Evans-Searles FT
Crooks FT
Jarzynski equality

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Evans-Searles FT

Denis J Evans, Ezechiel DG Cohen, Gary P Morriss (1993)
Denis J Evans, Debra J Searles (1994)

$$\frac{P(\Omega = S)}{P(\Omega = -S)} = e^{S}$$

S is entropy change in k_B units.

Evans and Searles (2002) Advances in Physics, 51: 1529

Crooks FT

For a small driven system which is in contact with a thermostat:

$$\frac{P_F(A \to B, W)}{P_R(A \leftarrow B, -W)} = e^{\frac{W-\Delta G}{k_B T}}$$

W is the work done when the system is driven from the state A of the control parameter to B.

ΔG is the free enthalpy difference between the states A and B

G. E. Crooks, J. Stat. Phys. (1998) 90: 1481

Jarzynski equality

Relates the work done during non-equilibrium processes with the free enthalpy difference of the initial and end states.

$$\left\langle e^{\frac{-W}{k_B T}} \right\rangle = e^{\frac{-\Delta G}{k_B T}}$$

W is the work that is done when the system is moved from the equilibrium state defined by the control parameter A to the equilibrium state determined by the control parameter B.

The transformation is not required to occur through equilibrium states.

C. Jarzynski, Phys. Rev. Lett. (1997) 78: 2690

Experimental verification of the fluctuation theorems

General strategy:

small system for a short time, under the influence of small forces

energy / work must be measured with the accuracy of a fraction of $k_B \cdot T$

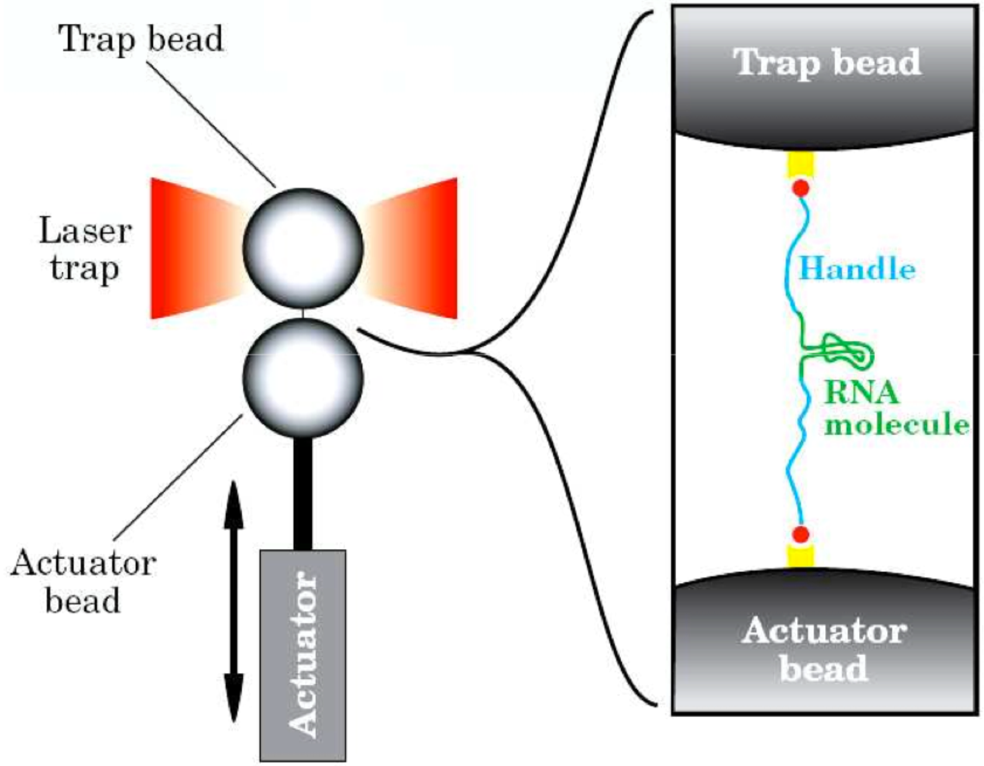
both equilibrium and non-equilibrium ranges should be accessible in the experiments

the experiment must be repeated many times

Verification of the Crooks FT

$$\frac{P(A \rightarrow B, W)}{P(A \leftarrow B, -W)} = e^{\frac{W-\Delta G}{k_B T}}$$

$$W = \sum F_i \cdot \Delta x_i$$



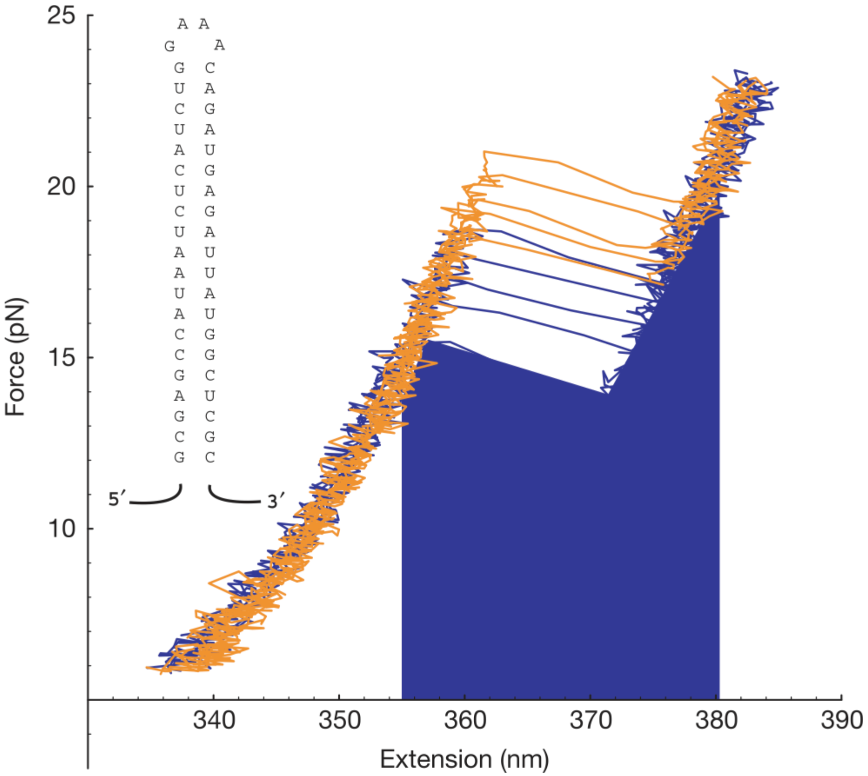
force-guided unfolding of viral RNA using laser tweezers

Collin D et al. (2005) Nature 437: 231

Verification of the Crooks FT

$$W = \sum F_i \cdot \Delta x_i$$

The work done is the integral of the force-elongation curve.



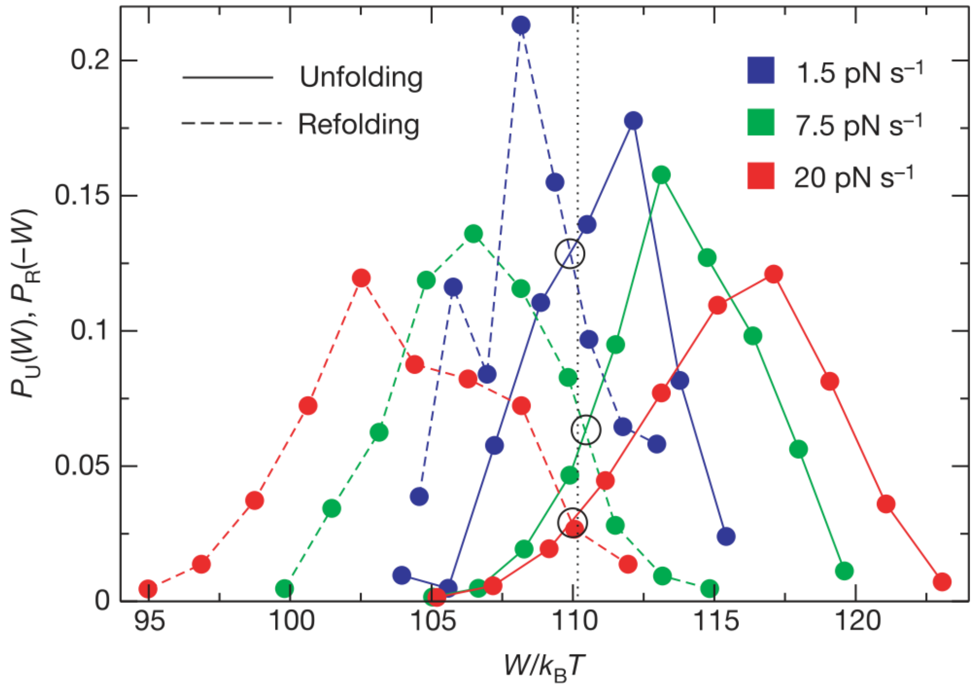
Collin D et al. (2005) Nature 437: 231

Verification of the Crooks FT

Force-controlled unfolding of an RNA hairpin molecule using laser tweezers at different pulling speeds

$$\Delta G = 110.3 \pm 0.5\ k_B T$$

$$\frac{\mathrm{P}(A \rightarrow B, W)}{\mathrm{P}(A \leftarrow B, -W)} = e^{\frac{W-\Delta G}{k_B T}}$$



Collin D et al. (2005) Nature 437: 231

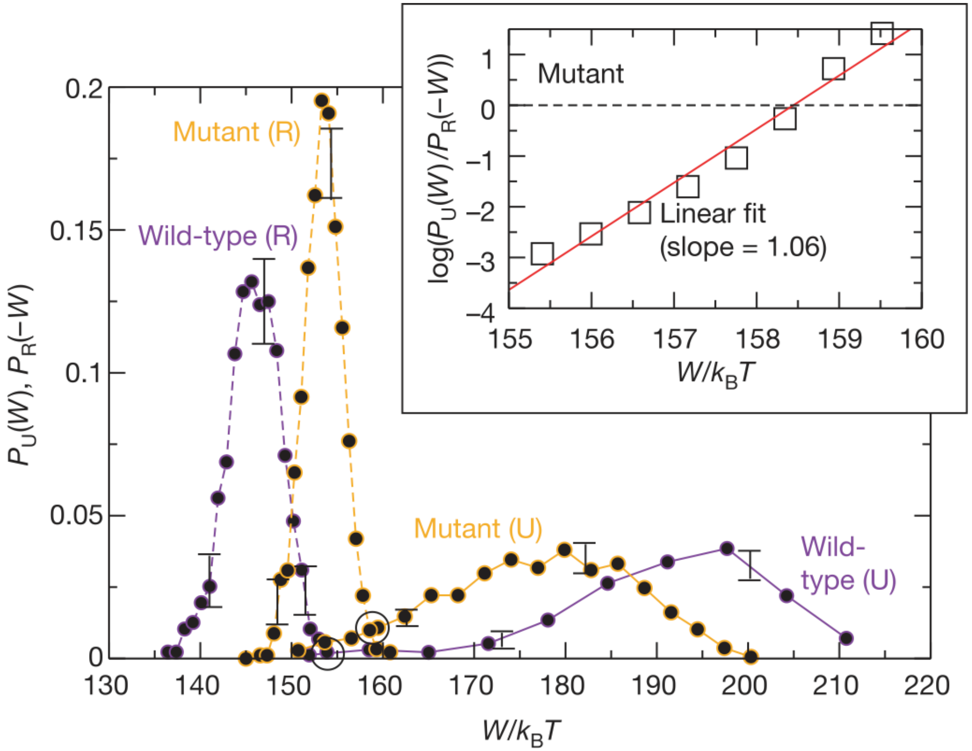
Verification of the Crooks FT

S15 three-helix junction

very far from balance

The probabilities depend on the drawing speed, but their ratio and the location of their intersection do not depend on it.

$$\frac{\mathrm{P}(A \rightarrow B, W)}{\mathrm{P}(A \leftarrow B, -W)} = e^{\frac{W-\Delta G}{k_B T}}$$

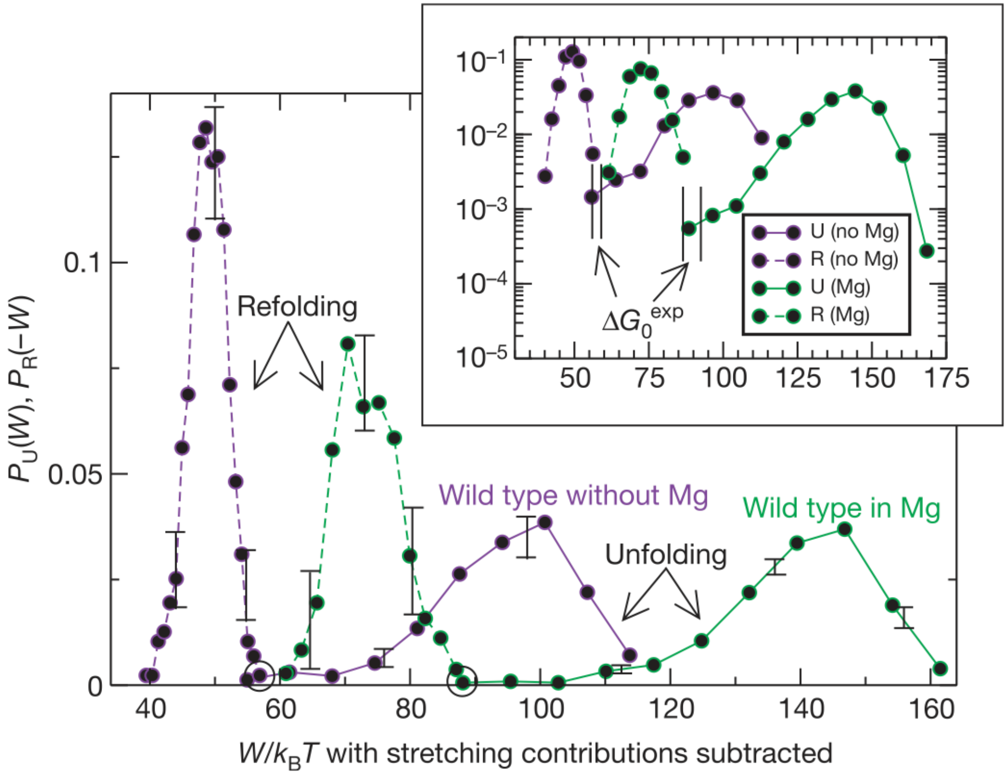


Collin D et al. (2005) Nature 437: 231

The stabilizing effect of Mg $^{2+}$ on RNA estimated based on the Crooks FT

The stabilizing effect of Mg^{2+} on the RNA structure:

$\Delta\Delta G = 31.7 \pm 2\ k_B T$



Collin D et al. (2005) Nature 437: 231

Operation of molecular motors

Szabolcs Osváth

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Properties of nanosystems

- Certain properties are quantized
- Gravity is negligible compared to the other forces
- Surface/mass ratio is very large
- Dissipation of heat is virtually instantaneous
- The role of different binding forces is large
- Molecular level recognition
- Self-organization
- The effect of inertia is negligible
- Increased role of viscosity and thermal movement

Properties of biological motors

- Made of soft material (biopolymers)
- Function is governed by non-covalent forces
- There are no smooth frictionless surfaces
- Fuel: ATP (NADH), transmembrane gradient
- Work in solutions – high viscosity
- Their power is: 100-1000 ATP/s, i.e. 10^{-16} – 10^{-17} W
- The power of Brown motion is: 10^{-8} W
- The working principle uses Brown motion

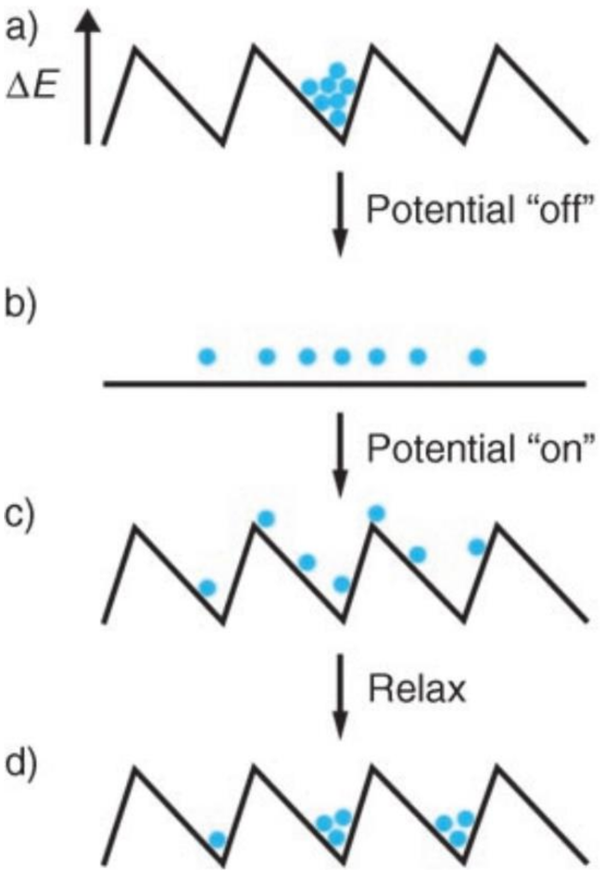
Function of the Brownian ratchet

- Random mixing

- Energy source

- Asymmetric energy surface along the reaction coordinate

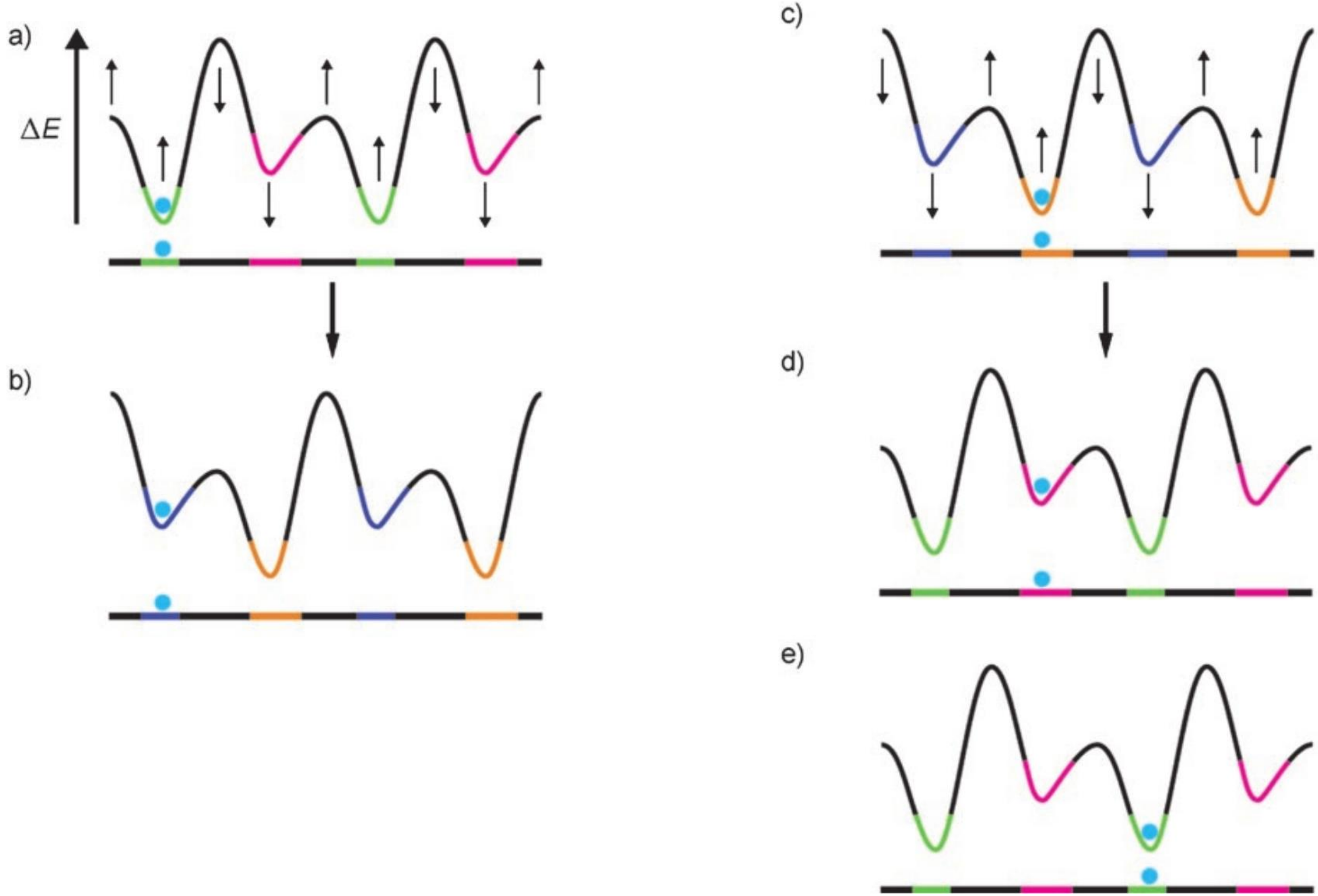
Pulsating ratchet



The potential should be turned of for a short time only, otherwise the transport happens with equal probabilities in both directions.

Kay et al. (2007) Angev. Chem. 46: 72

Flashing ratchet



The working principles of biological motors

- Break the isotropy of the transport resulting from fluctuations

- Kinetic coupling between substrate and motor

- Substrate movement is always localized

- Manipulating localization is important element of the transport

- Localization is the result of non-covalent interactions

Biological application of Nonequilibrium thermodynamics

Experimental verification of the ft-s (revision)

General strategy:

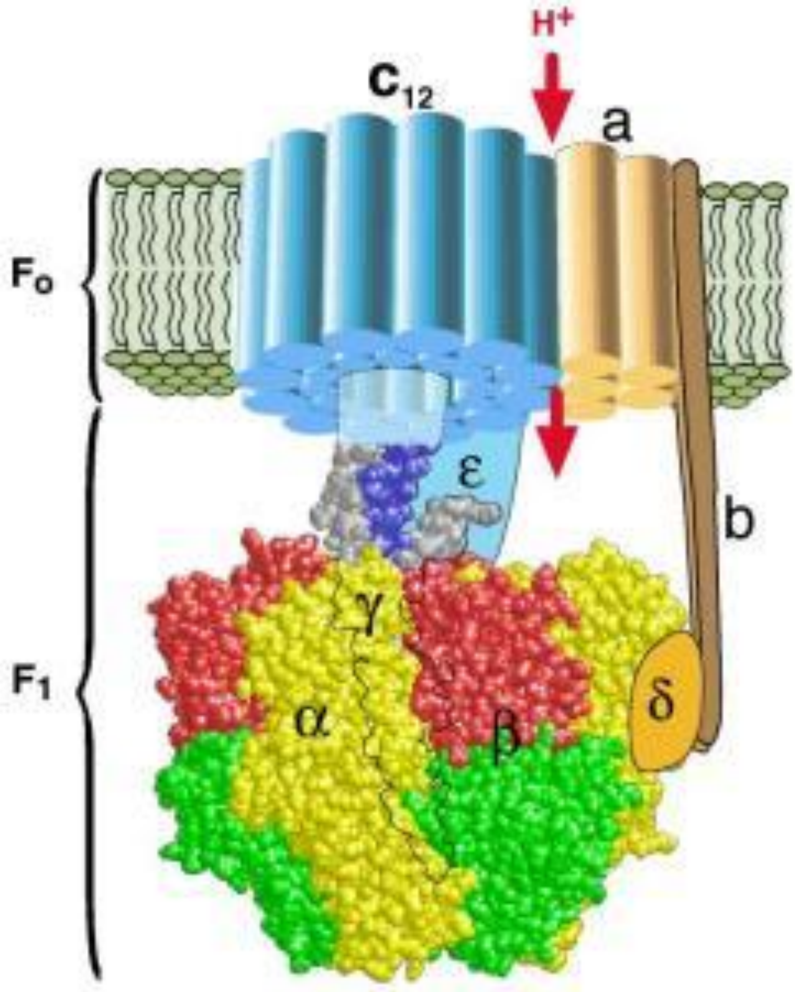
small system for a short time, under the influence of small forces

energy / work must be measured with the accuracy of a fraction of $k_B \cdot T$

both equilibrium and non-equilibrium ranges should be accessible in the experiments

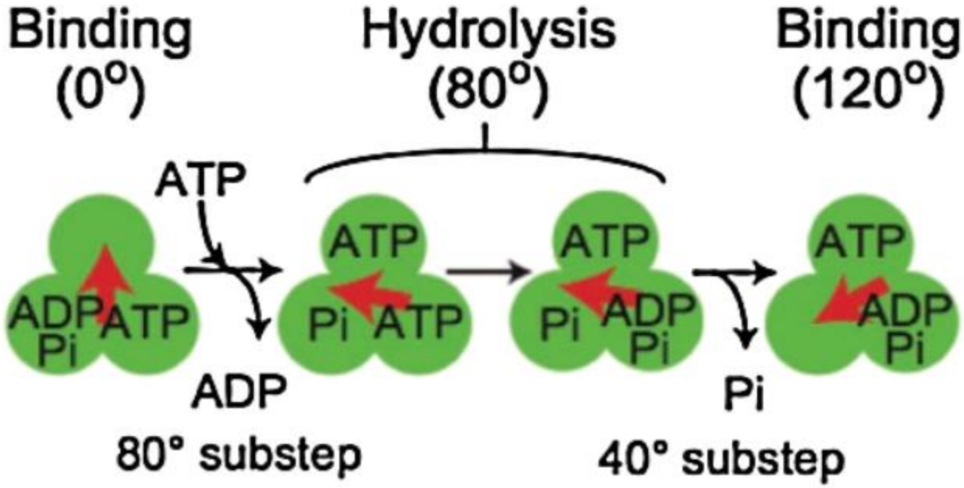
the experiment must be repeated many times

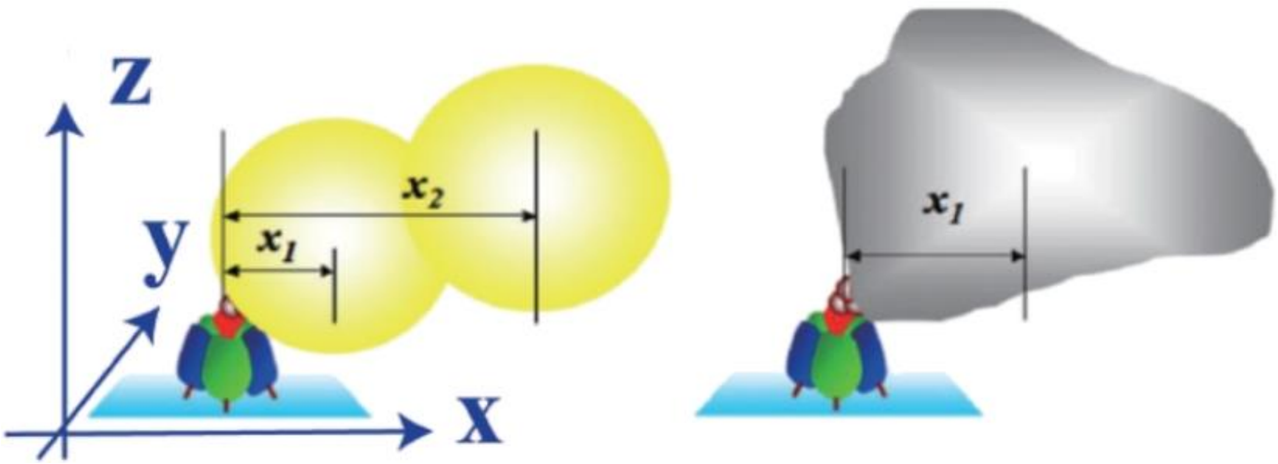
Structure of the F_1-ATP-ase motor



H. Wang and G. Oster (1998). Nature 396:279-282.

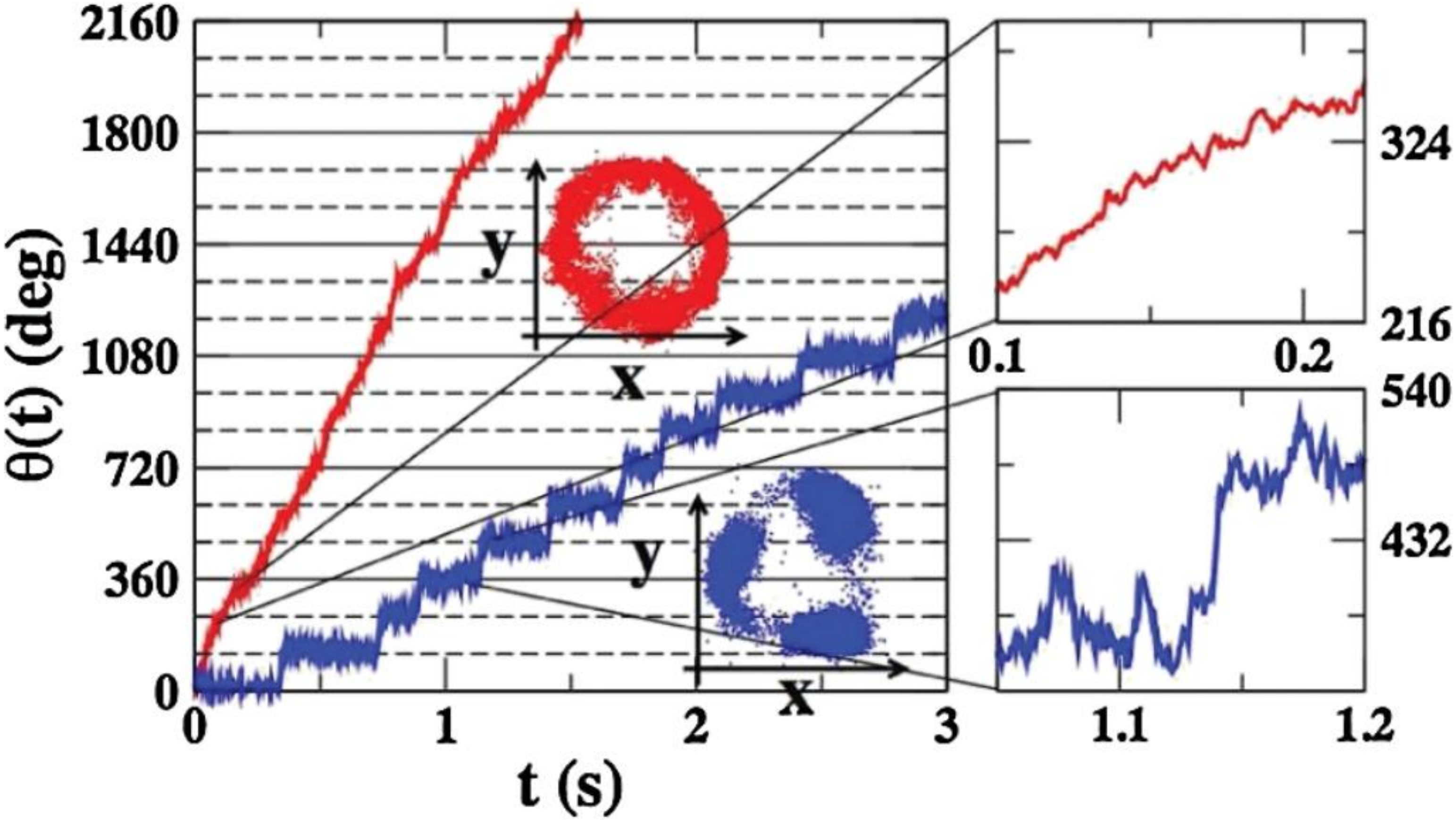
Rotation of F_1-ATP-ase motor





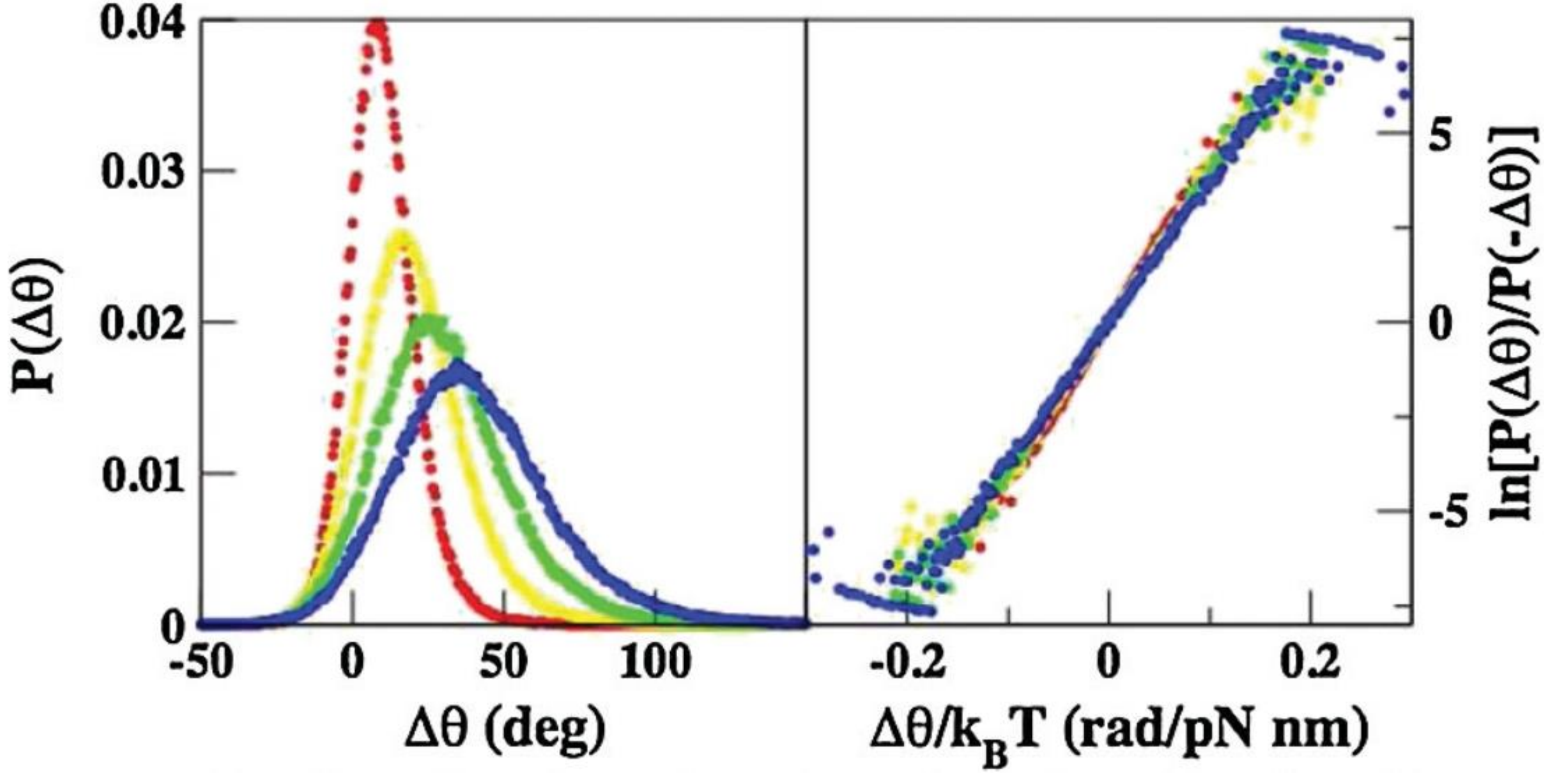
Hayashi et al. (2010) Phys. Rev. Lett. 104: 218103

Rotation of F_1-ATP-ase motor (experiment)



Hayashi et al. (2010) Phys. Rev. Lett. 104: 218103

Fluctuation theorem for the F_1-ATP-ase motor



red: 2.5 ms; yellow: 5.0 ms; green: 7.5 ms; blue: 10 ms

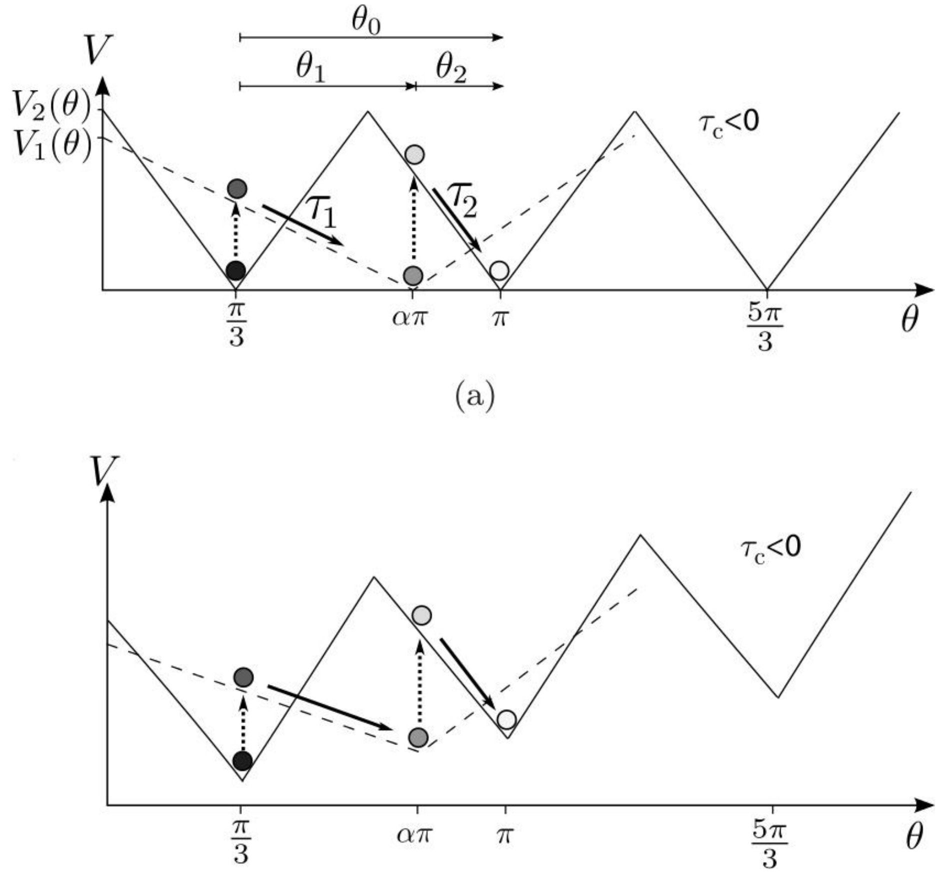
Hayashi et al. (2010) Phys. Rev. Lett. 104: 218103

F_1-ATP-ase flashing ratchet mechanism

Rotation mechanism of the free-rotating and the loaded F_1-ATP-ase motor.

relaxed state:
continuous line

nucleotide binding state:
dashed line



Sancho and Perez-Carrasco (2010) Fluct. Noise. Lett. 11: 1240003