Fluctuation Theorems in Small-System Thermodynamics: Evans–Searles, Crooks, and Jarzynski Relations

Dr. Szabolcs Osváth
Semmelweis University

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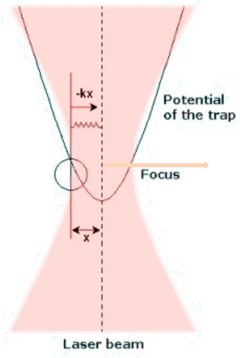
Fluctuations in Small Systems: Optical Trap Experiment

- A small bead is trapped in a laser focus and immersed in water.
- Trap is translated at a constant speed through the fluid, creating a non-equilibrium steady state.
- Thermal fluctuations occasionally drive the bead forward or backward, leading to transient negative entropy changes (apparent second-law violations).



Wang G.M. et al. (2002) Phys. Rev. Lett. **89**: 050601

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Evans-Searles fluctuation theorem

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

where S is the entropy production in k_B units

- Quantifies the probability of observing negative entropy production in small systems over finite observation times.
- Reformulates the second law in statistical terms.

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

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The significance of Evans-Searles fluctuation theorem

- Extends the second law of thermodynamics to finite-time, small-system dynamics.
- Provides an explicit expression for the probability of entropy-reducing fluctuations.
- Valid far from equilibrium and beyond the linear regime.
- Demonstrates that nanosystems exhibit fundamentally different behavior from macroscopic systems.

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The state of the small system

- The state of a small system is defined by the control parameters rather than macroscopic thermodynamic variables.
- These parameters determine the instantaneous potential energy profile of the system.
- Thermal noise causes fluctuations around each control parameter value.

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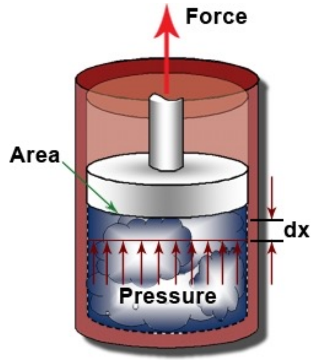
Control parameter

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.



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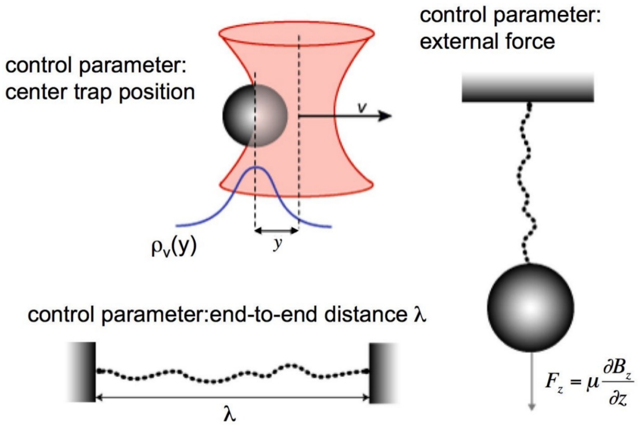
Exasmples of control parameter



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Work and the Control Parameter

- When the control parameter changes with time, the potential energy of the system also changes.
- This means that we perform work on the system.
- The amount of work depends on how the potential energy changes as the control parameter varies.
- Because the system is small and affected by thermal noise, the work fluctuates from one experiment to another — even when the same protocol is repeated.

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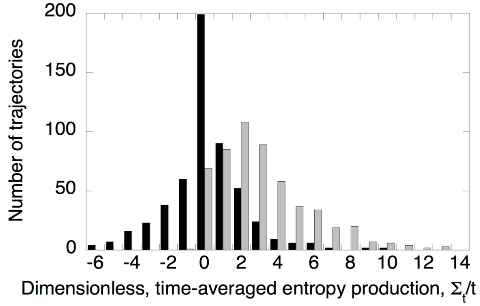
Evans-Searles FT (IFT) – violations of the second law



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Wang G.M. et al. (2002) Phys. Rev. Lett. 89: 050601

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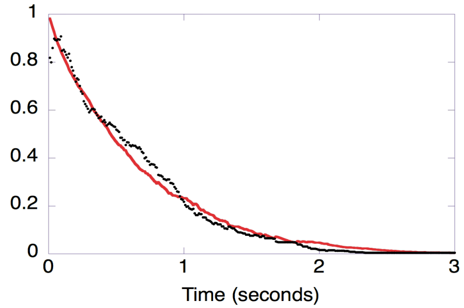
Evans-Searles FT (IFT) – violations of the second law



$$\frac{Pr(\Sigma_t < 0)}{Pr(\Sigma_t > 0)} = \langle \exp(-\Sigma_t) \rangle_{\Sigma_t > 0}$$

Wang G.M. at al. (2002) Phys. Rev. Lett. 89: 050601

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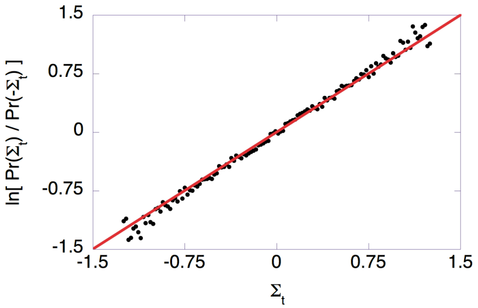
Evans-Searles FT (IFT) – violations of the second law



Wang G.M. at al. (2002) Phys. Rev. Lett. 89: 050601

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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

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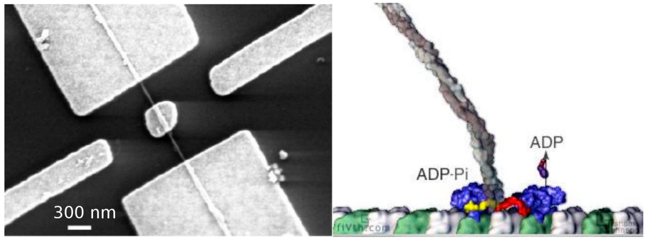
Enzymes and nano size engines



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

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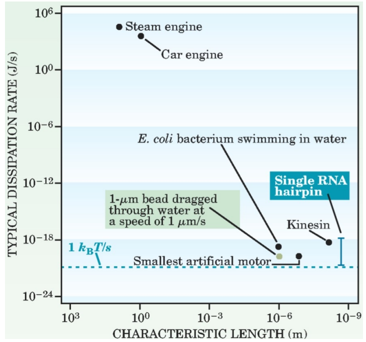
Enzymes and nano size engines



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

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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

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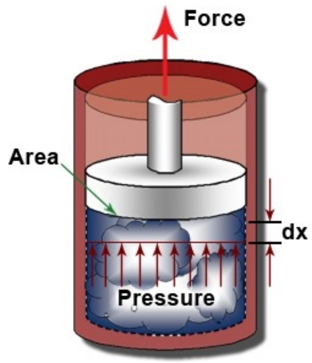
Crooks FT

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

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



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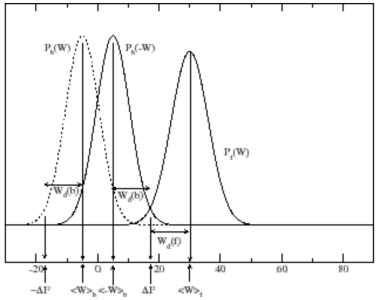
Crooks FT – distribution of microscopic work



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

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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)

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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

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Jarzynski equality

It creates a bridge between equilibrium thermodynamics and inequilibrium measurements.

During the transformation, the intensive thermodynamic parameters need not be defined.

An equilibration process is allowed to happen at the final value of an extensive control parameter, since this does not involve work.

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Relationship between the Jarzynski equality, the Crooks FT and the Evans-Searles FT

Crooks FT can be derived from Evans-Searles FT if the initial state is steady state or equilibrium.

Crooks FT can be derived from more general conditions than the Evans-Searles FT.

The Jarzynski equation can be derived from the Crooks FT ifboth the initial and final states are equilibrium.

The Crooks FT is generally more robust than the Jarzynski equation and gives a more accurate estimation of the free enthalpy based on the experimental results.

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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

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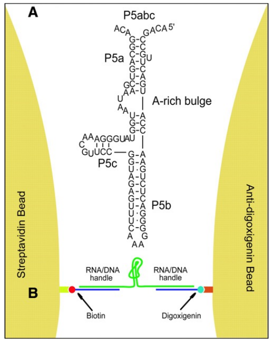
Verification of the Jarzynski equality

The work done along each trajectory was calculated from the force-displacement function measured using the optical trap.

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



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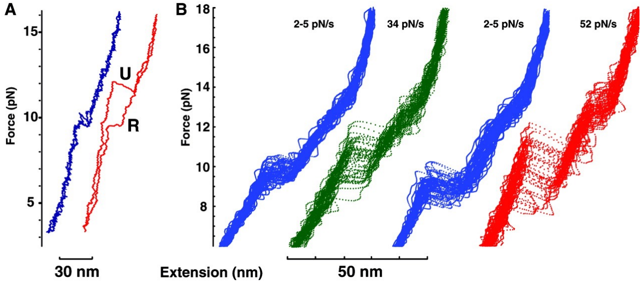
Verification of the Jarzynski equality



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Verification of the Jarzynski equality

Three different ways to estimate the free enthalpy difference :

average work
(thermodynamics, quasi-static)

$$W_A = \langle w \rangle$$

based on the fluctuation dissipation theorem (near equilibrium)

$$W_{FD} = \langle w \rangle - \frac{\sigma^2}{2 \cdot k_B T}$$

based on the Jarzynski equality (can be arbitrarily far from equilibrium)

$$W_{JE} = -k_B T \cdot ln\left(\left\langle e^{\frac{-w}{k_B T}} \right\rangle\right)$$

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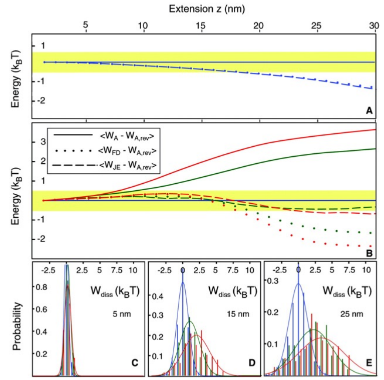
Verification of the Jarzynski equality

A:
in the reversible range

B:
in the irreversible range

C, D, E:
the distribution of the work w under different conditions



blue: 2-5 pN/s; green: 34 pN/s; red: 52 pN/s

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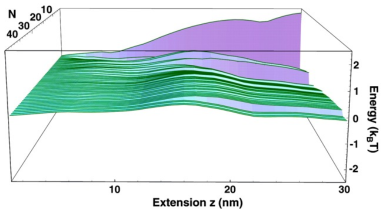
Verification of the Jarzynski equality

The free enthalpy calculated from Jarzynski's equation converges slowly as the number of measurements increases.

$\Delta G = 59.6 \pm 0.2\ k_B T$

green: 34 pN/s
red: 52 pN/s



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Verification of the Jarzynski equality - summary

- free enthalpy can be determined with an accuracy of: $0.5\ k_B T$
- the Jarzynski equality gave the best estimate for non-equilibrium measurements (within $1\ k_B T$)
- the Jarzynski equation makes it possible to derive the equilibrium free enthalpy from non-equilibrium measurements
- the free enthalpy calculated from the Jarzynski equation converges slowly if the measurements are done very far from equilibrium (requires many measurements)

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