



Frontiers of Complex Systems Science: Soft Matter, Biophysics, and Statistical Physics

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How to apply the concepts of stochastic thermodynamics to experiments

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Stochastic energetics

$$0 = -\frac{\partial U(x, a)}{\partial x} - \gamma \frac{dx}{dt} + \xi(t) \quad (\text{overdamped}),$$

Work

$$W = \int_{\alpha_i}^{\alpha_f} \frac{\partial U}{\partial \alpha} d\alpha$$

Heat

$$Q = \int_{x_i}^{x_f} \frac{\partial U}{\partial x} dx$$

U : potential

α : control parameter

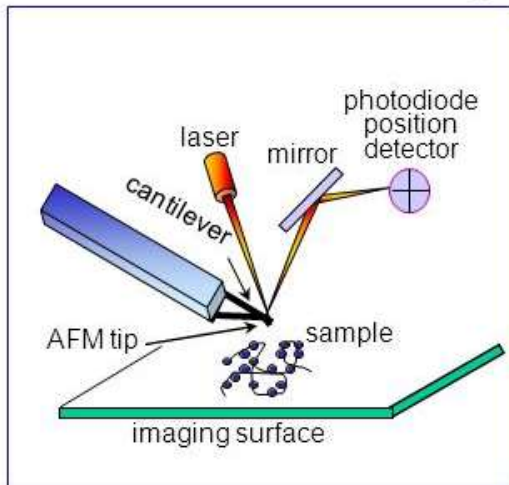
- Isolates potential and medium from rest of universe
- Just need to know $U[x(t), t]$ and $x(t)$

- K. Sekimoto, Journal of the Physical Society of Japan (1997)
- K. Sekimoto, *Stochastic Energetics* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2010).
- U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).

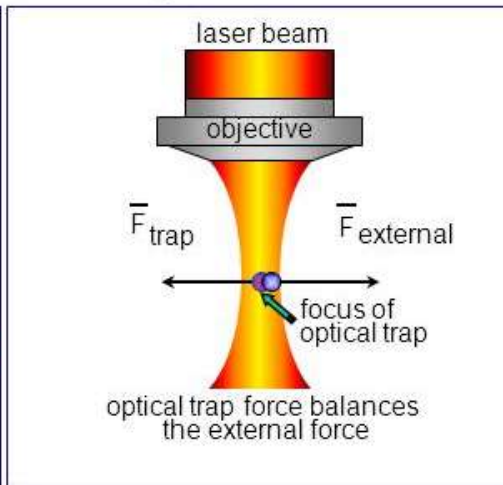
Technical advances

- Manipulation of single molecules

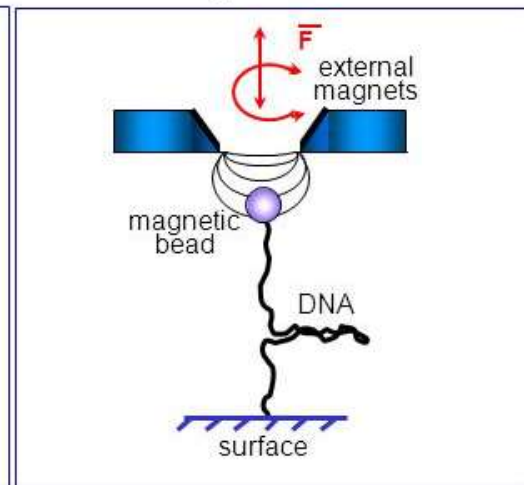
Atomic Force Microscope



Optical Tweezers



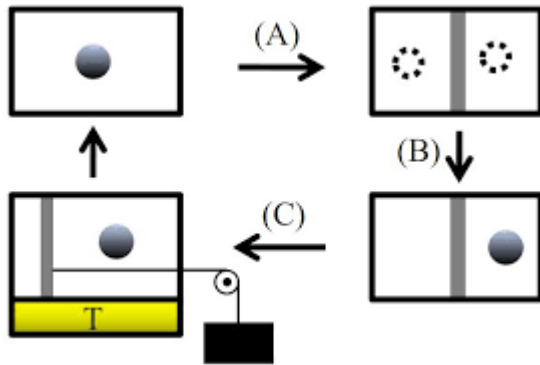
Magnetic Tweezers



Jordanka, *et al.*, Journal of molecular biology (2003)

- Y. Seo and W. Jhe, Reports on Progress in Physics (2008)
- R. W. Bowman and M. J. Padgett, Reports on progress in physics. (2013).
- C. Gosse and V. Croquette, Biophysical Journal (2002).

Gedanken to real experiment



• Szilard engine

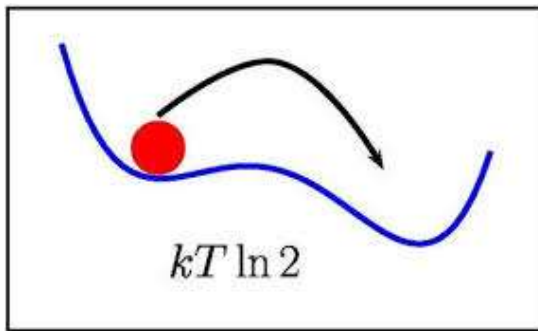
- S. Toyabe, *et al.*, Nat. Phys. **6**, 1 (2010).
- J. V. Koski, *et al.*, Proc. Natl. Acad. Sci. **111**, 13786 (2014).

<https://physicsforme.com/tag/szilard-engine/>

• Landauer memory erasure

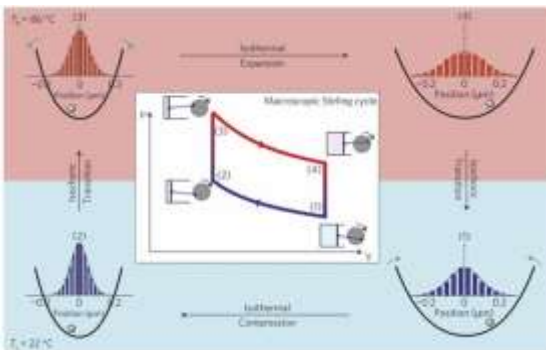
- A. Bérut, *et al.*, Nature **483**, 187 (2012).
- Y. Jun, M. Gavrilov, and J. Bechhoefer, PRL, **113**, 190601 (2014).

<https://www.kurzweilai.net/proof-that-erasing-information-produces-heat#!prettyPhoto>



• Microscopic heat engine

- V. Blickle and C. Bechinger, Nat. Phys. **8**, 143 (2011).
- I. A. Martínez, *et al.*, Nat. Phys. **12**, 67 (2015).
- S. Krishnamurthy *et al.*, Nat. Phys. **12**, 1 (2016).
- P. A. Quinto-Su, Nat. Commun. **5**, 5889 (2014).

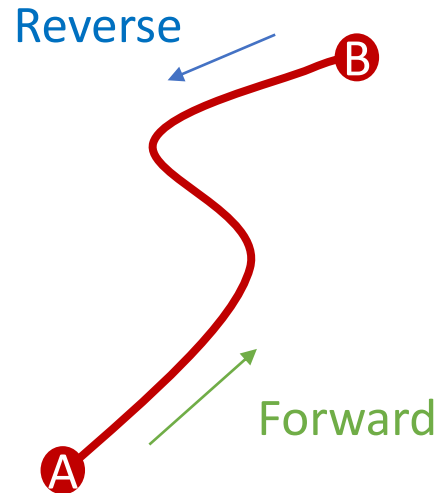


V. Blickle and C. Bechinger, Nat. Phys. **8**, 143 (2011).

Application to experiment

Verification of Crooks fluctuation theorem

Crooks fluctuation theorem (CFT)



$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta F}{k_B T}\right)$$

- $P_F(W)$ is the probability distribution for Forward (F) process.
- $P_R(W)$ analogously for the reverse (R) process.

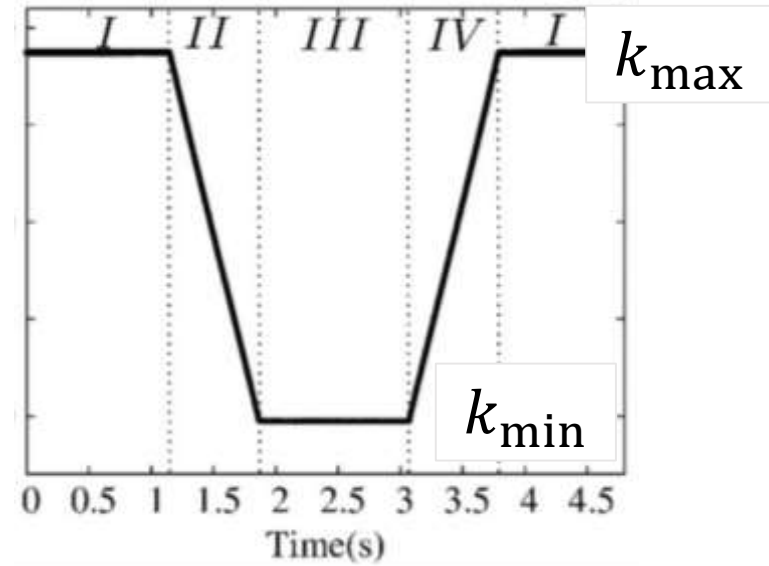
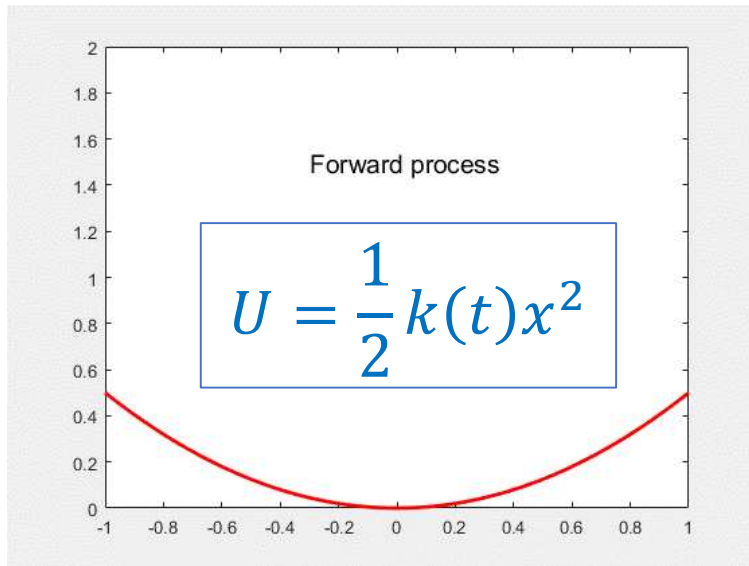
G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).

Crooks fluctuation theorem (CFT)

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta F}{k_B T}\right)$$

- It predicts a symmetry relation in the work fluctuations that a system undergoes as it is driven away from thermal equilibrium.
- The CFT has drawn a lot of attention because of its usefulness in experiment. This theorem makes it possible to experimentally measure the **free energy difference of the system during a non-equilibrium process**.

Time-varying harmonic potential

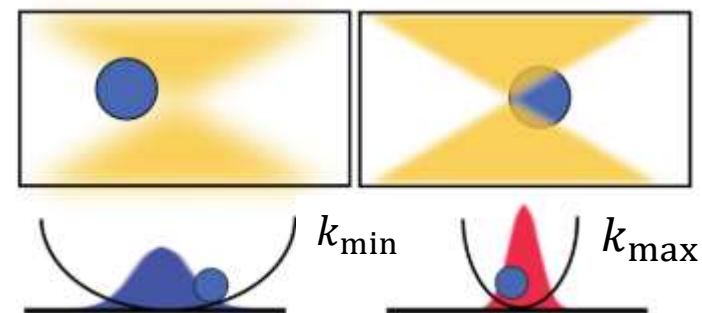


For the forward quasistatic process

$$\frac{\langle W_F \rangle}{k_B T} = \frac{1}{2} \ln \left(\frac{k_{\max}}{k_{\min}} \right) \equiv \frac{\Delta F}{k_B T}$$

For the reverse quasistatic process

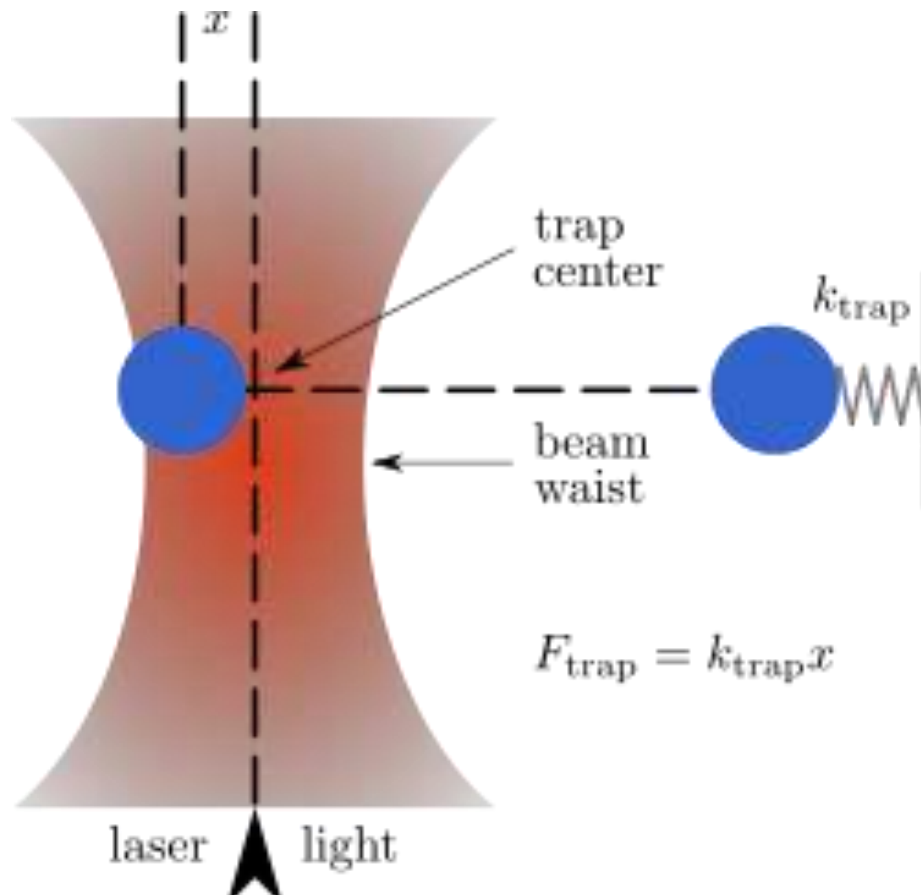
$$\frac{\langle W_R \rangle}{k_B T} = \frac{1}{2} \ln \left(\frac{k_{\min}}{k_{\max}} \right) \equiv -\frac{\Delta F}{k_B T}$$



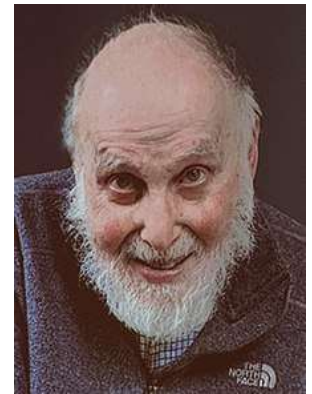
Martínez, et al., Soft Matter (2017).

Optical tweezers

Optical tweezers as a spring



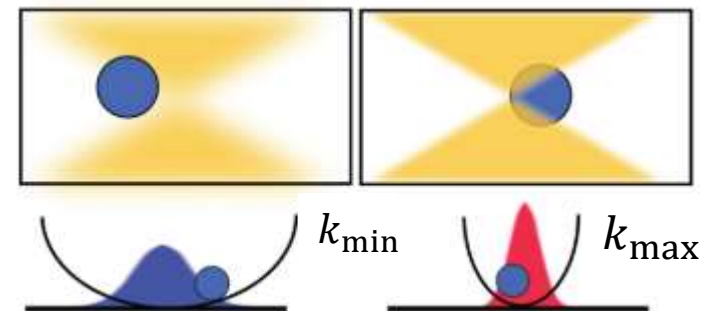
https://en.wikipedia.org/wiki/Optical_tweezers



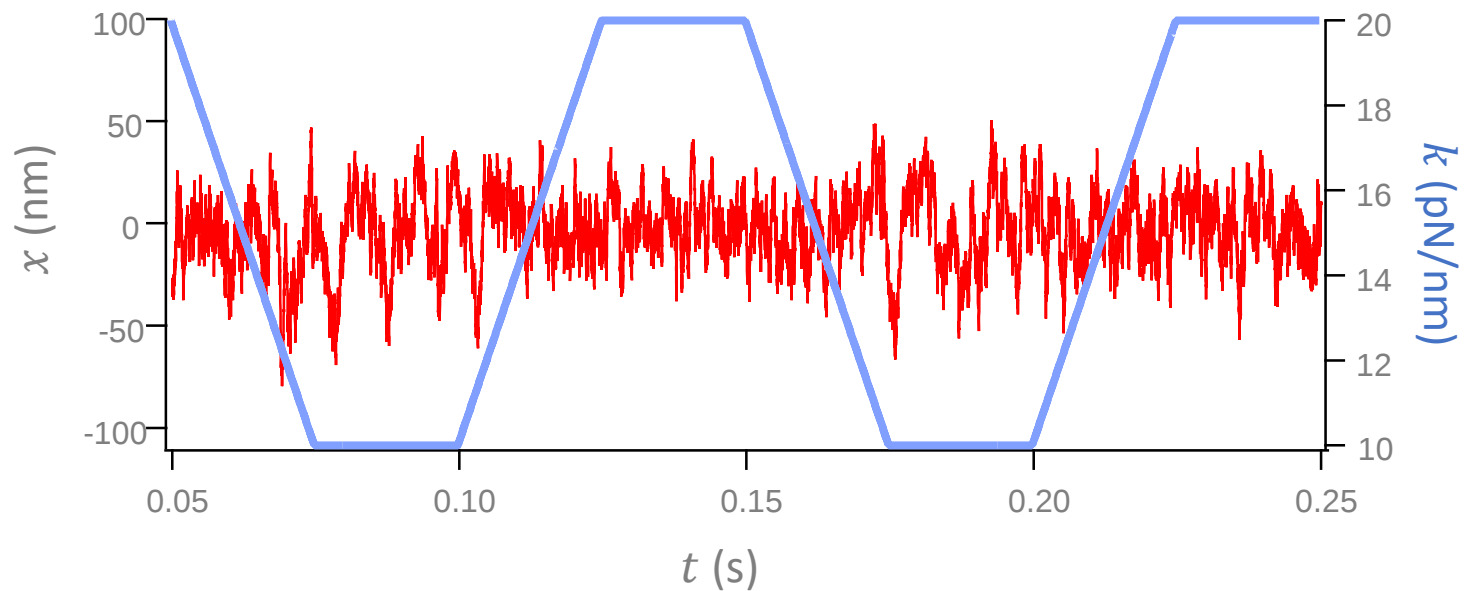
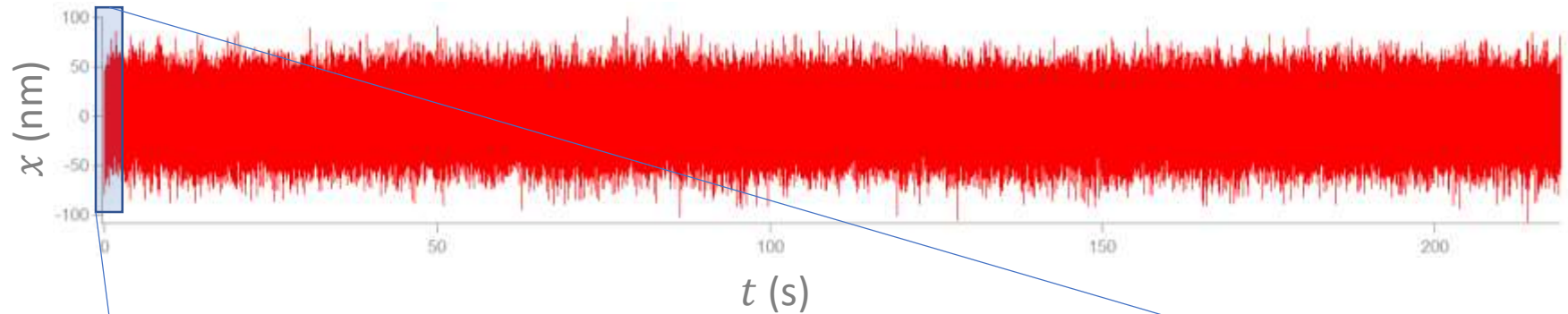
Arthur Ashkin
Nobel laureate
(2018)

https://en.wikipedia.org/wiki/Arthur_Ashkin

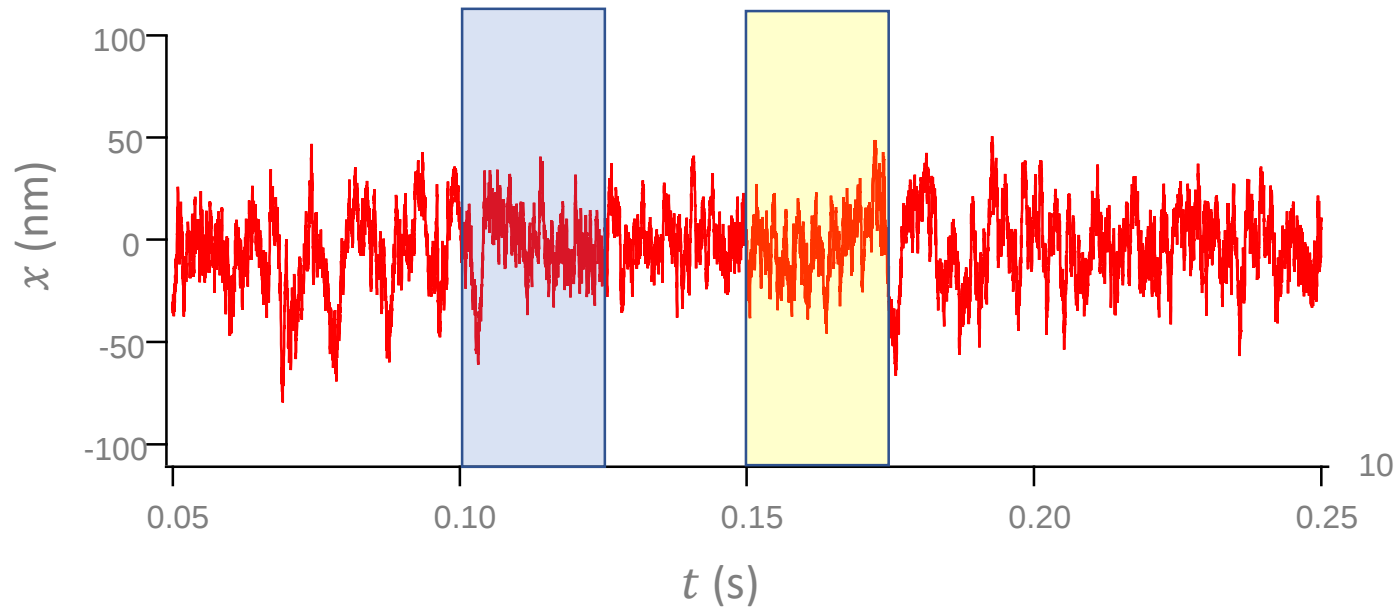
$$U = \frac{1}{2} kx^2$$



Trajectories of a particle



Discrete stochastic energetics



$$W = \int_{\alpha_i}^{\alpha_f} \frac{\partial U}{\partial \alpha} d\alpha, \quad U = \frac{1}{2} k(t) x^2$$

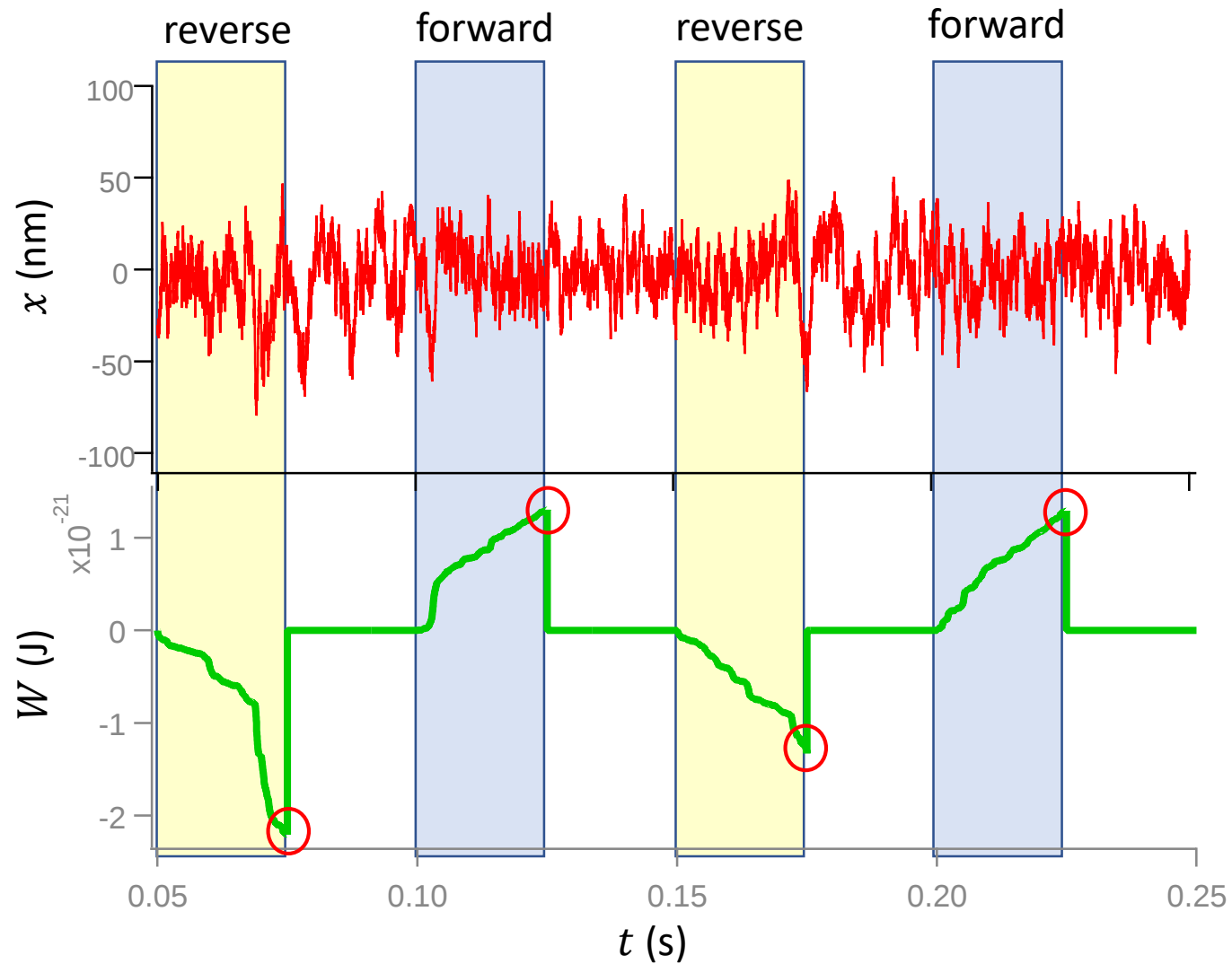
Discrete version of stochastic thermodynamics:

$$W = \sum_i^N \frac{\Delta U}{\Delta k} \Delta k = \frac{1}{2} \dot{k} \Delta t \sum_i^N x_i^2$$

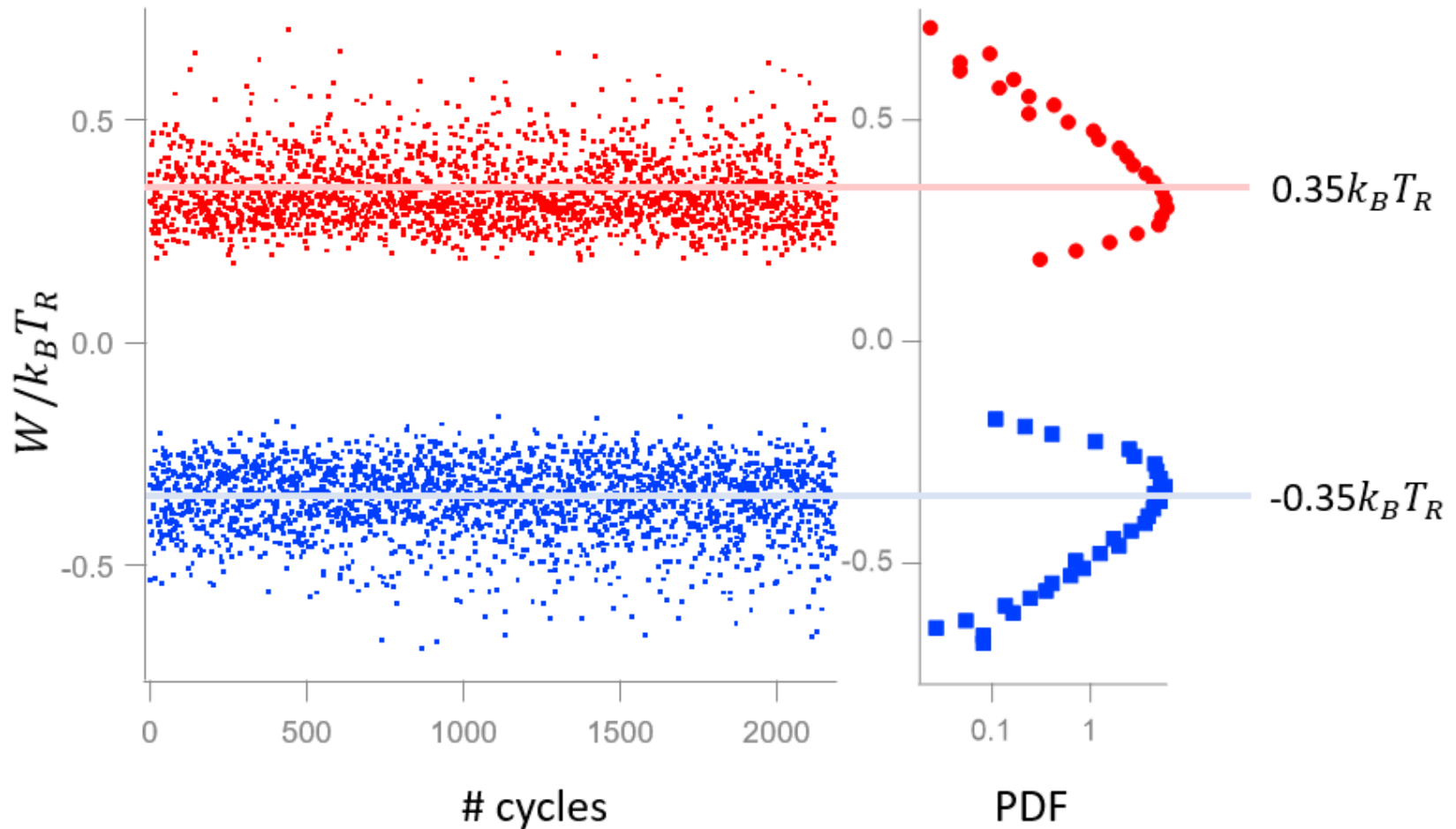
where $\tau = 25\text{ms}$, $t = 10\mu\text{s} \rightarrow N = \tau/\Delta t = 2500$

Sekimoto, 1998

Cumulative work



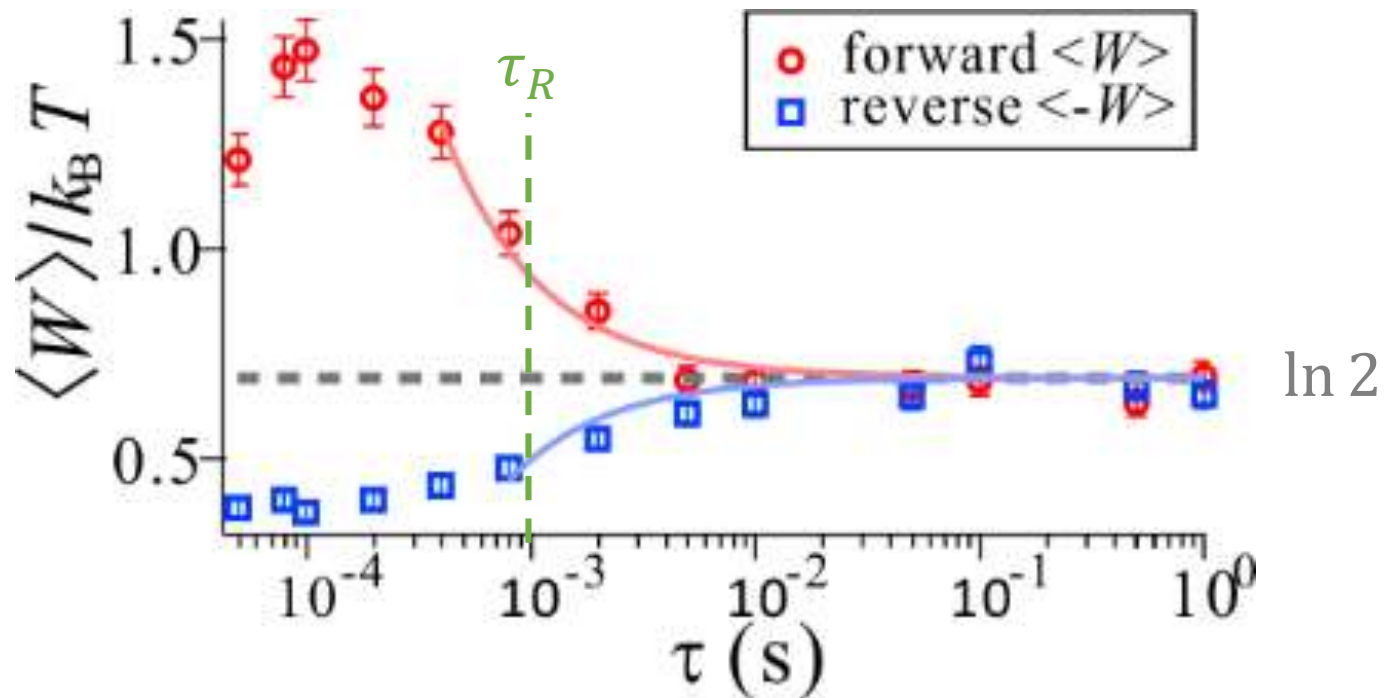
Distribution of forward and reverse work



Mean work

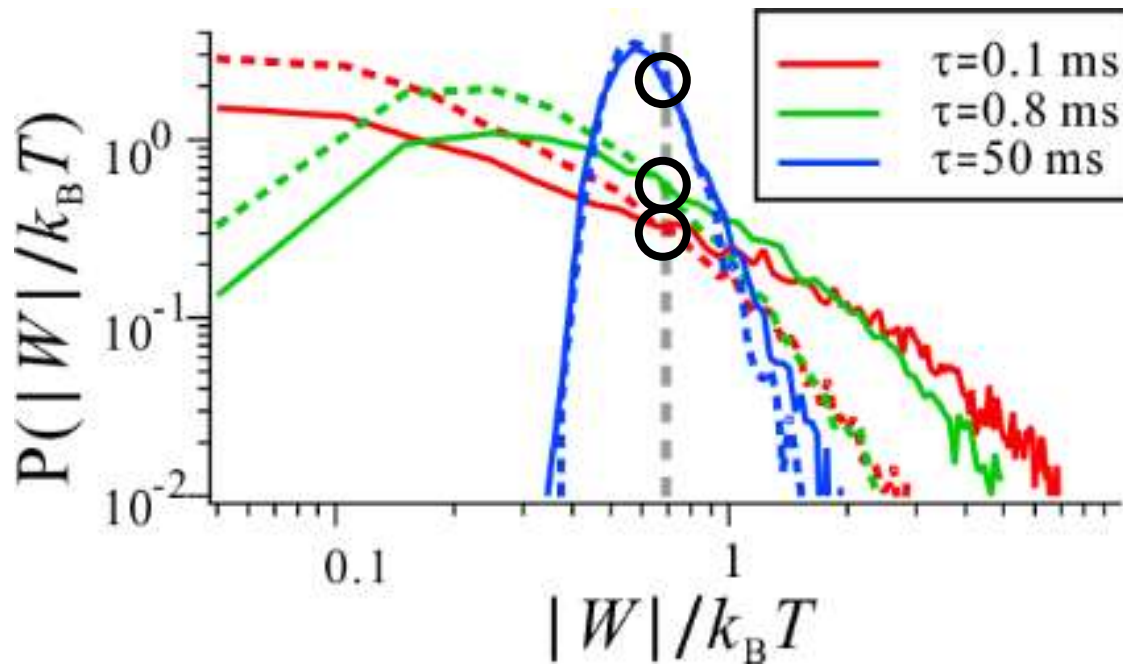
- For quasistatic process: $k_f/k_i = 4$

$$\frac{\langle W \rangle}{k_B T} = \frac{1}{2} \ln \left(\frac{k_f}{k_i} \right) \equiv \frac{\Delta F}{k_B T} = \ln 2$$



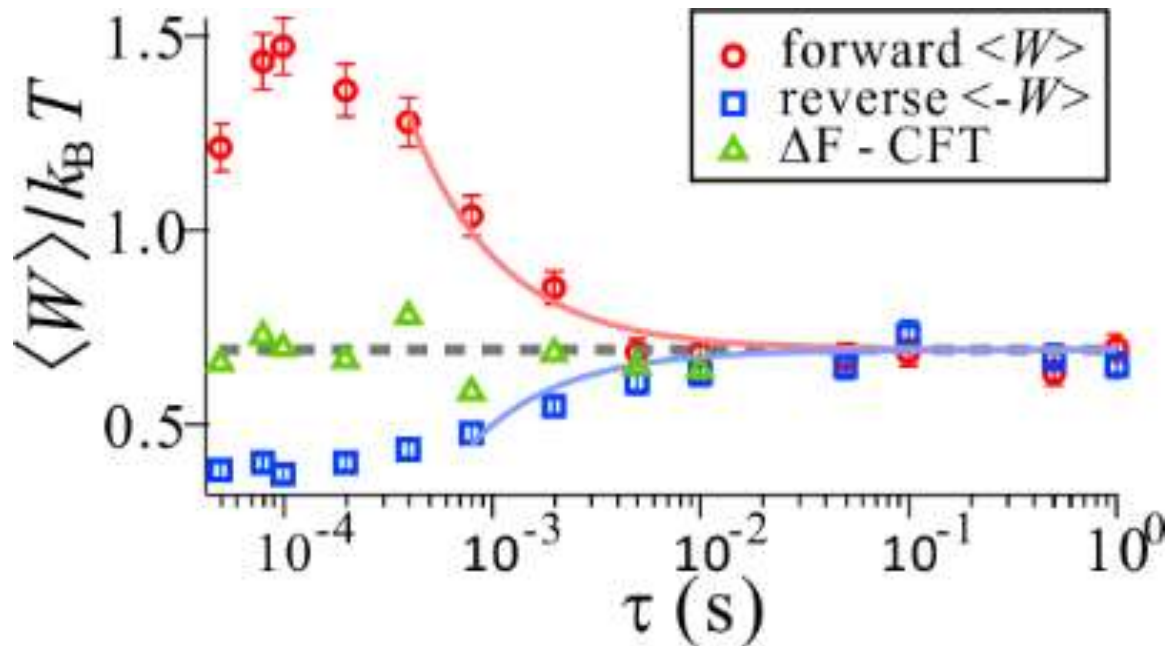
Work probabilities distribution function

$$\frac{P_F(W)}{P_R(-W)} = \exp\left(\frac{W - \Delta F}{k_B T}\right) = 1 \Rightarrow W = \Delta F$$



Albay, Paneru, Pak, and Jun, Opt. Express (2018)

Crooks fluctuation theorem works even in highly nonequilibrium regime!



Albay, Paneru, Pak, and Jun, Opt. Express (2018)