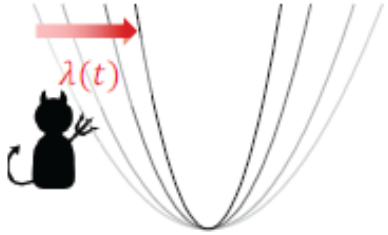
# Second-Law violating events are not Rare in Non-equilibrium non-steady states

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Dept. of Physics & Center for Complex Systems, National Central Univ., Taiwan
Email: pylai@phy.ncu.edu.tw

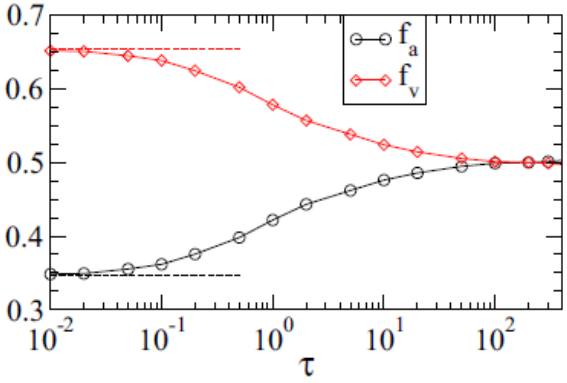
EAJSSP Seoul, 2025

- 2nd Law of Thermodynamics
- rare events of negative entropy production in non-equilibrium steady states
- non-equilibrium steady states: Brownian particle in a time-dependent trapping potential




- negative entropy production events can be the majority

- Analytical results, simulations, experiments

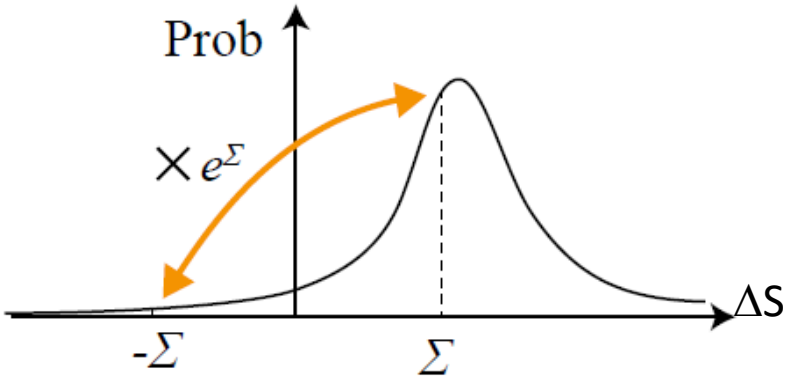


# Measure of irreversibility → Fluctuation Theorems (>1993): precise description of entropy production & irreversibility

$\langle \Delta S \rangle \geq 0$, 2nd Law

$$\langle e^{-\Delta S} \rangle = 1 \qquad \frac{P(\Delta S)}{P(-\Delta S)} = e^{\Delta S}$$

Integral FT FT (for NESS)

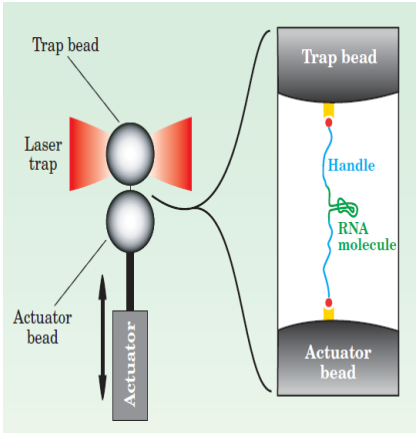



from Shiraishi, An Intro. to stochastic thermodyn.

Entropy decreasing (rare) events are possible, especially in strongly fluctuating and small systems or in mesoscopic scales (trajectory level)

Stochastic Thermodynamics

Information Thermodynamics– information → useful work

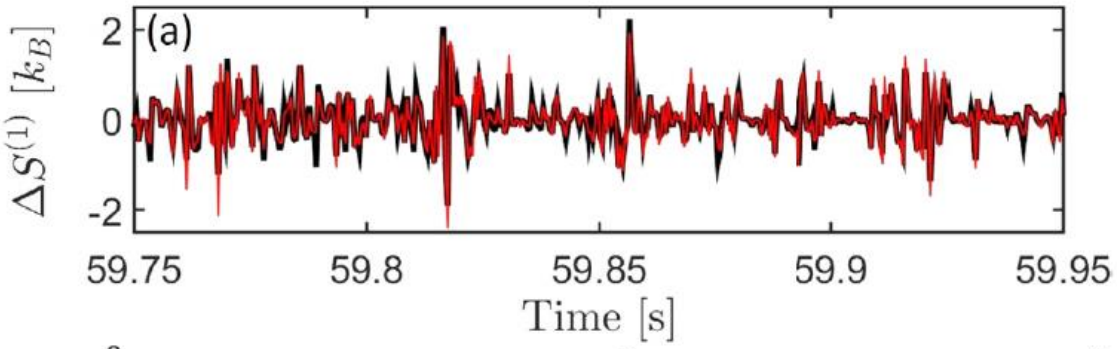


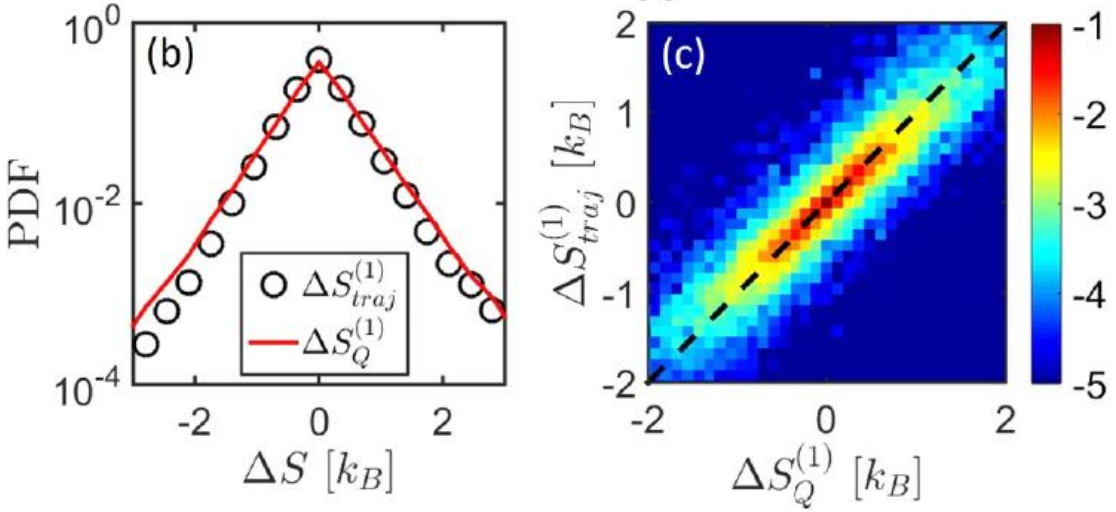
# Stochastic Entropy production in NESS

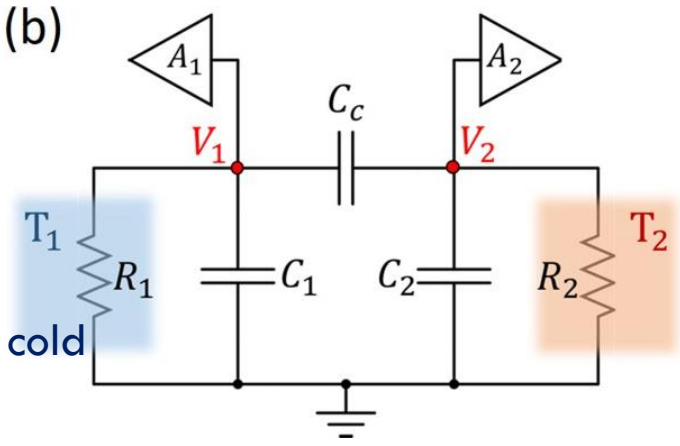
## NESS: injected currents or temperature difference

$$\Delta S^{(n)}_{\text{traj}} \equiv k_B \ln \frac{P_F[V(t) \xrightarrow{n} V(t+\tau)|V(t)]}{P_R[V(t+\tau) \xrightarrow{n} V(t)|V(t+\tau)]}$$

$$\Delta S^{(n)}_Q = \sum_t^{t+\tau} V i_R \Delta t / T$$



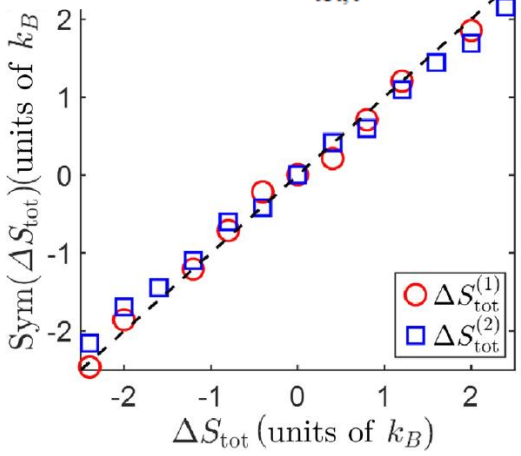




Phys. Rev. E **95,** 012158 (2017)

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

$$\text{sym}(\Delta S_{\text{tot},\tau}) \equiv \ln \frac{P(\Delta S_{\text{tot},\tau} = a)}{P(\Delta S_{\text{tot},\tau} = -a)}$$

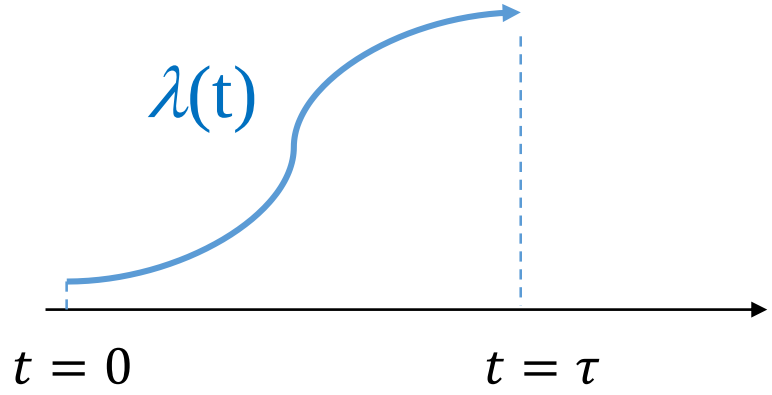


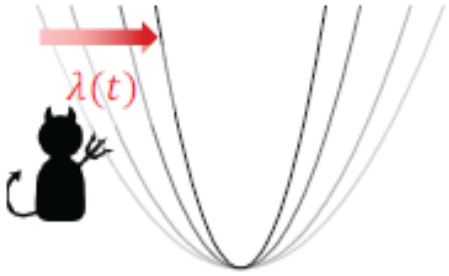
# Brownian particle in a time-dependent trapping potential

**Paradigm System:** $U(x,\lambda(t)) = \frac{1}{2}\lambda(t)x^n$ (harmonic n=2, anharmonic n=4,6...)

Protocol: from t=0 to t=$\tau$

Compression (stiffness λ increases) or Expansion (λ decreases)



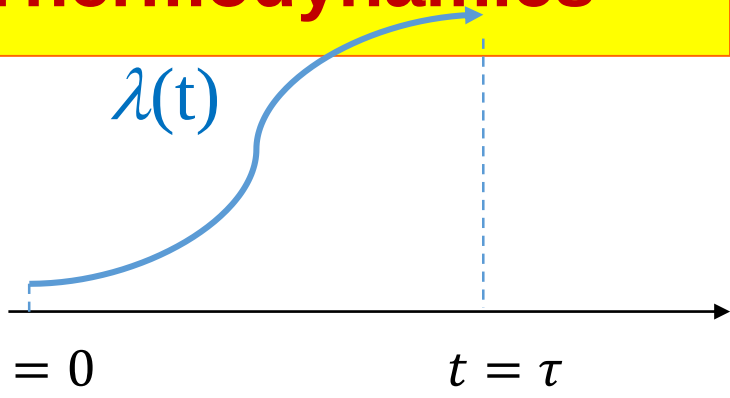




1-dim. overdamped Langevin dynamics (analytic results & simulations)

Experiment: single colloidal bead in water under feedback traps.
Particle tracking and recording trajectories

# Key Quantities in Stochastic Thermodynamics

## Non-steady state




$$U(x, \lambda(t)) = \tfrac{1}{2}\lambda(t)x^n$$

**For each trajectory $x(t)$:-**

**Free Energy Change:** $\Delta F(t) = \frac{k_B T}{n} \ln \frac{\lambda(t)}{\lambda(0)}$

**Stochastic Work:** $W(t) = \frac{1}{2}\int_0^t \dot{\lambda}(t)x^n(t)dt$

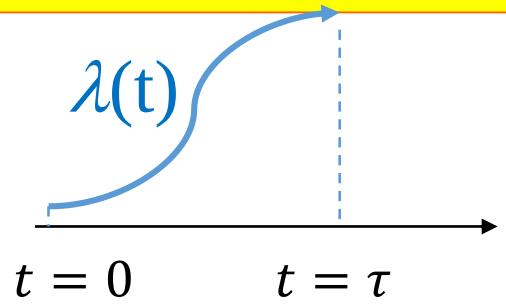
**Total stochastic Entropy Production:** $\Delta S(t) = W(t) - \Delta F(t)$

a trajectory is "second-law violating" if it's $\Delta S < 0$
"second-law abiding" if it's $\Delta S \geq 0$

$f_v$ : fraction of trajectories with ΔS < 0 (violating the law).
$f_a$ : fraction with ΔS ≥ 0 (abiding the law). $f_a + f_v = 1$

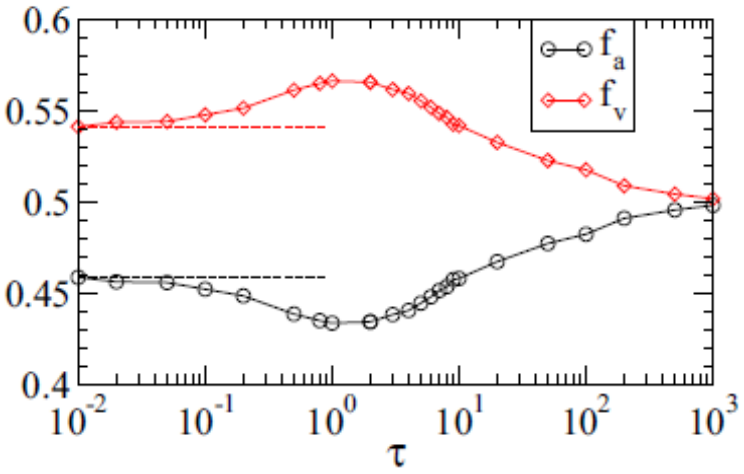
$f_a$ & $f_v$ calculated theoretically, measured in simulations and experiments
.

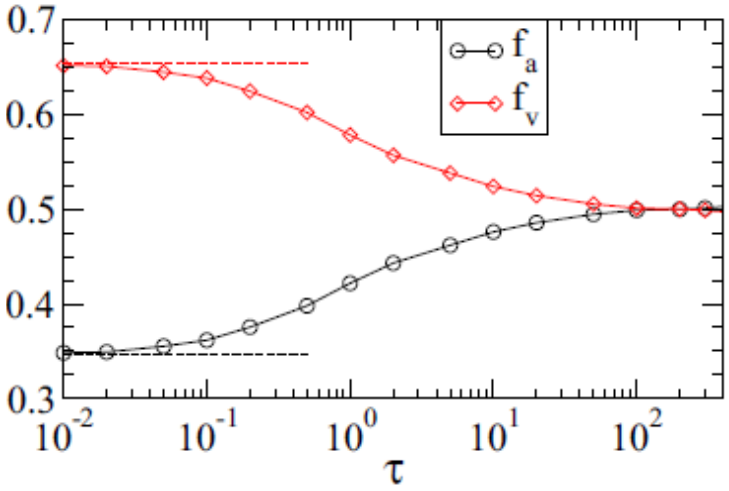
# Simulation Results – fraction of 2nd-Law violating events




$$\lambda(t) = \lambda(0)[1 + b(1 - \cos\tfrac{\pi t}{\tau})]. \qquad U(x, \lambda(t)) = \tfrac{1}{2}\lambda(t)x^n$$

$f_v$ & $f_a$ vs. τ= driving duration (in unit of relaxation time)




Harmonic Trap, n=2 (b=1, λ tripled) anharmonic, n=4

**for fast compression, the violating trajectories are the majority.**

The phenomenon is robust and potentially enhanced in non-harmonic potentials.

# 2nd-Law violators can outnumber the abiders

$f_v > f_a$ is possible (and not uncommon) in non-equilibrium non-steady states

**For NE Steady States: 2nd-Law violating events are always rare: $f_a > f_v$.**
Guaranteed by the Fluctuation Theorem NESS:

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

$$1 = \int_{-\infty}^{\infty} P(\Delta S)d\Delta S \quad = \quad f_a + f_v$$

$$= \int_{0}^{\infty} P(\Delta S)d\Delta S + \int_{0}^{\infty} P(\Delta S)e^{-\Delta S/k_B}d\Delta S \quad \Longrightarrow \quad f_a > f_v \text{ always for NESS}$$

$f_a$ $f_v$

For NE non-steady states: detailed FT relates forward and reverse protocols:

$$P(\Delta S) = P_R(-\Delta S)e^{\Delta S/k_B}$$

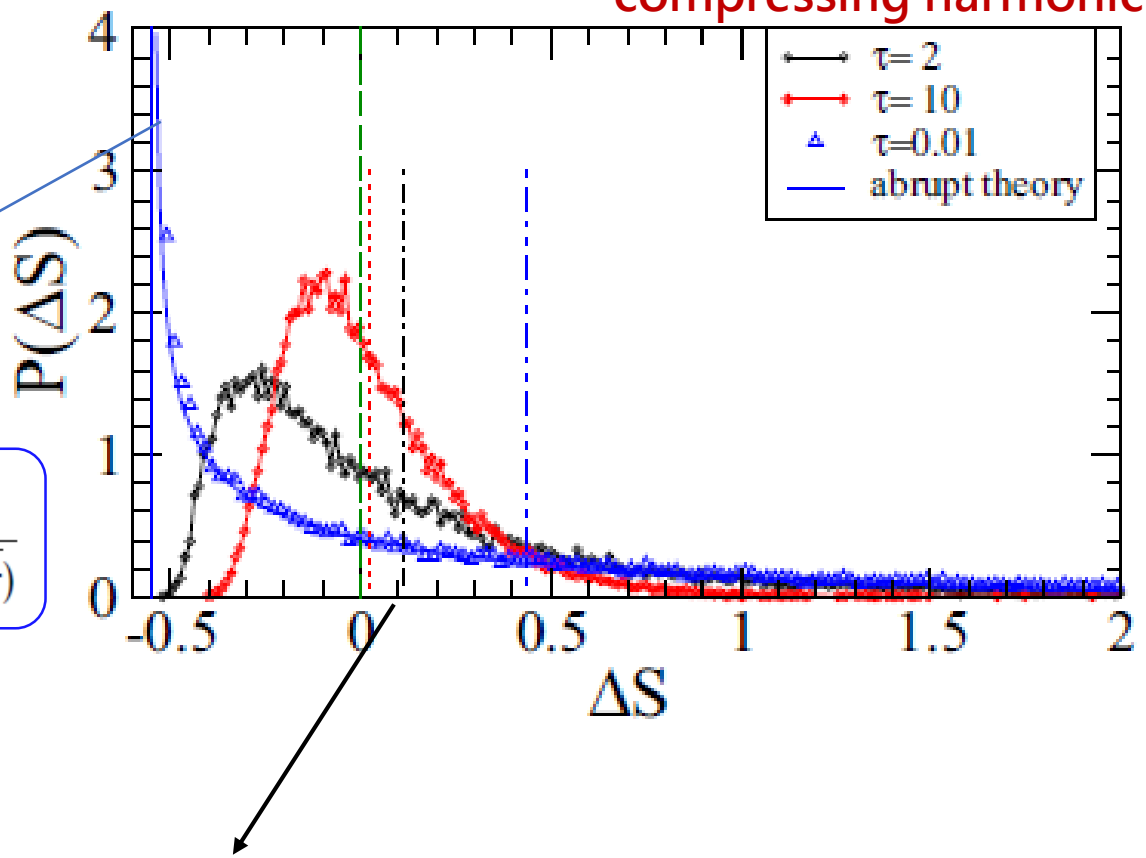
$$1 = \int_{-\infty}^{\infty} P(\Delta S)d\Delta S$$

But $P_R \neq P$. for non-steady states !

$$= \int_{0}^{\infty} P(\Delta S)d\Delta S + \int_{0}^{\infty} P_R(\Delta S)e^{-\Delta S/k_B}d\Delta S.$$

# Entropy production Distribution P(ΔS)

compressing harmonic trap




exact P(ΔS) for τ →0

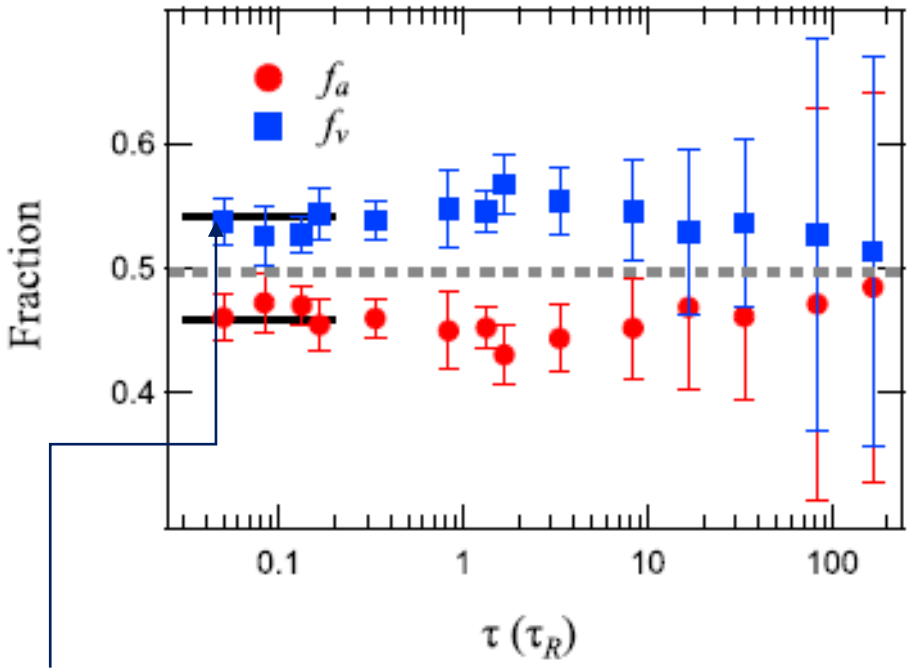
$$\Theta\left(\Delta S+\frac{1}{2}\ln r\right)\frac{e^{-\frac{\Delta S+\frac{1}{2}\ln r}{r-1}}}{\sqrt{\pi(r-1)\left(\Delta S+\frac{1}{2}\ln r\right)}}$$

**The Average:** ⟨ΔS⟩ > 0 (vertical dotted line), macroscopic 2nd Law holds !

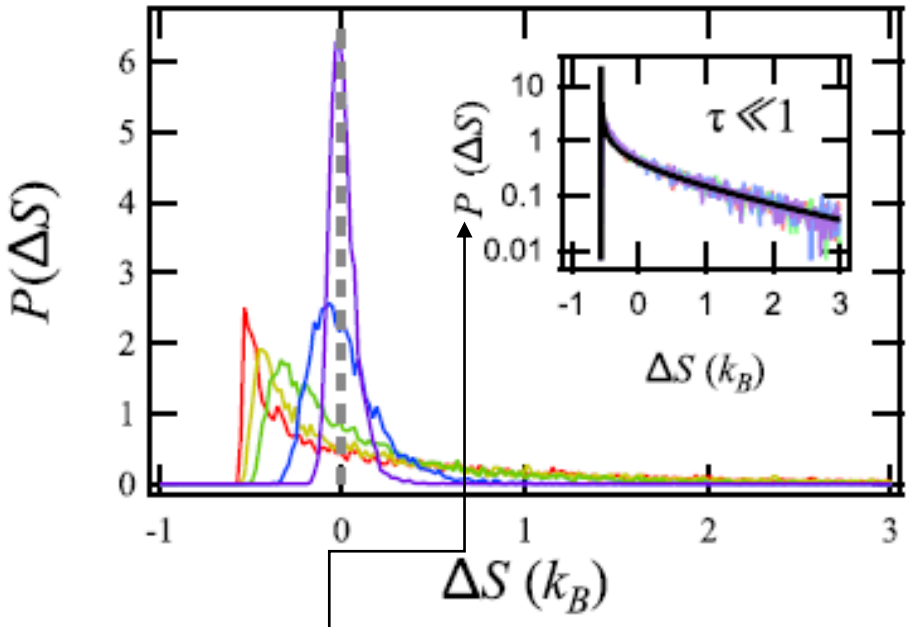
Many small "wins" (negative ΔS), a few huge "losses" (positive ΔS) → ⟨ΔS⟩ > 0

# Experimental results

- 1 μm polystyrene particles are immersed in water and trapped in the time-dependent harmonic potential, $U(x, \lambda(t)) = \lambda(t)x^2/2$ created by a dual optical tweezers system.
- The stiffness of one optical trap keeps fixed at the stiffness $\kappa$ = 15 pN/μm,
- A second trap shifts the position based on the particle position to apply the feedback force onto the particle such that the stiffness of the harmonic potential can be changed.
- The stiffness of the potential of the compressing and expanding processes are
  $\lambda(t) = \lambda_i(1 + (1 - \cos(\pi t/\tau)))$ (stiffness tripled for compression)




$$f_v = \mathrm{erf}(\tfrac{1}{2}\sqrt{\ln 3}) \approx 0.5414.$$




$$\Theta\left(\Delta S + \frac{1}{2}\ln r\right)\frac{e^{-\frac{\Delta S + \frac{1}{2}\ln r}{r-1}}}{\sqrt{\pi(r-1)\left(\Delta S + \frac{1}{2}\ln r\right)}}$$

$r$=3

# Analytic results for abrupt protocol: $\tau \to 0$

- Infinitely fast compression/expansion. Stiffness jumps from initial to final values.
- The particle does not have time to move/respond, so its distribution remains the initial Boltzmann distribution.

$$U(x,\lambda(t)) = \tfrac{1}{2}\lambda(t)x^n$$

- **Analytic Result for $P(\Delta S)$:**

[also for the reversed process $P_R(\Delta S)$]

$$P(\Delta S) = \Theta\left(\Delta S + \frac{1}{n}\ln r\right) \times \frac{e^{-\frac{\Delta S + \frac{1}{n}\ln r}{r-1}}}{\Gamma\left(\frac{1}{n}\right)(r-1)^{1/n}\left[\Delta S + \frac{1}{n}\ln r\right]^{1-1/n}} \qquad r \equiv \frac{\lambda(\tau)}{\lambda(0)}$$

$$\xrightarrow{n=2} \Theta\left(\Delta S + \frac{1}{2}\ln r\right)\frac{e^{-\frac{\Delta S + \frac{1}{2}\ln r}{r-1}}}{\sqrt{\pi(r-1)\left(\Delta S + \frac{1}{2}\ln r\right)}},$$

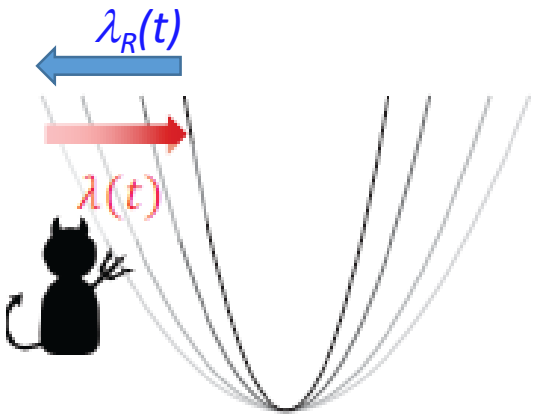
- $f_v$ & $f_a$ :

$$f_v = 1 - \frac{\Gamma_{\frac{1}{n}}\left(\frac{\ln r}{n(r-1)}\right)}{\Gamma\left(\frac{1}{n}\right)} \xrightarrow{n=2} \operatorname{erf}\left(\sqrt{\frac{\ln r}{2(r-1)}}\right),$$

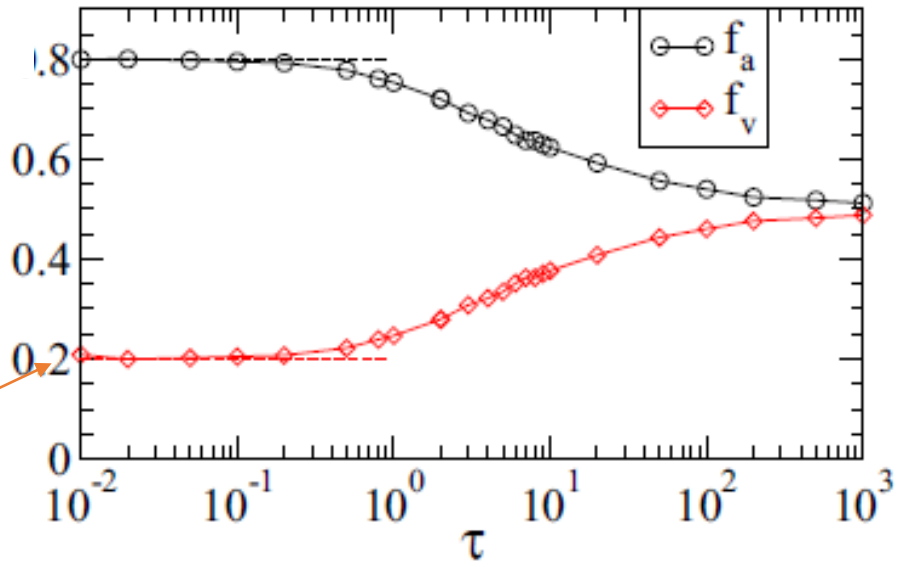
[also for the reversed process--expansion]

- Confirmed in simulations and experiment for fast compression/expansion

# 2nd-Law violating event are less in Expansion: $f_v < f_a$




the reversed process--expansion




$n=2,\ r=3$

abrupt expansion:

$$f_v^R = \frac{\Gamma_{\frac{1}{n}}\left(\frac{\ln r}{n(1-1/r)}\right)}{\Gamma\left(\frac{1}{n}\right)}$$

$\Rightarrow f_v^R < \frac{1}{2}$ always!

**Fluctuations are strong in a compressing trap → higher chance to achieve $\Delta S < 0$**

**Fluctuations are less strong in an expanding trap → less chance to achieve $\Delta S < 0$**

# Fluctuations in ΔS : Analytic results

the compressing process has larger fluctuations

Abrupt protocol (τ→0) for harmonic & anharmonic traps: $U(x,\lambda(t)) = \frac{1}{2}\lambda(t)x^n$

$$\langle \Delta S \rangle = \frac{1}{n}(r - \ln r - 1), \quad \sigma_{\Delta S} = \frac{r-1}{\sqrt{n}}$$

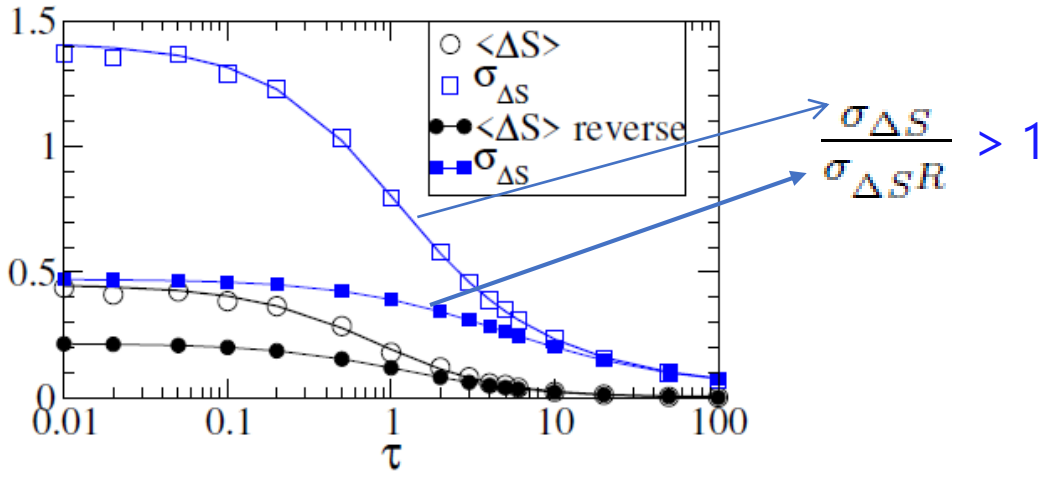
$$\langle \Delta S^R \rangle = \frac{1}{n}(\frac{1}{r} + \ln r - 1), \quad \sigma_{\Delta S^R} = \frac{1-1/r}{\sqrt{n}}$$

forward(compressing) $r \equiv \frac{\lambda(\tau)}{\lambda(0)}$ reverse(expanding)

$$\frac{\sigma_{\Delta S}}{\sigma_{\Delta S^R}} = r > 1$$

Finite τ protocol for harmonic trap: $U(x,\lambda(t)) = \frac{1}{2}\lambda(t)x^2$

$$\sigma^2_{\Delta S} = \int_0^\tau dv \dot{\lambda}(v) \left[\mu(v)\left(\frac{1}{\lambda(0)} + 2\int_0^v \frac{dx}{\mu^2(x)}\right)\right]^2 \int_v^\tau du \dot{\lambda}(u)\mu^2(u). \qquad \mu(t) \equiv e^{-\int_0^t \lambda(s)ds}$$




$\frac{\sigma_{\Delta S}}{\sigma_{\Delta S^R}}$ > 1

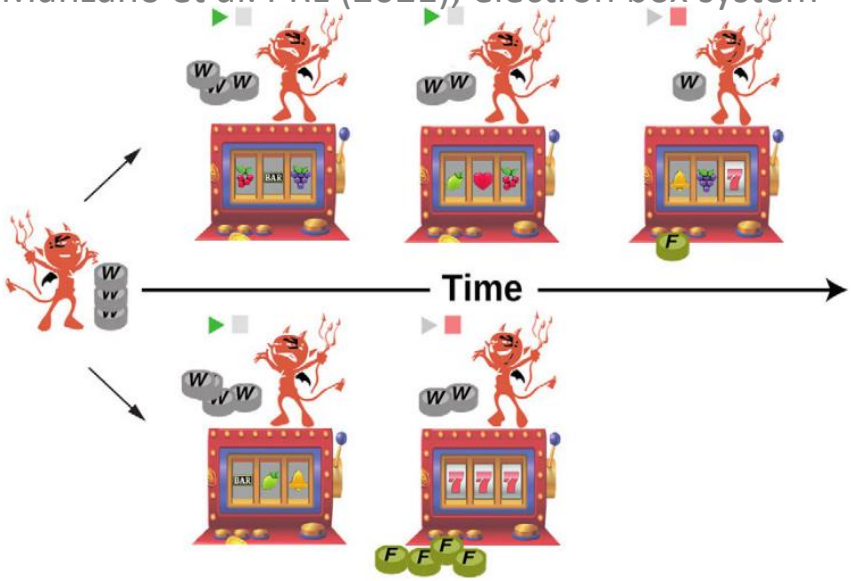
# Gambling Analogy: Gambling Demon

Winning: win over (beat) the 2nd-Law, $\Delta S < 0$ event
Losing: abiding the 2nd-Law, $\Delta S > 0$
Macroscopic 2nd-Law always holds: on average $\langle \Delta S \rangle > 0$

$\Rightarrow$ many small "wins" (negative ΔS, violating trajectories), but a few catastrophic "losses" (large positive ΔS) renders a losing gambler (although the gambler experienced many times winning !)

Gambling demon --still win ($\langle \Delta S \rangle < 0$) on average by stopping at the right moment
stopping-time Fluctuation Theorem

Manzano et al. PRL (2021), electron box system

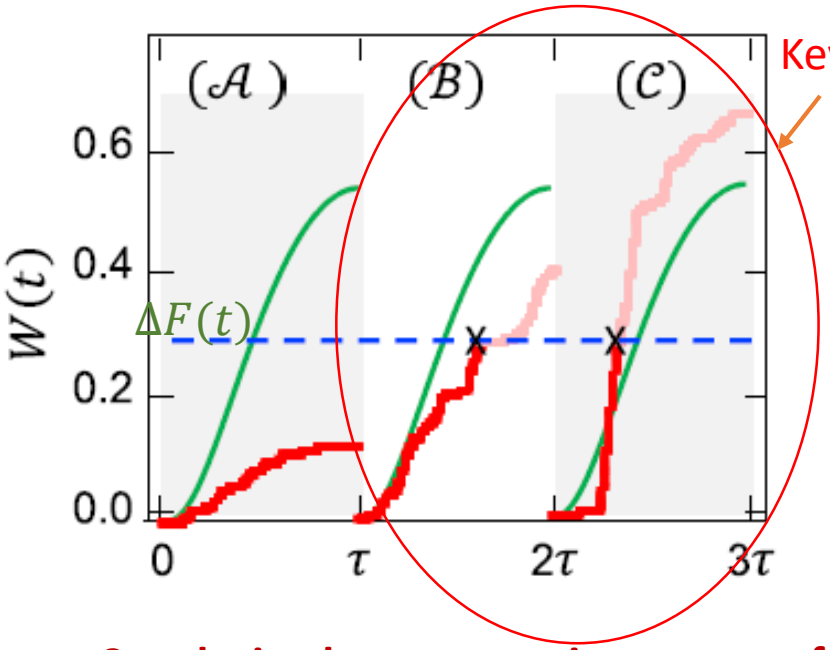



win (extract useful work) by exploiting information & decide to stop under some prescribed condition

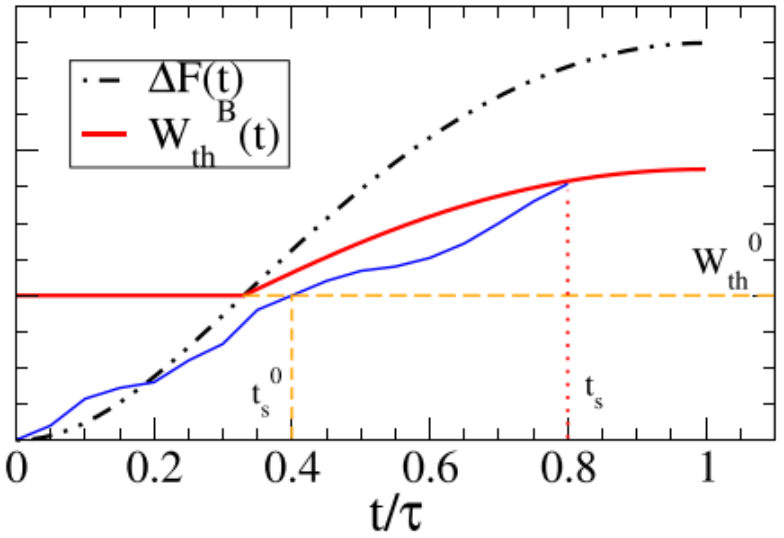
Gambling demon realized in the compressing trap of a Brownian bead with stopping criteria of $W(t) > W_{th}$

# Two main factors to achieve overall(average) winning

- **Win: $W \leq \Delta F$ when stopped/finished**
- **Three type of trajectories:**
- **Simply lucky: [trajectory *A* ] demon does nothing**
- **cut the (expected and potentially big) loss by early stopping [trajectory *C* ] when the cumulative work reaches the threshold.**
- **stop and harvest some appropriate winning profit without taking the risk till the end of the journey [trajectory *B* ]**




Key winning factors




- **Can design better stopping strategy for the demon to win more**

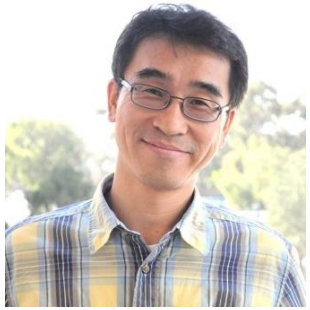
$\tau$

# Summary

- In **non-steady, far-from-equilibrium** processes, **Second-law violating trajectories ($\Delta S < 0$) can be the majority and** not rare.
- Demonstrated in a Brownian bead under a **compressing trap** via theory, simulation, and experiment.
- 
- For the **reverse process** of an expanding trap, **Second-law violating trajectories are always the minority.**
- Derived **analytic results** for the extreme case of abrupt compression/expansion.
- The asymmetry between compression and expansion is key, linked to larger **$\Delta S$** fluctuations during compression.
- **Potential Applications:** By exploiting these statistics, as in the "gambling demon", work can be extracted (winning) if sufficiently far from equilibrium;
  design optimal control protocols in small systems, extract work more efficiently in micro- information/heat engines

# Collaborators:

## Yonggun Jun田溶根, J.A.C. Albay, Yi-Hung Liao (NCU)



*"Second-Law violating events are not Rare in Non-equilibrium non-steady states ",* Phys. Rev. E 111, L022103 (2025).

"*Winning Strategies of a Gambling Demon in a Squeezing Potential",* Phys. Rev. Research, 5, 023115 (2023).

"*Gambling demon & Stopping-time fluctuation relation of a Brownian particle under a time-dependent trapping potential"* Phys. Rev. E 109, 014124 (2024).

Thank you for your attention