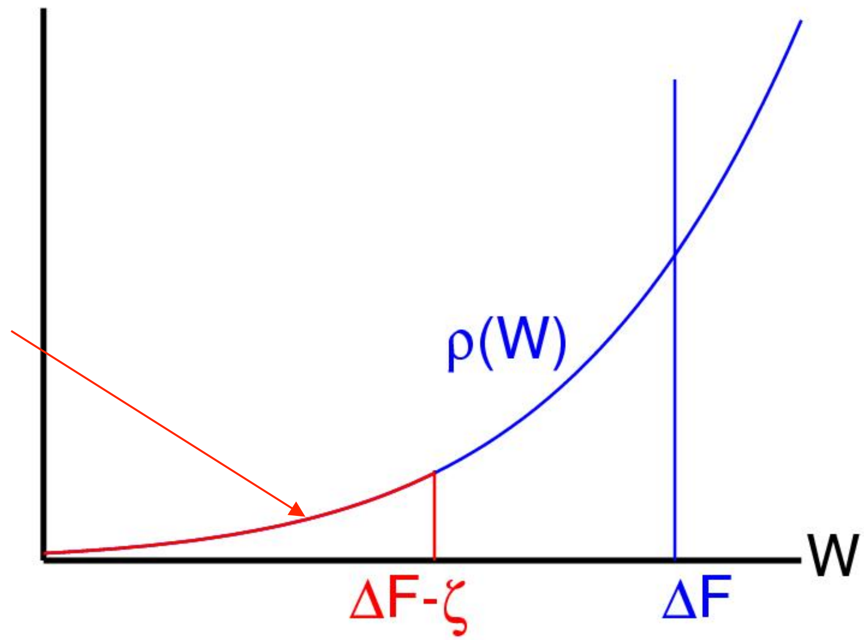


Irreversibility in microscopic systems

$$\left\langle e^{-\beta W} \right\rangle = e^{-\beta \Delta F} \quad \text{implies} \quad \begin{cases} \left\langle W \right\rangle \geq \Delta F \\ \Pr[W \leq \Delta F - \zeta] \leq \exp(-\zeta / k_B T) \end{cases}$$

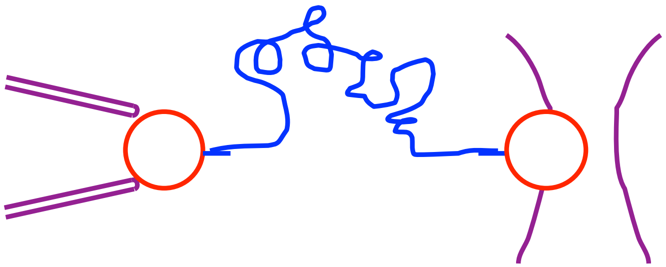
What is the probability that the 2nd law is "violated" by at least ζ ?

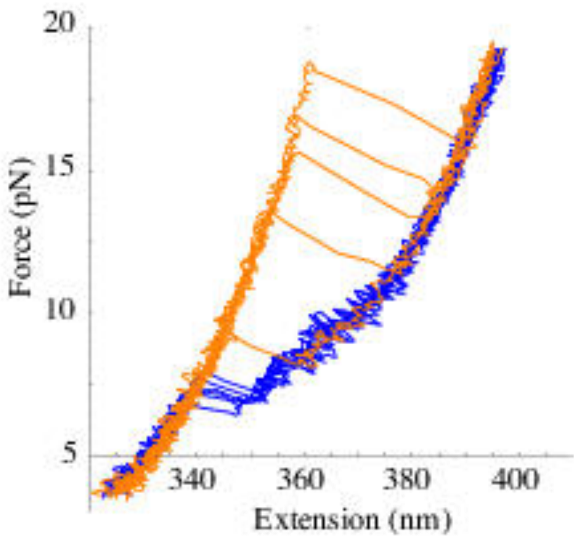
$$\Pr[W \leq \Delta F - \zeta]$$



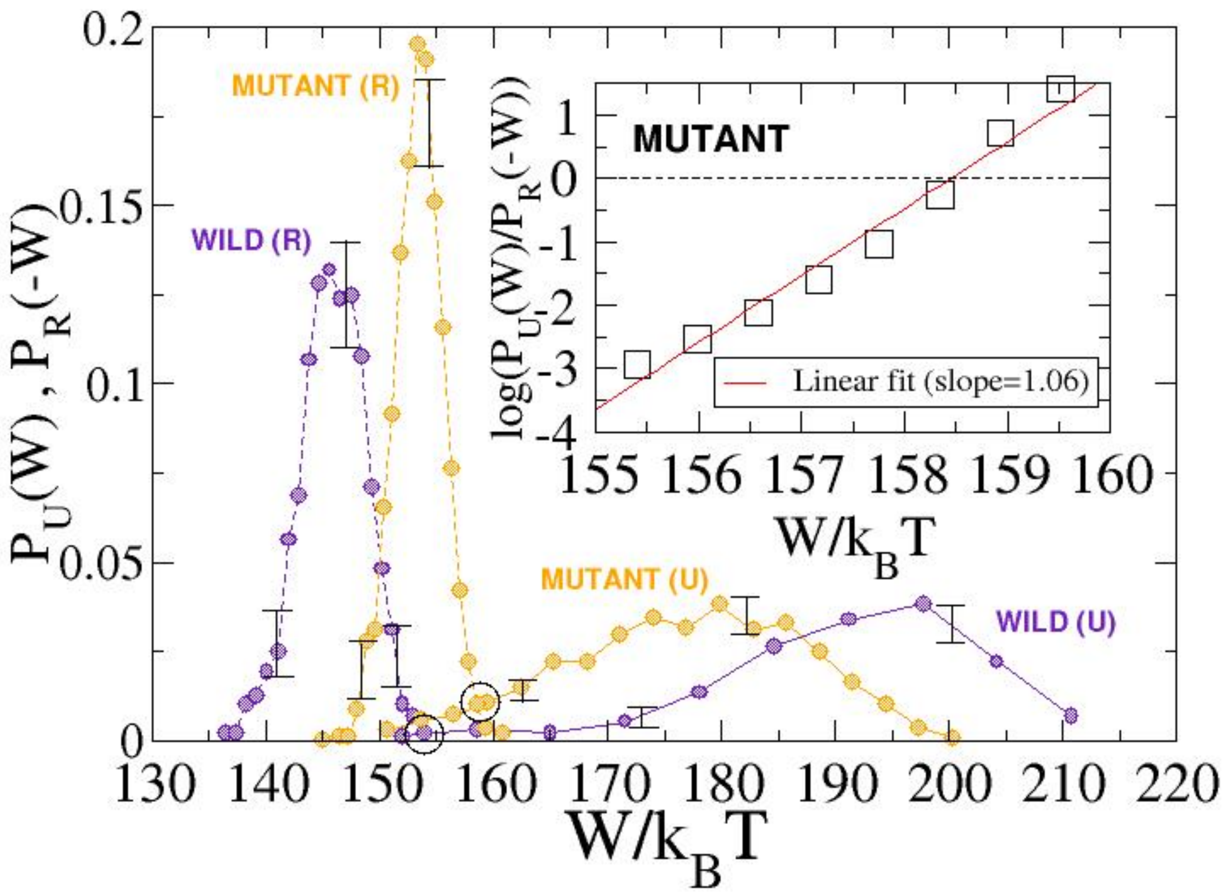
Unfolding & refolding of ribosomal RNA

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

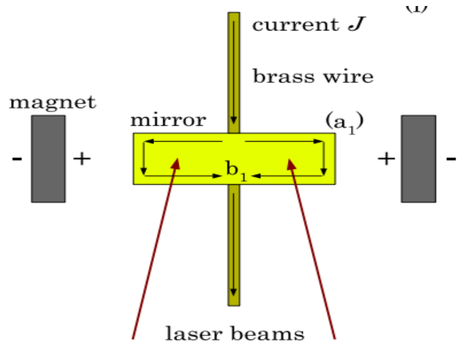




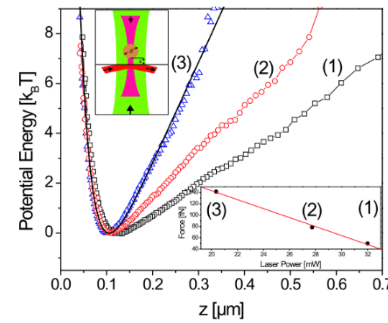
Collin *et al*, *Nature* **437**, 231 (2005)



Further experimental verification



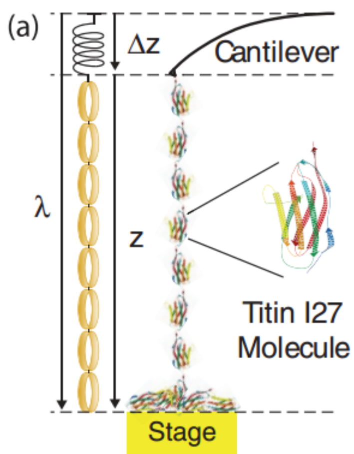
Mechanical oscillator
Douarche *et al, EPL* **70**, 593 (2005)



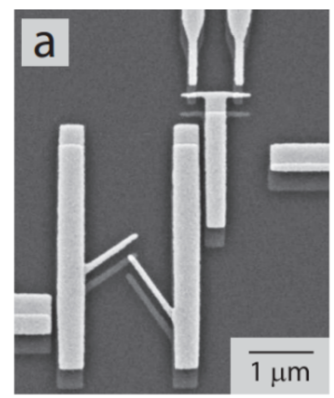
Trapped colloidal particle
Blickle *et al, PRL* **96**, 070603 (2006)

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

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



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

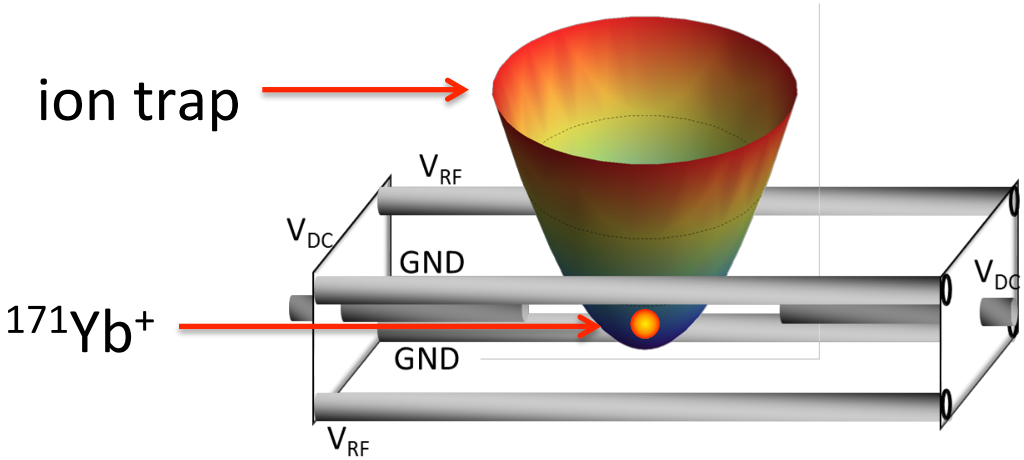


Single electron box
Saira *et al, PRL* **109**, 180601 (2012)

& others …

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

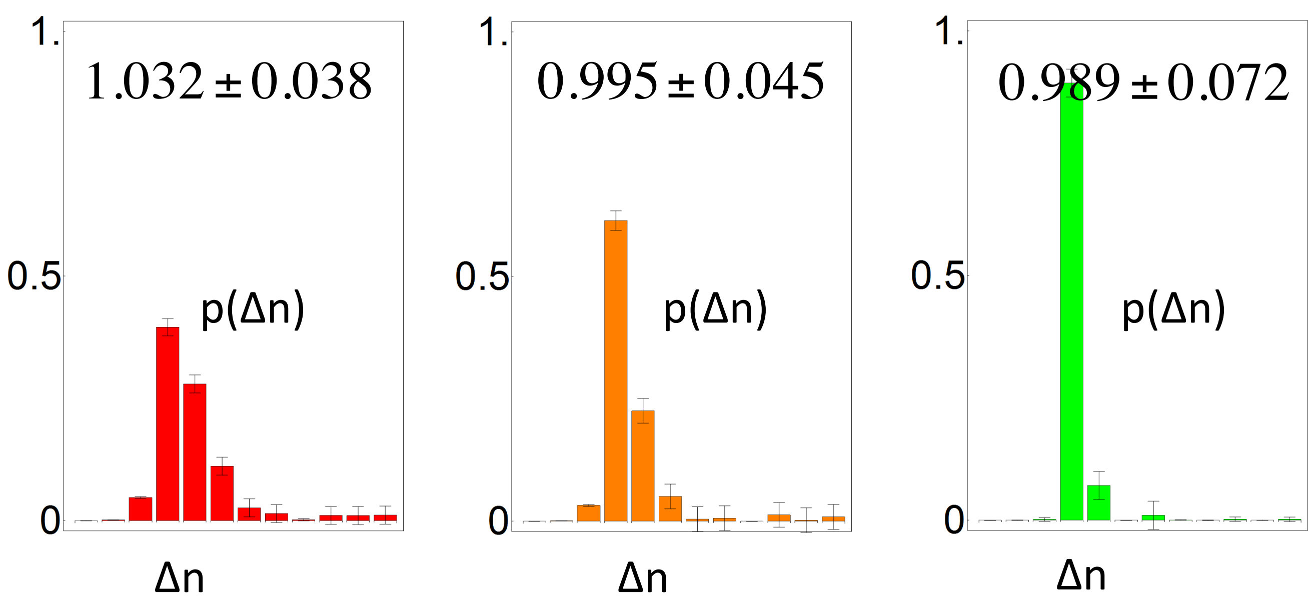
Mukamel, *PRL* **90**, 170604 (2003)
Kurchan, cond-mat/0007360 ; Tasaki, cond-mat/0009244



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

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

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



$$\Delta F = 0$$

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

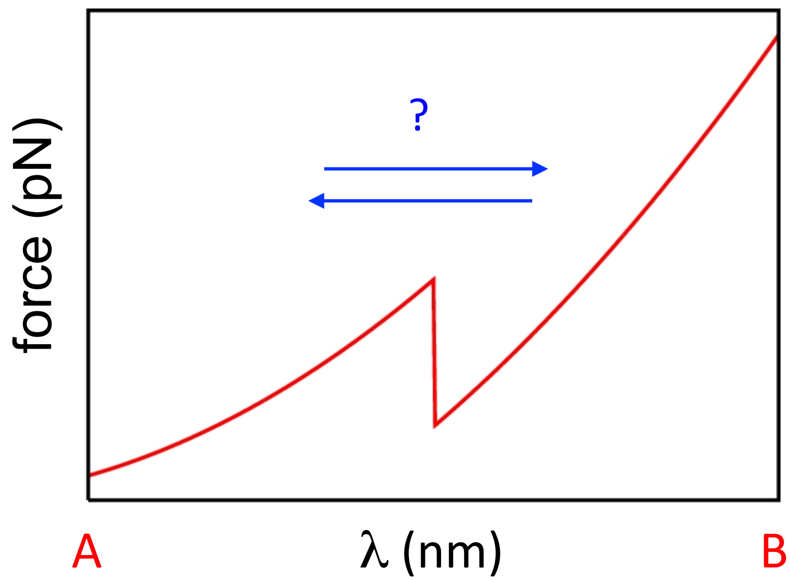
$$= 1$$

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.

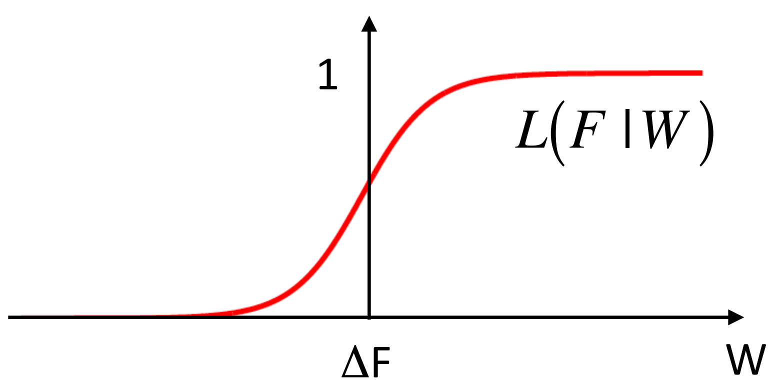
e.g.



Two hypotheses:

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

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



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

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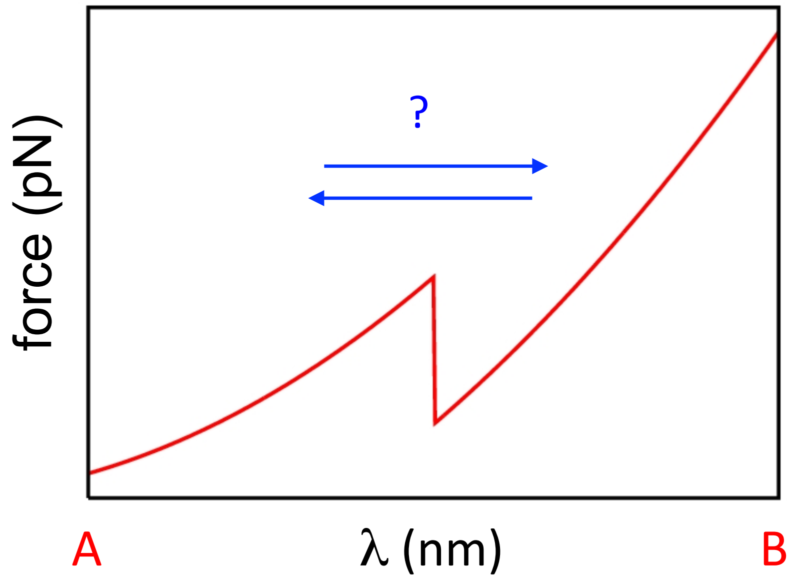

Two hypotheses:

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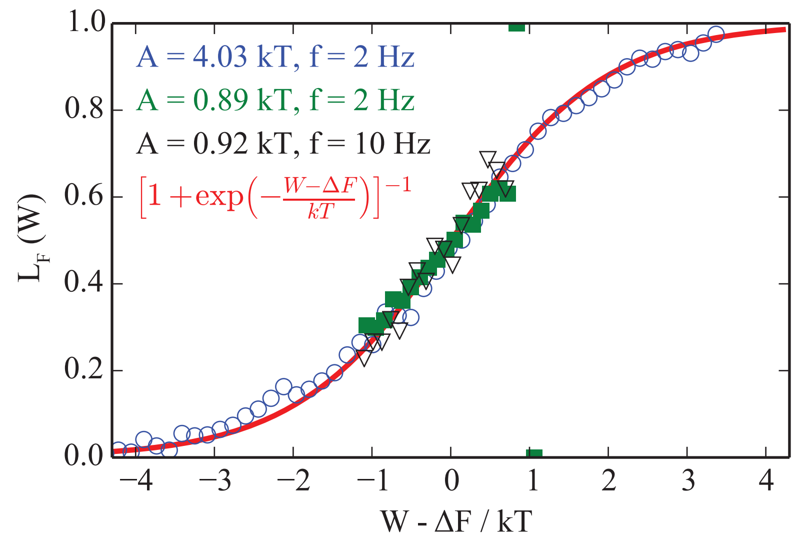
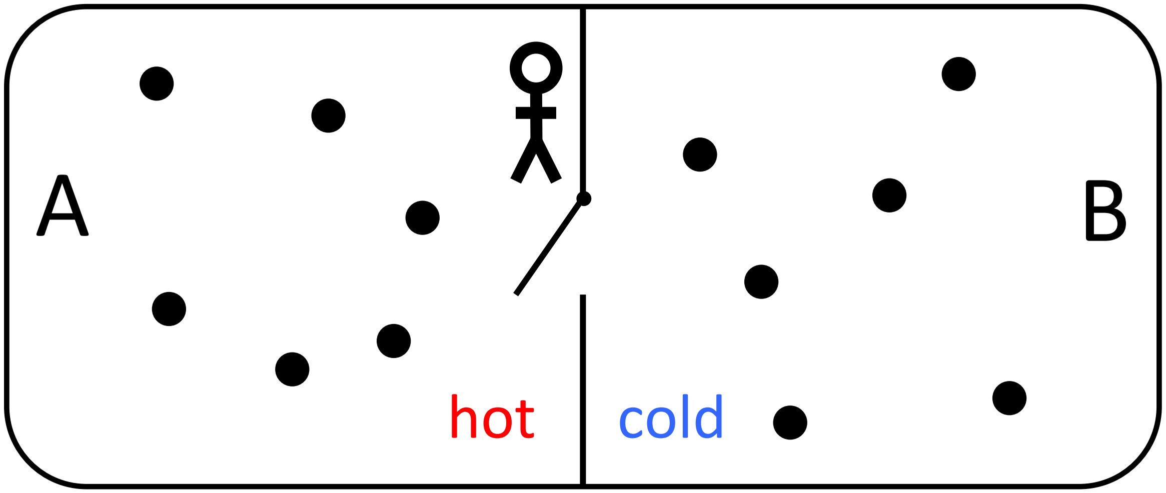
Hofmann *et al*, *Phys Status Solidi* **254**, 1600546 (2017)



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

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

Nanoscale feedback control: Maxwell's demon

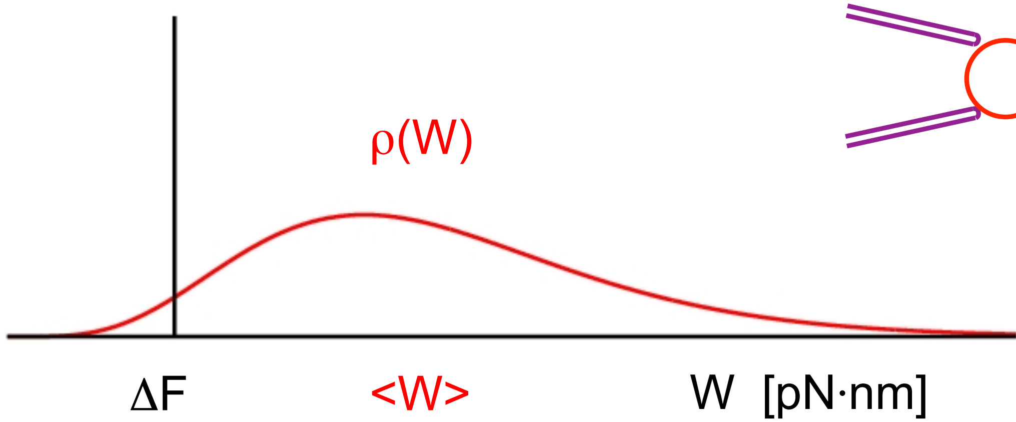


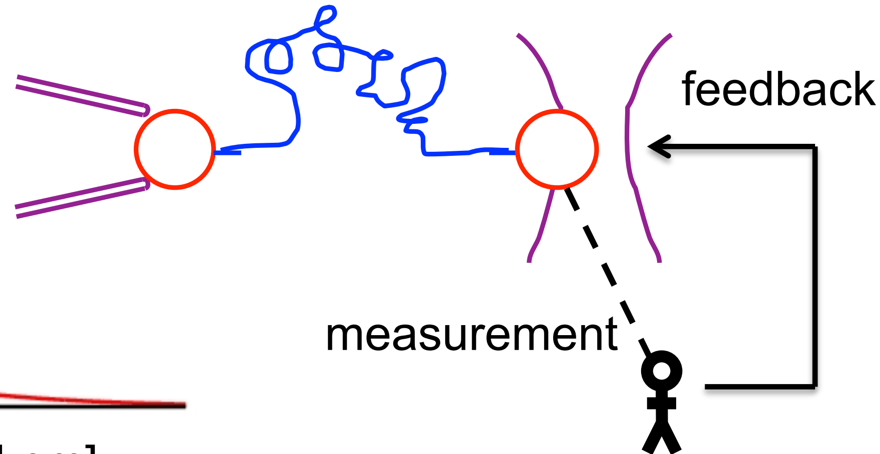
"… the energy in A is increased and that in B diminished; that is, the hot system has got hotter and the cold colder and yet no work has been done, only <u>the intelligence</u> of a very observant and neat-fingered being has been employed"

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

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)

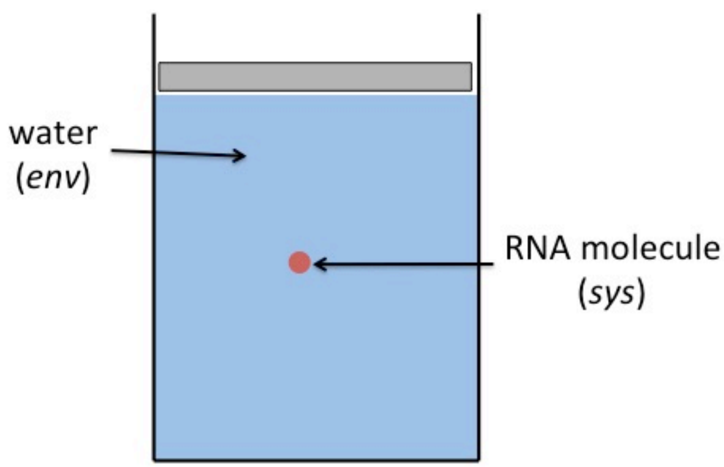
experiment:

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

Strong system-environment coupling

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

- 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



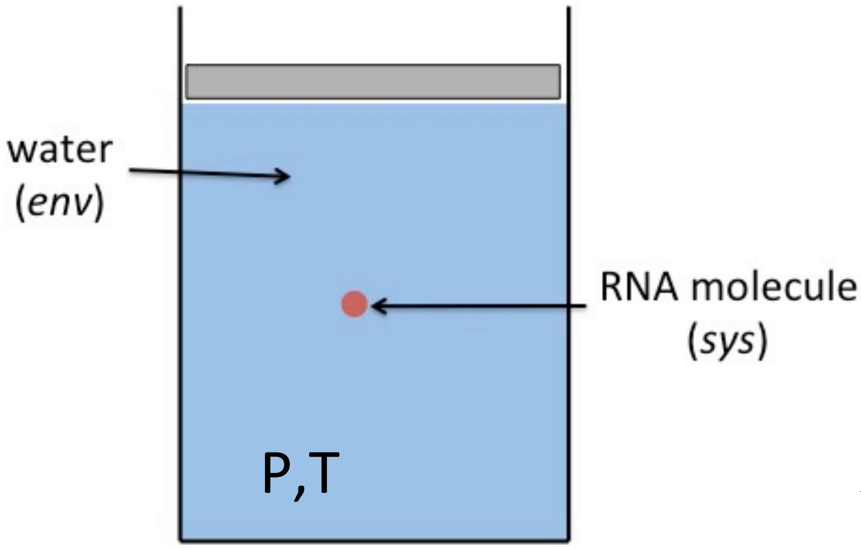
Total energy of *sys* + *env*:

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

non-negligible!

Strong system-environment coupling

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

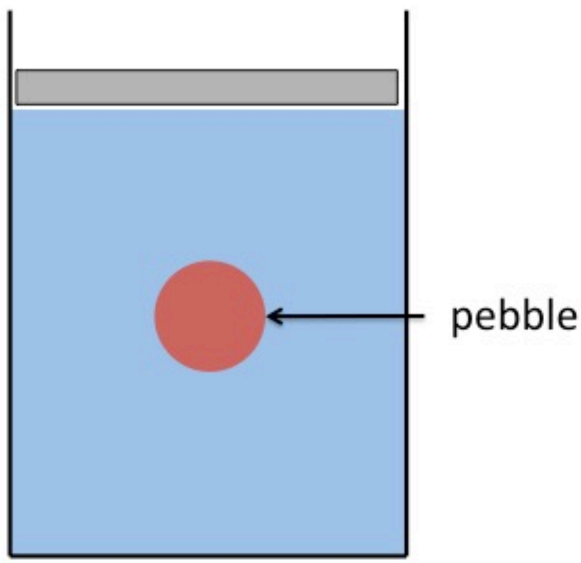


$$U_{S+E} = U_{sys} + U_{env} + U_{\text{int}}$$

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

microscopic configuration of molecule

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



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

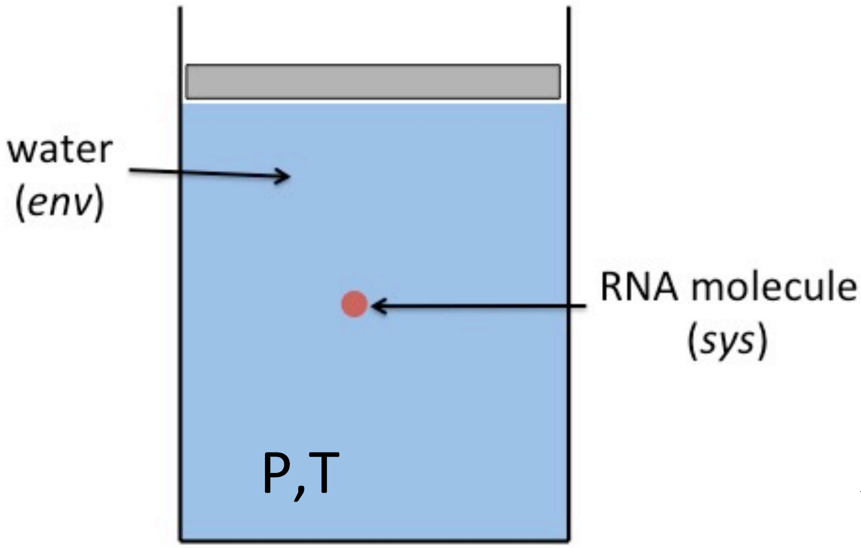
= $P \times V_{pebble}$

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

"thermodynamic volume"

Strong system-environment coupling

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



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

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

↑ microscopic configuration of molecule

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

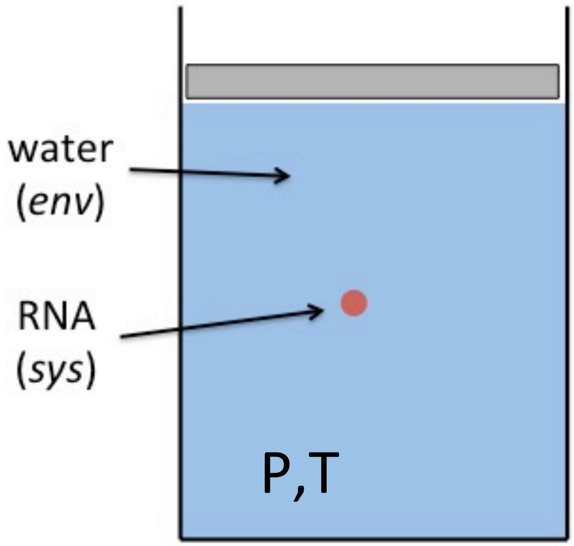
$$\rightarrow \frac{1}{Z}\exp\left[-\beta\left(U_{sys} + Pv\right)\right]$$

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

Strong system-environment coupling

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

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



$$v \equiv \phi / P$$

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

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