

# Crooks Fluctuation Theorem

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# Evans-Searles fluctuation theorem

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

Denis J Evans, Debra J Searles (1994)

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

where  $S$  is the entropy production in  $k_B$  units

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

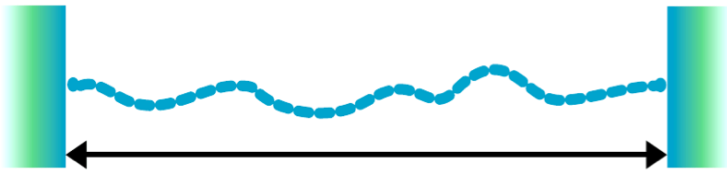
## **The significance of Evans-Searles fluctuation theorem**

- extension of the second law
- gives an analytical expression for the probability of the phenomena
- valid in the non-linear range
- valid for small systems (no thermodynamic limit)
- it is very general, with many version developed for a wide variety of systems and dissipations
- nano-systems are not reduced versions of their macroscopic counterpart, they behave fundamentally differently

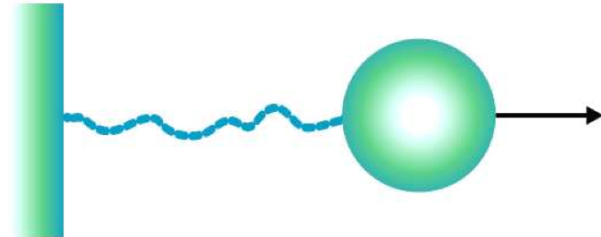
# The state of the small system

The state of the small system is described by the control parameter.

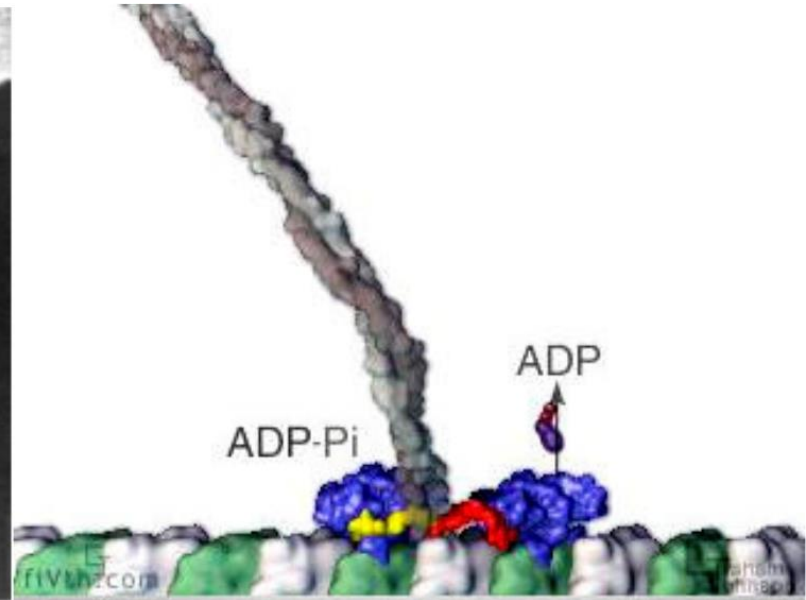
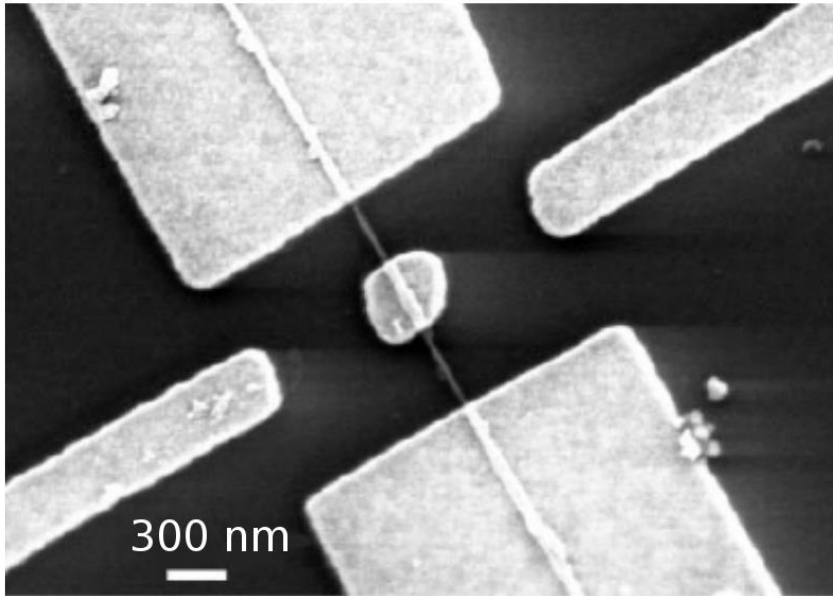
Control parameter: length



Control parameter: force

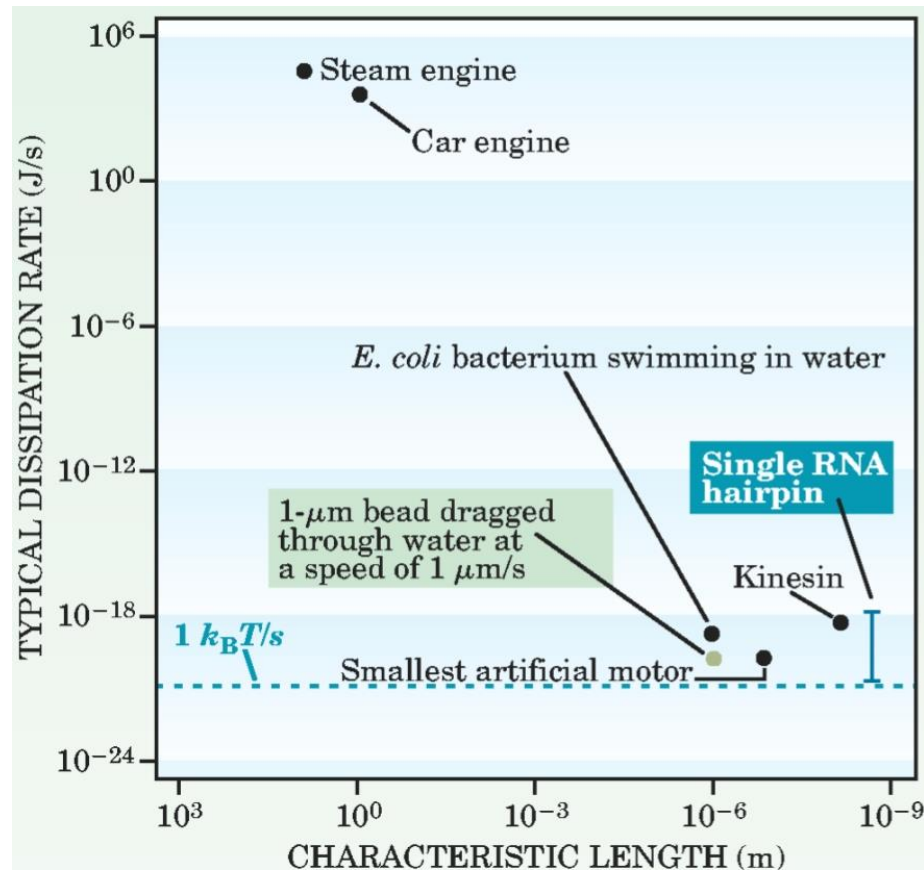


# Enzymes and nano size engines



Bustamante et al. (2005) arXiv preprint cond-mat/0511629

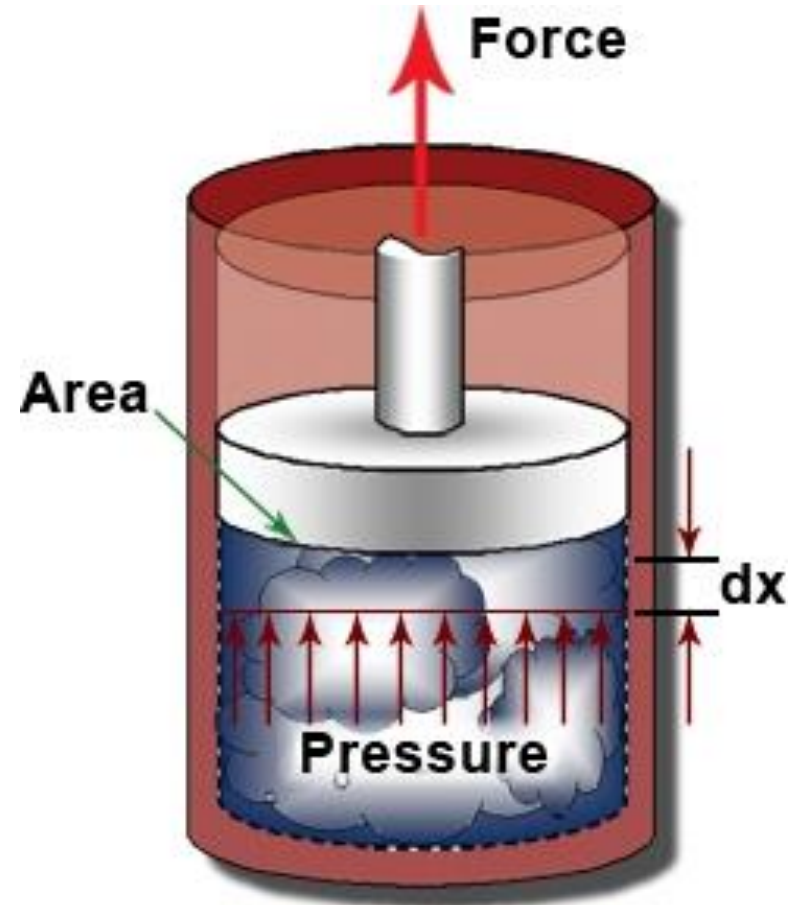
# Enzymes and nano size engines



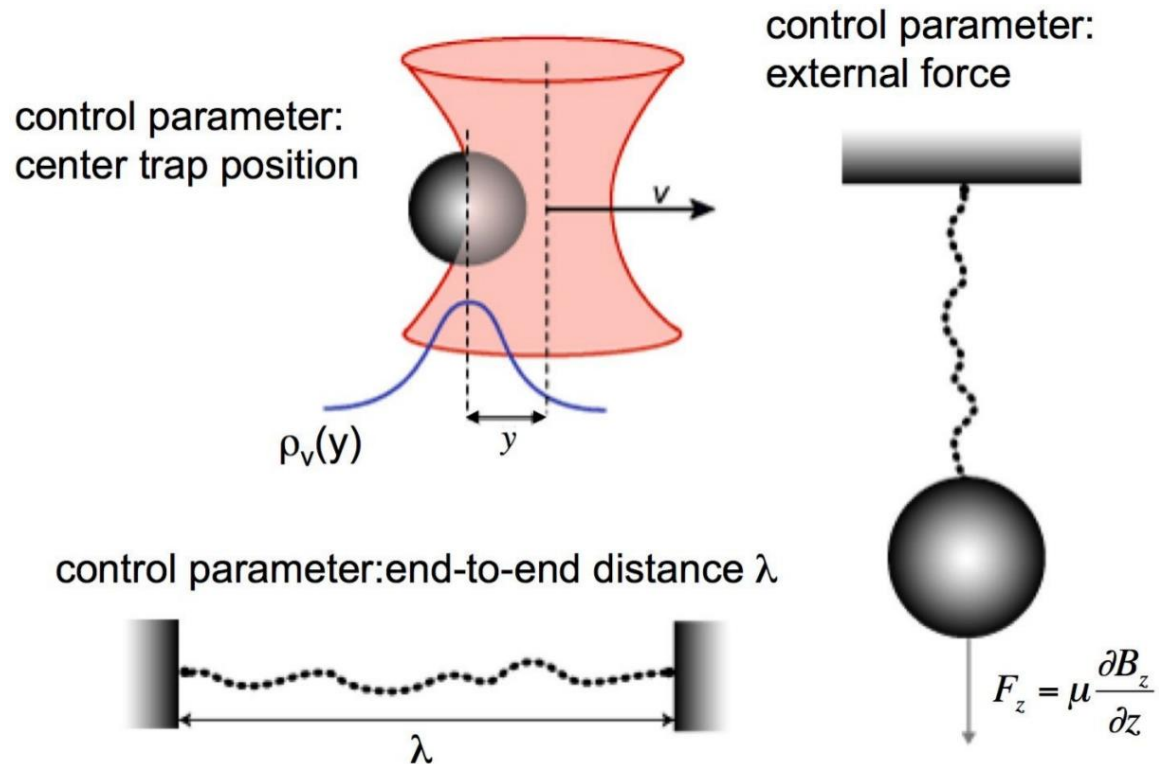
Bustamante et al. (2005) arXiv preprint cond-mat/0511629

# Control parameter

For small systems, the control parameter plays the role of the external variables (such as temperature, pressure, volume) used to specify the state of the system in macroscopic thermodynamic systems.



# Control parameter



Bustamante, et al. (2005) arXiv preprint cond-mat/0511629.



## Crooks FT

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

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

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

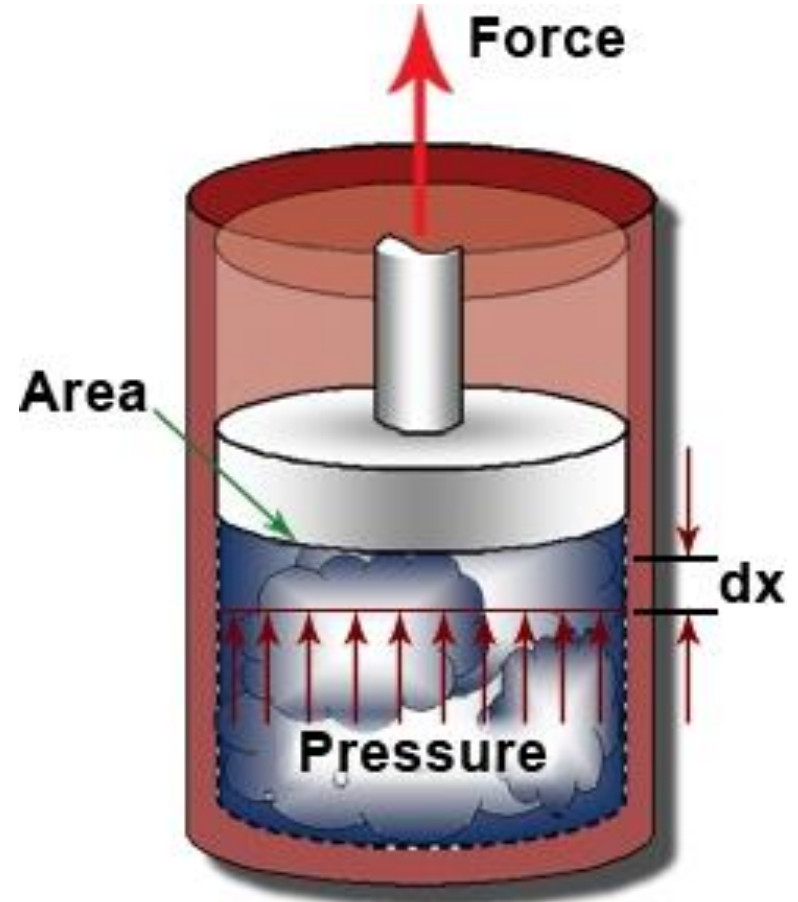
$\Delta G$  is the free enthalpy difference between the states  $A$  and  $B$

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

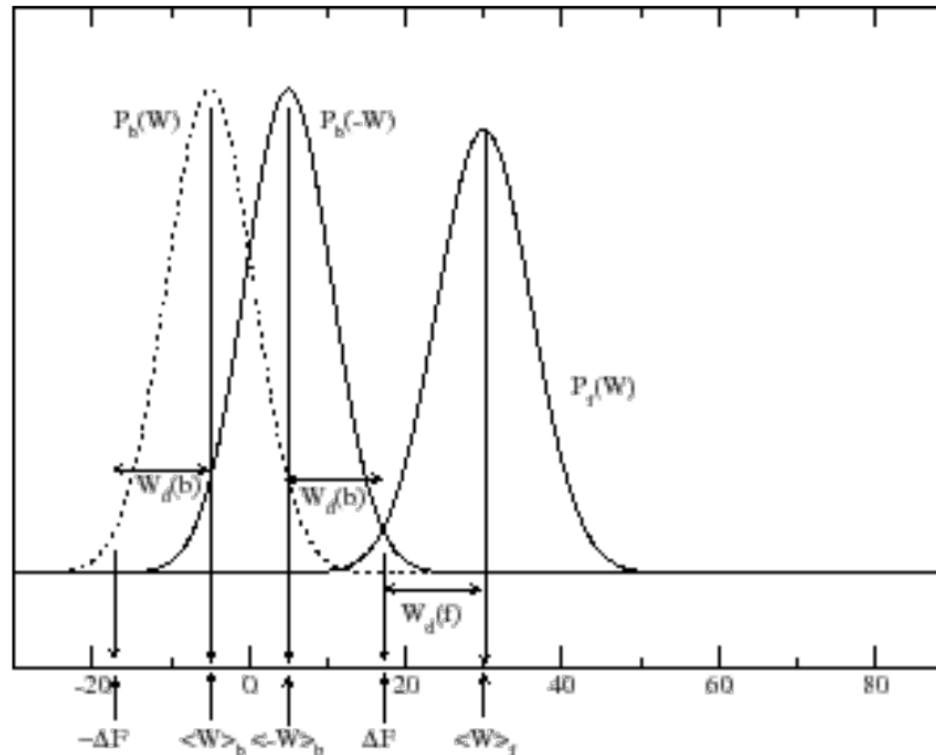
# Crooks FT

Both the forward (F) and reverse (R) paths are started from equilibrium.

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



# Crooks FT – distribution of microscopic work



The distribution curves of the work measured during forward (F) and reverse (R) transitions intersect at the equilibrium free enthalpy change value ( $\Delta F$ ), commonly referred to in biology as the Gibbs free energy change ( $\Delta G$ ).

## When can we use the Crooks FT

Systems that meet the basic assumptions of molecular dynamics calculations and experiments:

- equilibrium steady state system with time-symmetric microscopic dynamics
- processes that start at equilibrium (it is not necessary to go through equilibrium states or end at equilibrium)