Hierarchy of fluctuation theorems and experimental test of the differential fluctuation theorem

Rui Pan

Peking University

In collaboration with:

Tongcang Li group, Purdue University

2018/06/27, KITP

Reference: Phys. Rev. Lett. 120, 080602 (2018)

Outline

Background

- Length of time's arrow
- Stochastic thermodynamics and fluctuation theorems (FTs)
- Motivation

Hierarchy of fluctuation theorems

- Microscopic reversibility (MR)
- Differential fluctuation theorem (DFT)
- A generalized Jarzynski equality (GJE) for arbitrary initial states

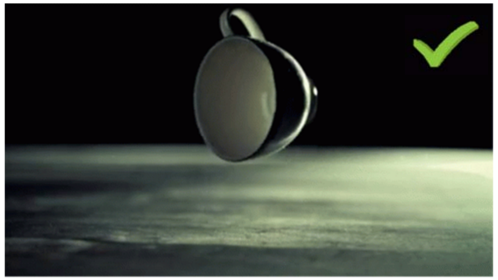
Experimental test

- Setup and data
- Generate arbitrary initial states

Summary

Length of time's arrow

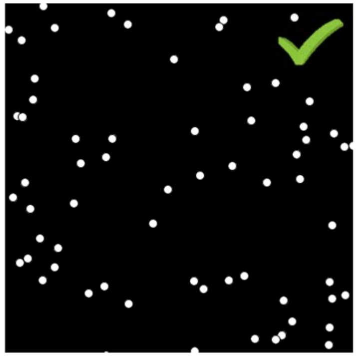
Macroscopic



- Thermal fluctuations are negligible
- Deterministic
- Newton's equation

- $W \geq \Delta F$
- $\Delta S \geq 0$

Microscopic



- Thermal fluctuations are dominant
- Stochastic
- Langevin equation
- Fokker-Planck equation

- $\langle W \rangle \geq \Delta F$
- $\langle \Delta S \rangle \geq 0$

Stochastic thermodynamics and Fluctuation theorems (FTs)

Thermodynamic quantities based on stochastic trajectories:

Work [1,2]: $W[\Gamma(t)] = \int_0^\tau \frac{\partial H}{\partial \lambda} \dot{\lambda} dt$

Heat [1,2]: $Q[\Gamma(t)] = \int_0^\tau (-\gamma v_t + \xi_t) \circ dx_t = \int_0^\tau \frac{\partial H}{\partial \Gamma} \dot{\Gamma} dt$

Entropy production [4]:

$$S_{sys}(t) = -\ln \rho(\Gamma_t, t)$$

$$\Delta S_{tot} = \Delta S_{sys} - \frac{Q}{T}$$

$\Gamma_t \coloneqq (x_t, p_t)$

- **Jarzynski equality** (JE) [1]:

$$\left\langle e^{-\beta(W-\Delta F)} \right\rangle = 1$$

- **Crooks fluctuation theorem** (CFT) [3]:

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

- **Hummer-Szabo relation** (HSR) [5]:

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

- **FT of entropy production** [4]:

$$\frac{P_R(-\Delta S_{tot})}{P_F(\Delta S_{tot})} = e^{-\Delta S_{tot}/k_B}$$

$$\left\langle e^{-\Delta S_{tot}} \right\rangle = 1$$

- **Hatano-Sasa relation** [6]:

$$\langle e^{-Y} \rangle = 1, \ Y \coloneqq \int_0^\tau \frac{\partial \phi}{\partial \alpha}(x(t), \alpha(t)) \dot{\alpha} dt$$

- **Sagawa-Ueda relation** [7]:

$$\left\langle e^{-\beta(W-\Delta F)-I} \right\rangle = 1$$

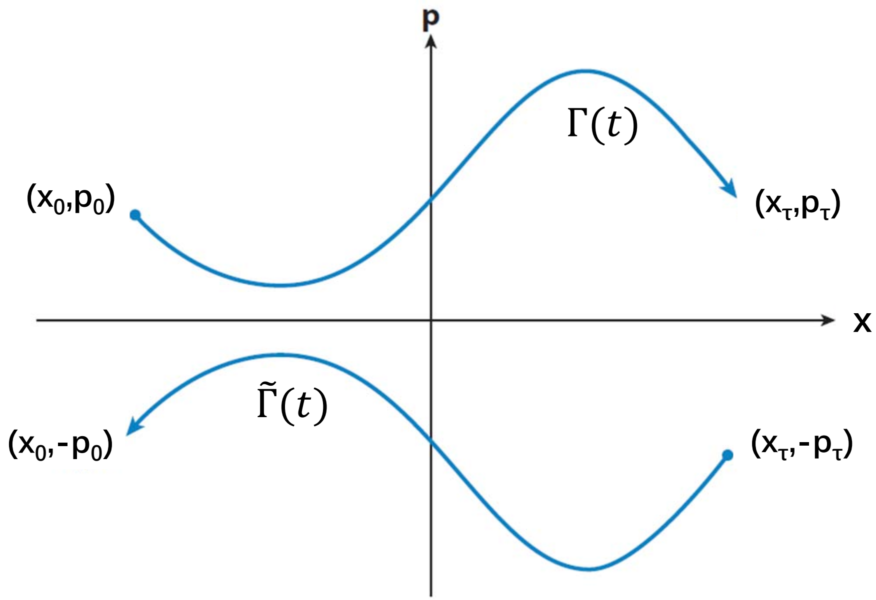
……

What is the origin of fluctuation theorems?

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

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

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



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).

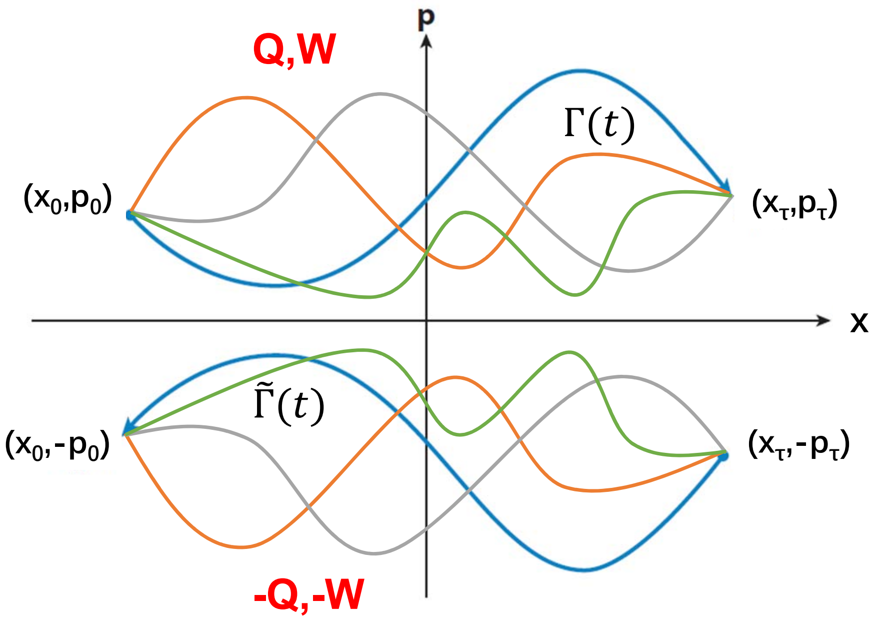
Differential fluctuation theorem (DFT)

- **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]:

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

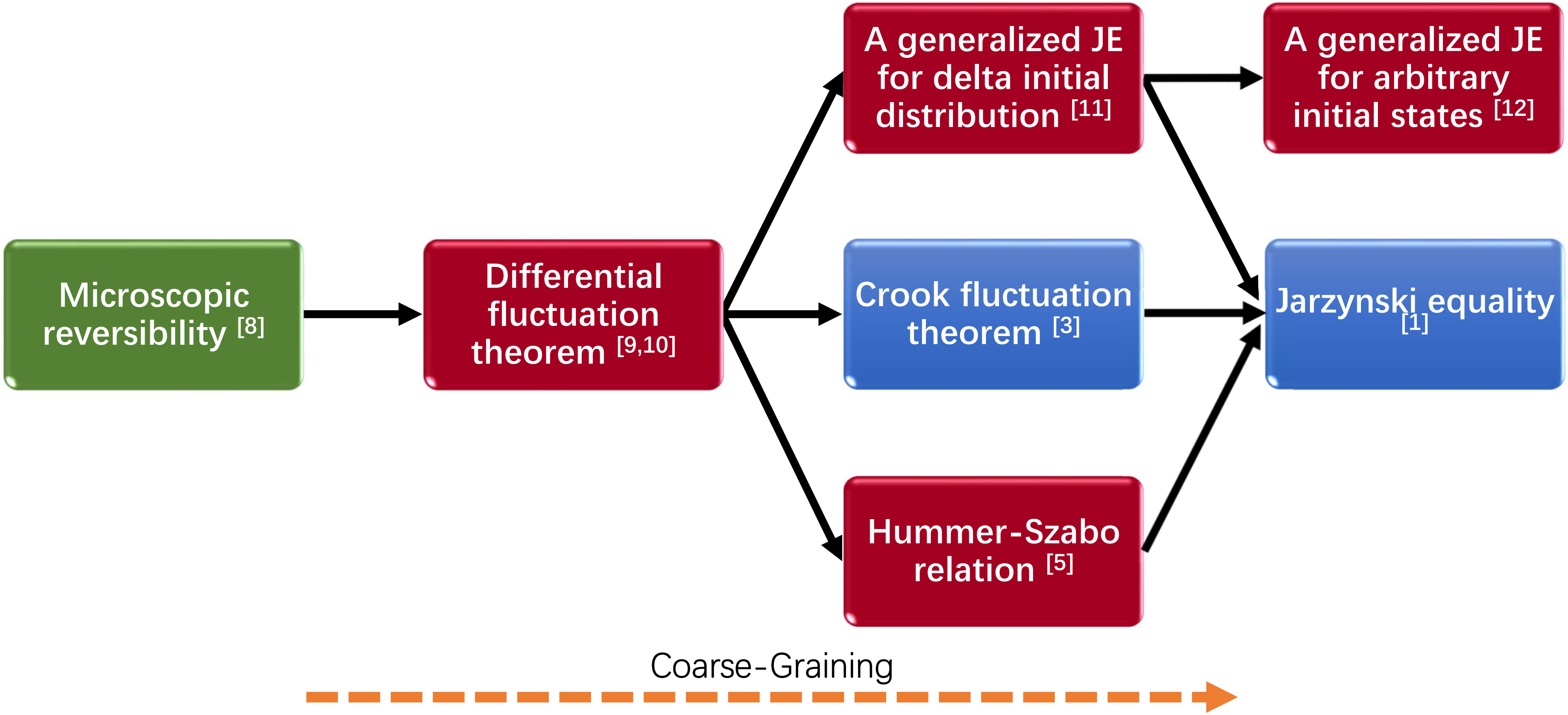


The most detailed fluctuation theorem that can be tested **experimentally**.

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

[11] R. Kawai, et al. Phys. Rev. Lett. 98, 080602 (2007).
[12] Z. Gong and H. T. Quan, Phys. Rev. E 92, 012131 (2015).

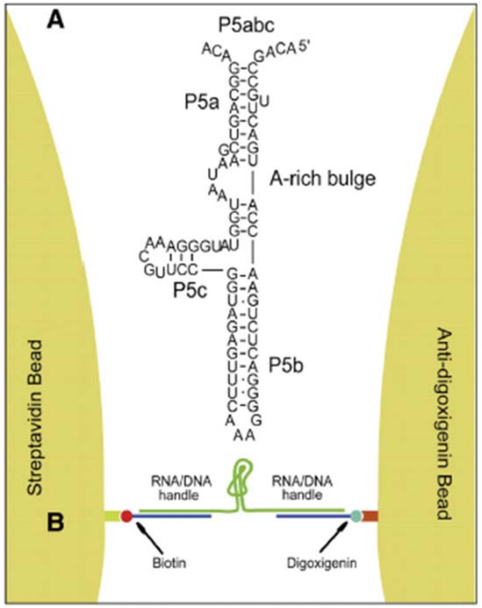
Hierarchy of fluctuation theorems

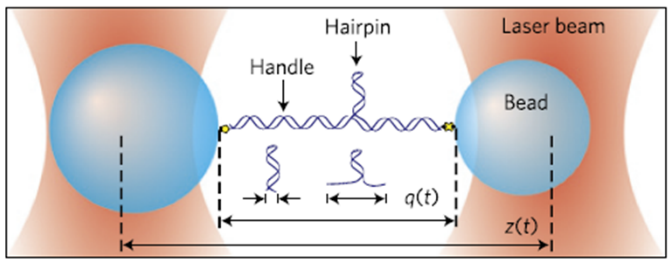


Previous experiments

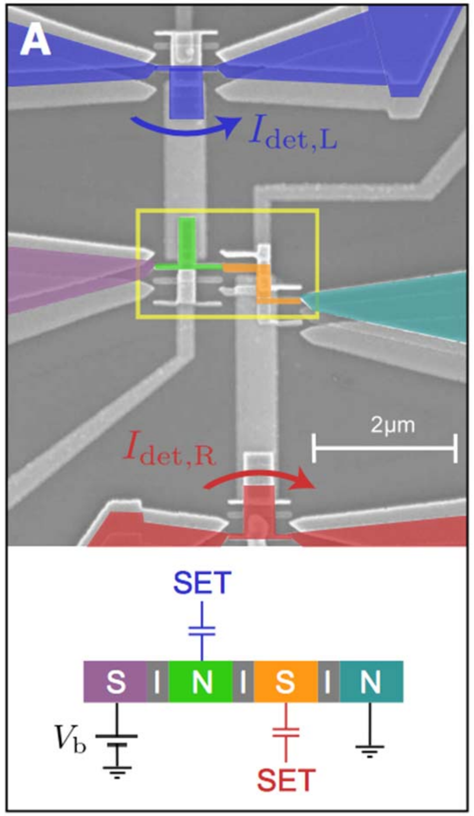
[13] J. Liphardt, et al. Science 296, 1832 (2002).
[14] D. Collin, et al. Nature (London) 437, 231 (2005).
[15] A. N. Gupta, et al. *Nature Physics* 7,631 (2011).
[16] E. Trepagnier, et al. Proc. Natl. Acad. Sci. 101, 15038 (2004).
[17] D. Y. Lee, et al. Phys. Rev. Lett. 114, 060603 (2015).
[24] J. P.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

Stretching RNA molecules [13-15]

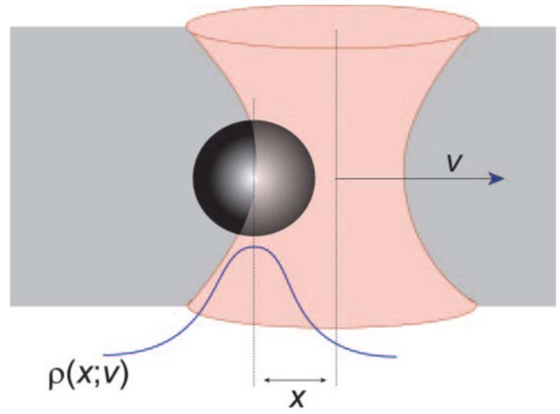


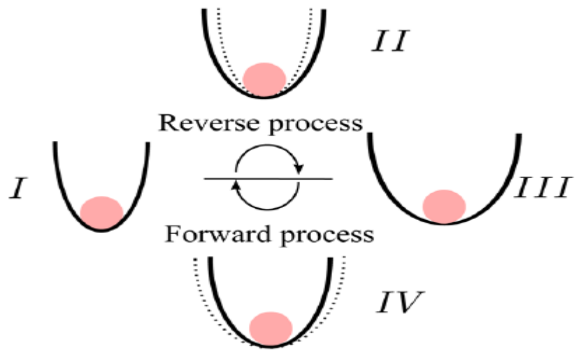


Electronic circuit [24,25]



Brownian particle trapped in water [16,17]

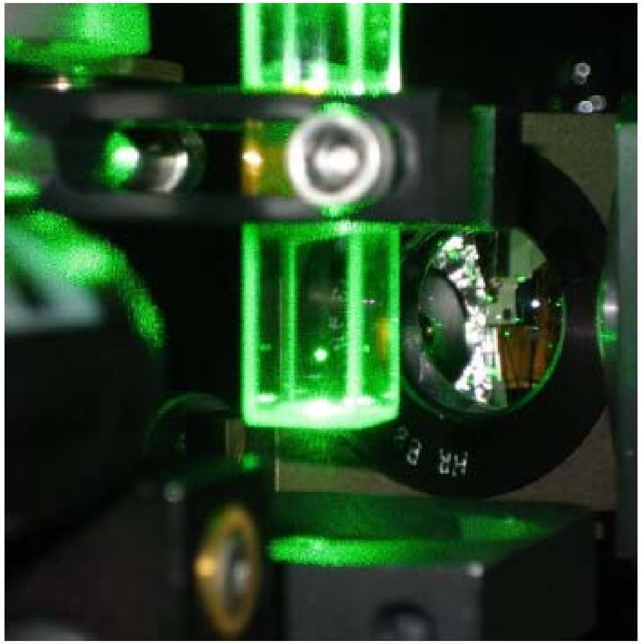




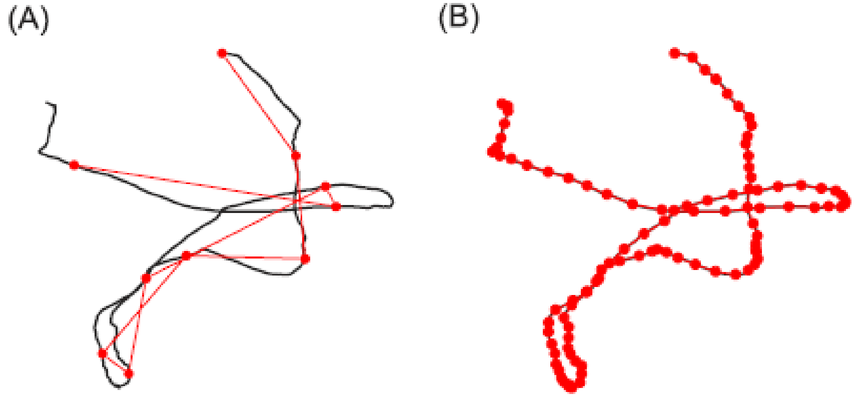
Our experiment

[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).

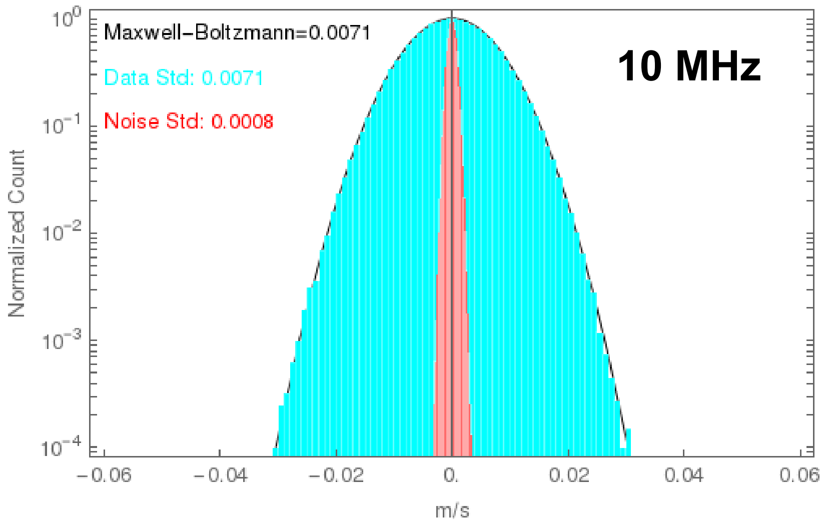
Silica nanosphere levitated in **AIR** using optical tweezers [18-20]



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



Measurement of the instantaneous velocity



Our experiment

- In air, room temperature (296K)

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

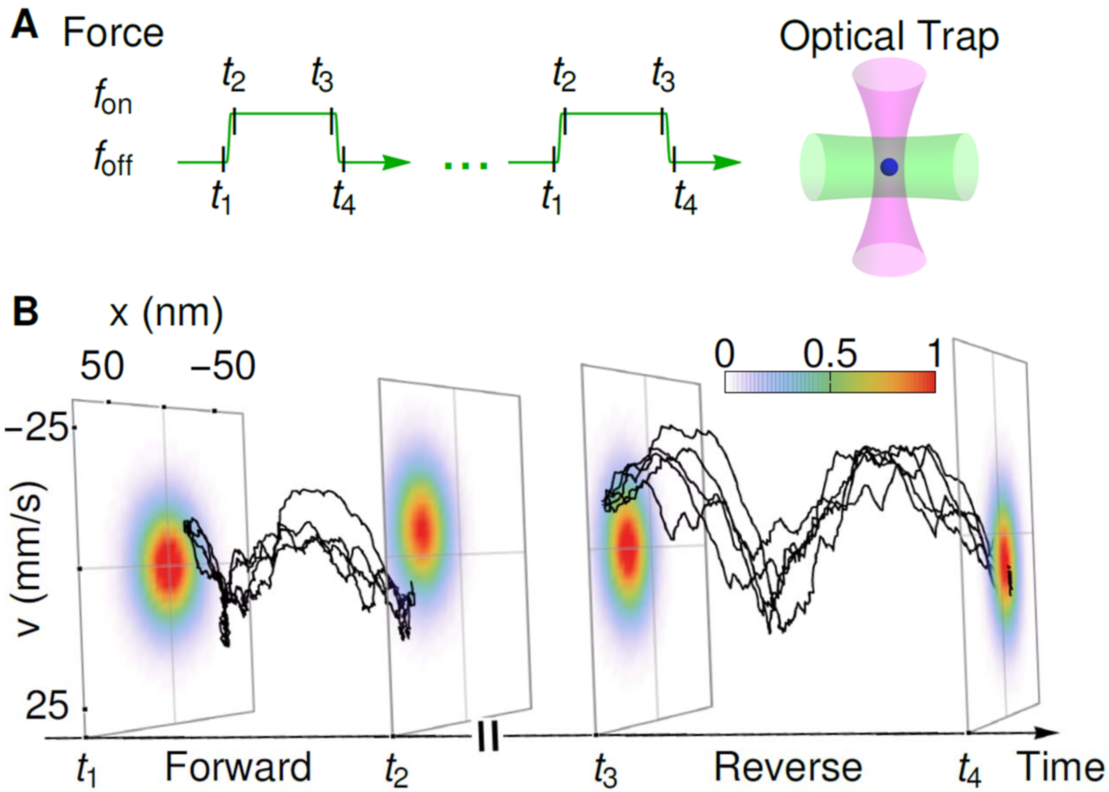
$f(t)$: $f_{off} \rightarrow f_{on}$

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

- Challenges of our experiment:
  - ➢ Very large statistics

    > **one million** cycles, $500\ \mu s$ /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

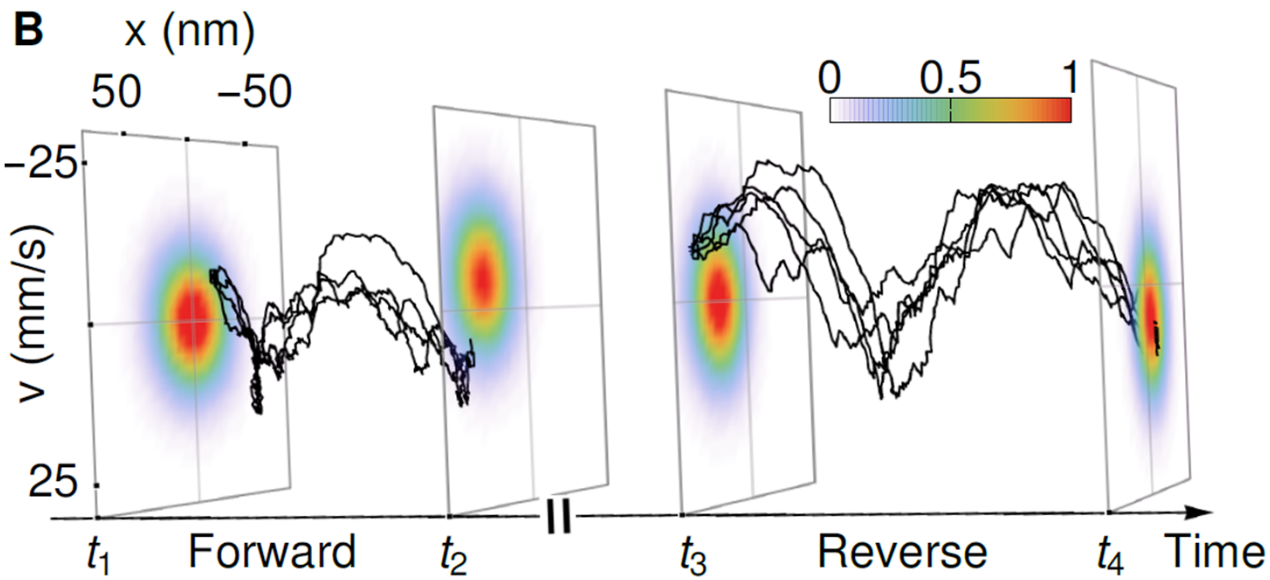
- Underdamped regime (50 Torr)

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

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

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

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



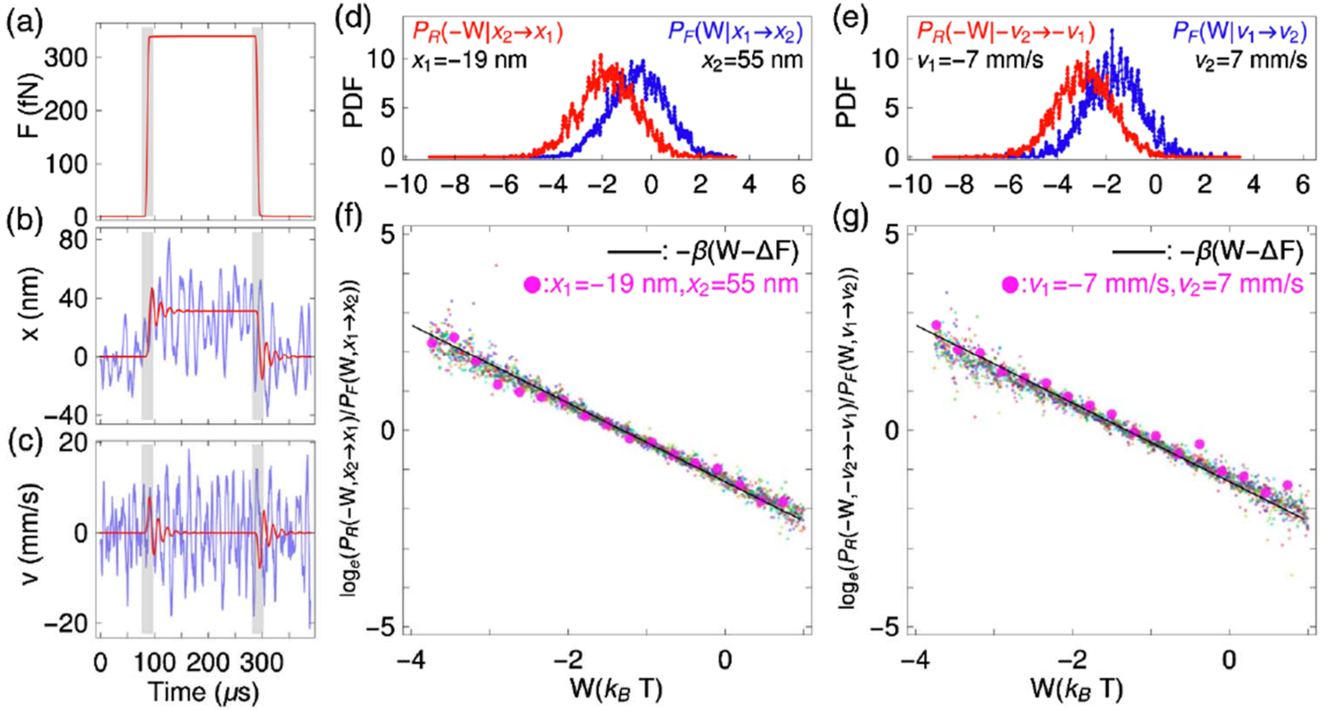
Test the differential fluctuation theorem

- 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:**

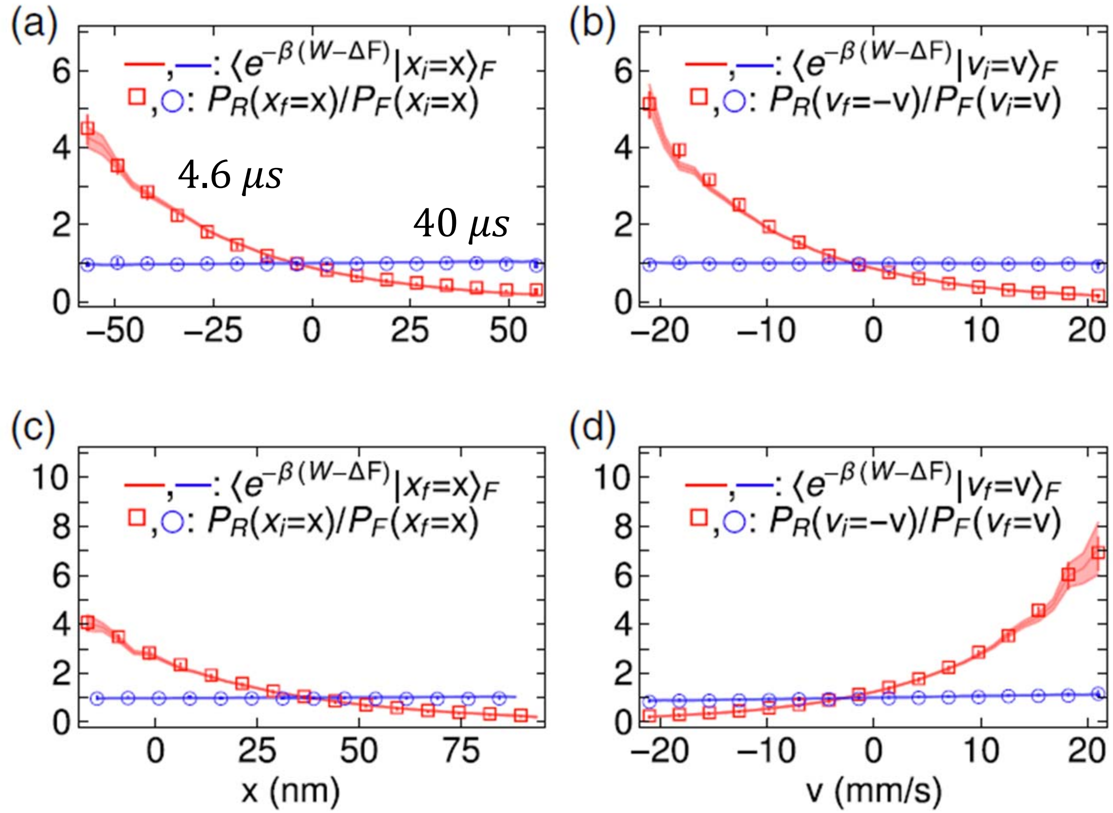
$$\left\langle e^{-\beta(W-\Delta F)} \middle| x_i = x \right\rangle_F = \frac{P_R(\tilde{x}_f = x)}{P_F^{eq}(x_i = x)}$$

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

- **HSR:**

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

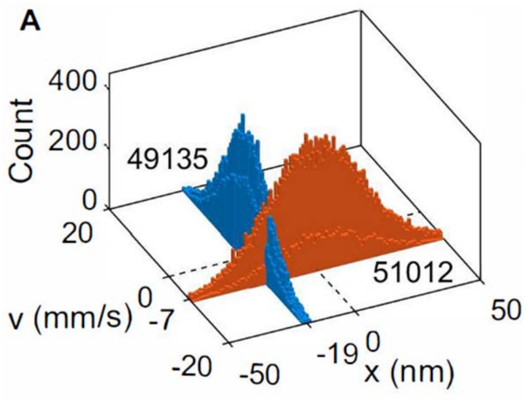
$$\left\langle e^{-\beta(W-\Delta F)} \middle| v_f = v \right\rangle_F = \frac{P_R^{eq}(\tilde{v}_i = -v)}{P_F\ (v_f = v)}$$



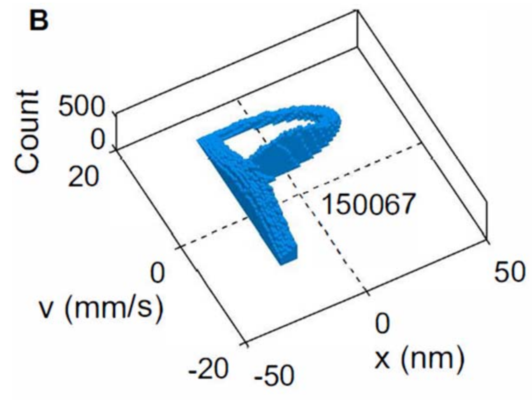
Test the GJE for arbitrary initial states

- GJE for arbitrary initial states

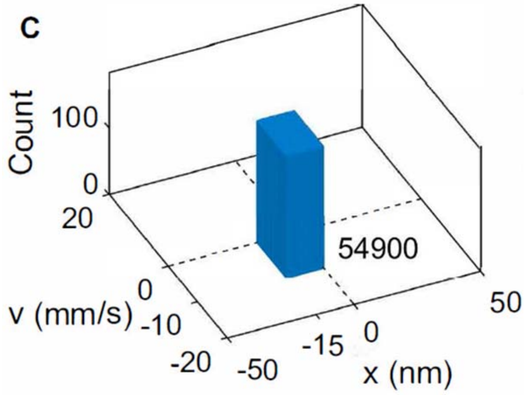
$$\left\langle e^{-\beta(W-\Delta F)}\right\rangle_{P_{ini}(x_i,v_i)} = \int \frac{P_R(\tilde{x}_f = x, \tilde{v}_f = -v)}{P_F^{eq}(x_i = x, v_i = v)} P_{ini}(x_i = x, v_i = v)\, dx dv$$



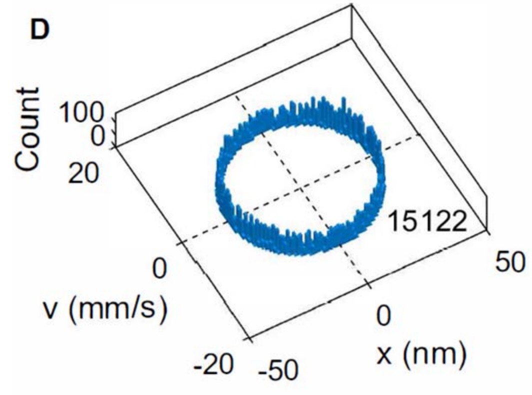
Delta distribution
See last slide



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)

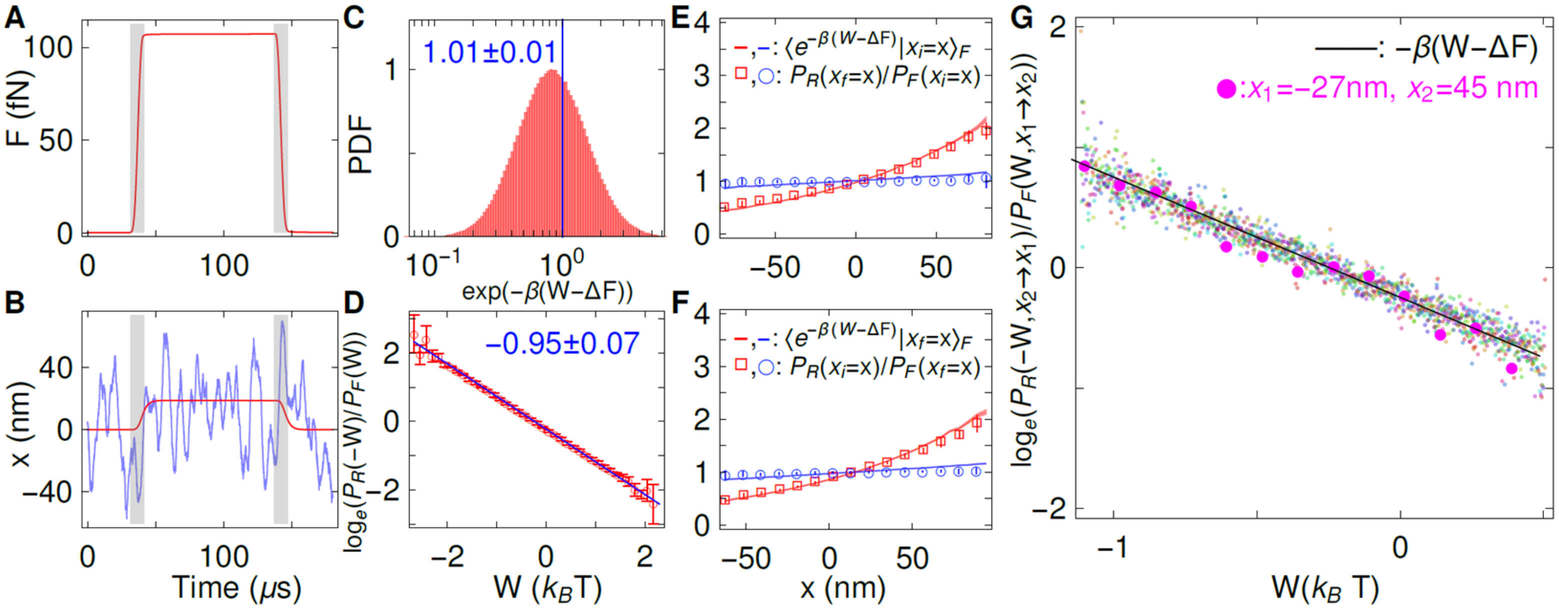
➢ $f_{off} = 0, f_{on} = 107\ fN$

➢ Ramp time ~$4.8\ \mu s$

➢ Particle size $r = 145 \pm 5\ nm$

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

➢ $\Delta F = -0.24\ k_B T$



[12] Z. Gong and H. T. Quan, Phys. Rev. E 92, 012131 (2015).
[21] E. H. Feng and G. E. Crooks, Phys. Rev. Lett. 101, 090602 (2008).
[23] T. Li et al. *Nature Physics* 7, 527 (2011).

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]

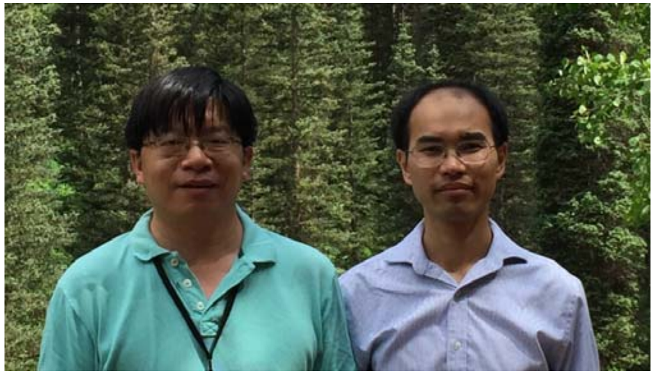
Collaborators

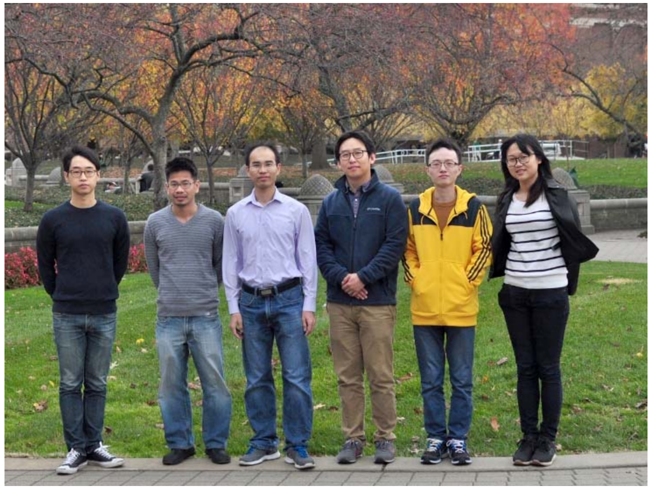
Haitao Quan group (Peking University):

Haitao Quan, Rui Pan

Tongcang Li group (Purdue University):

Tongcang Li, Thai M. Hoang, Jonghoon Ahn, Jaehoon Bang





References

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

[2] K. Sekimoto. Progr. Theor. Phys. Suppl. 130 (1998).

[3] G. E. Crooks, Phys. Rev. E 60, 2721 (1999).

[4] U. Seifert, Phys. Rev. Lett. 95, 040602 (2005).

[5] G. Hummer and A. Szabo, Proc. Natl. Acad. Sci. 98, 3658 (2001).

[6] T. Hatano, and S. Sasa. Phys. Rev. Lett. 86, 3463 (2001).

[7] T. Sagawa and M. Ueda, Phys. Rev. Lett. 104, 090602 (2010).

[8] G. E. Crooks. *Journal of Statistical Physics* 90.5-6 (1998).

[9] C. Jarzynski, J. Stat. Phys. 98, 77 (2000).

[10] P. Maragakis, et al. J. Phys. Chem. B 112, 6168 (2008).

[11] R. Kawai, et al. Phys. Rev. Lett. 98, 080602 (2007).

[12] Z. Gong and H. T. Quan, Phys. Rev. E 92, 012131 (2015).

[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).

[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).

[21] E. H. Feng and G. E. Crooks, Phys. Rev. Lett. 101, 090602 (2008).

[22] C. Jarzynski, Annu. Rev. Condens. Matter Phys. 2, 329 (2011).

[23] T. Li et al. *Nature Physics* 7, 527 (2011).

[24] J. P. Pekola, Nat. Phys. 11, 118 (2015).

[25] S. Singh, et al. *arXiv:1712.01693* (2017).

Thanks for your attention!

A generalized JE (GJE) for arbitrary initial states

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

$\iint d\Gamma_0 d\Gamma_\tau$: $\quad e^{-\beta(W-\Delta F)} P_F(W) = P_R(-W)$ **(CFT)**

$\iint d\Gamma_0 dW$: $\quad \left\langle e^{-\beta(W-\Delta F)} | \Gamma(\tau) = \Gamma_\tau \right\rangle_F = \frac{P_R^{eq}(\widetilde{\Gamma}(0)=\Gamma_\tau^\dagger)}{P_F(\Gamma(\tau)=\Gamma_\tau)}$ **(HSR)**

A generalized JE (GJE) for delta initial distribution [11]**:**

$\iint d\Gamma_\tau dW$: $\quad \left\langle e^{-\beta(W-\Delta F)} | \Gamma(0) = \Gamma_0 \right\rangle_F = \frac{P_R(\widetilde{\Gamma}(\tau)=\Gamma_0^\dagger)}{P_F^{eq}(\Gamma(0)=\Gamma_0)}$

A generalized JE (GJE) for arbitrary initial states [12]**:**

$$\left\langle e^{-\beta(W-\Delta F)} \right\rangle_{P_{ini}(\Gamma(0)=\Gamma_0)} = \int \frac{P_R\left(\widetilde{\Gamma}(\tau)=\Gamma_0^\dagger\right)}{P_F^{eq}(\Gamma(0)=\Gamma_0)} P_{ini}(\Gamma(0) = \Gamma_0) d\Gamma_0$$