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

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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

\[
\text{Work: } dw = \frac{\partial H}{\partial \lambda} \dot{\lambda} dt \quad \text{Heat: } dq = \frac{\partial H}{\partial x} \dot{x} dt
\]


For overdamped Langevin Dynamics

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

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 \( dx \)

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

\[ dE = \Delta W + \Delta Q \]

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

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)
  \[ \langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \]
  \[ \langle e^{-\beta W} \rangle \geq e^{\beta \Delta F} \]

- Hummer-Szabo relation (2001)
  \[ \langle \delta(\Gamma - \Gamma')e^{-\beta W} \rangle = \frac{e^{-\beta U_{\tau}(\Gamma)}}{Z_0} \]

- Crooks Fluctuation Theorem (1998)
  \[ \frac{P_R(-W)}{P_F(W)} = e^{-\beta(W-\Delta F)} \]

- Differential Fluctuation Theorem (2008)
  \[ P_F(W, \Gamma_0 \rightarrow \Gamma_{\tau})e^{-\beta(W-\Delta F)} = P_R(-W, \Gamma_{\tau} \rightarrow \Gamma_{0}^*) \]

Time reversed:
\[ \overline{\lambda}, = \lambda_{\tau-t} \]
What is the origin of fluctuation theorems?

Microscopic reversibility \[^{[3,4,8,22]}\]:

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

\[\lambda_{\tau-i}, \tilde{\Gamma}_i := \langle x_{\tau-i}, -p_{\tau-i} \rangle\]

Impossible to test it in experiment!

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

Proof of the microscopic reversibility

- Path integral representation
  - “Boltzmann factor for a whole trajectory”
    \[
    p[\zeta(\tau)] \sim \exp \left[ -\int_0^t d\tau \frac{\zeta^2(\tau)}{4D} \right]
    \]
    \[
    p[x(\tau)|x_0] \sim \exp \left[ -\int_0^t d\tau \frac{(\dot{x} - \mu F)^2}{4D} \right]
    \]
  
- “time reversal” \( \tilde{x}(\tau) \equiv x(t - \tau) \) and \( \tilde{\lambda}(\tau) \equiv \lambda(t - \tau) \)

- Ratio of forward to reversed path
  \[
  \frac{p[x(\tau)|x_0]}{\tilde{p}[\tilde{x}(\tau)|\tilde{x}_0]} = \frac{\exp \left[ -\int_0^t d\tau \frac{(\dot{x} - \mu F)^2}{4D} \right]}{\exp \left[ -\int_0^t d\tau \frac{(\dot{\tilde{x}} - \mu F)^2}{4D} \right]}
  = \exp \beta \int_0^t d\tau \dot{x} F = \exp \beta q[x(\tau)] = \exp \Delta s_m
  \]

Differential fluctuation theorem (DFT)

- **DFT version 1** (2000, Jarzynski) \cite{9}:

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

- **DFT version 2** (2008, Karplus) \cite{10}:

\[
\frac{P_R(-W, \Gamma_\tau^\dagger \to \Gamma_0^\dagger)}{P_F(W, \Gamma_0 \to \Gamma_\tau)} = e^{-\beta (W - \Delta F)}
\]

The most detailed fluctuation theorem that can be tested experimentally.

The Hierarchy of Fluctuation Theorems

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

\[
\frac{P_F(W,x_0 \rightarrow x_\tau)}{P_R(-W,x_\tau \rightarrow x_0^*)} = e^{-\beta(W-\Delta F)}
\]

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

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

Previous experiments

Stretching RNA molecules \cite{13-15}

Electronic circuit \cite{24,25}

Brownian particle trapped in water \cite{16,17}

\begin{enumerate}
\item J. P. Pekola, Nat. Phys. 11, 118 (2015).
\end{enumerate}
Experimental test of Jarzynski’s equality

- Nano-world Experiment: Stretching RNA

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

- distributions of $W_{\text{diss}}$: 
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


...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 $\theta$, and, indeed, in a totally irregular manner.

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

$\theta = 3.3 \times 10^{-7}$ seconds.
Technical breakthrough:

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

Measurement of instantaneous velocity of a Brownian Motion
Our experiment

Silica nanosphere levitated in AIR using optical tweezers \cite{18-20}

We can study the thermodynamics of the phase space.

\cite{19} T. Li, et al. Science 329, 1673 (2010).
\cite{19} S. Kheifets et al. Science 343, 1493 (2014).
Our experiment

- In air, room temperature (296K)
  \[ H(x, v, t) = \frac{1}{2} k x^2 - f(t) x + \frac{1}{2} m v^2 \]
  \[ f(t): f_{\text{off}} \rightarrow f_{\text{on}} \]
  \[ \Delta F = -\frac{f_{\text{on}}^2 - f_{\text{off}}^2}{2k}, \quad W = \int_0^T \frac{\partial H}{\partial f} \hat{f}(t) dt \]

- Challenges of our experiment:
  - Very large statistics
    - one million cycles, 500 µs /cycle
  - \( \sim 10^{10} \) 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)

\[
\frac{P_R(-W, x_2 \rightarrow x_1)}{P_F(W, x_1 \rightarrow x_2)} = e^{-\beta (W - \Delta F)}
\]

\[
\frac{P_R(-W, -v_2 \rightarrow -v_1)}{P_F(W, v_1 \rightarrow v_2)} = e^{-\beta (W - \Delta F)}
\]

\[(x, v) = (x \pm \frac{\sigma_x}{11}, v \pm \frac{\sigma_v}{11})\]

121 combinations of \(\{x_1, x_2\}\) or \(\{v_1, v_2\}\)
Test the differential fluctuation theorem

- Underdamped regime (50 Torr)

\[
\frac{P_R(-W, x_2 \rightarrow x_1)}{P_F(W, x_1 \rightarrow x_2)} = e^{-\beta(W - \Delta F)}
\]

\[
\frac{P_R(-W, -v_2 \rightarrow -v_1)}{P_F(W, v_1 \rightarrow v_2)} = e^{-\beta(W - \Delta F)}
\]

- \( f_{off} = 0, f_{on} = 340 \text{ fN} \)
- Ramp time \( \sim 4.6 \mu s \)
- Particle size \( r = 209 \pm 9 \text{ nm} \)
- \( \Omega = 60.4 \pm 0.3 (2\pi \cdot \text{kHz}) \)
- \( \Delta F = -1.3 k_B T \)
Test the GJE for delta distribution and the HSR

**GJE for delta distribution:**
\[
\langle e^{-\beta(W-\Delta F)} | x_i = x \rangle_F = \frac{p_R(\tilde{x}_f = x)}{p_F(\tilde{x}_i = x)} \\
\langle e^{-\beta(W-\Delta F)} | v_i = v \rangle_F = \frac{p_R(\tilde{v}_f = -v)}{p_F(\tilde{v}_i = v)}
\]

**HSR:**
\[
\langle e^{-\beta(W-\Delta F)} | x_f = x \rangle_F = \frac{p_R^e(\tilde{x}_i = x)}{p_F(x_f = x)} \\
\langle e^{-\beta(W-\Delta F)} | v_f = v \rangle_F = \frac{p_R^e(\tilde{v}_i = -v)}{p_F(v_f = v)}
\]
Test the GJE for arbitrary initial states

- GJE for arbitrary initial states

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

![Graph A: Delta distribution](image)

- See last slide

![Graph B: P-shaped state](image)

- Lhs: 0.92 ± 0.02
- Rhs: 0.90

![Graph C: Uniform distribution](image)

- Lhs: 1.42 ± 0.03
- Rhs: 1.42

![Graph D: Microcanonical ensemble](image)

- 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 $r = 145 \pm 5 \, nm$
  - $\Omega = 76 \pm 3 \, (2\pi \cdot kHz)$
  - $\Delta F = -0.24 \, k_B T$
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.

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 $^{[21]}$
  - Unpreceidentedly detailed level
- Technique to generate arbitrary initial states
  - Post-selection of trajectories
- Outlook: extension to quantum regime $^{[12,23]}$
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