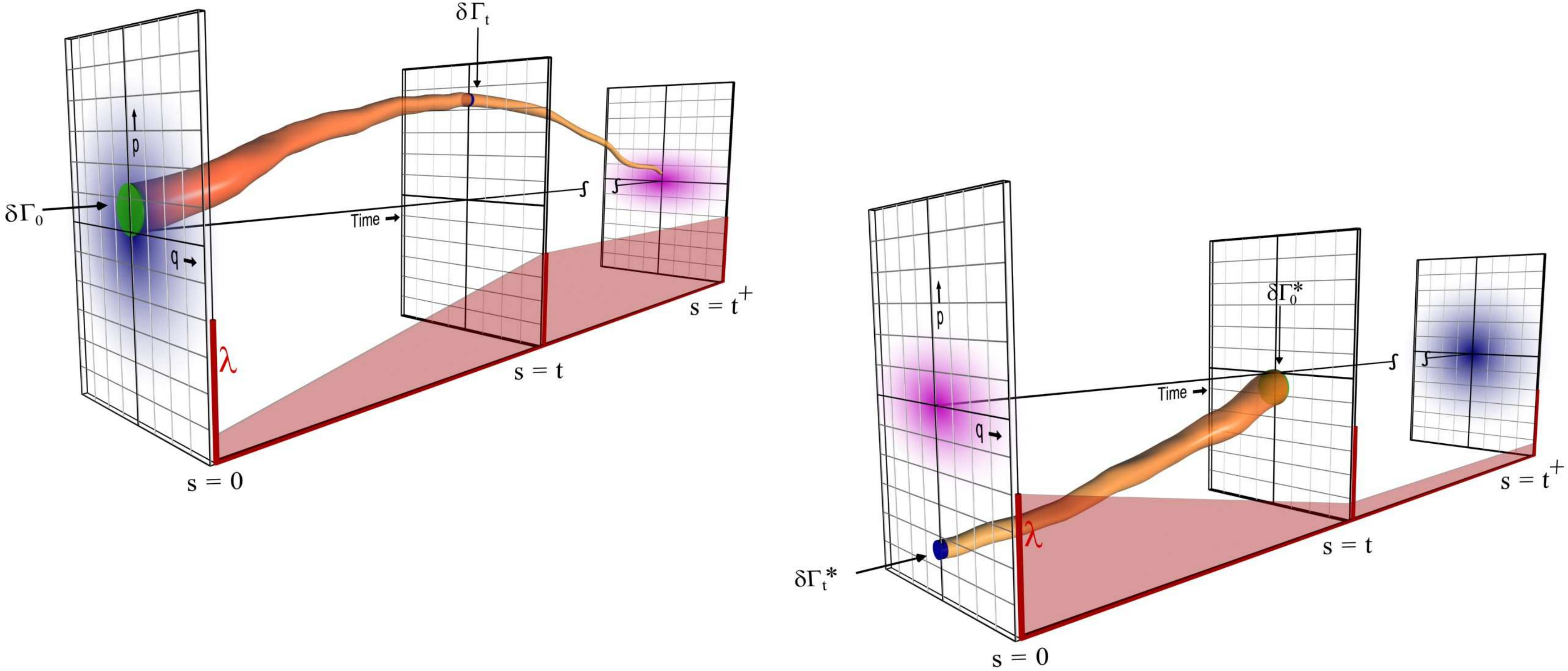
Fluctuation Relations: Experimental Demonstrations



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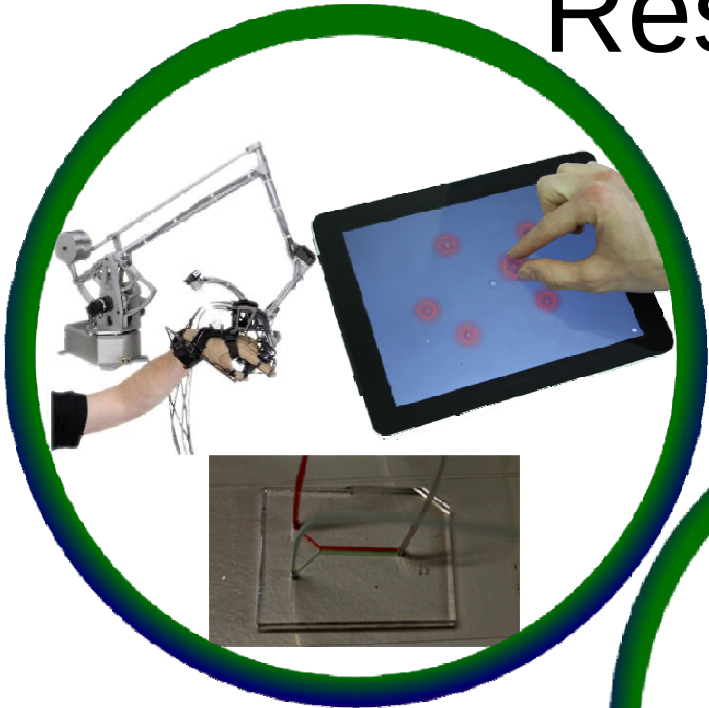
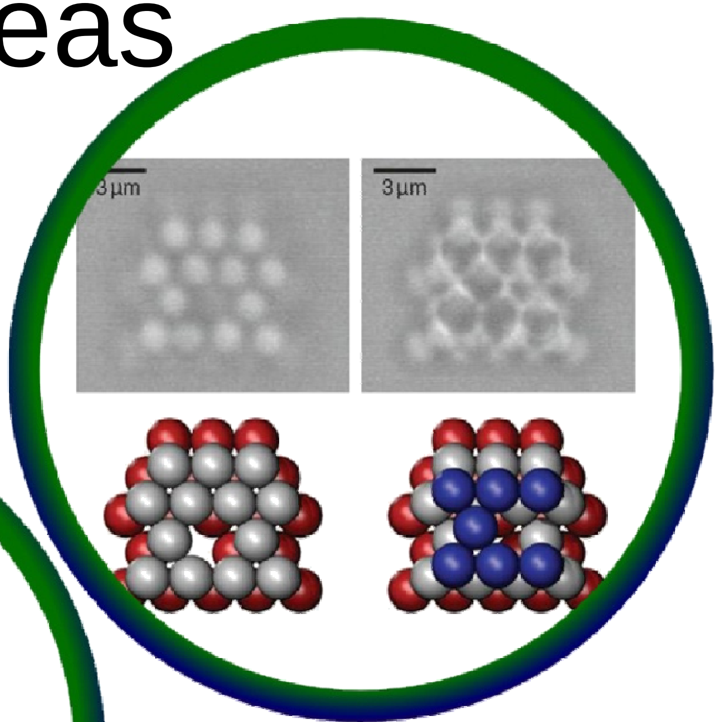
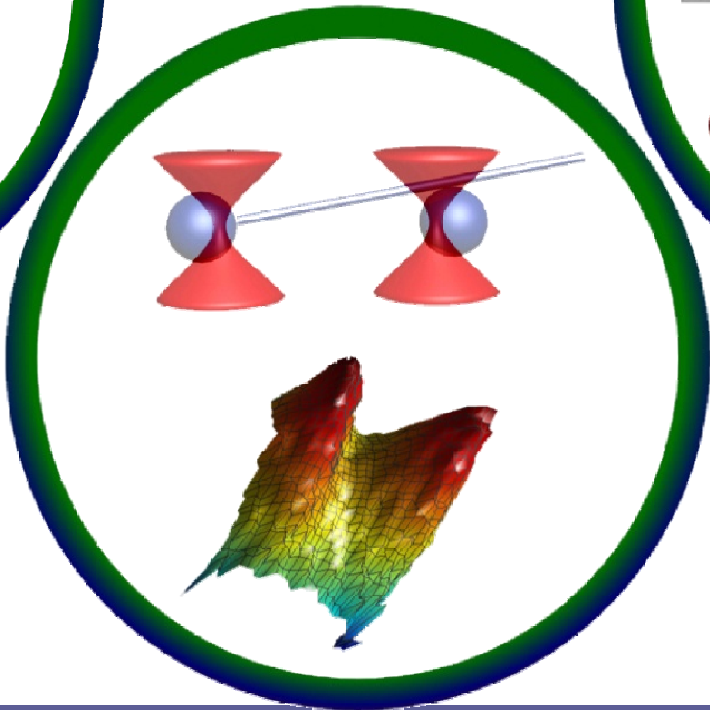
Research Areas







Outline

- Optical Tweezers
- Overview of the Fluctuation Theorem + Crooks' Relation
- The FT, IFT and KI – experiments
- The CR and WR – experiments

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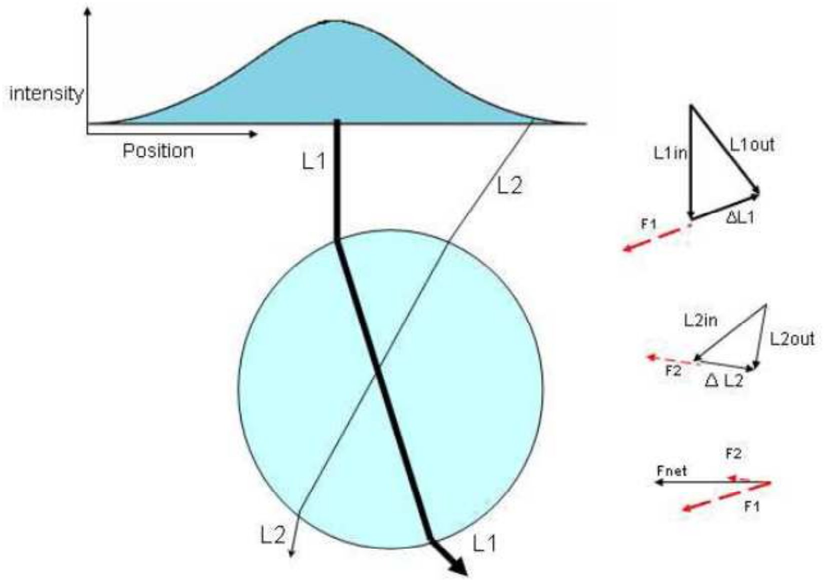
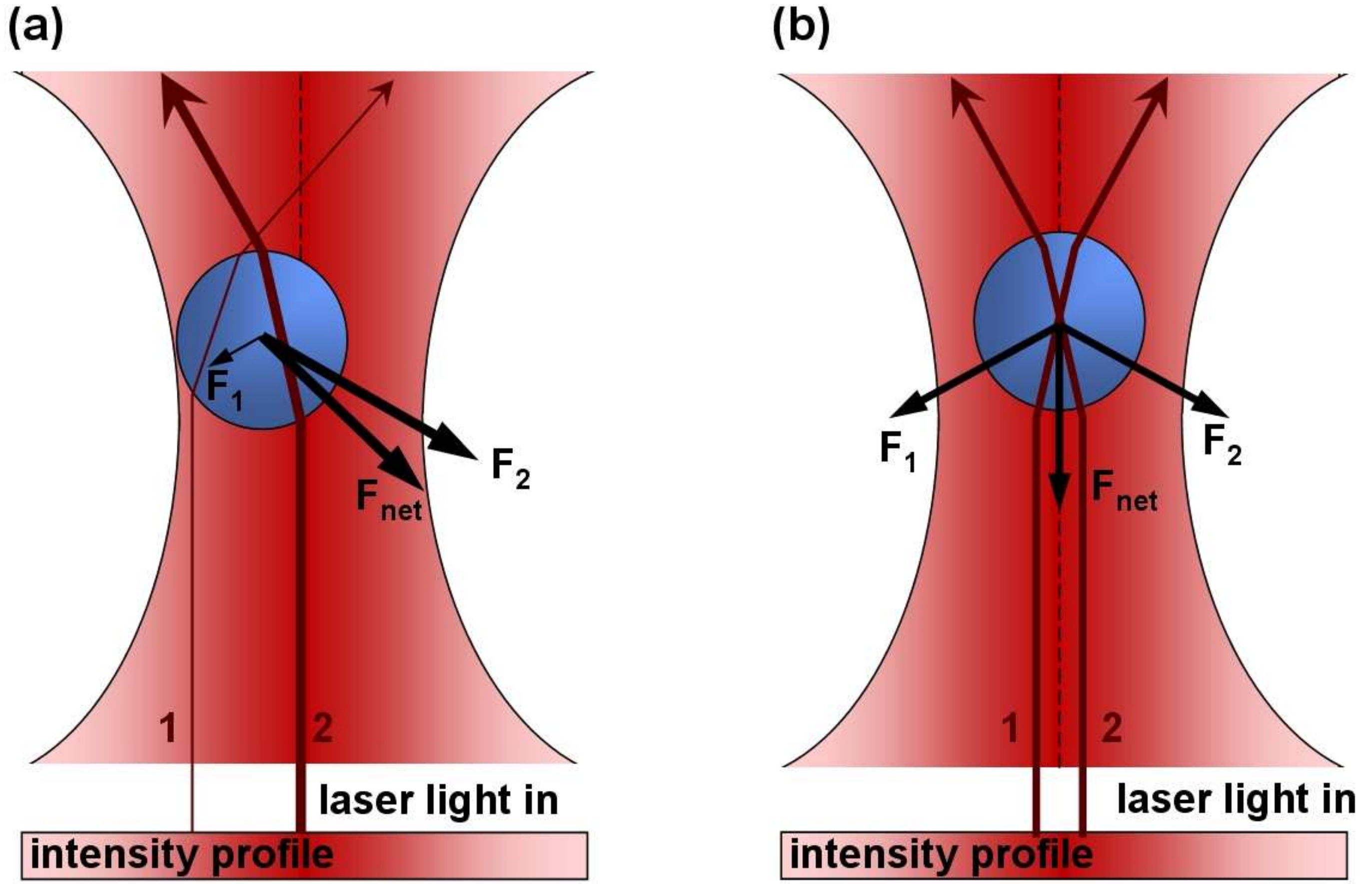
Optical Traps

The refraction of light through a transparent object changes the momentum of the light <u>and</u> of the object.



http://www.physics.gla.ac.uk/Optics/projects/tweezers/trapsimulation/

An optical trap



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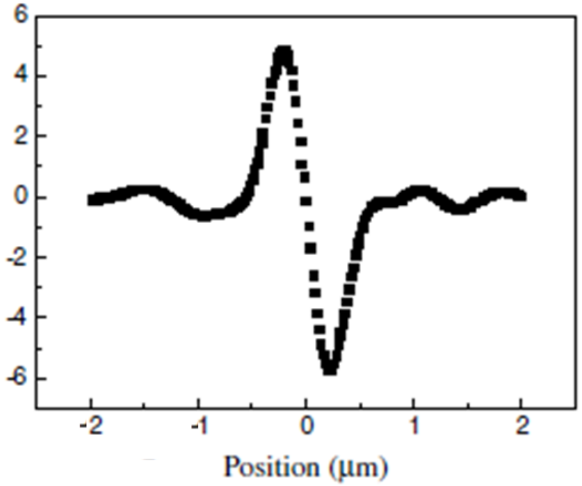
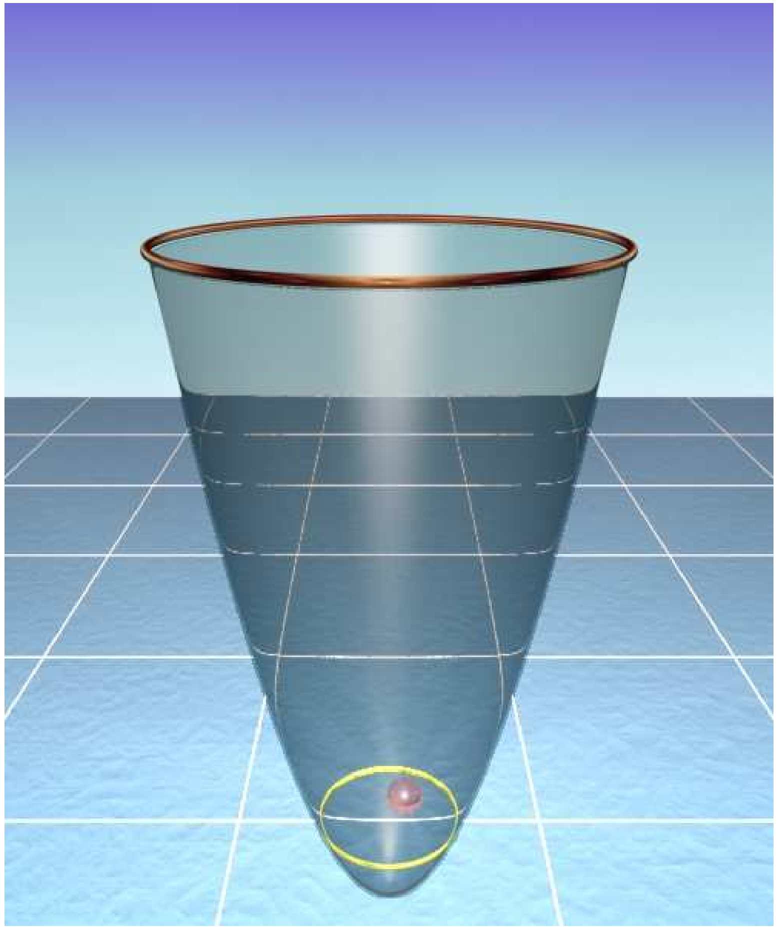
Optical Forces

$$\mathbf{F} = -k\mathbf{x}$$

$$\mathbf{F} = \frac{\partial \mathbf{U}}{\partial \mathbf{x}}$$





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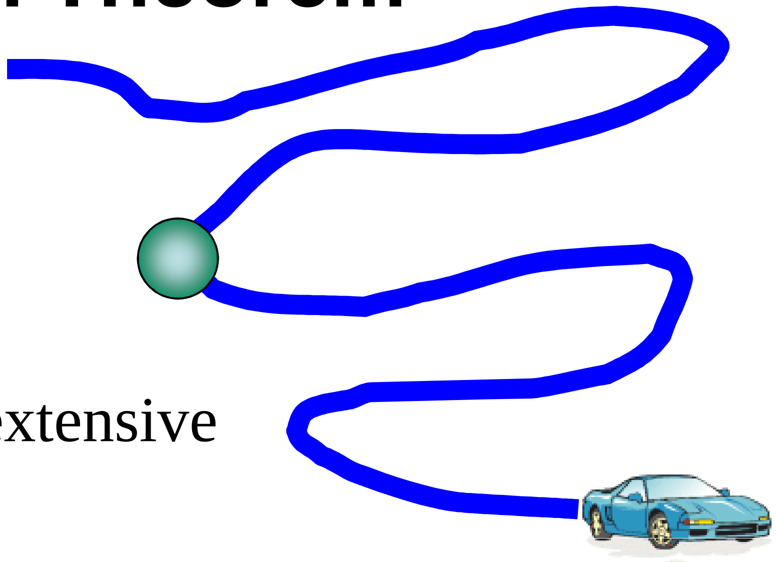
The 2nd Law

- 2nd Law: entropy of the universe always increases
- Large systems for long times

The Fluctuation Theorem (FT): A Second-Law like Relation

- D.J. Evans, E.G.D. Cohen, G.P. Moriss, *Phys.Rev.Lett.* **71**, 2401 (1993).
- D.J. Evans, D.J. Searles, *Phys.Rev.E.* **50**, 1645 (1994)
- small systems/short timescales, or systems NOT described by the thermodynamic limit

The Fluctuation Theorem



$$\frac{P(\Omega_t = -a)}{P(\Omega_t = a)} = \exp(-a)$$

Ω_t is a dimensionless energy, extensive measure of a path

$$\frac{P(\Omega_t < 0)}{P(\Omega_t > 0)} = \langle \exp(-\Omega_t) \rangle_{\Omega_t > 0}$$

- paths with $\Omega_t \geq 0$ consistent with Second Law

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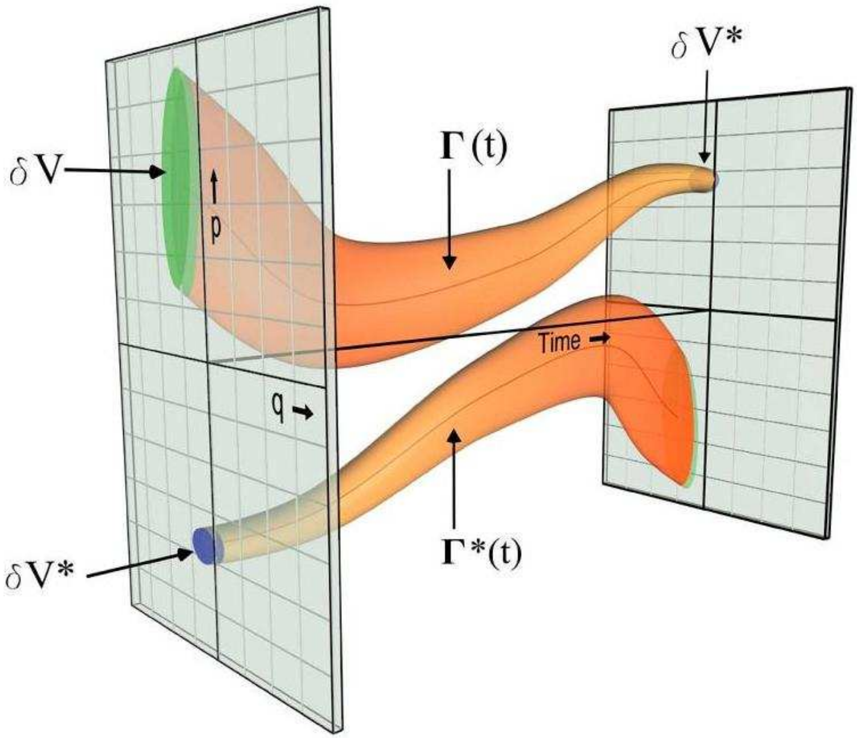
Definition of the dissipation function, Ω_t



$$\Omega_t \equiv \ln\left[\frac{P(\delta V)}{P(\delta V^*)}\right]$$

. . . a measure of irreversibility

$\Omega_t = 0$ for vanishingly small t, indicative of perfect reversibility at short time scales

$\langle \Omega_t \rangle \geq 0$ with larger t, indicative of irreversibility predicted by 2nd Law

$\langle \Omega_t \rangle \geq 0$, entropy like quantity

Reid, Carberry, Wang, Sevick, Searles & Evans, *Phys. Rev. E* (2004)

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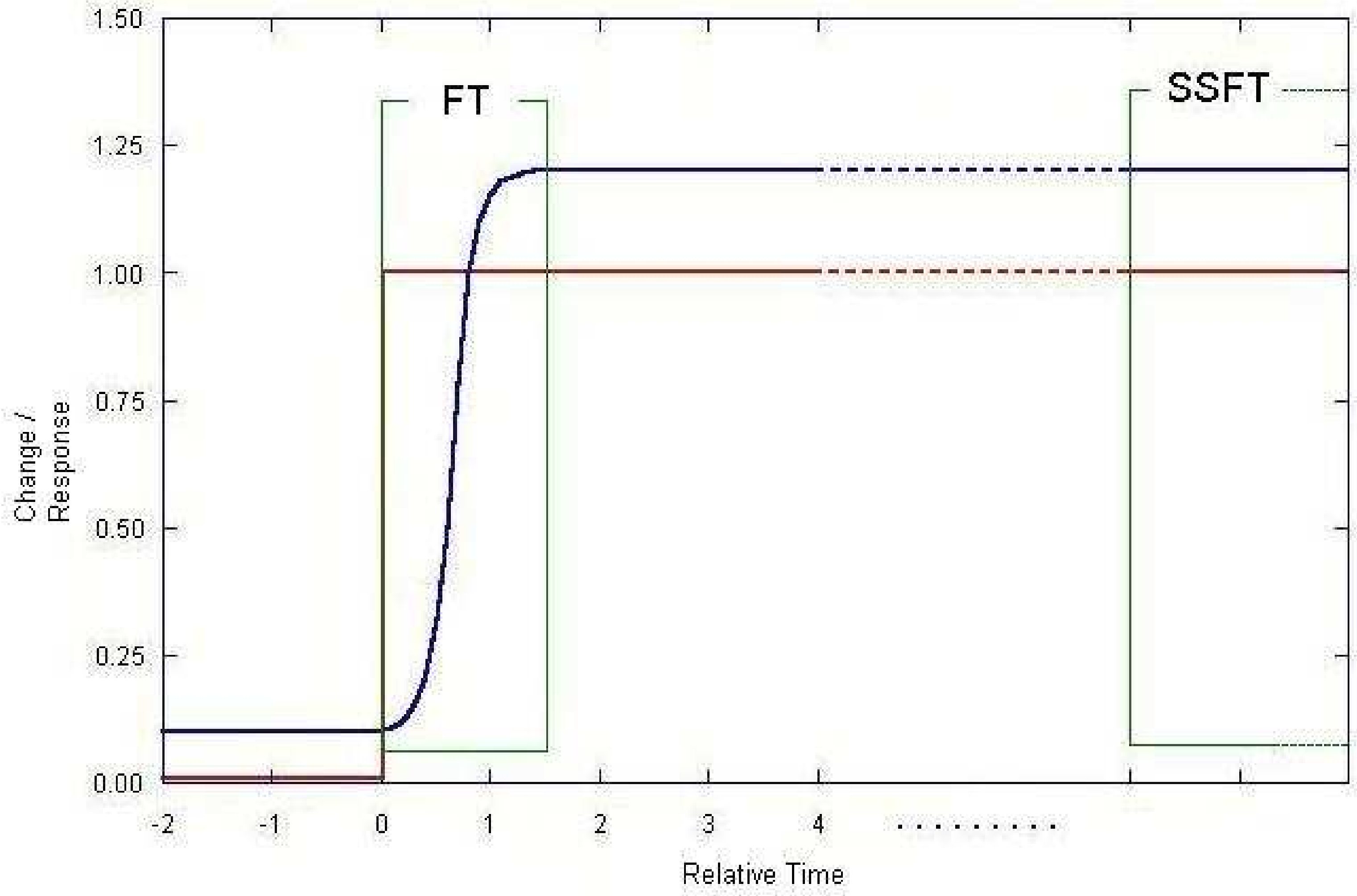
Areas of Application



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The Work Relation (WR): Anathema to classical thermodynamics

- Chris Jarzynski, 1997
- ΔF evaluated over non-equilibrium paths
- $\langle \exp(-\beta \Delta W) \rangle = \exp(-\Delta F)$

The Crooks Relation: FT-like relation for systems with ΔF

- Gavin Crooks, 1998
- $\dfrac{P_{1\to 2}(\beta \Delta W = a)}{P_{2\to 1}(\beta \Delta W = -a)} = \exp(\beta \Delta F - \beta \Delta W)$

Summary of Equations

Fluctuation Theorem

$$\frac{P_{1\to 2}(\Omega_t = a)}{P_{1\to 2}(\Omega_t = -a)} = \exp(a)$$

Kawasaki Identity

$$\langle \exp(-\Omega_t) \rangle = 1$$

Crooks Equality

$$\frac{P_{1\to 2}(\Delta w = a)}{P_{2\to 1}(\Delta w = -a)} = \exp(a)\exp(-\Delta F)$$

Work Relation (Jarzynski equality)

$$\langle \exp(-\Delta w) \rangle = \exp(-\Delta F)$$

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Some other little FT bits

$$\langle \Omega_t \rangle = \langle \Omega_t (1 - \exp(-\Omega_t)) \rangle_{\Omega_t \geq 0} \qquad \geq 0 \quad \forall t.$$

2nd law inequality

$$\boxed{\frac{P(\Omega_t < 0)}{P(\Omega_t > 0)} = \langle \exp(-\Omega_t) \rangle_{\Omega_t > 0}.}$$

Integrated FT

$$\lim_{t \to \infty} \frac{P(\Omega_t^{ss} < 0)}{P(\Omega_t^{ss} > 0)} = \langle \exp(-\Omega_t^{ss}) \rangle_{\Omega_t^{ss} > 0}.$$

ISSFT

$$\left\langle \exp(-\Omega_t) \right\rangle = 1$$

KI

Rare anti-trajectory events are essential for the Kawasaki Identity to hold.

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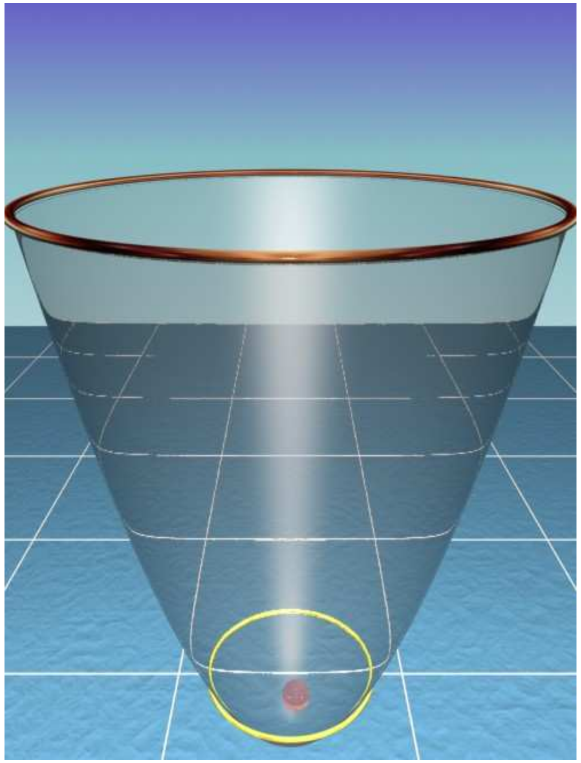
Drag Experiment (2002)



$$\Omega_t = \frac{1}{k_B T}\int_0^t ds\left(\mathbf{F}_{opt}(s)\cdot\mathbf{v}_{opt}\right)$$

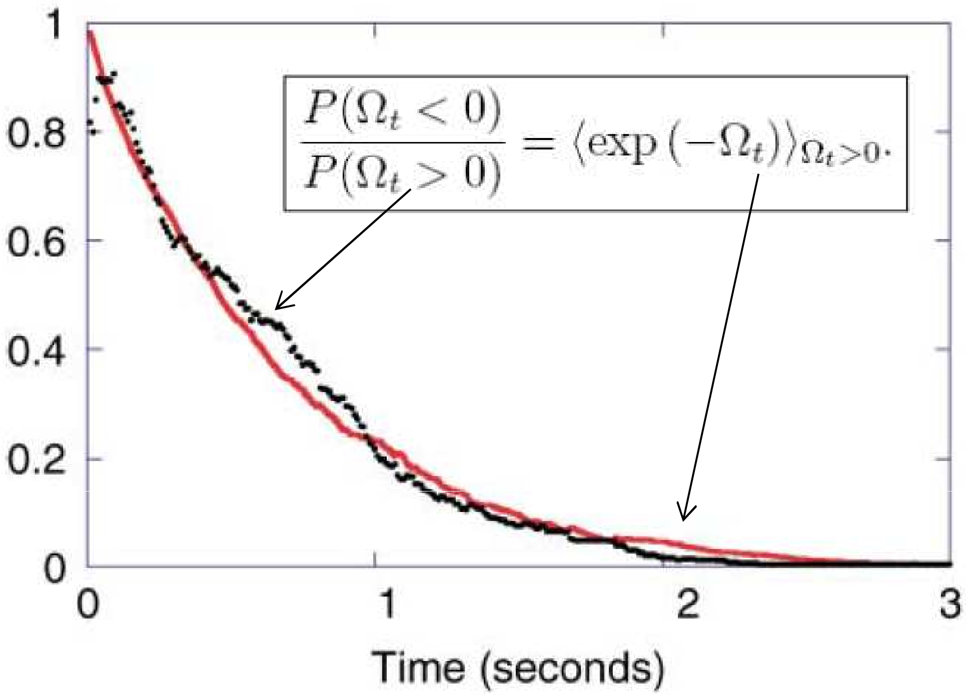
540 Trajectories

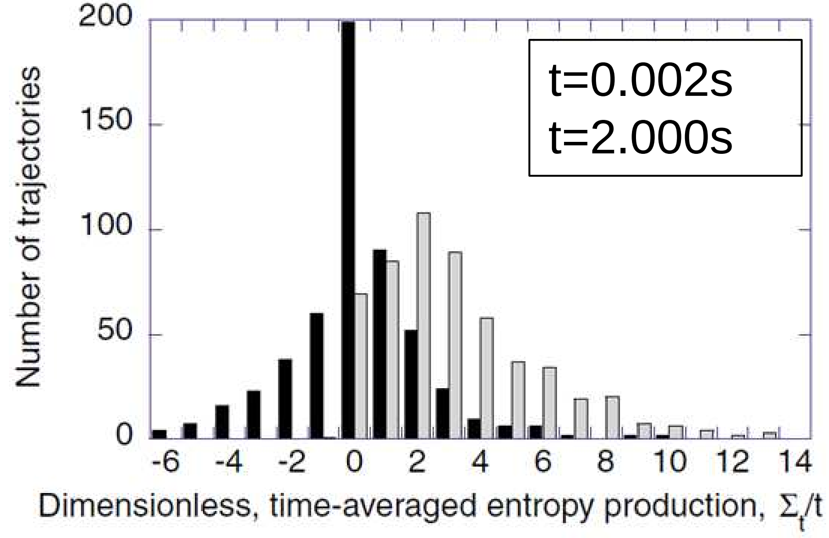
2s stationary,
10s per translation

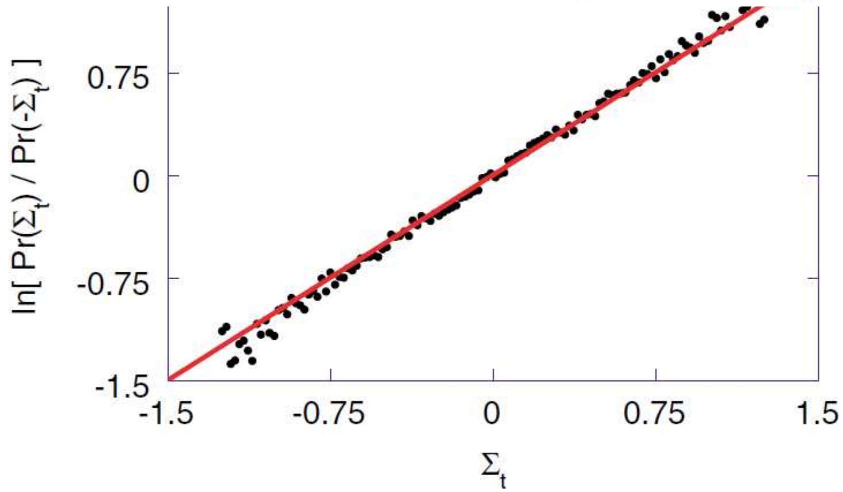
Solution: H_2O;
v=1.25um/s

G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, *Phys. Rev. Lett.* **89**, 050601 (2002).

Drag Results







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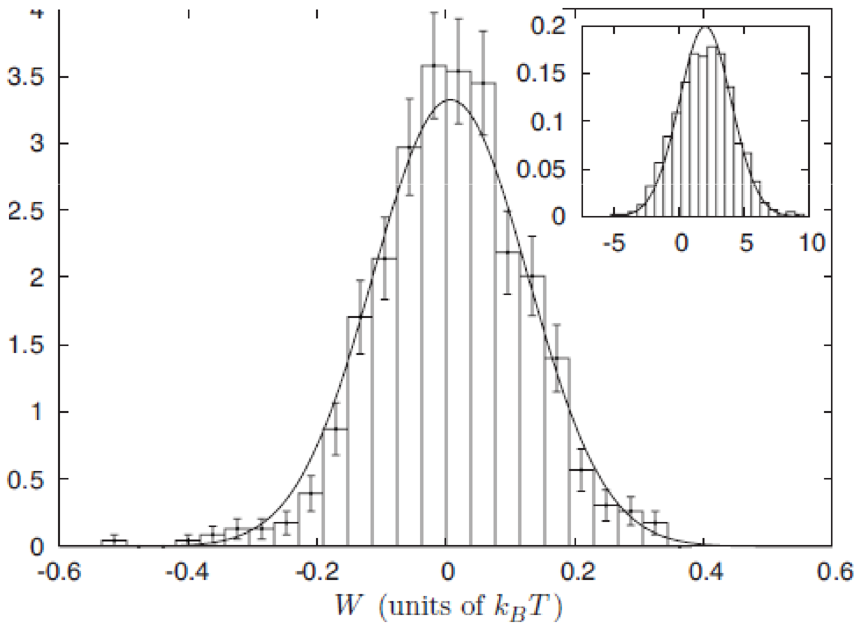
Drag Experiment + Heat (2007)

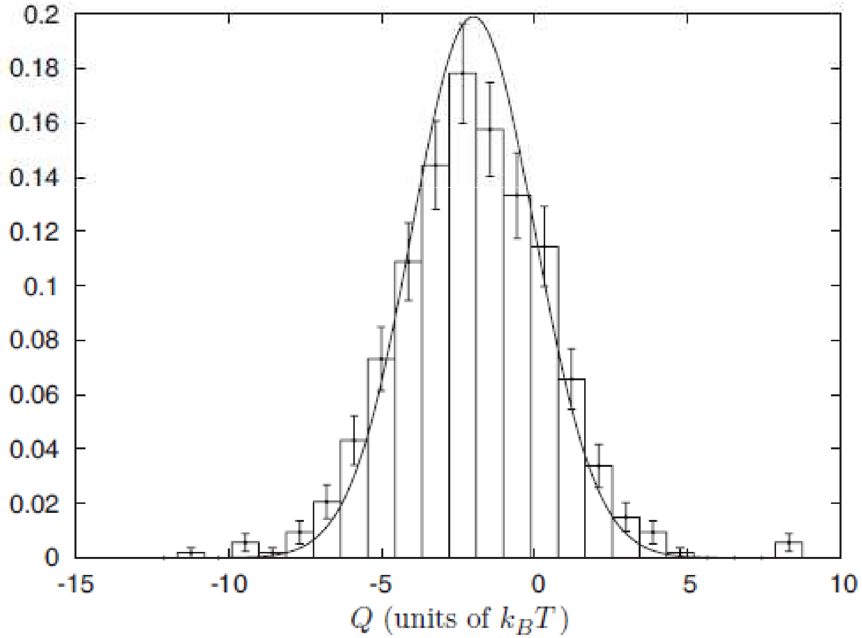
Solution: H_2O;
v=1.um/s

$$\Omega_t = \frac{1}{k_B T}\int_0^t ds\left(\mathbf{F}_{opt}(s)\cdot\mathbf{v}_{opt}\right)$$

$$W = \int dX \frac{\partial U}{\partial X} = \int_0^t dt'\dot{X}(t')\frac{\partial U}{\partial X}.$$

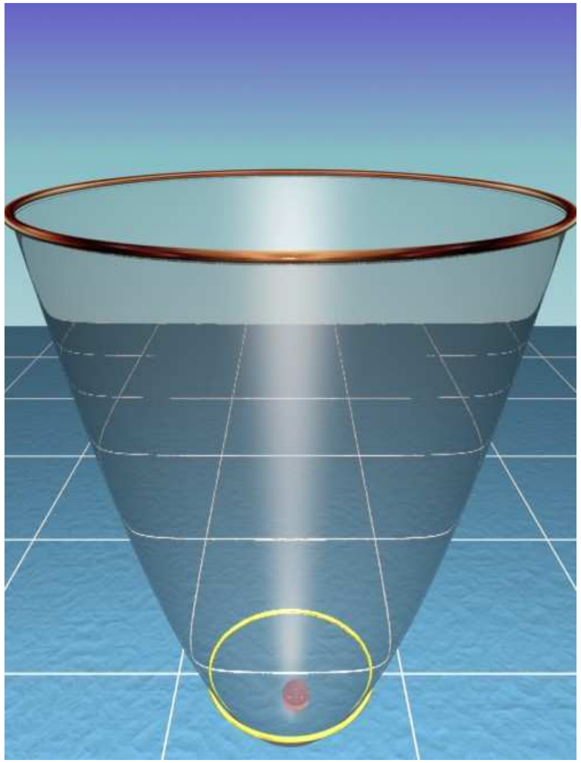
$$Q = \int dx \frac{\partial U}{\partial x} = \int_0^t dt'\dot{x}(t')U'[x(t'),X(t')].$$





A. Imparato, L. Peliti, G. Pesce, G. Rusciano, and A. Sasso, *Phys. Rev. E* **76**, 050101 (2007).

Capture Experiment (2004)

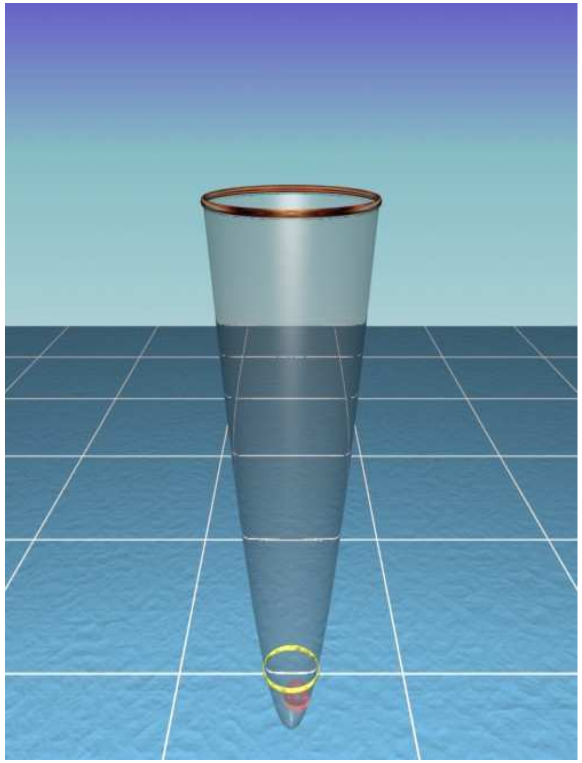


$$\Omega_t = \frac{1}{2k_B T}\int_0^t ds\left(\Delta\mathbf{F}_{opt}\cdot\mathbf{v}_{opt}\right)$$

2100 cycles

10s per state

Solution: H_2O



D.M. Carberry, J.C. Reid, G.M. Wang, E.M. Sevick, D.J. Searles, and D.J. Evans, *Physical Review Letters* **92**, 140601, (2004).

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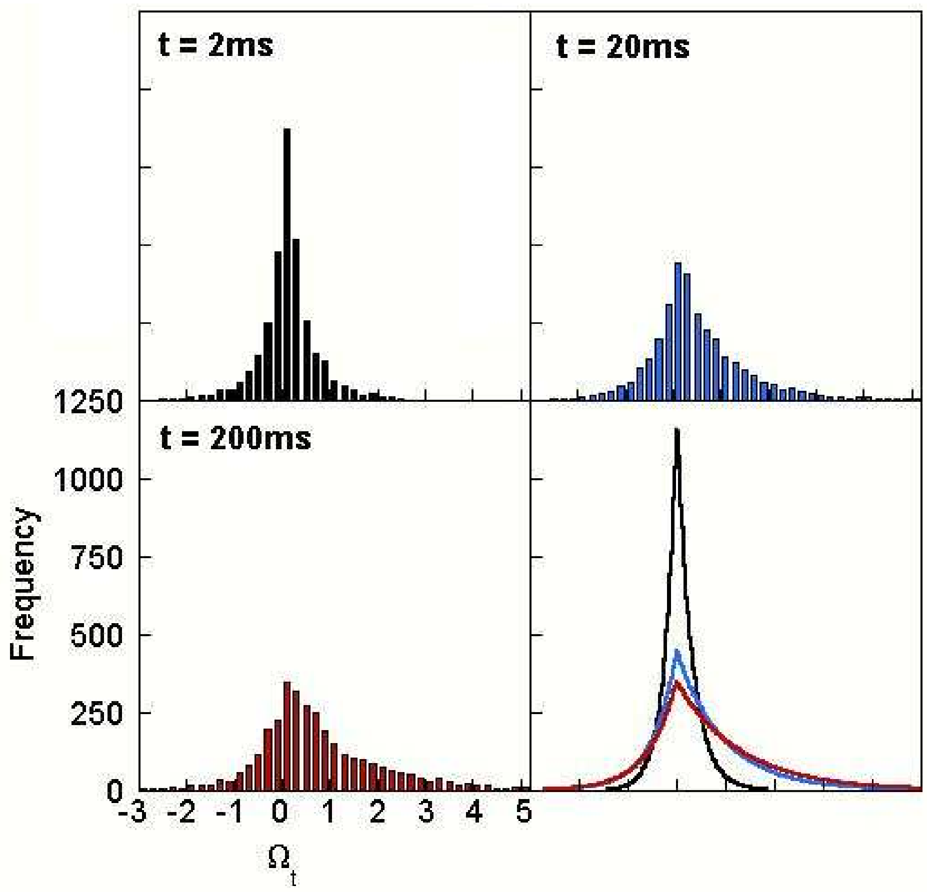
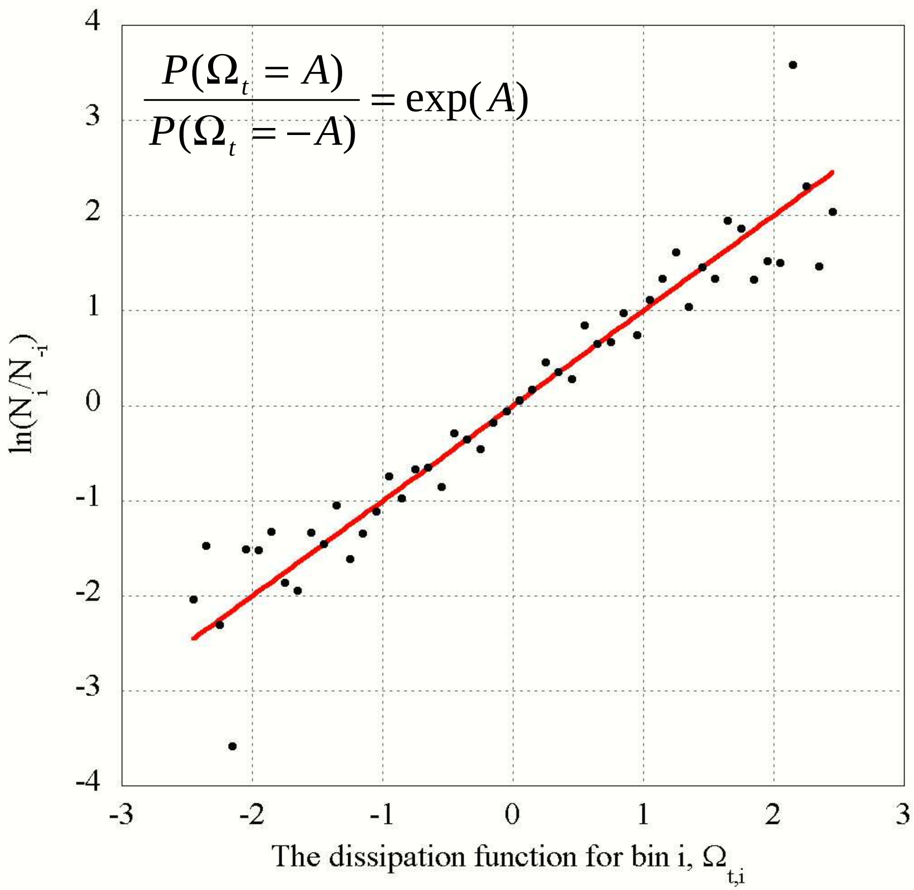
Capture Experiment Results





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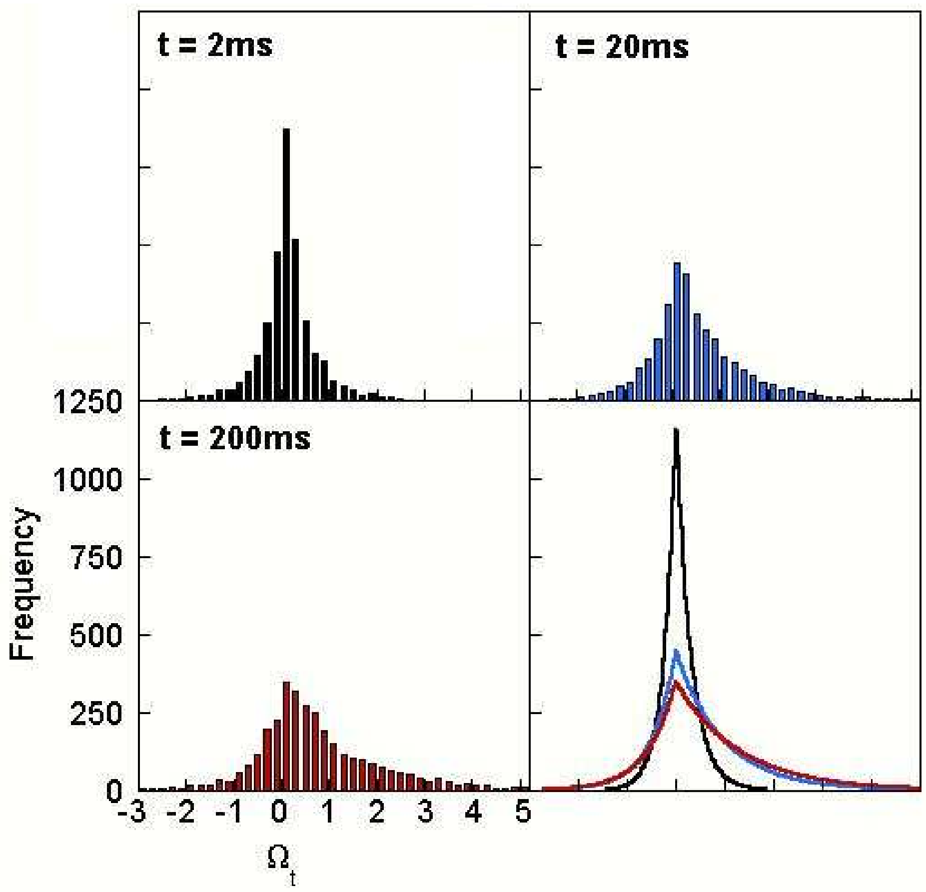
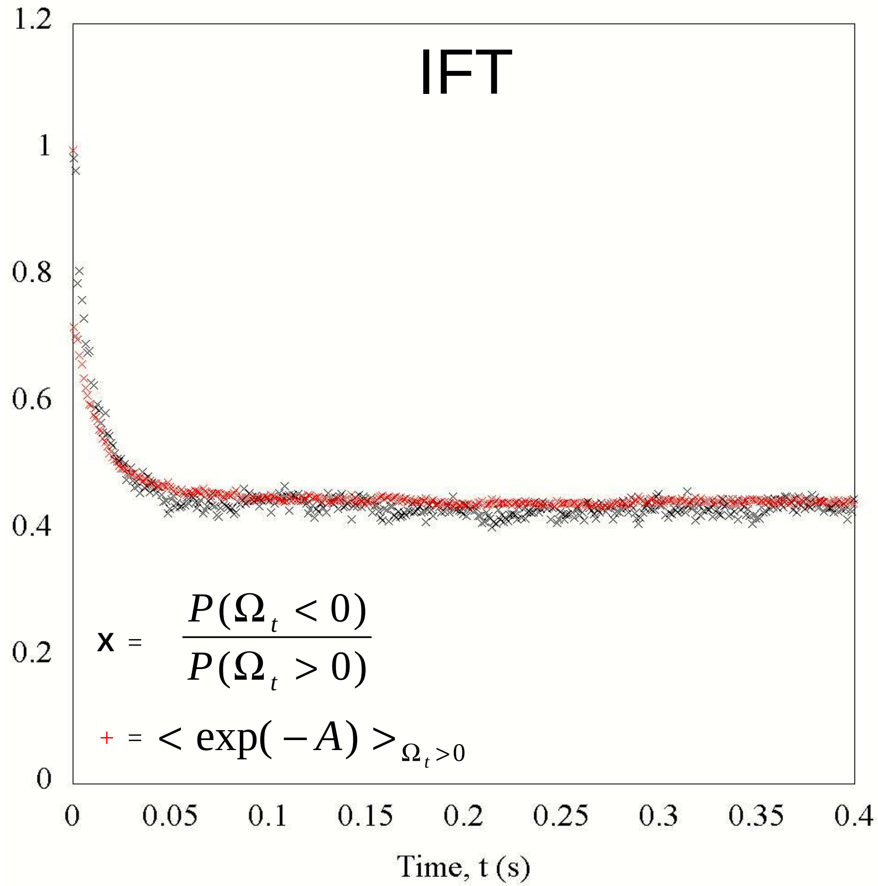
Capture Experiment Results





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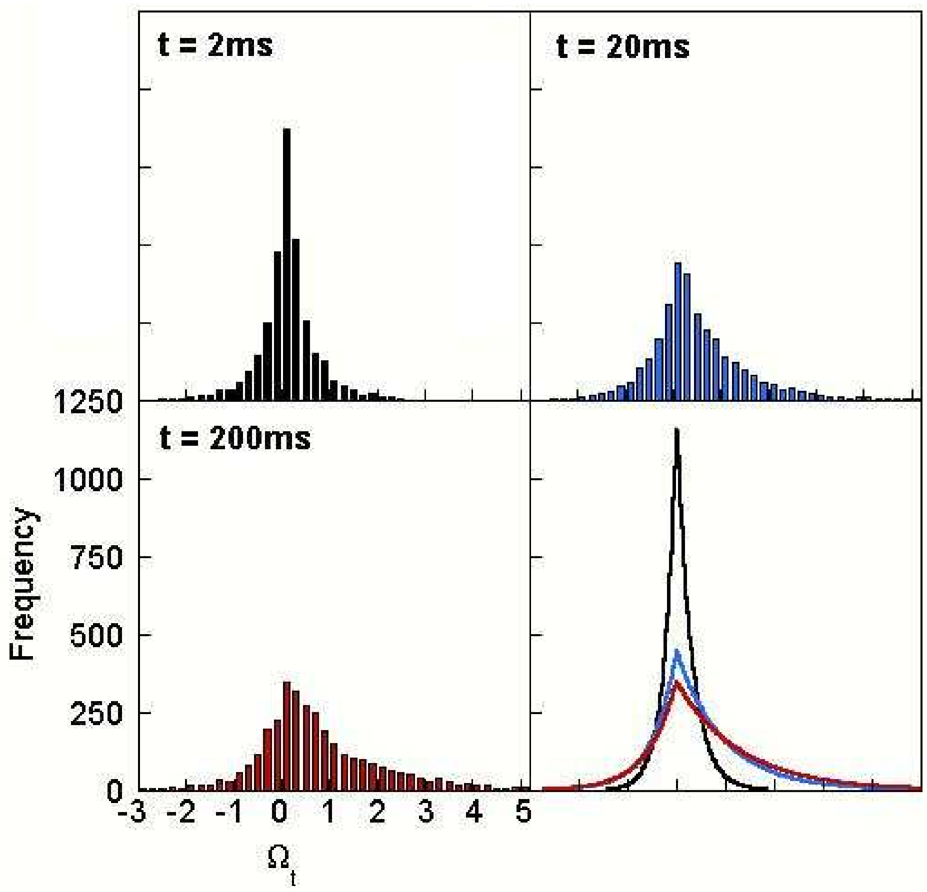
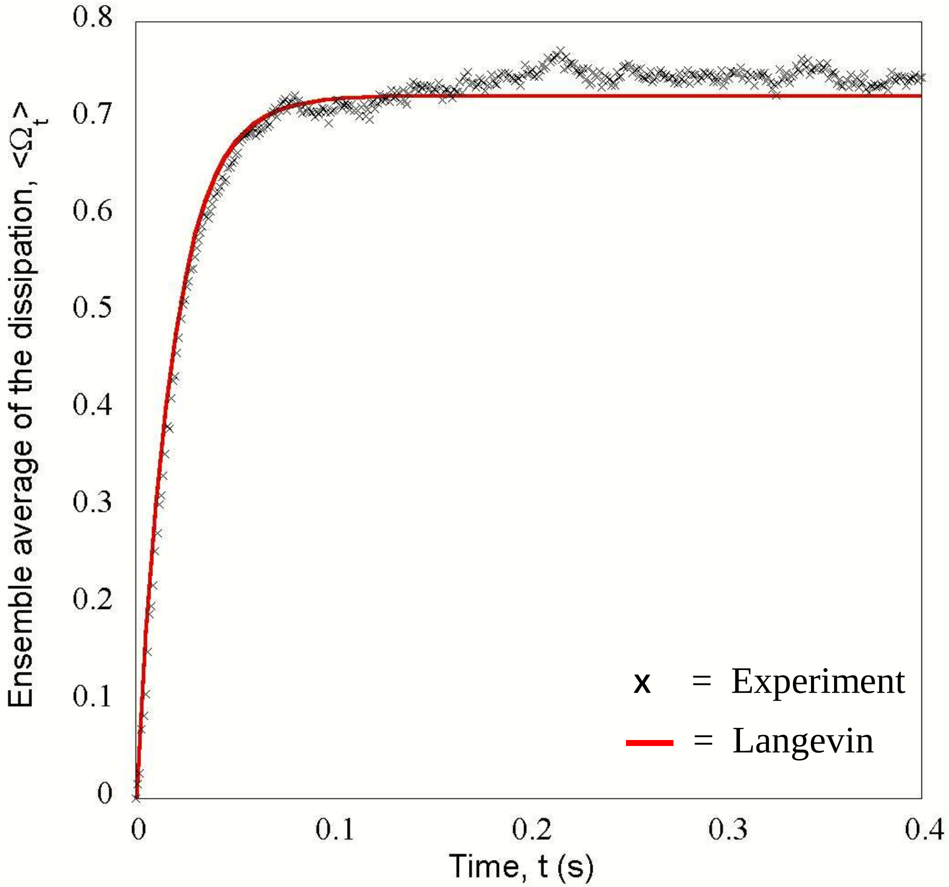
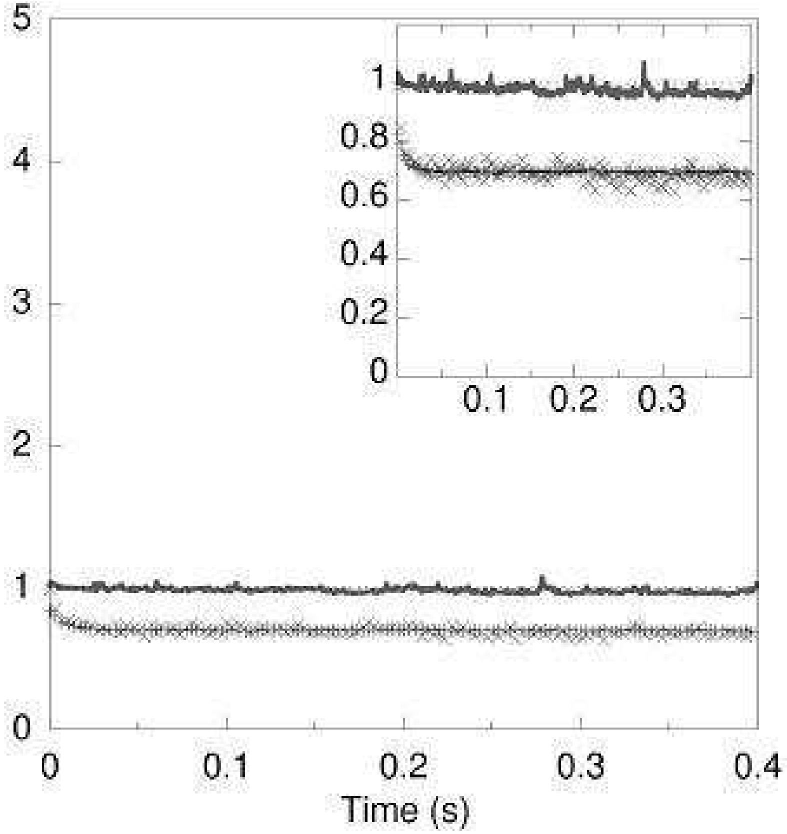
Capture Experiment Results

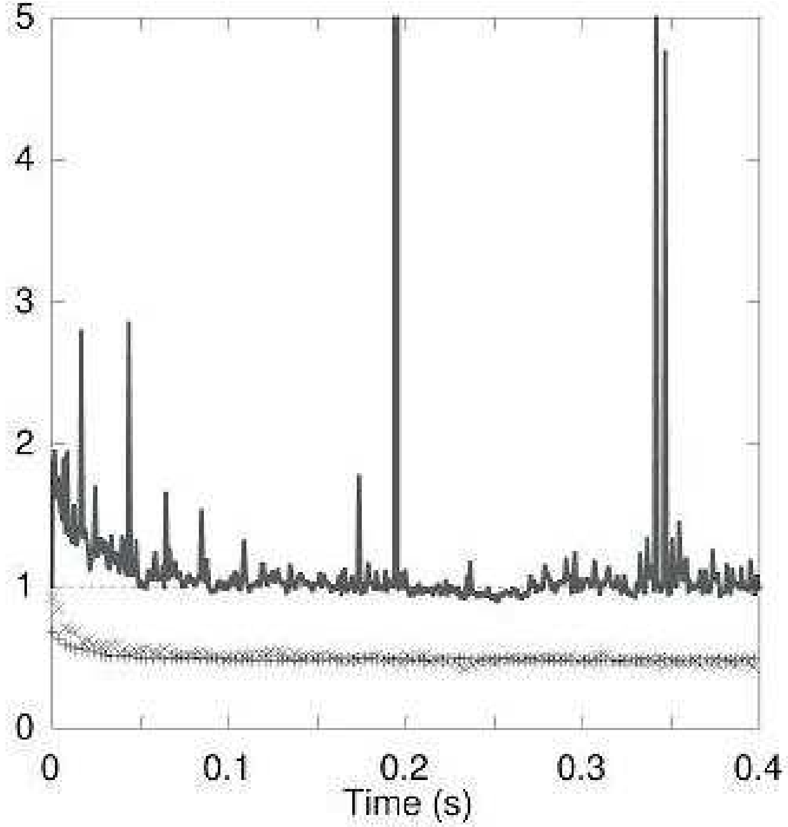




Applications of the Kawasaki Identity

$$\langle \exp(-\Omega_t) \rangle = 1$$





D.M. Carberry, S.R. Williams, G.M. Wang, E.M. Sevick, D.J. Evans, *J. Chem. Phys.* **121**, 8179 (2004).

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The Steady-State Fluctuation Theorem (SSFT)

Dissipation Fn:

$$\Omega_t = \ln\left[\frac{P(\partial V)}{P(\partial V^*)}\right]$$

Under deterministic dynamics, *t=0* must correspond to an equilibrium state

$$\Omega_t = \int_0^t ds\dot{\Omega}(s)$$

$$= \int_0^\tau ds\dot{\Omega}(s) + \underbrace{\int_\tau^t ds\dot{\Omega}(s)}_{\Omega_t^{ss}}$$

$$\lim_{t/\tau\to\infty} \Omega_t^{ss} \approx \Omega_t$$

$$\frac{P(\Omega_t = -A)}{P(\Omega_t = A)} = \exp(-A)$$

$$\lim_{t/\tau\to\infty} \frac{P\left(\Omega_t^{ss} = -A\right)}{P\left(\Omega_t^{ss} = A\right)} \approx \exp(-A)$$

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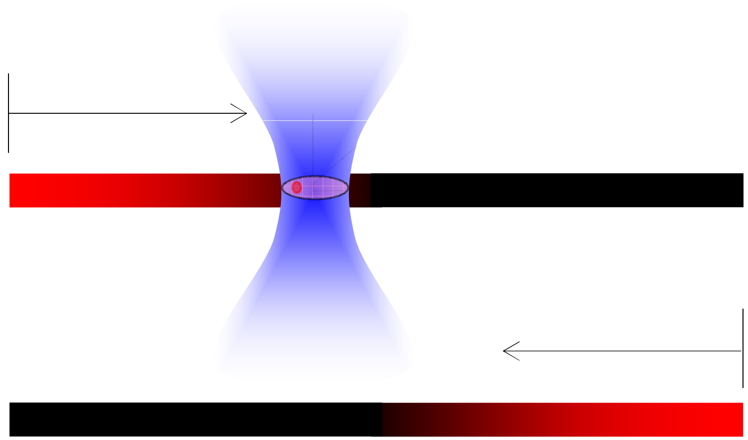
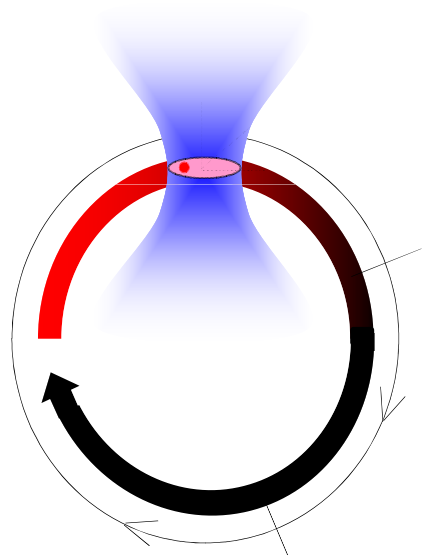
Fluctuation Theorem (FT) under transient & steady-state conditions

0 < t < 20 second trajectories
0.29 μm/s linear velocity
k = 0.48 pN/μm

7.3 μm diameter at 4 mHz
0.18 μm/s linear velocity
k = 0.12 pN/μm



Multiple linear drag trajectories



Single circular drag trajectory

Wang, *et al.*, Phys. Rev. E **71**, 046142 (2005).

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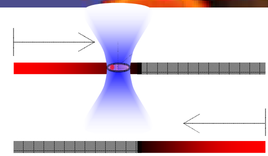
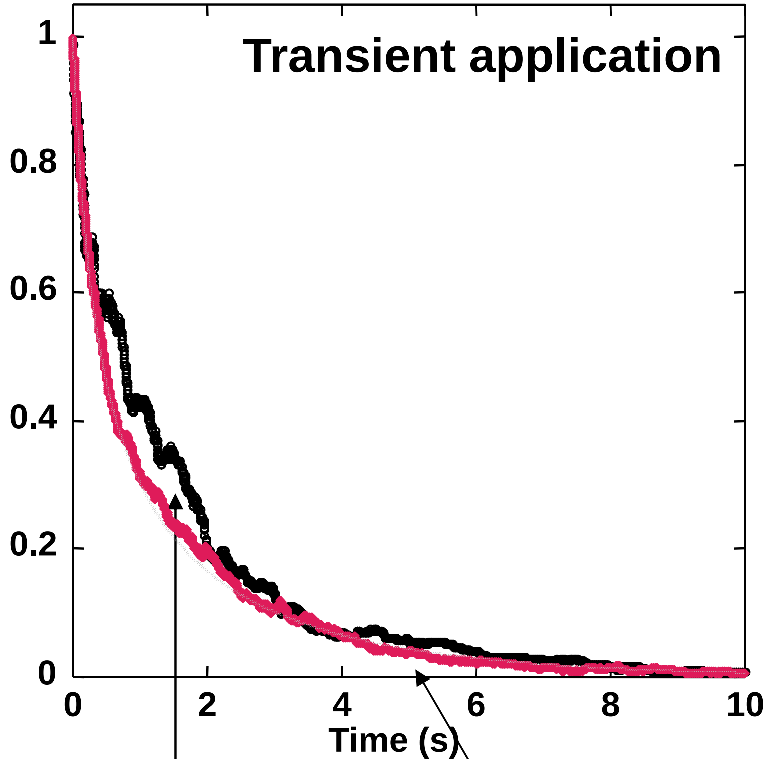
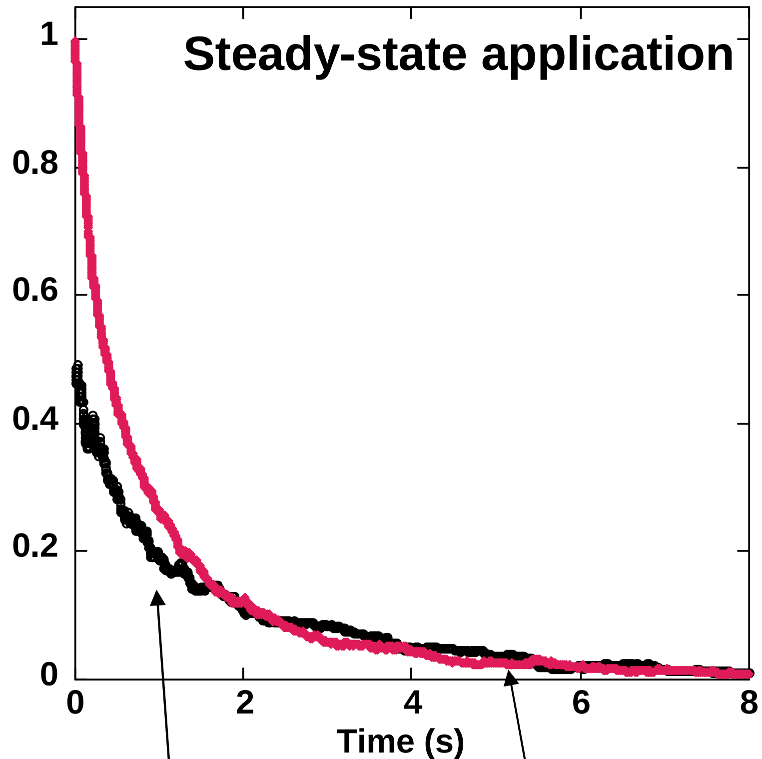
Deterministic dissipation function:



$$\Omega_t = \frac{1}{k_B T}\int_0^t ds\, \boldsymbol{F}_{opt}\cdot \boldsymbol{v}_{opt}$$





$$\frac{P(\Omega_t<0)}{P(\Omega_t>0)} = \left\langle \exp(-\Omega_t)\right\rangle_{\Omega_t>0}$$

$$\lim_{t\to\infty}\frac{P(\Omega_t^{ss}<0)}{P(\Omega_t^{ss}>0)} = \left\langle\exp(-\Omega_t^{ss})\right\rangle_{\Omega_t^{ss}>0}$$

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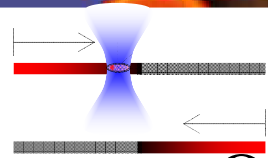
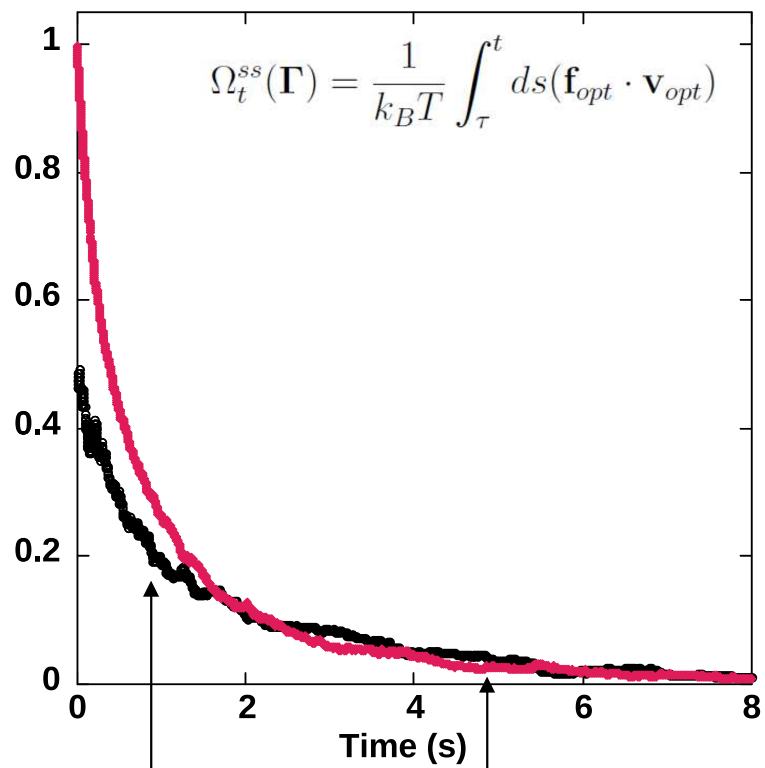
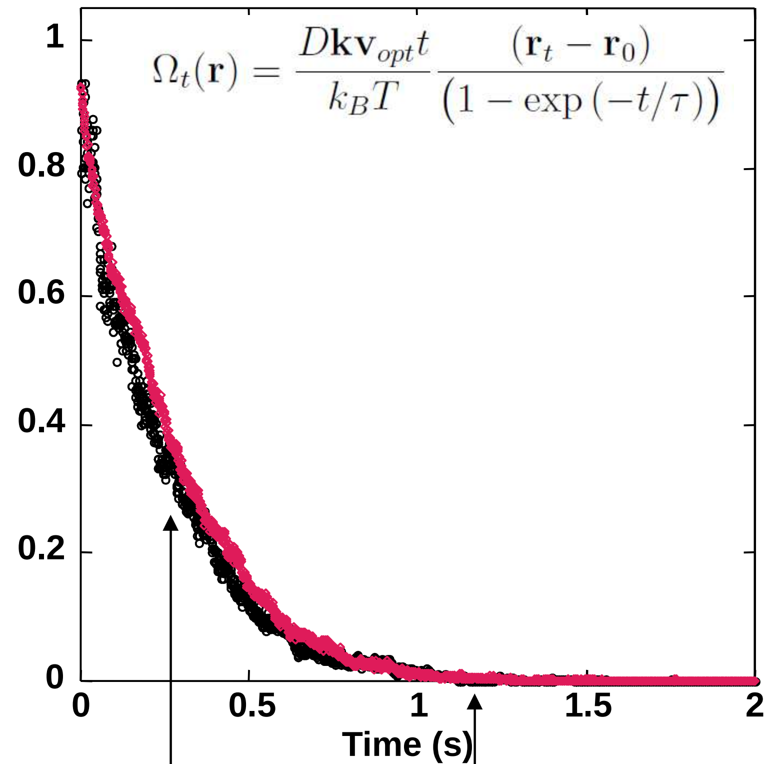


Deterministic (approx) Ω_t^{SS} — Stochastic (exact) Ω_t





$$\lim_{t\to\infty}\frac{P(\Omega_t^{ss}<0)}{P(\Omega_t^{ss}>0)} = \left\langle \exp(-\Omega_t^{ss})\right\rangle_{\Omega_t^{ss}>0}$$

$$\frac{P(\Omega_t<0)}{P(\Omega_t>0)} = \left\langle \exp(-\Omega_t)\right\rangle_{\Omega_t>0}$$

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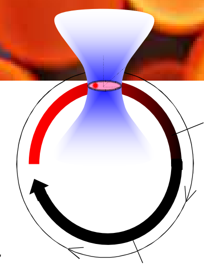
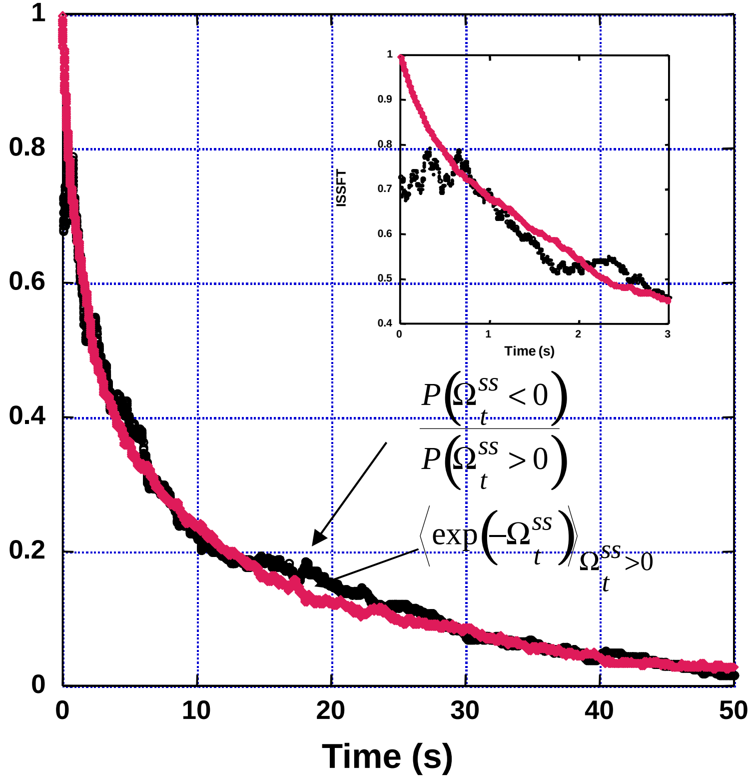
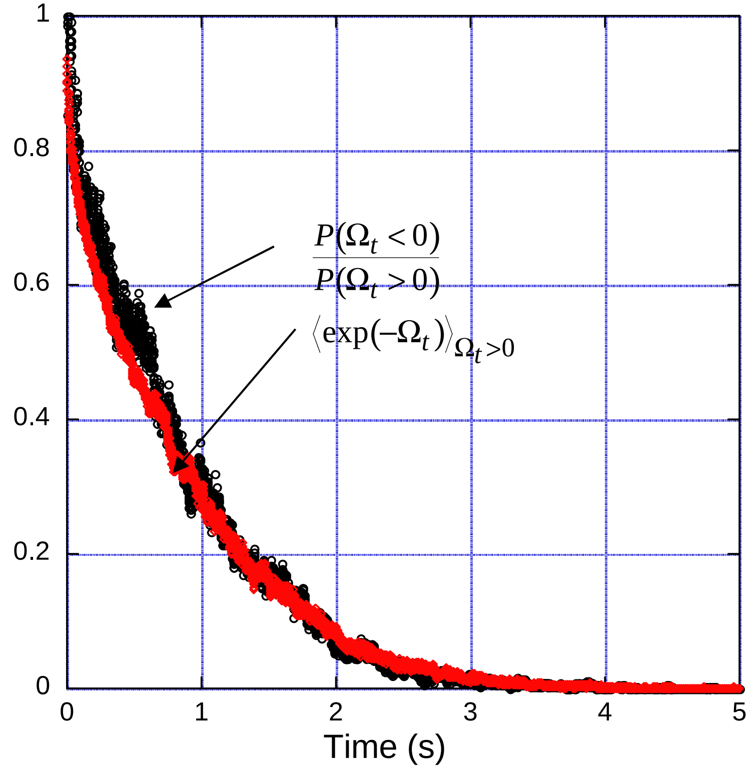


Steady-state circular drag

Deterministic (approx) Ω_t^{ss}



Stochastic (exact) Ω_t



$$\lim_{t\to\infty} \frac{P(\Omega_t^{ss}<0)}{P(\Omega_t^{ss}>0)} = \left\langle \exp(-\Omega_t^{ss}) \right\rangle_{\Omega_t^{ss}>0}$$

$$\frac{P(\Omega_t<0)}{P(\Omega_t>0)} = \left\langle \exp(-\Omega_t) \right\rangle_{\Omega_t>0}$$

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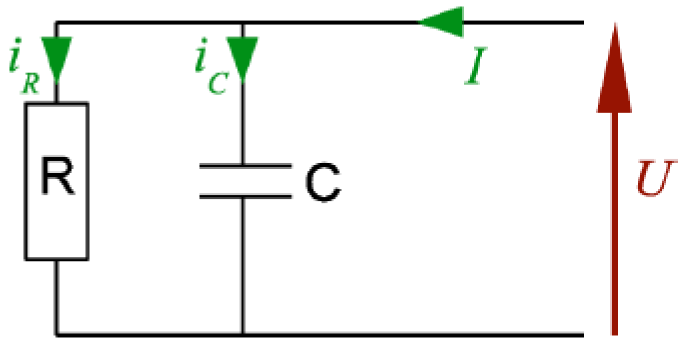
Other FT Experiments

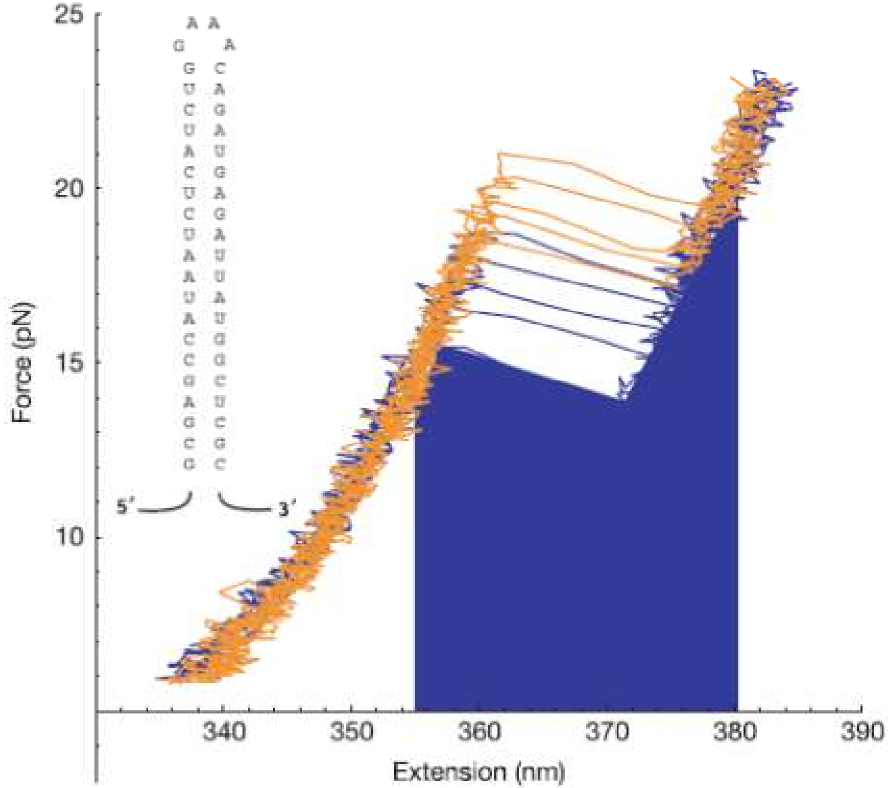
N. Garnier, and S. Ciliberto, "Nonequilibrium fluctuations in a resistor," *Phys. Rev. E* **71**, 060101 (2005). doi:10.1103/PhysRevE.71.060101

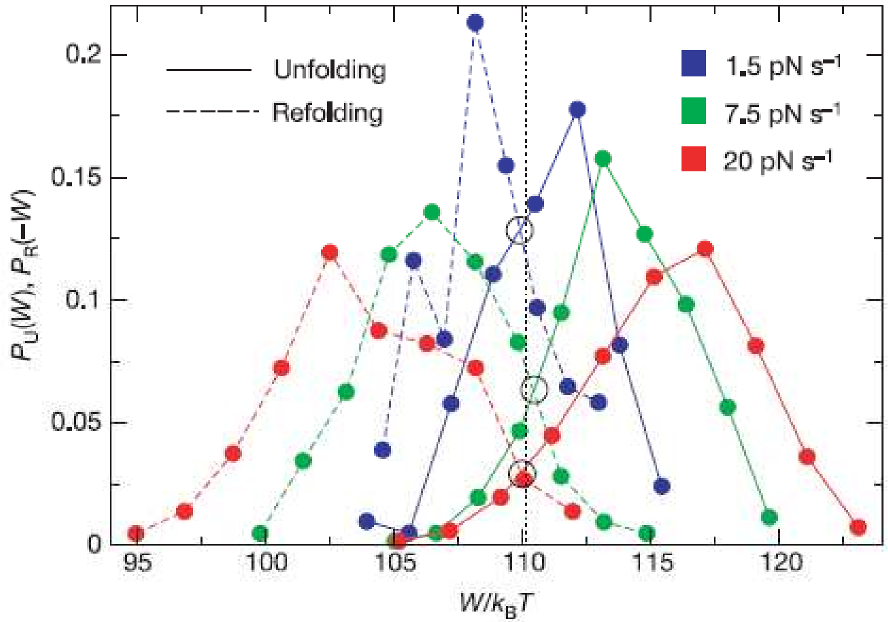


C. Tietz, S. Schuler, T. Speck, U. Seifert, and J. Wrachtrup, "Measurement of Stochastic Entropy Production," *Phys. Rev. Lett.* **97**, 050602 (2006). doi:10.1103/PhysRevLett.97.050602

V. Blickle, T. Speck, L. Helden, U. Seifert, and C. Bechinger, "Thermodynamics of a Colloidal Particle in a Time-Dependent Nonharmonic Potential," *Phys. Rev. Lett.* **96**, 070603 (2006). doi:10.1103/PhysRevLett.96.070603

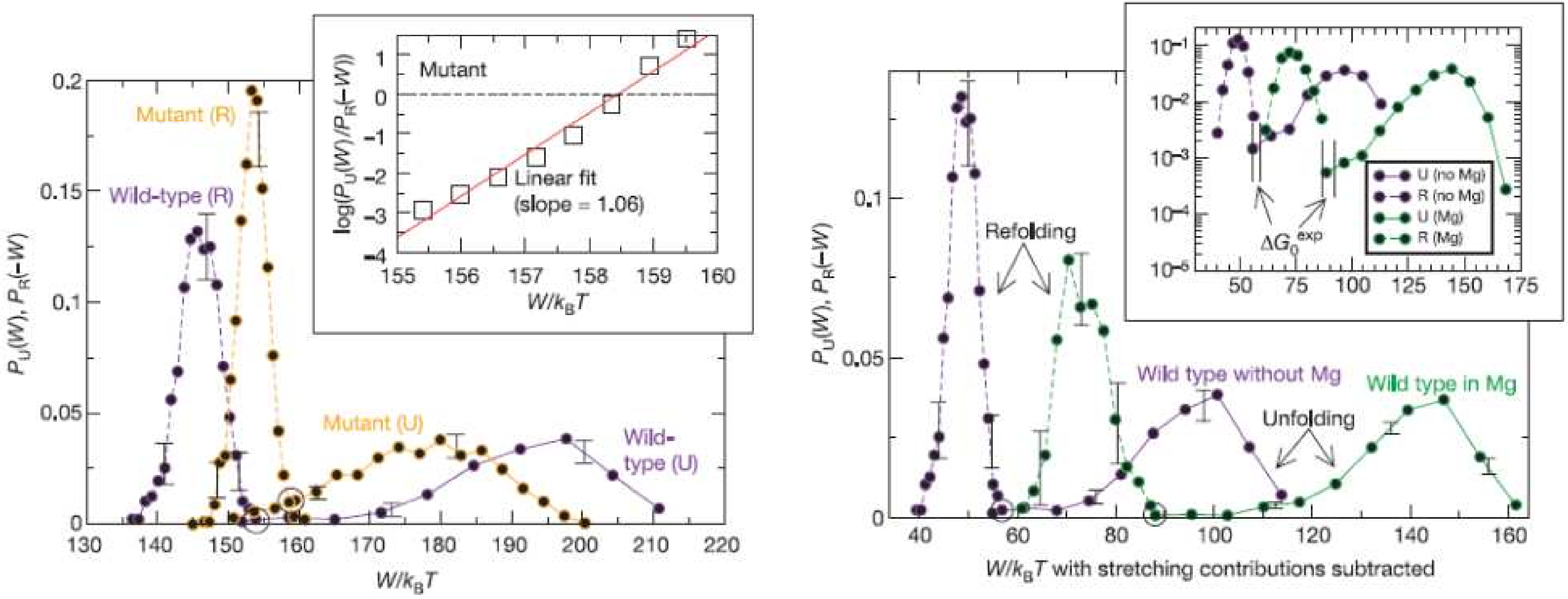
CR/JE Experiments





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

CR/JE Experiments



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

Conclusions

- FT applies to paths, results in 2nd law irreversibility – end points must be time reversible!
- The CR and WR tell the Free Energy change between two states.
- Almost ANY nanoscience experiments which uses energy is likely to be affected in some way by this! Whether it be a molecular motor walking along a fibril, or measuring the reaction kinetics between lipids.

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