The 5th East Asian Joint Seminars on Statistical Physics
2019.10.22-2019.10.25

Hierarchic Structure of Fluctuation Theorems and Experimental Tests of Differential Fluctuation Theorems

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Reference: Phys. Rev. E 92, 012131 (2015)
Phys. Rev. Lett., 120, 080602 (2018)

outline

- Background and Motivation
- Hierarchic Structure of Fluctuation Theorems
- Experimental Verification
- Summary

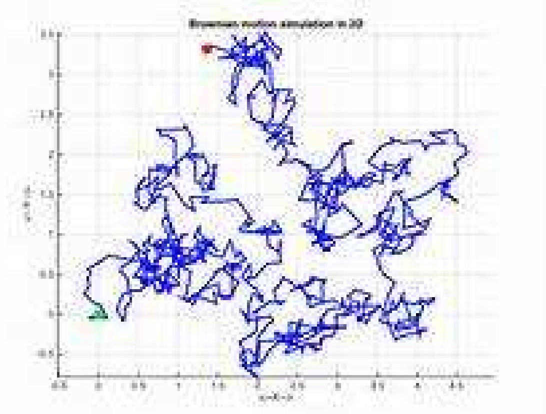
Basic notions of stochastic thermodynamics

Work, heat and Entropy as functionals of a trajectory

Work: $dw = \frac{\partial H_\lambda(x(t))}{\partial \lambda} \dot{\lambda} dt$ Heat: $dq = \frac{\partial H_\lambda(x(t))}{\partial x} \dot{x} dt$

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

K. Sekimoto, J. Phys. Soc. Jap. 66, 1234 (1



For overdamped Langevin Dynamics

$$\dot{x} = \mu F(x,\lambda) + \zeta = \mu[-\partial_x V(x,\lambda) + f(\lambda)] + \zeta,$$

$$\langle \zeta(\tau)\zeta(\tau')\rangle = 2D\delta(\tau - \tau')$$

Heat: $dq = (1/\mu)(\dot{x} - \zeta)dx$

Work: $dw = f dx + \partial_\lambda V(x,\lambda) d\lambda$

Ken Sekimoto,
Stochastic Energetics
(2010)

First Law in stochastic thermodynamics

First Law: energy balance for a trajectory

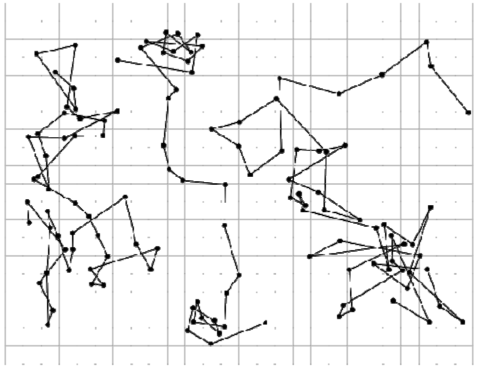
$$m\ddot{x} = -\frac{\partial U(x,\lambda)}{\partial x} + [-\gamma\dot{x} + \xi(t)]$$

for a small step dx

$$d[\frac{1}{2}m\dot{x}^2 + U(x,\lambda)] = \frac{\partial U(x,\lambda)}{\partial \lambda}d\lambda + [-\gamma\dot{x} + \xi(t)]dx$$

$$dE \quad = \quad \Delta W \quad + \quad \Delta Q$$

change of internal energy	work by external operation	heat production in the medium

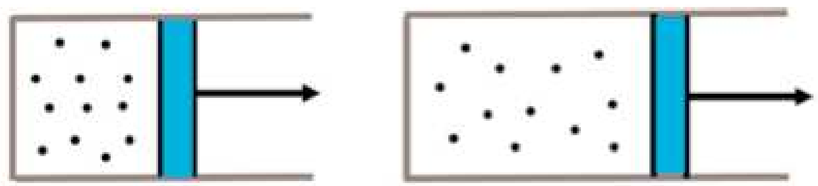


K. Sekimoto, *Progr. Theor. Exp. Phys.*, 130:17–27, 1998

Timeline of the second law

- Maximum Work Principle (1876)

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



- Fluctuation-Dissipation relation (1950)

$$\langle W\rangle - \Delta F = \frac{1}{2}\beta\sigma_W^2$$

- Jarzynski equality (1997)

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

$$\langle e^{x}\rangle \geq e^{\langle x\rangle}$$

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

- Crooks Fluctuation Theorem (1998)

$$\frac{P_R(-W)}{P_F(W)} = e^{-\beta(W-\Delta F)}$$

- Hummer-Szabo relation (2001)

$$\langle \delta(\tilde{\Gamma}-\Gamma_\tau)e^{-\beta W}\rangle = \frac{e^{-\beta U_\tau(\tilde{\Gamma})}}{Z_0}$$

- Differential Fluctuation Theorem (2008)

$$P_F(W,\Gamma_0\to\Gamma_\tau)e^{-\beta(W-\Delta F)} = P_R(-W,\Gamma_\tau^*\to\Gamma_0^*)$$

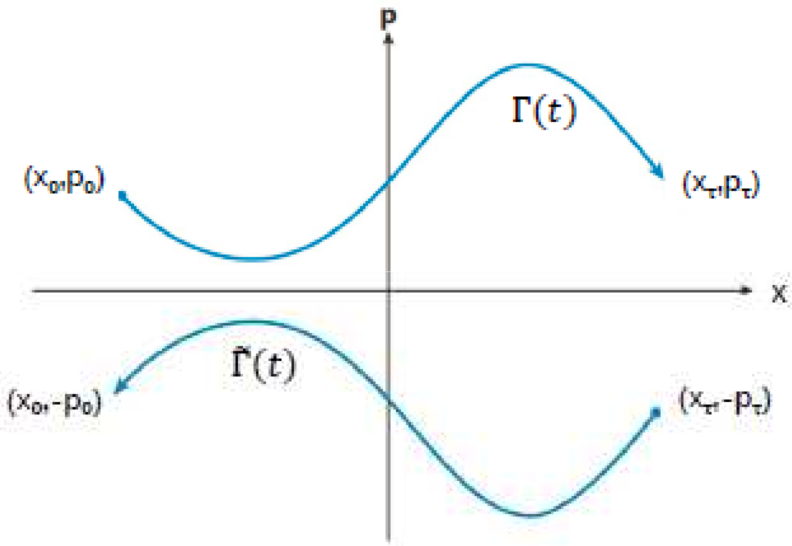
Time reversed: $\bar{\lambda}_t = \lambda_{\tau-t}$

What is the origin of fluctuation theorems?

Microscopic reversibility [3,4,8,22]:

$$\ln \frac{p(\Gamma(t)|\Gamma_0)}{\tilde{p}(\tilde{\Gamma}(t)|\tilde{\Gamma}_0)} = -\beta Q[\Gamma(t)]$$

$$\tilde{\lambda}_t := \lambda_{\tau-t}, \tilde{\Gamma}_t := (x_{\tau-t}, -p_{\tau-t})$$



Impossible to test it in experiment!

How about it if we do a little bit coarse-graining?

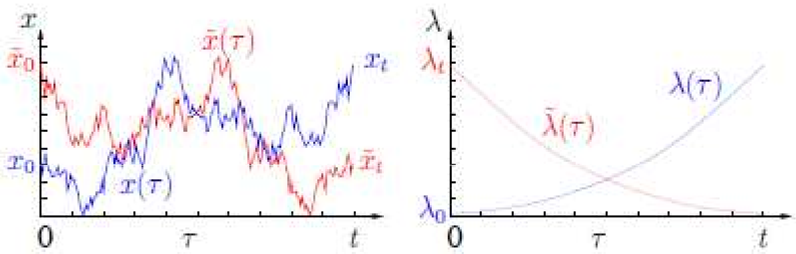
[3] G. E. Crooks, Phys. Rev. E 60, 2721 (1999).
[4] U. Seifert, Phys. Rev. Lett. 95, 040602 (2005).
[8] G. E. Crooks. *Journal of Statistical Physics* 90.5-6 (1998).
[22] C. Jarzynski, Annu. Rev. Condens. Matter Phys. 2, 329 (2011).

Proof of the microscopic reversibility

- Path integral representation
  - "Boltzmann factor for a whole trajectory"

$$p[\zeta(\tau)] \sim \exp\ [-\int_0^t d\tau\ \zeta^2(\tau)/4D]$$

$$p[x(\tau)|x_0] \sim \exp\ [-\int_0^t d\tau\ (\dot{x} - \mu F)^2/4D]$$



Lars Onsager

  - "time reversal" $\tilde{x}(\tau) \equiv x(t-\tau)$ and $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$
  - Ratio of forward to reversed path

$$\frac{p[x(\tau)|x_0]}{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]} = \frac{\exp\ [-\int_0^t d\tau\ (\dot{x} - \mu F)^2/4D]}{\exp\ [-\int_0^t d\tau\ (\dot{\tilde{x}} - \mu \tilde{F})^2/4D]}$$

$$= \exp\ \beta \int_0^t d\tau\ \dot{x}F = \exp\ \beta q[x(\tau)] = \exp \Delta s_m$$

L. Onsager, S. Machlup, Phys. Rev. 91, 1505 (1953).

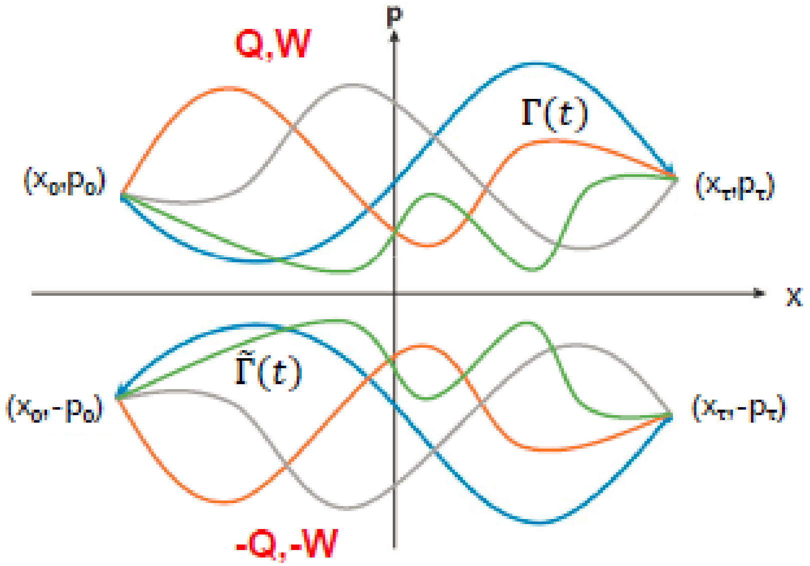
Differential fluctuation theorem (DFT)

- **DFT version 1** (2000, Jarzynski) [9]:

$$\frac{P_R\left(-Q,\Gamma_0^\dagger|\Gamma_\tau^\dagger\right)}{P_F(Q,\Gamma_\tau|\Gamma_0)} = e^{\beta Q}$$

- **DFT version 2** (2008, Karplus) [10]:

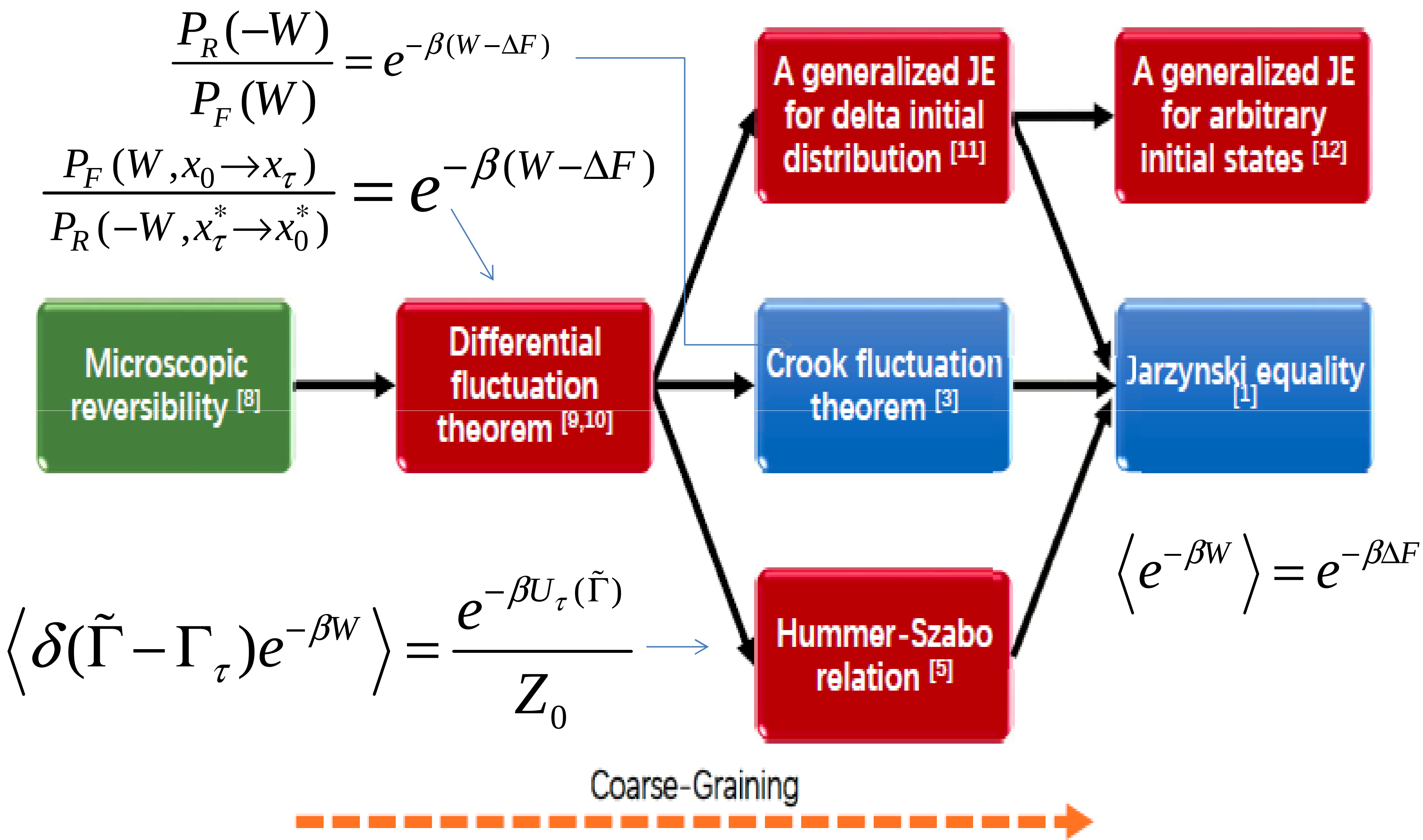
$$\frac{P_R\left(-W,\Gamma_\tau^\dagger\rightarrow\Gamma_0^\dagger\right)}{P_F(W,\Gamma_0\rightarrow\Gamma_\tau)} = e^{-\beta(W-\Delta F)}$$



The most detailed fluctuation theorem that can be tested **experimentally**.

[9] C. Jarzynski, J. Stat. Phys. 98, 77 (2000).
[10] P. Maragakis, et al. J. Phys. Chem. B 112, 6168 (2008).

Hierarchy of fluctuation theorems

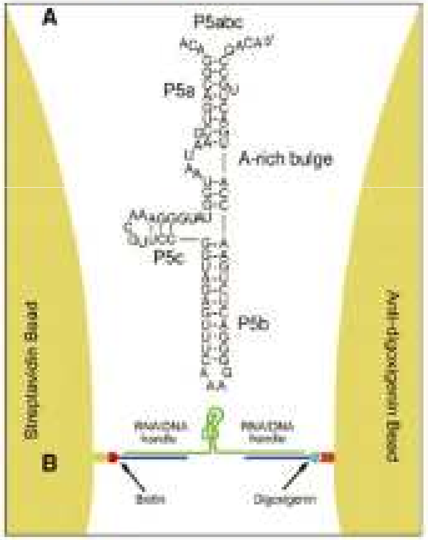


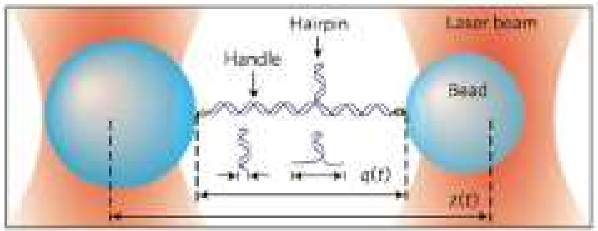
Z. Gong, **HTQ**, Phys. Rev. E 92, 012131 (2015)

Previous experiments

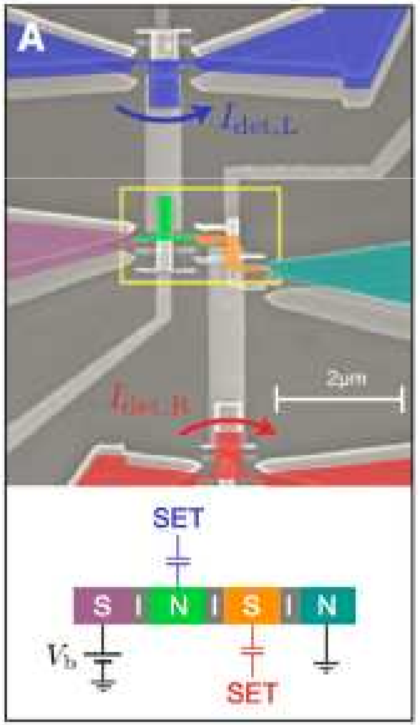
[13] J. Liphardt, et al. Science 296, 1832 (2002).
[14] D. Collin, et al. Nature (London) 437, 231 (2005).
[15] A. N. Gupta, et al. *Nature Physics* 7,631 (2011).
[16] E. Trepagnier, et al. Proc. Natl. Acad. Sci. 101, 15038 (2004)
[17] D. Y. Lee, et al. Phys. Rev. Lett. 114, 060603 (2015).
[24] J. P. Pekola, Nat. Phys. 11, 118 (2015).
[25] S. Singh, et al. *arXiv:1712.01693* (2017).

Stretching RNA molecules [13-15]

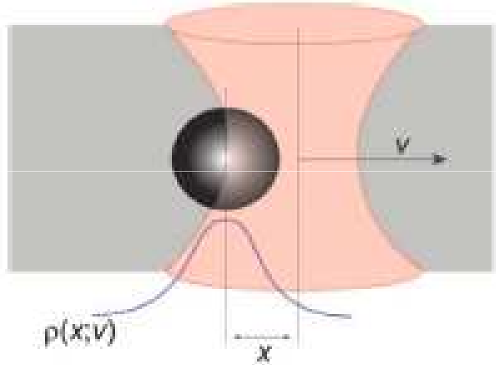


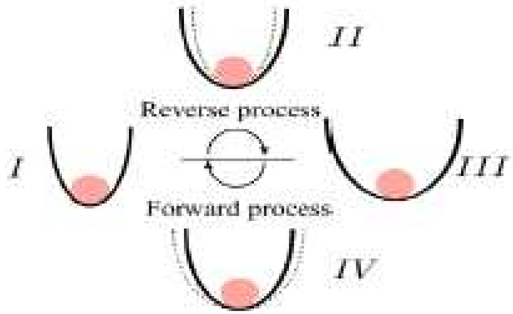


Electronic circuit [24,25]



Brownian particle trapped in water [16,17]

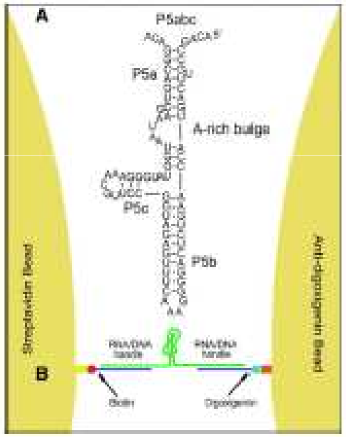


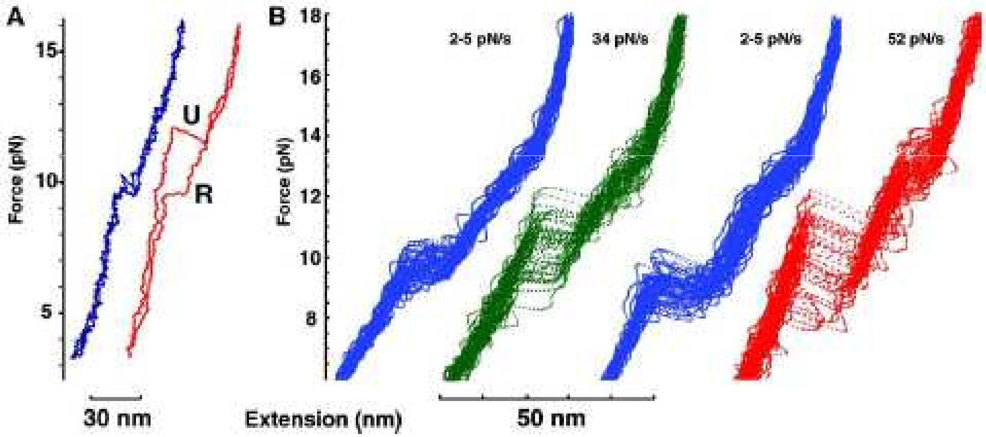


Experimental test of Jarzynski's equality

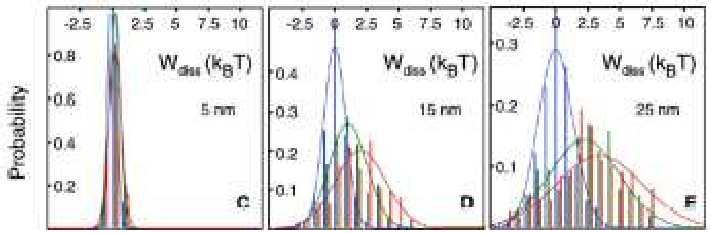
- Nano-world Experiment: Stretching RNA

  [Liphardt et al, Science **296** 1832, 2002.]



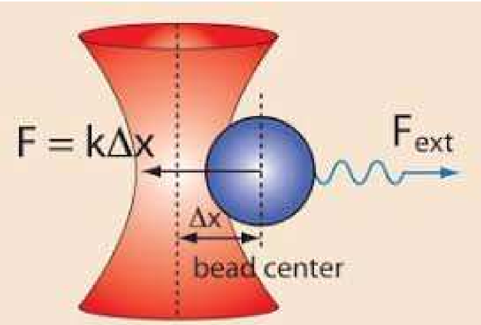


– distributions of W_{diss}:



Arthur Ashkin
“Optical tweezer”

Key application:
Study of Stochastic thermodynamics



KUNGL. VETENSKAPS-AKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

The Nobel Prize in Physics 2018

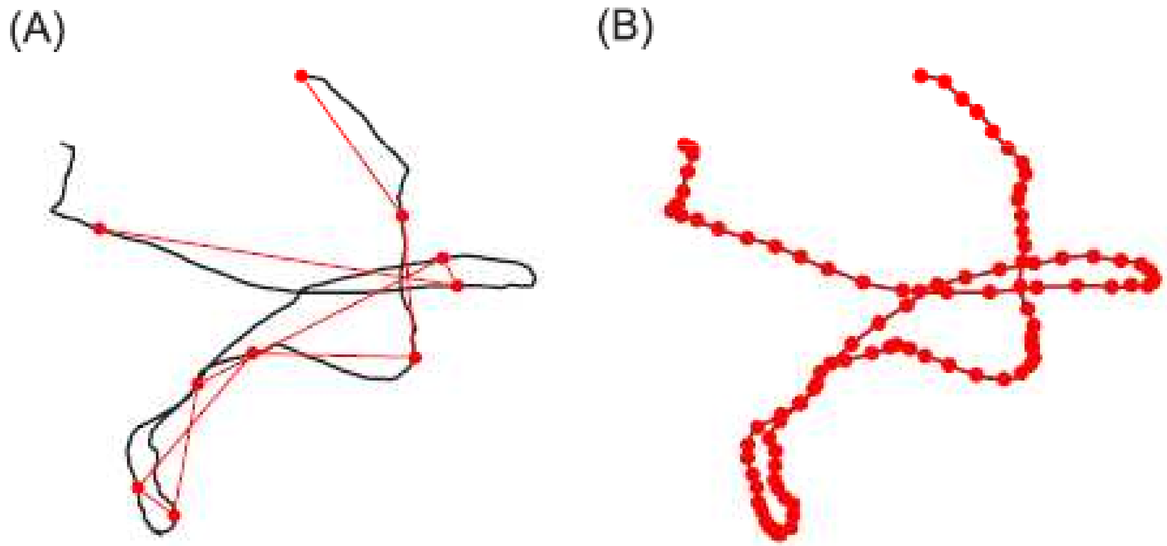
Ill. Niklas Elmehed. © Nobel Media
Arthur Ashkin
Prize share: 1/2

Ill. Niklas Elmehed. © Nobel Media
Gérard Mourou
Prize share: 1/4

Ill. Niklas Elmehed. © Nobel Media
Donna Strickland
Prize share: 1/4

RNA molecules under mechanical force [36]. Force-extension curves for an RNA molecule were subsequently used for the first experimental test [37] of Jarzynski’s equality in stochastic thermodynamics, which relates nonequilibrium work distributions to equilibrium free energy differences [38].

However, the experimental test of the differential fluctuation theorems requires that the measurement of the instantaneous velocity of the Brownian particle



T. Li et al Science, 328, 1673 (2010)

and it was thought to be impossible task by Einstein in 1907

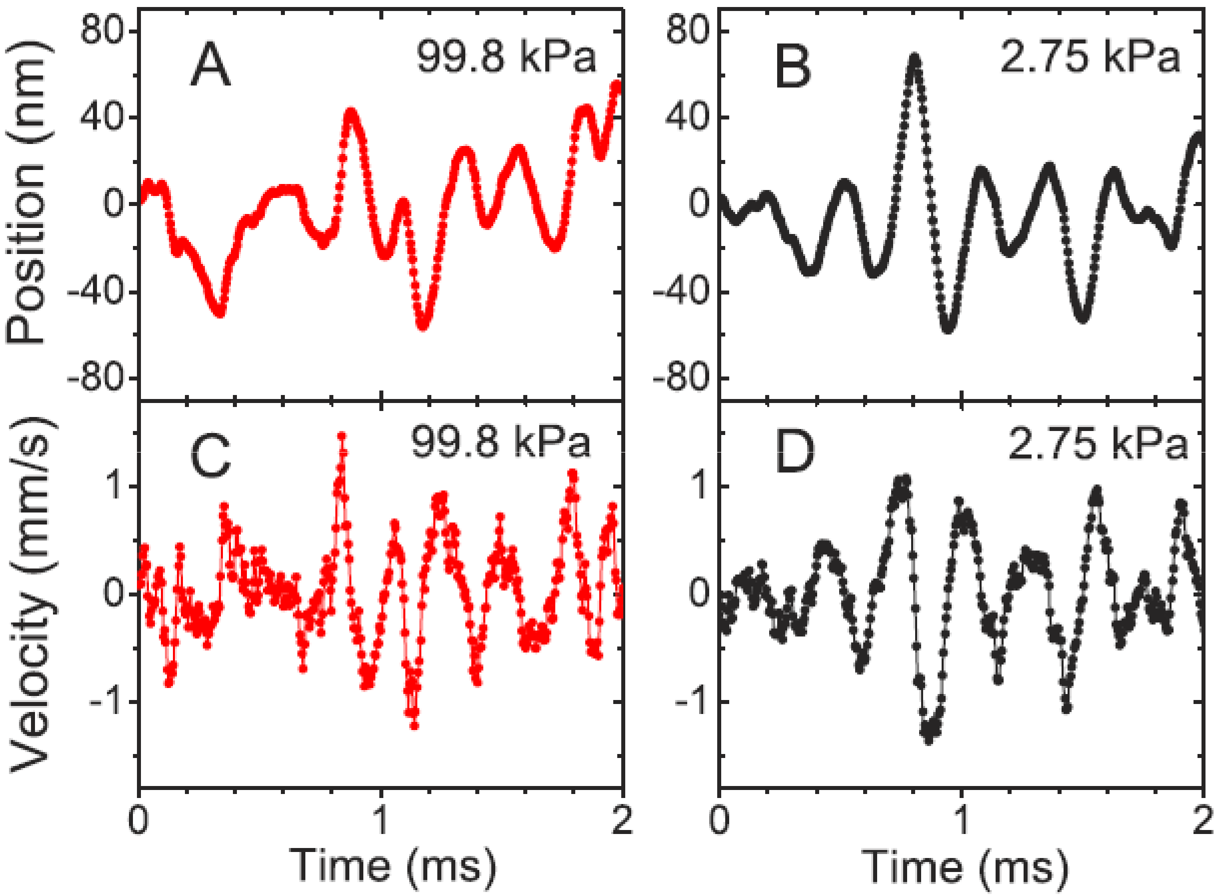
A. Einstein , *Zeit. F. Elektrochemie*, **13**, 41-42 (1907).
translated in A. Einstein, Investigations on the Theory of the Brownian movement, Dover, New York,1956

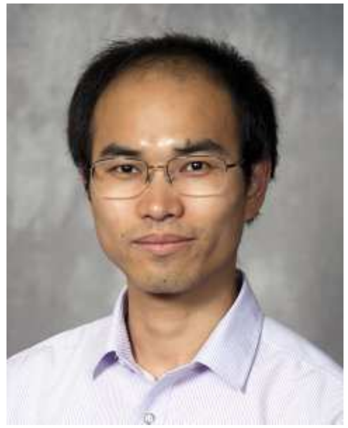
tion of motion and velocity of the particle, we must conclude that the velocity and direction of motion of the particle will be already very greatly altered in the extraordinary short time θ, and, indeed, in a totally irregular manner.

It is therefore impossible—at least for ultra-microscopic particles—to ascertain $\sqrt{\overline{v^2}}$ by observation.

$$\theta = 3 \cdot 3 \, . \, 10^{-7} \text{ seconds.}$$

Technical breakthrough:





Tongcang Li

(Purdue University)

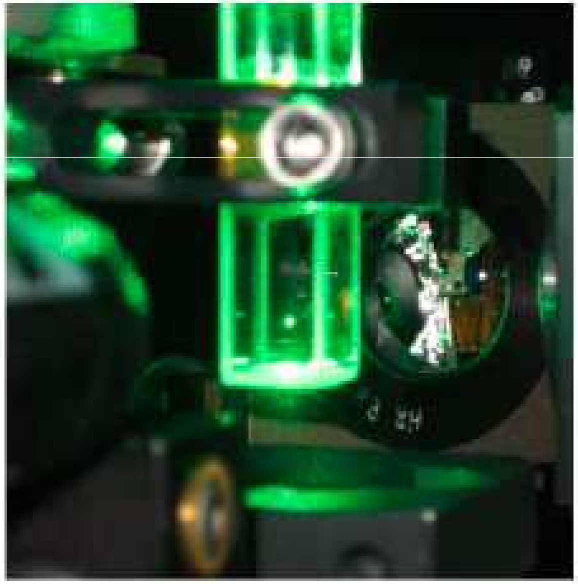
T. Li et al Science, 328, 1673 (2010)

Measurement of instantaneous velocity of a Brownian Motion

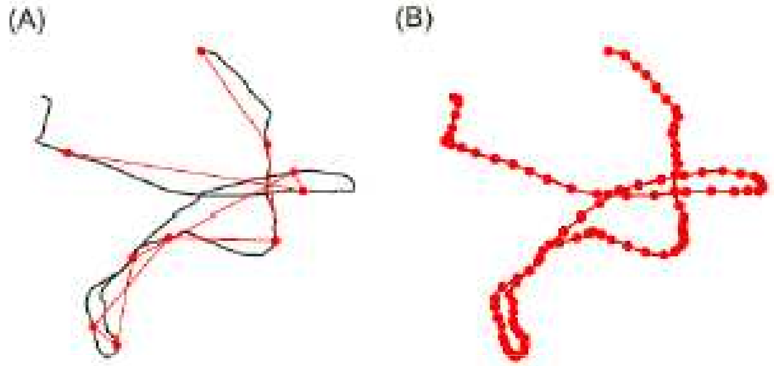
Our experiment

[18] T. Li, et al. Science 328, 1673 (2010).
[19] S. Kheifets et al. Science 343, 1493 (2014) .
[20] T. M. Hoang, et al. Nat. Commun. 7, 12250 (2016).

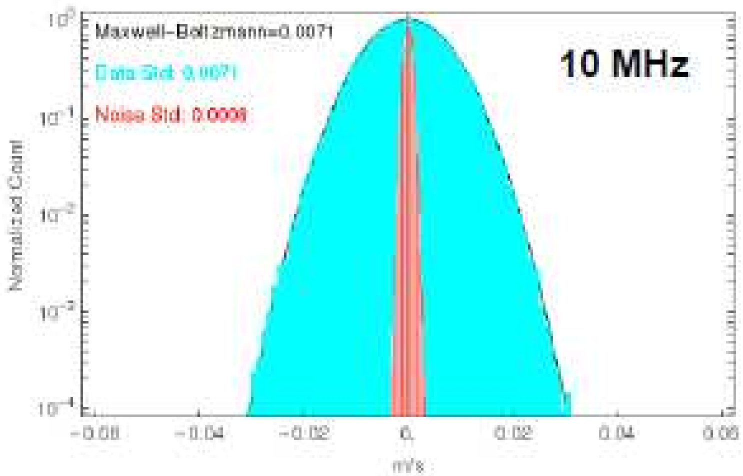
Silica nanosphere levitated in **AIR** using optical tweezers [18-20]



We can study the thermodynamics of the **phase space**.



Measurement of the instantaneous velocity



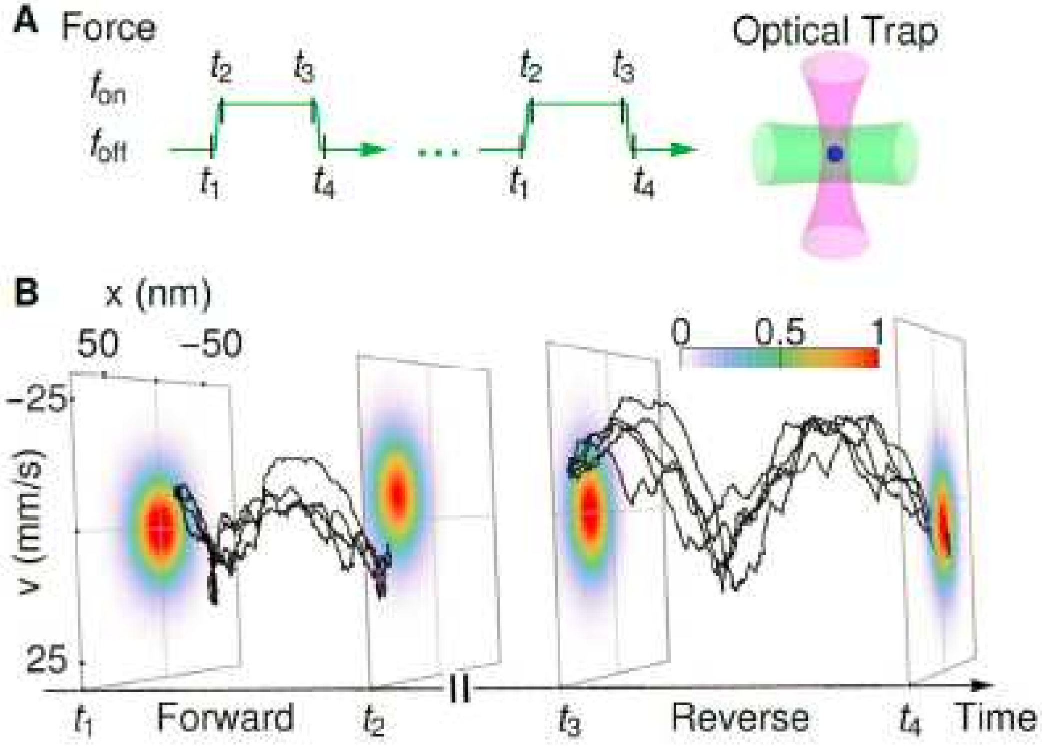
Our experiment

- In air, room temperature (296K)

  $H(x, v, t) = \frac{1}{2}kx^2 - f(t)x + \frac{1}{2}mv^2$

  $f(t)$: $f_{off} \rightarrow f_{on}$

  $\Delta F = -\frac{f_{on}^2 - f_{off}^2}{2k}$, $W = \int_0^{\tau} \frac{\partial H}{\partial f} \dot{f}(t) dt$



- Challenges of our experiment:
  - ➢ Very large statistics

    > **one million** cycles, **500** μs /cycle

    ~10^{10} data points in the phase space with 10 MHz acquisition rate
  - ➢ Track individual trajectories in the phase space (instantaneous velocity measurement)

Test the differential fluctuation theorem

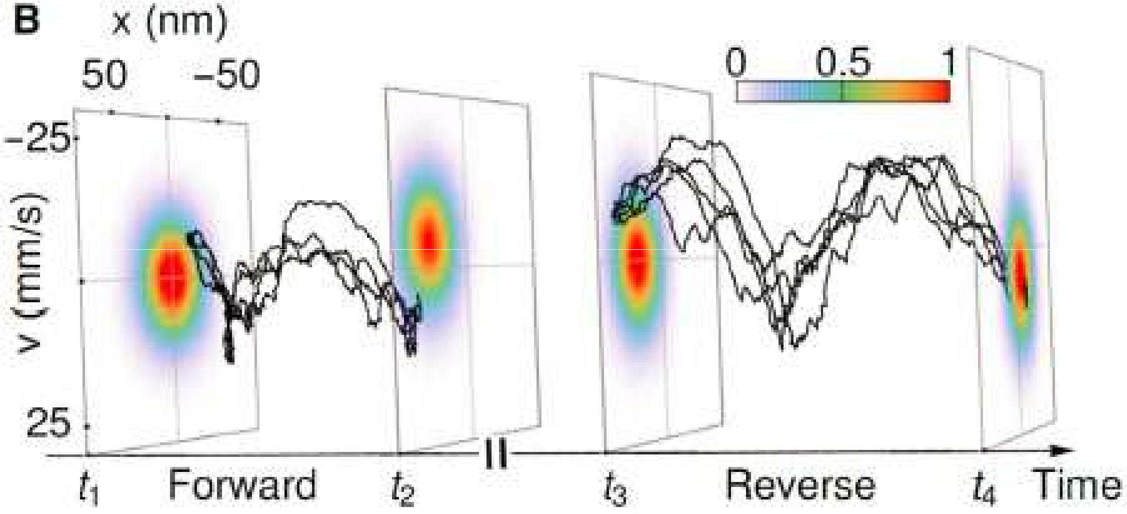
- Underdamped regime (50 Torr)

$$\frac{P_R(-W, x_2 \to x_1)}{P_F(W, x_1 \to x_2)} = e^{-\beta(W - \Delta F)}$$

$$\frac{P_R(-W, -v_2 \to -v_1)}{P_F(W, v_1 \to v_2)} = e^{-\beta(W - \Delta F)}$$

$(x, v) \coloneqq (x \pm \frac{\sigma_x}{11}, v \pm \frac{\sigma_v}{11})$

121 combinations of $\{x_1, x_2\}$ or $\{v_1, v_2\}$



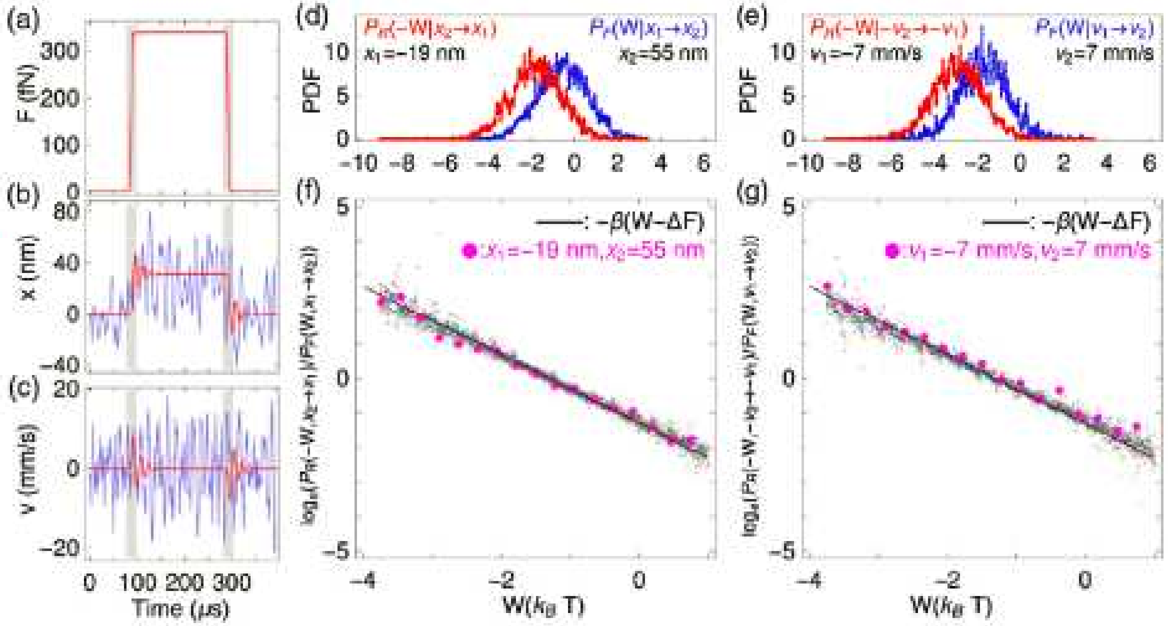
Test the differential fluctuation theorem

- Underdamped regime (50 Torr)

$$\frac{P_R(-W, x_2 \to x_1)}{P_F(W, x_1 \to x_2)} = e^{-\beta(W-\Delta F)}$$

$$\frac{P_R(-W, -v_2 \to -v_1)}{P_F(W, v_1 \to v_2)} = e^{-\beta(W-\Delta F)}$$

- $f_{off} = 0, f_{on} = 340\ fN$
- Ramp time $\sim 4.6\ \mu s$
- Particle size $r = 209 \pm 9\ nm$
- $\Omega = 60.4 \pm 0.3\ (2\pi \cdot kHz)$
- $\Delta F = -1.3\ k_B T$



Test the GJE for delta distribution and the HSR

- **GJE for delta distribution:**

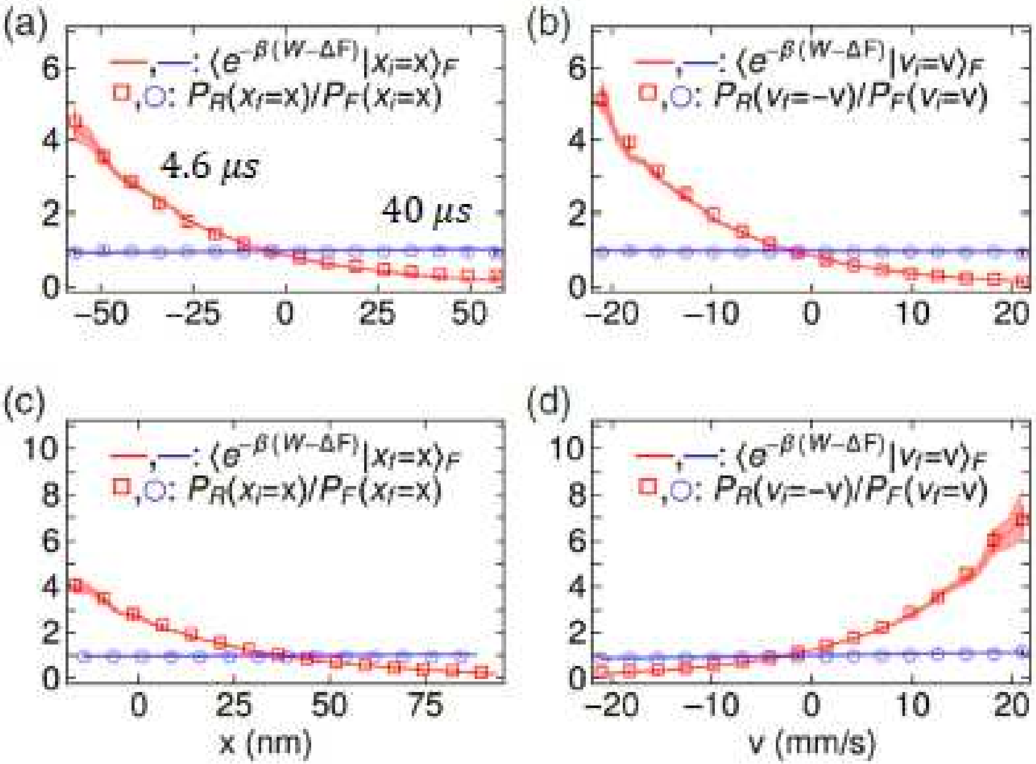
$$\left\langle e^{-\beta(W-\Delta F)} \middle| x_i = x \right\rangle_F = \frac{P_R(\tilde{x}_f = x)}{P_F^{eq}(x_i = x)}$$

$$\left\langle e^{-\beta(W-\Delta F)} \middle| v_i = v \right\rangle_F = \frac{P_R(\tilde{v}_f = -v)}{P_F^{eq}(v_i = v)}$$

- **HSR:**

$$\left\langle e^{-\beta(W-\Delta F)} \middle| x_f = x \right\rangle_F = \frac{P_R^{eq}(\tilde{x}_i = x)}{P_F\,(x_f = x)}$$

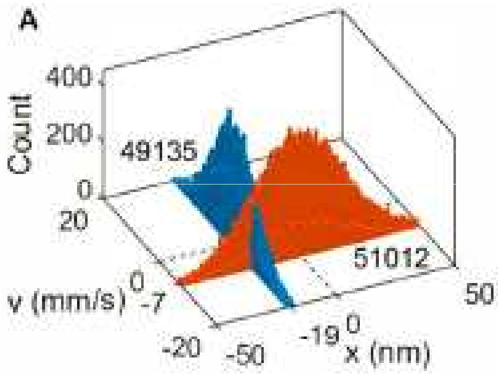
$$\left\langle e^{-\beta(W-\Delta F)} \middle| v_f = v \right\rangle_F = \frac{P_R^{eq}(\tilde{v}_i = -v)}{P_F\,(v_f = v)}$$



Test the GJE for arbitrary initial states

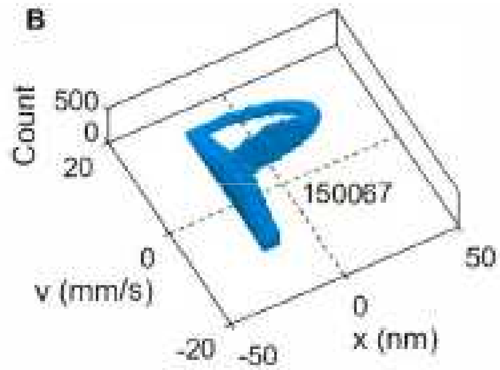
- GJE for arbitrary initial states

$$\left\langle e^{-\beta(W-\Delta F)}\right\rangle_{P_{ini}(x_i,v_i)} = \int \frac{P_R\left(\tilde{x}_f = x, \tilde{v}_f = -v\right)}{P_F^{eq}(x_i = x, v_i = v)} P_{ini}(x_i = x, v_i = v)\,dx\,dv$$



Delta distribution

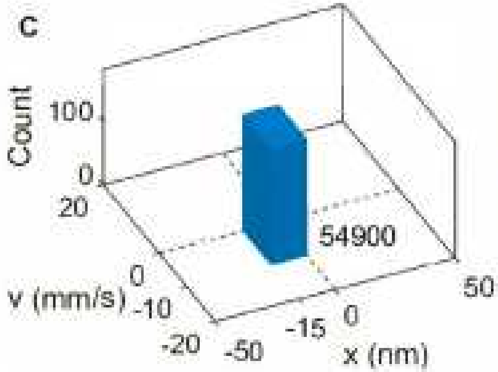
See last slide



P-shaped state

lhs: 0.92±0.02

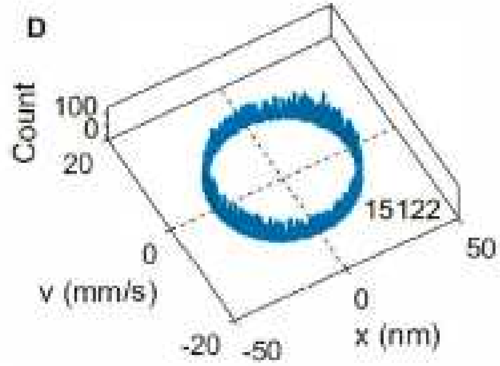
rhs: 0.90



Uniform distribution

lhs: 1.42±0.03

rhs: 1.42



Microcanonical ensemble

lhs: 1.08±0.02

rhs: 1.07

Data in the overdamped regime

- Overdamped regime (760 Torr)

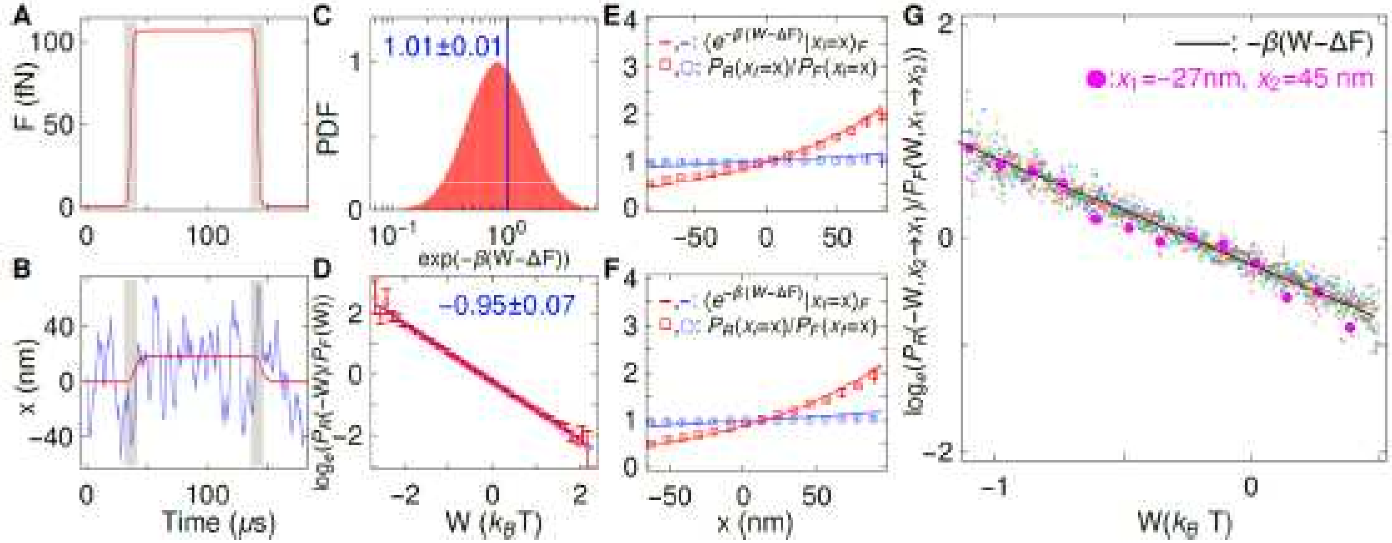
➢ $f_{off} = 0, f_{on} = 107\ fN$

➢ Ramp time $\sim 4.8\ \mu s$

➢ Particle size $r = 145 \pm 5\ nm$

➢ $\Omega = 76 \pm 3\ (2\pi \cdot kHz)$

➢ $\Delta F = -0.24\ k_B T$



APS physics | Physics

Synopsis: Fluctuation Theorems Tested with a Levitating Bead

February 22, 2018

Motion measurements of a nanosized bead—held aloft in an optical trap—confirm thermodynamic theories that describe fluctuations of microscopic objects.

PHYS.ORG

Researchers validate several fluctuation theorems for first time

23 February 2018, by Kayla Zacharias

A team of researchers from Purdue and Peking

Summary

- Test the DFT and the GJE in both underdamped and overdamped regimes
  - The most detailed fluctuation theorem that can be tested in experiment
  - DFT can unify most of the FTs
  - Length of time's arrow [21]
  - Unprecedentedly detailed level
- Technique to generate arbitrary initial states
  - Post-selection of trajectories
- Outlook: extension to quantum regime [12,23]

Acknowledgement

- Pan Rui 潘瑞 (Peking University)
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- Jaehoon Bang (Purdue University)
- Jonghoon Ahn (Purdue University)

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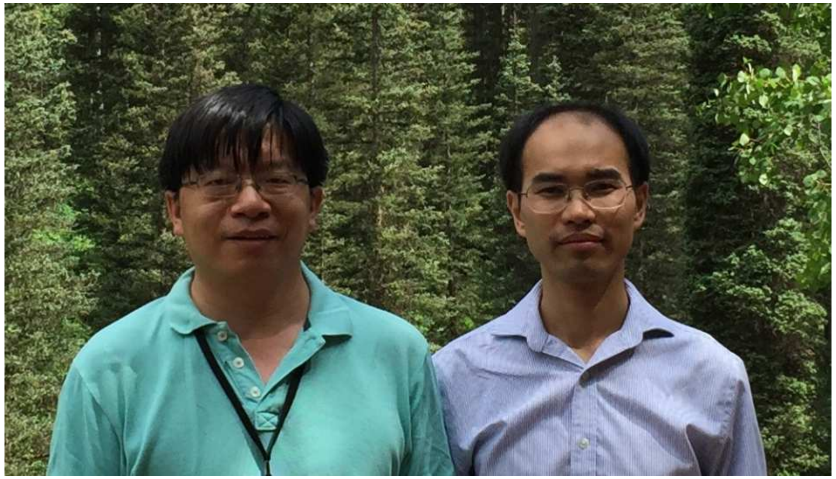

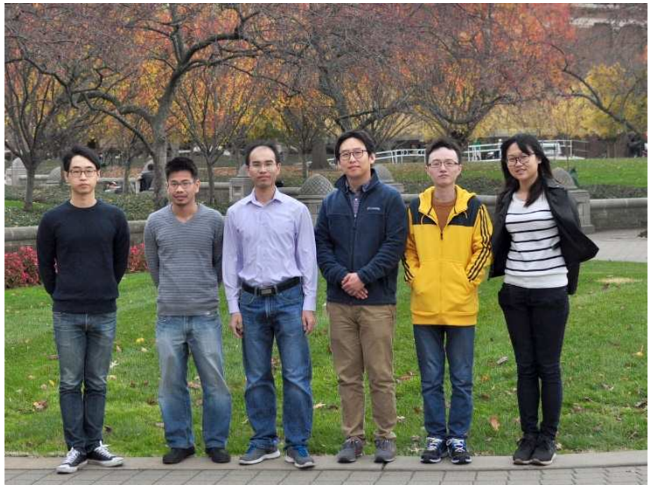

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