Hyunggyu Park 박 형 규 朴 炯 奎

Entropy production and Fluctuation theorems

1. Nonequilibrium processes
2. Brief History of Fluctuation theorems
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4. Experiments
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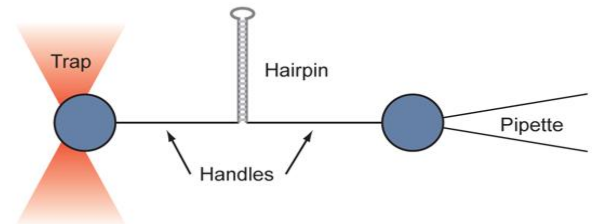
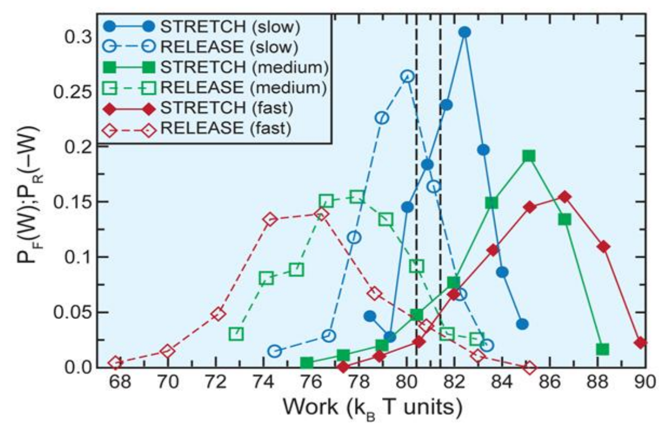


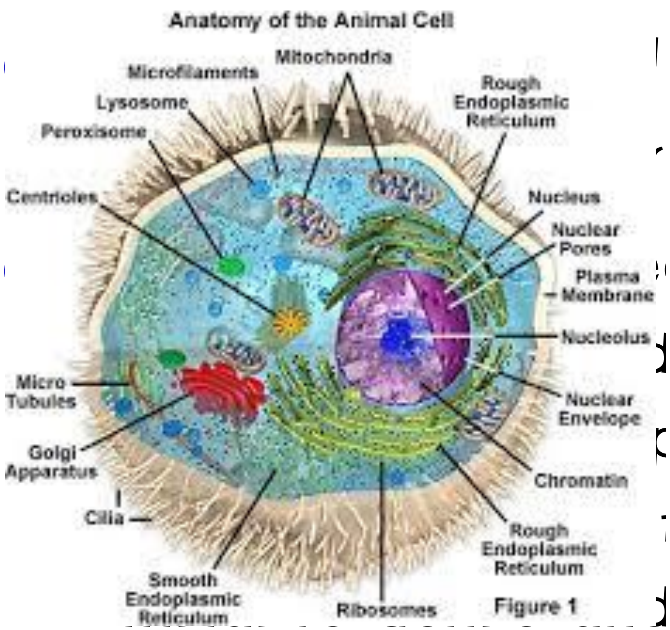


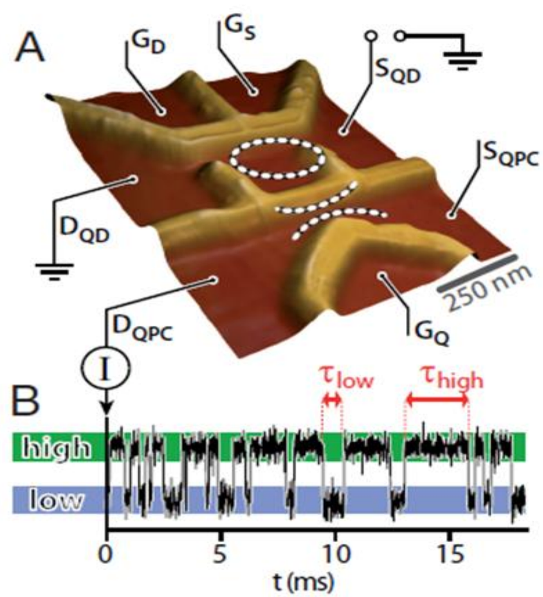
(Bustamante)

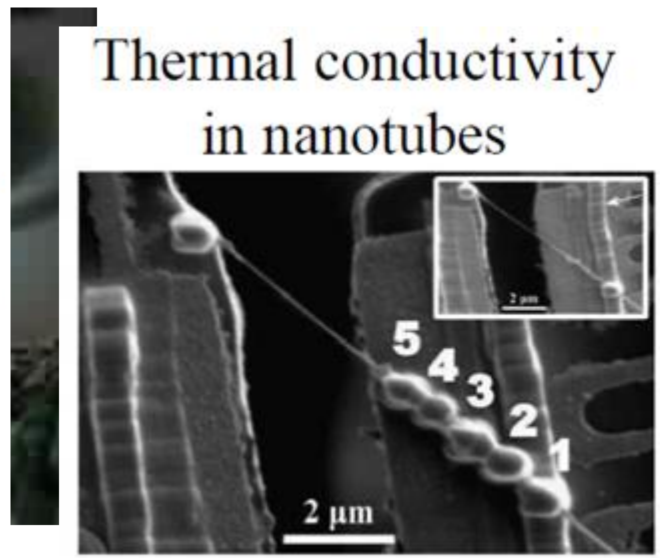
IAS program on frontiers of soft matter physics:
from nonequilibrium dynamics to active matter at IAS, Hong Kong (January 7, 2014)

Nonequilibrium processes

- Why NEQ processes?
  - biological cell (molecular motors, protein reactions, ⋯)
  - electron, heat transfer, .. in nano systems
  - evolution of bio. species, ecology, socio/economic sys., ...
  - moving toward equilibrium & NEQ steady states (NESS)
  - interface coarsening, ageing, percolation, driven sys., ⋯







Brief history of FT (I)

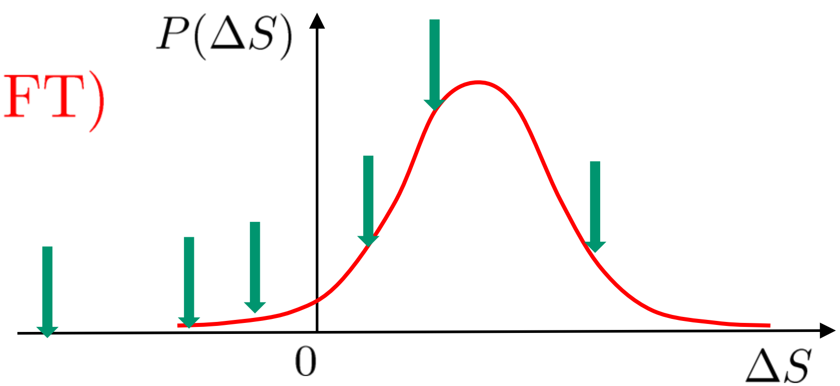
- Evans, Cohen, Morris (1993)

observation of FT in molecular dynamics simulations on fluid systems

- Gallavotti and Cohen (1995)

analytic derivation of FT in "deterministic" systems (NEQ steady state)

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



Gallavotti-Cohen symmetry

$$\langle e^{-\Delta S}\rangle = 1 = \int d(\Delta S) P(\Delta S) e^{-\Delta S}$$ (Integral FT)

➡ Jensen's inequality ($\langle e^{x}\rangle \geq e^{\langle x\rangle}$) leads to $\langle \Delta S\rangle \geq 0$.

- Thermodynamic 2nd law is a consequence of (GC symmetry FT).

$$\langle e^{y}\rangle \geq \langle 1+y\rangle$$
with $y = x - \langle x\rangle$

⋆ Special NEQ pocesses, NEQ steady state

Brief history of FT (II)

- Jarzynski (1997)

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

FT in Hamiltonian systems (work-free energy relation)

- Kurchan (1998)

FT in Langevin equation approach for stochastic systems

- Lebowitz and Spohn (1999)

⋆ Bochkov/Kuzovlev (1977)

FT in master equation approach for stochastic systems

- Crooks (1999)

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

DFT for stochastic systems

- Hatano and Sasa (2001)

FT in NEQ steady states

two independent FT
$\Delta S = \Delta S_{hk} + \Delta S_{ex}$

- Speck/Seifert/van den Broeck

Information entropy

- Sagawa/....
- Our group/Spinney/Ford

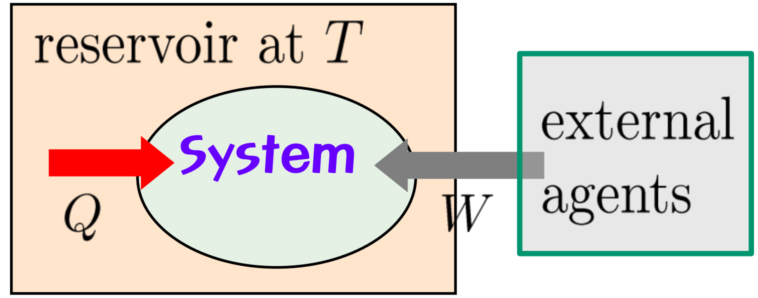
odd parity

- Experiments: Bustamante(2002, 2005), Ciliberto(2002,2005), ...

Thermodynamics

Themodyn. 1st law

$$\Delta E = Q + W$$



Themodyn. 2nd law

S: entropy

$$\Delta S_{\rm total} = \Delta S_{\rm s} + \Delta S_{\rm r}$$

$$\langle \Delta S_{\rm total} \rangle \geq 0$$

Phenomenological law

$dS \neq \frac{dQ}{T}$ $\quad \langle W \rangle \geq \Delta F$ $\quad dS \geq \frac{dQ}{T}$

Total entropy does not change during reversible processes.

Total entropy increases during irreversible (NEQ) processes.

- Work and Free energy $\quad (F = E - TS)$

$$\Delta S_r = -\frac{Q}{T}$$

$$W = \Delta E - Q = \Delta E + T\Delta S_{\rm r}$$
$$= \Delta E - T\Delta S_{\rm s} + T\Delta S_{\rm total} = \Delta F + T\Delta S_{\rm total}$$

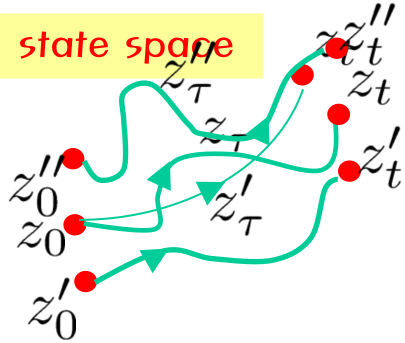
Jarzynski equality

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

Jarzynski equality & Fluctuation theorems

Simplest derivation in Hamiltonian dynamics

$H = \frac{p^2}{2m} + \frac{1}{2}\lambda_\theta x^2$
with $\lambda_\tau = \lambda(\tau)$



¶ state $z = (x, p)$
¶ Hamiltonian (deterministic) H dynamics w/o heat reser.
¶ consider a dynamic path z_τ with $0 < \tau < t$
¶ introduce a time-dependent parameter λ_τ : $H = H_\lambda$
¶ average over EQ initial ensemble $p(z_0, 0)$ at $T = 1/\beta$

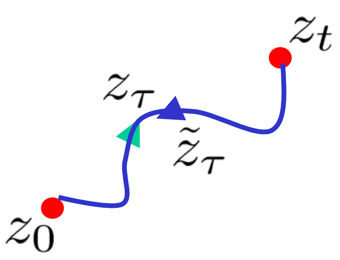
- $W[z_\tau] = H_{\lambda_t}(z_t) - H_{\lambda_0}(z_0)$ (no heat reservoir $Q = 0 \to W = \Delta E$)
- $\langle e^{-\beta W}\rangle = \int \mathcal{D}z_\tau \mathcal{P}_F(z_\tau) e^{-\beta W[z_\tau]} = \int dz_0 p(z_0, 0) e^{-\beta W}$ ($\mathcal{P}_F(z_\tau) = p(z_0, 0)$)
  - $p(z_0, 0) = e^{-\beta H_{\lambda_0}(z_0)}/Z_{\lambda_0}$ ($Z_{\lambda_0} = \int dz_0 e^{-\beta H_{\lambda_0}(z_0)}$: partition function)
  - Liouville theorem ($dp(z_\tau, \tau)/d\tau = 0$) guarantees Jacobian $|\partial z_t/\partial z_0| = 1$
- $\langle e^{-\beta W}\rangle = \frac{1}{Z_{\lambda_0}} \int dz_t e^{-\beta H_{\lambda_0}(z_0)} e^{-\beta(H_{\lambda_t}(z_t) - H_{\lambda_0}(z_0))}$
  $= Z_{\lambda_t}/Z_{\lambda_0} = e^{-\beta(F_{\lambda_t} - F_{\lambda_0})} = e^{-\beta \Delta F}$

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

-Intial distribution must be of Boltzmann (EQ) type. crucial
-Hamiltonian parameter changes in time. (special NE type). generalized
-In case of thermal contact (stochastic) ? still valid

Jarzynski equality & Fluctuation theorems

Crooks "detailed" fluctuation theorem



¶ Forward path z_τ with $0 < \tau < t$

¶ Backward (reverse) path $\tilde{z}_\tau$ with $\tilde{z}_\tau = z_{t-\tau}$ $(\tilde{p}_\tau = -p_{t-\tau})$

¶ Reverse protocol: $\tilde{\lambda}_\tau = \lambda_{t-\tau}$

odd variable

¶ EQ initial ensemble for both F(B)-paths.

- $$\frac{\mathcal{P}_F(z_\tau)}{\mathcal{P}_R(\tilde{z}_\tau)} = \frac{p(z_0,0)}{p(\tilde{z}_0,0)} = \frac{Z_{\lambda_t}}{Z_{\lambda_0}} \frac{e^{-\beta H_{\lambda_0}(z_0)}}{e^{-\beta H_{\lambda_t}(z_t)}} = e^{\beta(W-\Delta F)_F}$$

time-reversal symmetry
for deterministic dynamics

- $$\langle \mathcal{O}[z] \rangle_F = \int \mathcal{D}z_\tau \mathcal{P}_F(z_\tau)\mathcal{O}[z] = \int \mathcal{D}z_\tau \mathcal{P}_R(\tilde{z}_\tau) e^{\beta(W[z]-\Delta F)} \mathcal{O}[z]$$
$$= \langle \tilde{\mathcal{O}}[\tilde{z}] e^{-\beta W[\tilde{z}]} \rangle_R \cdot e^{-\beta \Delta F}$$ with $W[\tilde{z}] = -W[z]$

- For $\mathcal{O}[z] = \delta(W - W[z])$, we have $P_F(W) = \langle \delta(W + W[\tilde{z}]) \rangle_R \cdot e^{\beta W - \beta \Delta F}$

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

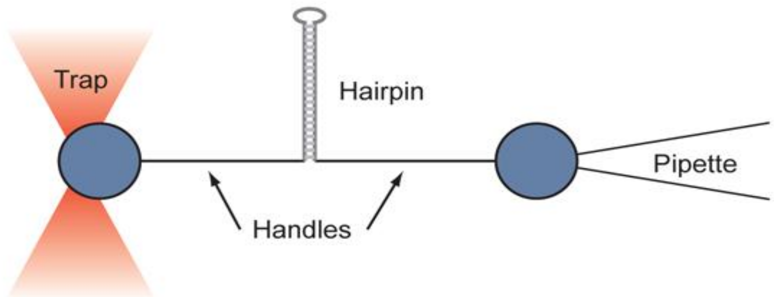
Crooks detailed FT for PDF of Work

- For $\mathcal{O}[z] = e^{-\beta W[z]}$, $\langle e^{-\beta W} \rangle_F = e^{-\beta \Delta F}$ (Jarzinsky equality)

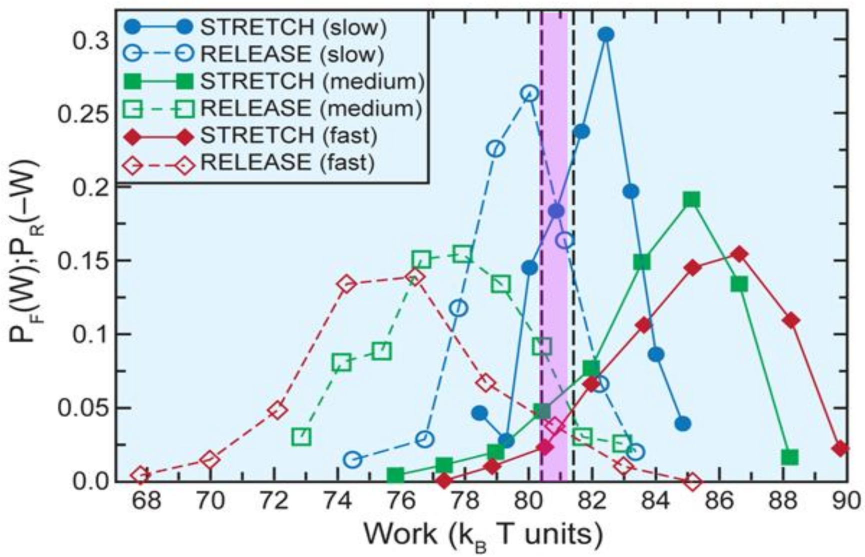
"Integral" FT

Experiments

DNA hairpin mechanically unfolded by optical tweezers

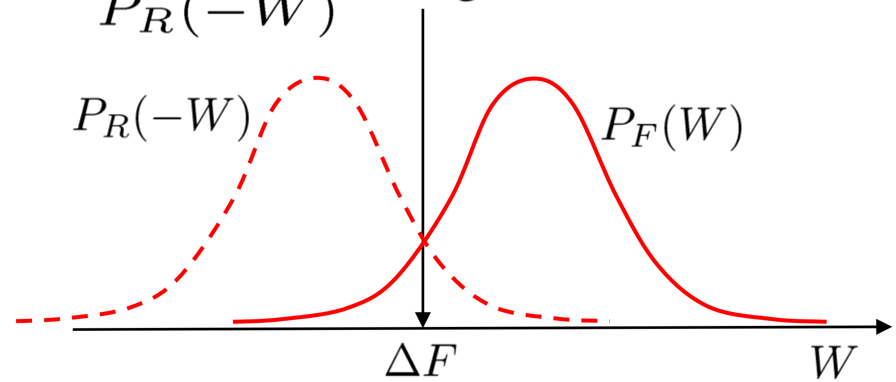


Collin/Ritort/Jarzynski/Smith/Tinoco/Bustamante, Nature, 437, 8 (2005)



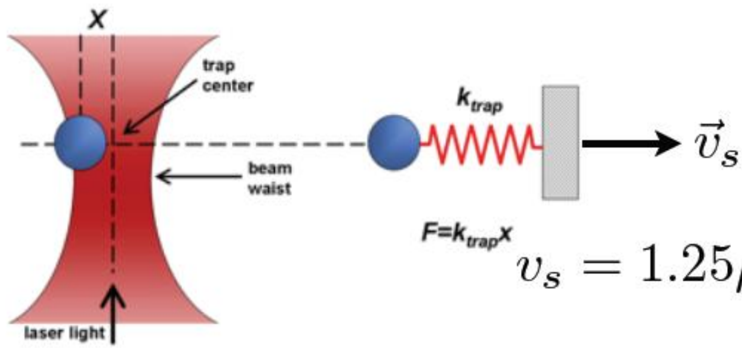
Detailed fluctuation theorem

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



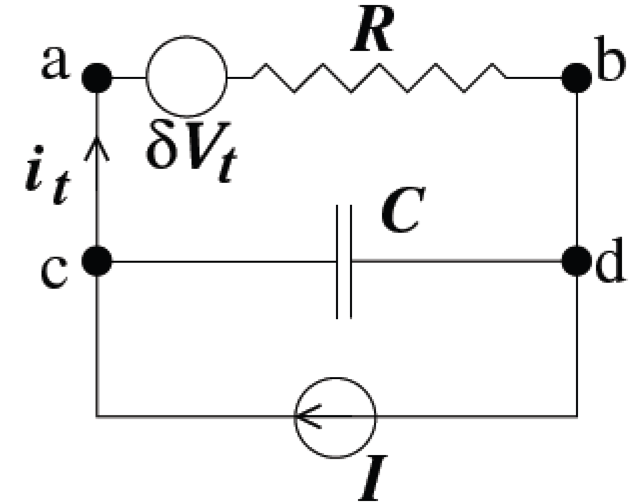
- At $P_F(W) = P_R(-W)$, W must be the same as ΔF, independent of intermediate processes.

- Considerable prob. for $W < \Delta F$
- Efficient measurement of ΔF



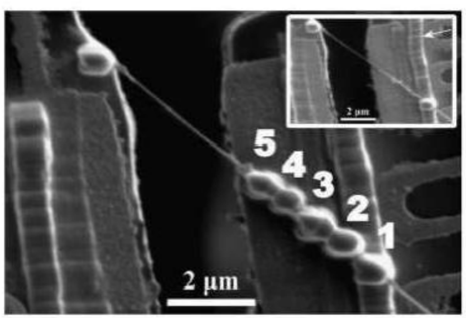
$v_s = 1.25\mu\text{m/s}$

[Wang et al `02] $\alpha/k = 3$ ms



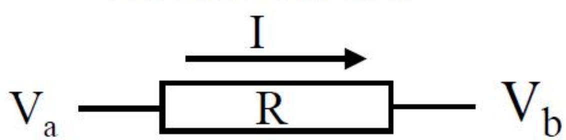
[Garnier&Ciliberto `05]

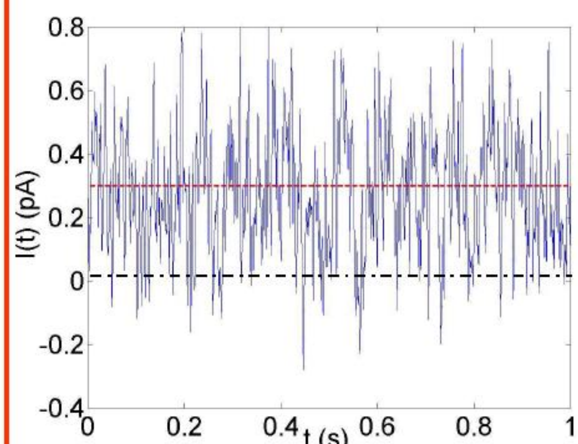
Thermal conductivity in nanotubes



C.W. Chang, et al.
PRL 101, 075903 (2008)

Electric current





R.Van Zon, et al
PRL 92, 130601 (2004).

N. Garnier, S. Ciliberto
PRE 71, 060101 (2005)

$$\bar{I} = \frac{(V_b - V_a)}{R}$$

Injected power
$10^{-19} W$

PNAS 106, 10116 (2009)

Universal oscillations in counting statistics

C. Flindt[a,b,1], C. Fricke[c], F. Hohls[c], T. Novotný[b], K. Netočný[d], T. Brandes[e], and R. J. Haug[c]

[a]Department of Physics, Harvard University, 17 Oxford Street, Cambridge, MA 02138; [b]Department of Condensed Matter Phys and Physics, Charles University, Ke Karlovu 5, 12116 Prague, Czech Republic; [c]Institut für Festkörperphysik, Leibniz Universität Germany; [d]Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Prague, Czech Republic; and Physik, Technische Universität Berlin, D 10623 Berlin, Germany

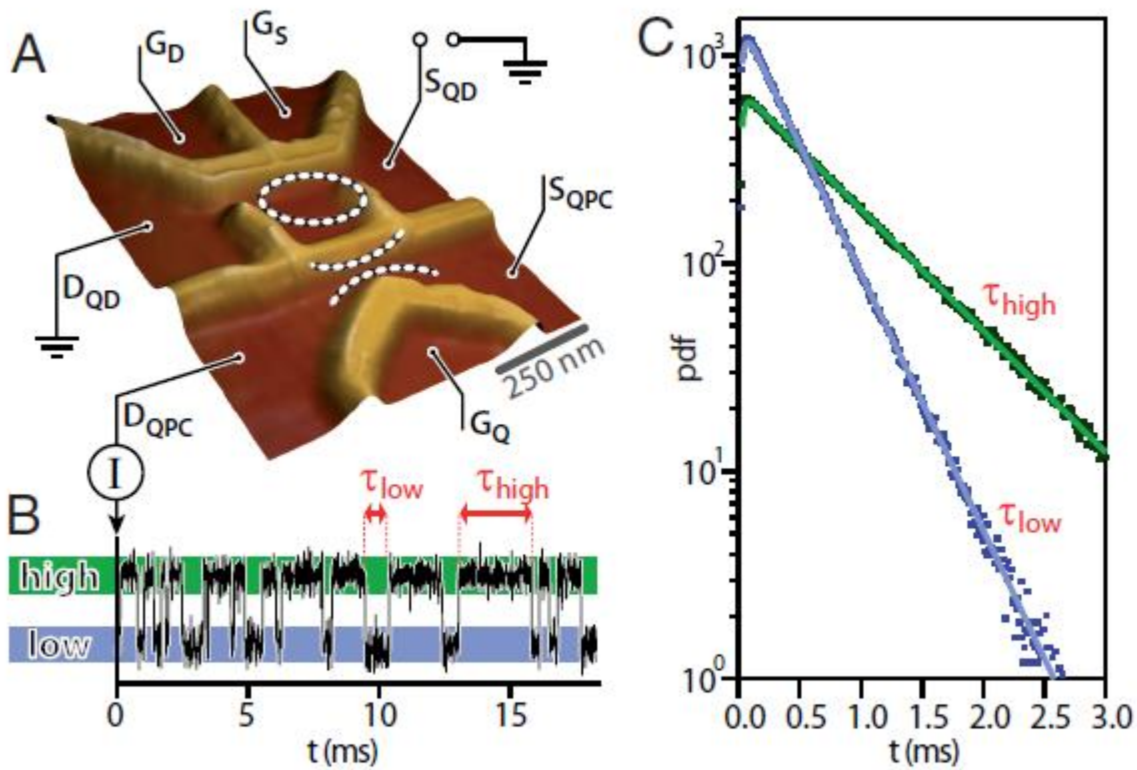


Fig. 1. Real-time counting of electrons tunneling through a quantum dot.

arXiv: 1008.1184

KEK-T

Non-Equilibrium Fluctuations of Black Hole Horizons

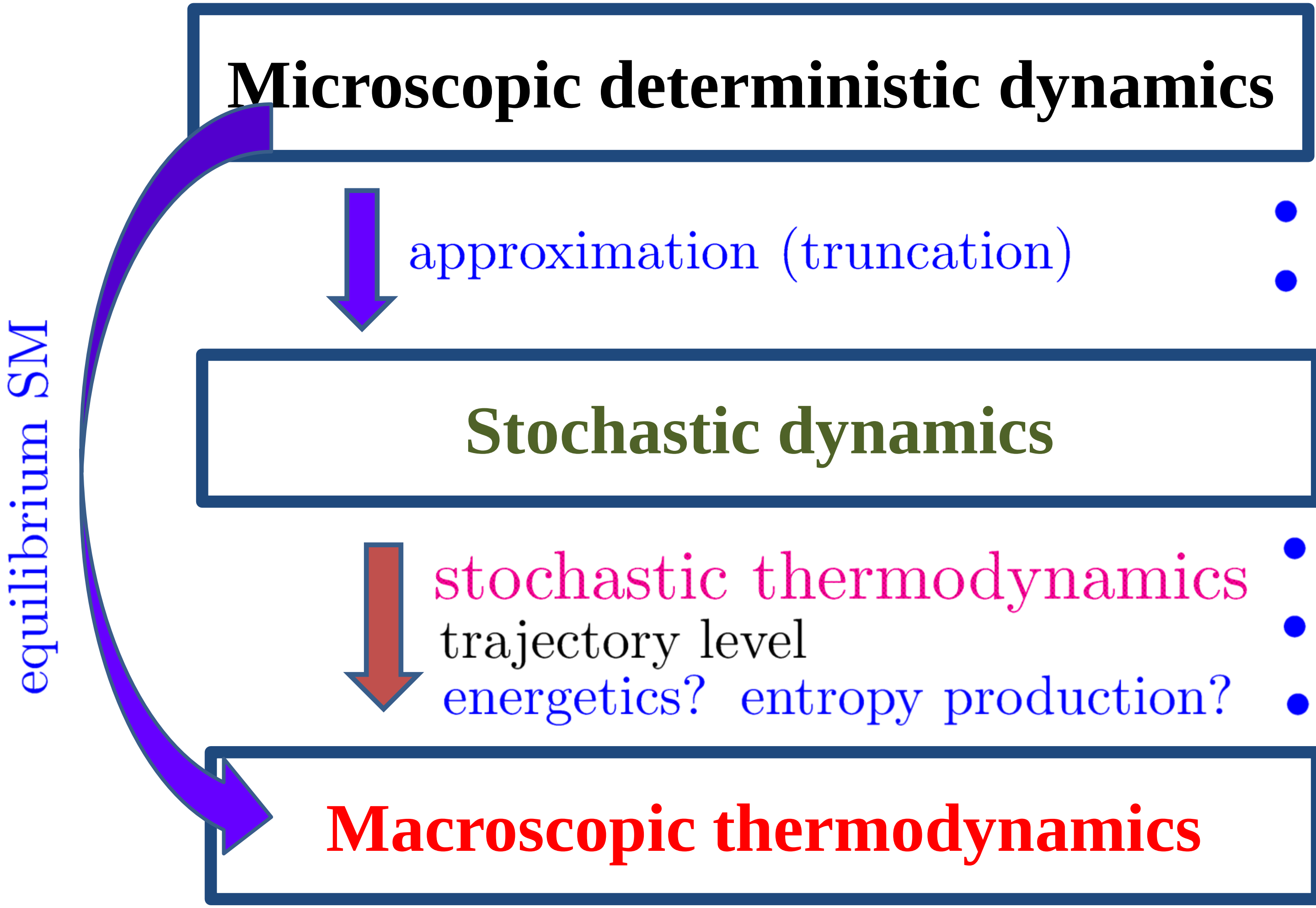
Satoshi Iso,[*] Susumu Okazawa,[†] and Sen Zhang[‡]
KEK Theory Center, Institute of Particle and Nuclear Studies,
High Energy Accelerator Research Organization(KEK)
and
The Graduate University for Advanced Studies (SOKENDAI),
Oho 1-1, Tsukuba, Ibaraki 305-0801, Japan

(Dated: August 9, 2010)

We investigate non-equilibrium nature of fluctuations of black hole horizons by applying the fluctuation theorems and the Jarzynski equality developed in the non-equilibrium statistical physics. These theorems applied to space-times with black hole horizons lead to the generalized second law of thermodynamics. It is also suggested that the second law should be violated microscopically so as to satisfy the Jarzynski equality.

Stochastic thermodynamics

[Sekimoto(1998),Seifert(2005)]



- Hamilton equation
- TR symmetry

- Langevin equation
- Master equation
- TR symmetry broken

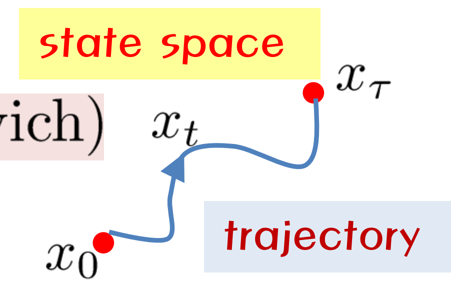
- NOT really dynamics
- TR symmetry broken

Langevin (stochastic) dynamics

¶ Brownian particle in a potential V with protocol $\lambda(t)$ & external force $g(x)$

$$\dot{v} = -\partial_x V(x;\lambda) + g(x) - \gamma v + \xi \quad (v = \dot{x} \ \& \ m = 1) \ \text{thermal reservoir}$$

with $\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')$ and $\gamma = \beta D$ (Einstein relation)



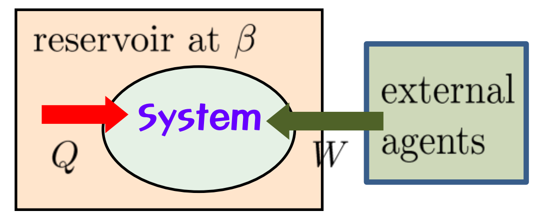
- Kinetic energy K and Total energy E:

(Stratonovich)

$$\dot{K} = \frac{d}{dt}\left[\frac{1}{2}v^2\right] = v\dot{v} = -v\partial_x V + vg + v(-\gamma v + \xi)$$

$$\dot{E} = \dot{K} + \dot{V}(x;\lambda) = \dot{K} + \dot{x}(\partial_x V) + \dot{\lambda}(\partial_\lambda V)$$

$$= v(-\gamma v + \xi) + vg + \dot{\lambda}(\partial_\lambda V) \quad = \dot{Q} + \dot{W}$$



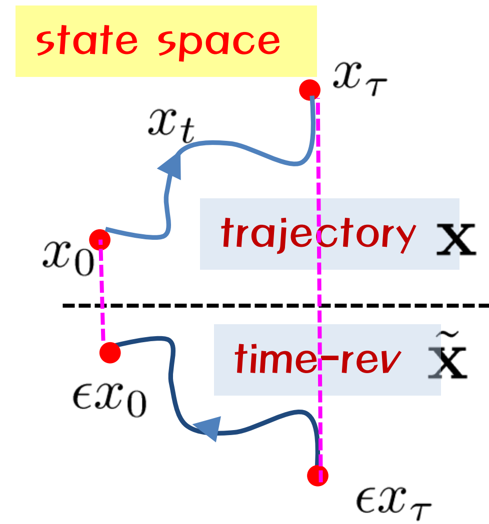
- Heat Q and Work W (at the trajectory level)

$$\dot{Q} \equiv v(-\gamma v + \xi) \quad \text{and} \quad \dot{W} \equiv vg + \dot{\lambda}(\partial_\lambda V) \qquad \text{(Jarzynski work)}$$

- Entropy production $\Delta S_{\rm tot}$: $\Delta S_{\rm tot} = \Delta S_{\rm res} + \Delta S_{\rm sys}$??? (trajectory)

$$\Delta S_{\rm res} = -\beta Q \quad \text{and} \quad \Delta S_{\rm sys} = -\ln(p_{x_\tau}/p_{x_0}) \ \text{(Shannon entropy)}$$

Stochastic process, Irreversibility & Total entropy production



¶ Dynamic trajectory in state space
with a set of state variables: $x = (s_1, s_2, \cdots)$

- under time-reversal operation: $s_i \to \epsilon_i s_i$ (ϵ_i : parity)
- odd-parity variable: $\epsilon_i = -1$ (momentum, ...)
  even-parity variable : $\epsilon_i = 1$ (position, ...)
- "time-reversed" (mirror) state : $\epsilon x = (\epsilon_1 s_1, \epsilon s_2, \cdots)$

¶ Irreversibility (total entropy production)

$$\Delta S_{\rm tot}[\mathbf{x}] = \ln \frac{\mathcal{P}[\mathbf{x}]}{\mathcal{P}[\tilde{\mathbf{x}}]}$$

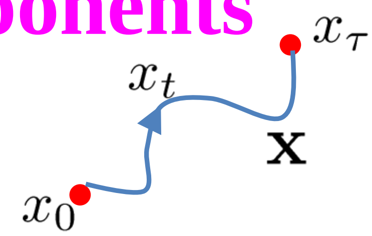
$P(\mathbf{x})$:probability of traj. $\mathbf{x}$
$\tilde{\mathbf{x}}$: time-reversed traj.

Time-reversed dynamics ??

- *integral* fluctuation theorem (FT) : automatic
  $\langle e^{-\Delta S_{\rm tot}} \rangle = \sum_{\mathbf{x}} \mathcal{P}[\mathbf{x}] e^{-\Delta S_{\rm tot}} = \sum_{\tilde{\mathbf{x}}} \mathcal{P}[\tilde{\mathbf{x}}] = 1$ (Jacobian $|\partial \tilde{\mathbf{x}} / \partial \mathbf{x}| = 1$).
  (valid for any finite-time "transient" process) $\langle \Delta S_{\rm tot} \rangle \geq 0$
- *detailed* fluctuation theorem (FT) : involution, i.c.-sensitive
  $P(\Delta S_{\rm tot}) / \tilde{P}(-\Delta S_{\rm tot}) = e^{\Delta S_{\rm tot}}$

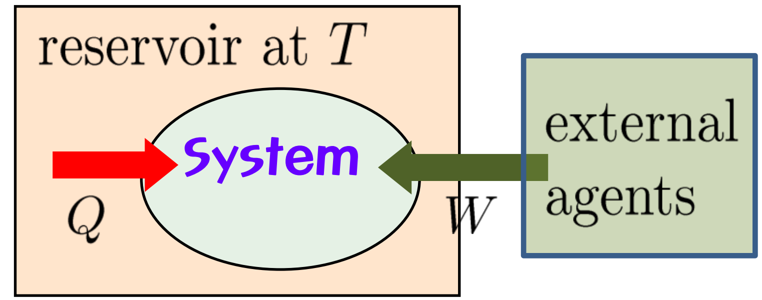
[Seifert(2005), Esposito/vdBroeck(2010)]

Total entropy production and its components



$\langle e^{-\Delta S_{\rm tot}}\rangle = 1,\ P(\Delta S_{\rm tot})/P(-\Delta S_{\rm tot}) = e^{\Delta S_{\rm tot}}$

[A] $\Delta S_{\rm tot}[\mathbf{x}] = \Delta S_{\rm sys}[\mathbf{x}] + \Delta S_{\rm env}[\mathbf{x}]$



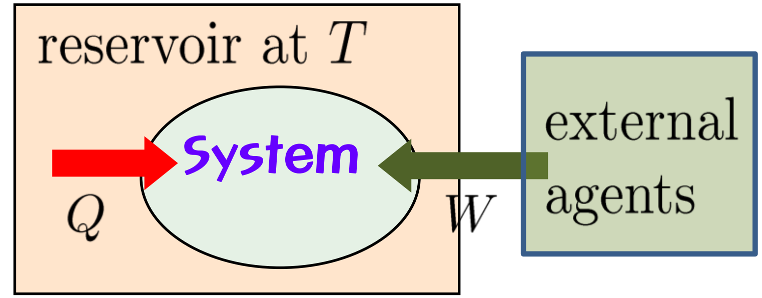
- $\Delta S_{\rm sys} = -\ln(p_{x_\tau}/p_{x_0})$ (Shannon entropy)
- $\Delta S_{\rm env} = \Delta S_{\rm res} = -\frac{Q}{T}$
  without feedback control
  changing external agents (information entropy: Maxwell's demon)
- $\Delta S_{\rm sys}, \Delta S_{\rm res}$: not FT variables

[B] $\Delta S_{\rm tot}[\mathbf{x}] = \Delta S_{\rm hk}[\mathbf{x}] + \Delta S_{\rm ex}[\mathbf{x}]$

- $\Delta S_{\rm hk}$: EP to maintain the NESS [Hatano/Sasa(2001), Speck/Seifert(2005)]
- $\Delta S_{\rm ex}$: EP regarding transitions between steady states ($\lambda(t)$)
- $\Delta S_{\rm ex}, \Delta S_{\rm hk}$: FT variables $\langle e^{-\Delta S_{\rm ex}}\rangle = 1, \langle e^{-\Delta S_{\rm hk}}\rangle = 1$ • 2nd laws
- $\Delta S_{\rm hk}$: adiabatic, $\Delta S_{\rm ex}$: non-adiabatic ($\Delta S_{\rm ex}$ vanishes in $\dot{\lambda} \to 0$ limit)

(even-parity variable only: overdamped case) [Esposito/vdBroeck(2010)]

Fluctuation theorems



$$\langle e^{-\beta W_d} \rangle = 1 \qquad (W_d = W - \Delta F\text{: dissipated work})$$

$$\langle e^{-\Delta S_t} \rangle = 1 \qquad (S_t = S + S_r\text{: total entropy})$$

$$\langle e^{-\Delta S_{ex}} \rangle = 1 \qquad (\Delta S_{ex} = \Delta S - \beta Q_{ex})$$

$$\langle e^{-\Delta S_{hk}} \rangle = 1 \qquad (\Delta S_{hk} = -\beta Q_{hk})$$

Integral fluctuation theorems

Fluctuation theorems

Integral fluctuation theorems

$$\langle e^{-R} \rangle = 1 \quad (R = \Delta S_t, \beta W_d, \Delta S - \beta Q_{ex}, -\beta Q_{hk}, \cdots)$$

Jensen's inequality ($\langle e^x \rangle \geq e^{\langle x \rangle}$) leads to $\langle R \rangle \geq 0$.

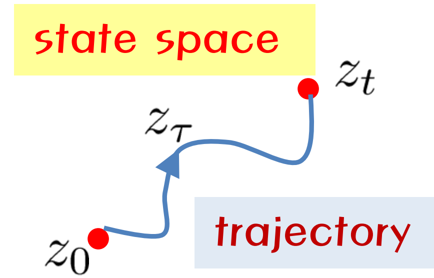
Thermodynamic 2nd laws

Detailed fluctuation theorems

$$\frac{P(R)}{\tilde{P}(-R)} = e^R \qquad \int dR P(R) e^{-R} = 1$$

Probability theory

- Consider two normalized PDF's : $\mathcal{P}(z_\tau)$, $\tilde{\mathcal{P}}(\tilde{z}_\tau)$



$$\sum_{z_\tau} \mathcal{P}(z_\tau) = 1, \; \sum_{\tilde{z}_\tau} \tilde{\mathcal{P}}(\tilde{z}_\tau) = 1 \quad \text{with } \tilde{z}_\tau = \pi(z_\tau)$$

- Define "relative entropy"

$$|J(\pi)| = 1$$

$$R(z_\tau) \equiv \ln \frac{\mathcal{P}(z_\tau)}{\tilde{\mathcal{P}}(\tilde{z}_\tau)} \Rightarrow \langle e^{-R} \rangle_{\mathcal{P}} = \sum_{z_\tau} e^{-R(z_\tau)} \mathcal{P}(z_\tau)$$

$$= \sum_{\tilde{z}_\tau} \tilde{\mathcal{P}}(\tilde{z}_\tau) = 1$$

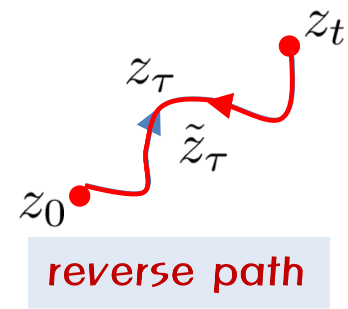
$$\Delta S_{\text{tot}}[\mathbf{x}] = \ln \frac{\mathcal{P}[\mathbf{x}]}{\mathcal{P}[\tilde{\mathbf{x}}]}$$

Integral fluctuation theorem $\quad \langle e^{-R} \rangle_{\mathcal{P}} = 1 \quad \langle R \rangle_{\mathcal{P}} \geq 0$

(Kullback-Leibler divergence)

(exact for any finite-time trajectory)

Probability theory



- Consider the mapping : $\tilde{\mathcal{P}}(\tilde{z}_\tau) = f \circ \mathcal{P}(z_\tau)$

- Require $f^2 = I$ (involution)

then, $\tilde{R}(\tilde{z}_\tau) = \ln \frac{\tilde{\mathcal{P}}(\tilde{z}_\tau)}{f \circ \tilde{\mathcal{P}}(\tilde{z}_\tau)} = \ln \frac{\tilde{\mathcal{P}}(\tilde{z}_\tau)}{\mathcal{P}(z_\tau)} = -R(z_\tau)$ $\quad R(z_\tau) \equiv \ln \frac{\mathcal{P}(z_\tau)}{f \circ \mathcal{P}(z_\tau)}$

$$P(R) = \sum_{z_\tau} \delta(R - R(z_\tau))\mathcal{P}(z_\tau)$$

$$= \sum_{\tilde{z}_\tau} \delta(R + \tilde{R}(\tilde{z}_\tau))e^{-\tilde{R}(\tilde{z}_\tau)}\tilde{\mathcal{P}}(\tilde{z}_\tau) = \tilde{P}(-R)e^R$$

Detailed fluctuation theorem $\quad \frac{P(R)}{\tilde{P}(-R)} = e^R$ **(exact for any finite t)**

$\langle \mathcal{O}(z_\tau) \rangle_{\mathcal{P}} = \langle \tilde{\mathcal{O}}(\tilde{z}_\tau) e^{-\tilde{R}(\tilde{z}_\tau)} \rangle_{\tilde{\mathcal{P}}}$ with $\mathcal{O}(z_\tau) = \tilde{\mathcal{O}}(\tilde{z}_\tau)$

(Generalized Crooks' relation)

Dynamic processes & Path probability ratio

¶ Hamiltonian (deterministic) dynamics without any heat reservoir with a time-dependent parameter λ_τ : $H = H_\lambda$

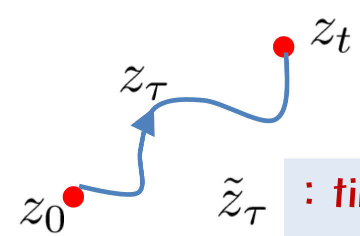
$H = \frac{p^2}{2m} + \frac{1}{2}\lambda_\tau x^2$ with $\lambda_\tau = \lambda(\tau)$

¶ Langevin (stochastic) dynamics with white noise and λ_τ and nonconservative force g : $\dot{z} = -\partial_z V(z;\lambda_\tau) + g(z) + \xi(\tau)$

¶ Markovian discrete (stochastic) dynamics with transition rate $w_{z,z'}$ for $z' \to z$: $\dot{p}_z = \sum_{z'} \left(w_{z,z'}(\lambda_\tau) p_{z'}(\tau) - w_{z',z}(\lambda_\tau) p_z(\tau) \right)$

¶ Thermostatted systems

⋆ Path probability ratio:

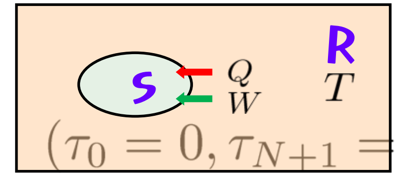


: time-reverse path

$$R(z_\tau) = \ln \frac{\mathcal{P}(z_\tau)}{\mathcal{P}(\tilde{z}_\tau)} = \ln \frac{p^0(z_0)\Pi(z_\tau)}{p^0(\tilde{z}_0)\Pi(\tilde{z}_\tau)}$$

($\Pi(z_\tau)$: conditional probability for path z_τ)

Markovian jump dynamics

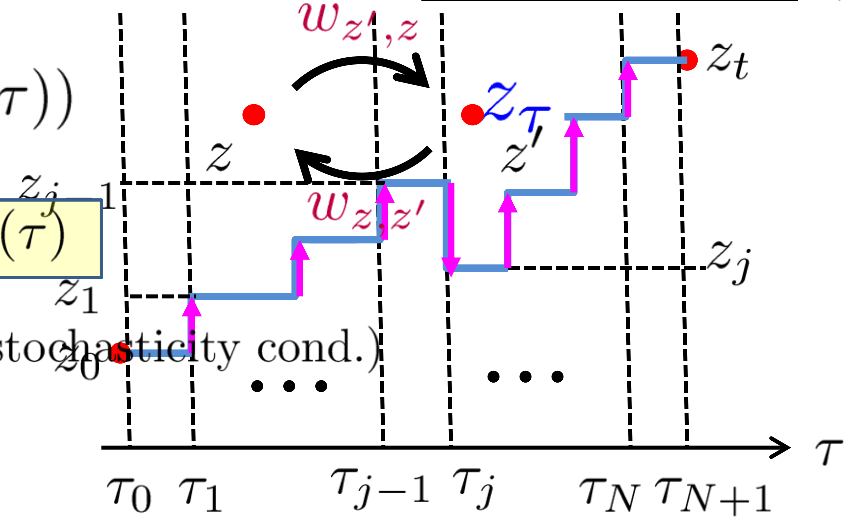


- Markovian discrete dynamics:

$$\dot p_z = \sum_{z'} \left(w_{z,z'}(\lambda_\tau) p_{z'}(\tau) - w_{z',z}(\lambda_\tau) p_z(\tau) \right)$$

$$\dot p_z = \sum_{z'} W_{z,z'}(\lambda_\tau) p_{z'}(\tau) \qquad \dot p_z = W_{z,z}(\lambda_\tau) p_z(\tau)$$

$$W_{z,z'} = \omega_{z,z'} - \delta_{z,z'} \sum_{z''} \omega_{z'',z} \qquad \sum_z W_{z,z'} = 0 \quad \text{(stochasticity cond.)}$$



- Conditional probability for trajectory z_τ with fixed $z(0) = z_0$ and λ_τ:

$$\boldsymbol{\Pi(z_\tau)} \sim \prod_{j=1}^N e^{\int_{\tau_{j-1}}^{\tau_j} d\tau' W_{z_{j-1},z_{j-1}}(\lambda_{\tau'})} W_{z_j,z_{j-1}}(\lambda_{\tau_j}) \cdot e^{\int_{\tau_N}^{t} d\tau' W_{z_N,z_N}(\lambda_{\tau'})}$$

$$e^{\int_{\tau_0}^{\tau_1} d\tau' W_{z_0,z_0}(\lambda_{\tau'})} * W_{z_1,z_0}(\lambda_{\tau_1}) * e^{\int_{\tau_1}^{\tau_2} d\tau' W_{z_1,z_1}(\lambda_{\tau'})} * W_{z_2,z_1}(\lambda_{\tau_2}) * \cdots$$

- For reverse trajectory $\tilde z_\tau$ with fixed $\tilde z(0) = z_t$ and $\tilde\lambda_\tau = \lambda_{t-\tau}$

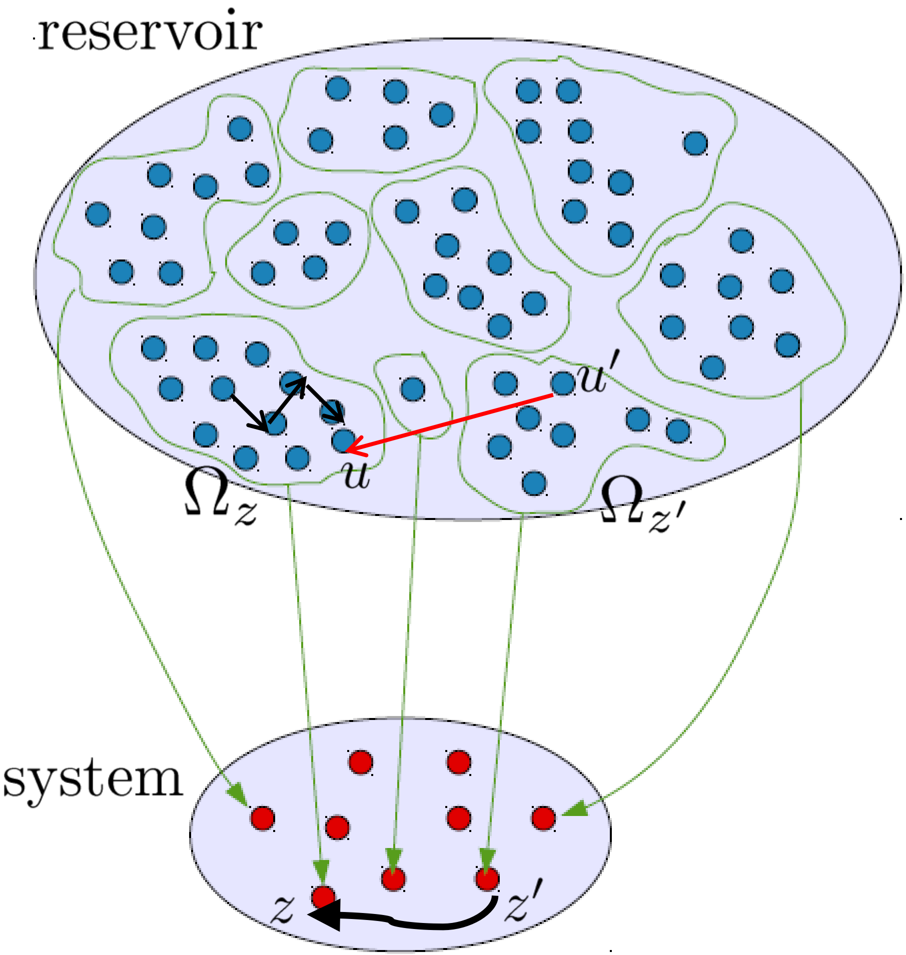
$$\tilde\Pi(\tilde z_\tau) \sim \prod_{j=1}^N e^{\int_{\tau_{j-1}}^{\tau_j} d\tau' W_{z_{j-1},z_{j-1}}(\lambda_{\tau'})} W_{z_{j-1},z_j}(\lambda_{\tau_j}) \cdot e^{\int_{\tau_N}^{t} d\tau' W_{z_N,z_N}(\lambda_{\tau'})}$$

¶ Log ratio: $$\ln \frac{\Pi(z_\tau)}{\tilde\Pi(\tilde z_\tau)} = \sum_{j=1}^N \ln \frac{W_{z_j,z_{j-1}}(\lambda_{\tau_j})}{W_{z_{j-1},z_j}(\lambda_{\tau_j})} = \Delta S_r(z_\tau) = -\beta Q(z_\tau)$$

Micro-reversibility (Schnakenberg, 1976) (reservoir EP)

Reservoir entropy change

Schnakenberg/Hinrichsen



$$\frac{w_{z,z'}}{w_{z',z}} \overset{?}{=} \frac{\sum w_{u,u'}}{\Omega_{z'}} \; \frac{\Omega_z}{\sum w_{u',u}}$$

instantaneous relaxation into a sector

Micro-reversibility :

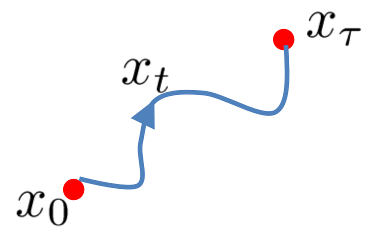
$w_{u,u'} p^s_{u'} = w_{u',u} p^s_u$ (detailed balance)

⇒ $w_{u,u'} = w_{u',u}$

- $\Delta S_r = \ln \frac{\Omega_z}{\Omega_{z'}} = \ln \frac{w_{z,z'}}{w_{z',z}}$
- $\Delta S_r(z_\tau) = \ln \frac{\Pi(z_\tau)}{\tilde{\Pi}(\tilde{z}_\tau)}$

More transparent in Langevin dynamics description

Langevin dynamics



¶ Brownian particle with "external" force $g(x)$

$$\dot{v} = g(x) - \gamma v + \xi \quad (v = \dot{x} \ \& \ m = 1)$$

with $\langle \xi(t)\xi(t') \rangle = 2D\delta(t - t')$ and $\gamma = \beta D$ (Einstein relation)

$$\Pi[x_t] \sim e^{-\int_0^\tau dt \frac{\xi^2}{4D}} \sim e^{-\int_0^\tau dt \frac{1}{4D}(\dot{v}+\gamma v - g)^2}$$ (Onsager-Machlup)

$$\Pi[\tilde{x}_t] \sim e^{-\int_0^\tau dt \frac{1}{4D}(\dot{v}-\gamma v - g)^2}$$

$v \to -v$
$t \to \tau - t$

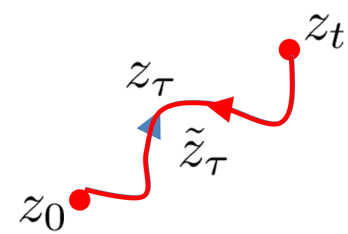
$$\ln \frac{\Pi(x_t)}{\Pi(\tilde{x}_t)} = -\frac{\gamma}{D}\int_0^\tau dt \ v(\dot{v} - g)$$

$$= -\beta \int_0^\tau dt \ v(-\gamma v + \xi) = -\beta Q(x_t) \quad = \Delta S_r(x_t)$$

Fluctuation theorems

$$\star\ R(z_\tau) = \ln \frac{\mathcal{P}(z_\tau)}{\mathcal{P}(\tilde{z}_\tau)} = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi(\tilde{z}_\tau)\tilde{p}^0_{\tilde{z}_0}}$$

$$\mathcal{P}(z_\tau) = \Pi(z_\tau)p^0_{z_0}$$



reverse path

Irreversibility (total entropy production)

- Choose $\tilde{p}^0_{\tilde{z}_0} = p_{z_t}(t)$ with arbitrary $p^0_{z_0}$.
- $R(z_\tau) = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi(\tilde{z}_\tau)p_{z_t}(t)} = \ln \frac{\Pi(z_\tau)}{\Pi(\tilde{z}_\tau)} + \ln \frac{p^0_{z_0}}{p_{z_t}(t)} = \Delta S_r + \Delta S = \Delta S_{\text{tot}}$

$$\langle e^{-\Delta S_{\text{tot}}}\rangle = 1 \text{ but } \langle e^{-\Delta S_r}\rangle \neq 1 \text{ and } \langle e^{-\Delta S}\rangle \neq 1$$

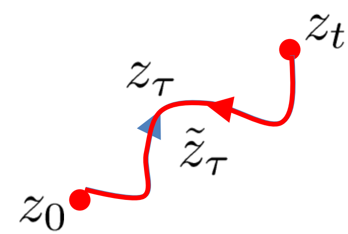
- NOT involutive ($f^2 \neq I$) due to i.c.
- Only if starting with the stationary distribution p^s_z with constant λ, then $f^2 = I$ and DFT holds.

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

Fluctuation theorems

$\star\ R(z_\tau) = \ln \frac{\mathcal{P}(z_\tau)}{\mathcal{P}(\tilde{z}_\tau)} = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi(\tilde{z}_\tau)\tilde{p}^0_{\tilde{z}_0}}$

$\mathcal{P}(z_\tau) = \Pi(z_\tau)p^0_{z_0}$



Work free-energy relation (dissipated work)

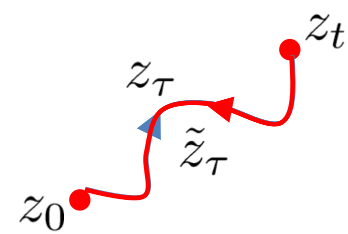
- Choose $p^0_{z_0} = e^{-\beta E(z_0;\lambda_0)+\beta F(\lambda_0)}$ and $\tilde{p}^0_{\tilde{z}_0} = e^{-\beta E(z_t;\lambda_t)+\beta F(\lambda_t)}$ [initially, start with equilibrium Boltzmann distribution.]
- $R(z_\tau) = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi(\tilde{z}_\tau)\tilde{p}^0_{\tilde{z}_0}} = \Delta S_r(z_\tau) - \beta\Delta F + \beta\Delta E(z_\tau)$

  $= -\beta Q(z_\tau) + \beta\Delta E(z_\tau) - \beta\Delta F = \beta(W(z_\tau) - \Delta F) \ = \beta W_d(z_\tau)$
- $f^2 = I.$
- $\langle e^{-\beta W_d}\rangle = 1$ or $\langle e^{-\beta W}\rangle = e^{-\beta\Delta F}$ and $\frac{P(W)}{\tilde{P}(-W)} = e^{\beta(W-\Delta F)}.$
- Other NEQ initial conditions? FT approx. valid for large t, but not for rare events with exponentially small probability.

  (Initial memory does not go away forever !)

Fluctuation theorems

$\star\ R(z_\tau) = \ln \frac{\mathcal{P}(z_\tau)}{\mathcal{P}(\tilde{z}_\tau)} = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi(\tilde{z}_\tau)\tilde{p}^0_{\tilde{z}_0}}$ $\mathcal{P}(z_\tau) = \Pi(z_\tau)p^0_{z_0}$



reverse path

House-keeping & Excess entropy production

- $\Delta S_{\rm tot}(z_\tau) = \Delta S_{hk}(z_\tau) + \Delta S_{ex}(z_\tau)$ $\tilde{p}^0_{\tilde{z}_0} = p_{z_t}(t)$

NEQ steady state (NESS) $p^s_z(\lambda_\tau)$ **for fixed** λ_τ $0 = \sum_{z'} W_{z,z'}(\lambda_\tau)p^s_{z'}$

- $\Pi(z_\tau) = \prod_{i=1}^N \Pi(z_{\tau_j}; z_{\tau_{j-1}})$
- $\Delta S_{hk}(z_\tau) = \sum_{j=1}^N \ln \frac{\Pi(z_{\tau_j};z_{\tau_{j-1}})p^s_{z_j}}{\Pi(z_{\tau_{j-1}};z_{\tau_j})p^s_{z_{j-1}}} = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi^+(z_\tau)p^{+0}_{z_0}}$ with $p^{+0}_{z_0} = p^0_{z_0}$
- $\Delta S_{ex}(z_\tau) = \sum_{j=1}^N \ln \frac{p^s_{z_j}(\lambda_{\tau_j})}{p^s_{z_{j-1}}(\lambda_{\tau_j})} + \ln \frac{p^0_{z_0}}{p_{z_t}(t)} = \ln \frac{\Pi(z_\tau)p^0_{z_0}}{\Pi^+(\tilde{z}_\tau)\tilde{p}^{+0}_{\tilde{z}_0}}$ with $\tilde{p}^{+0}_{\tilde{z}_0} = p_{z_t}(t)$

$W^+_{z,z'}(\lambda_\tau) \equiv \frac{W_{z',z}(\lambda_\tau)p^s_z(\lambda_\tau)}{p^s_{z'}(\lambda_\tau)}$ $\sum_z W^+_{z,z'} = 0$ $\langle e^{-\Delta S_{hk}}\rangle = 1$ and $\langle e^{-\Delta S_{ex}}\rangle = 1$

DB $\rightarrow W^+_{z,z'} = W_{z,z'} \rightarrow \Delta S_{hk} = 0$ $\frac{P(\Delta S_{hk})}{P^+(-\Delta S_{hk})} = e^{\Delta S_{hk}}$ & $\frac{P(\Delta S_{ex})}{\tilde{P}^+(-\Delta S_{ex})} \neq e^{\Delta S_{ex}}$

Dynamic processes with odd-parity variables?

¶ underdamped Brownian dynamics with potential $V(\mathbf{x})$

$$\dot{\mathbf{x}} = \mathbf{v}$$

$$\dot{\mathbf{v}} = -\gamma \mathbf{v} + \boldsymbol{\xi} - \nabla \mathbf{V}(\mathbf{x})$$

$$\langle \boldsymbol{\xi}(t) \boldsymbol{\xi}^T(t') \rangle = 2D\mathsf{I}\delta(t-t')$$

$$\gamma = \beta D \text{ (Einstein relation)}$$

$\mathbf{v}$: odd-parity variable ($\mathbf{v} \to -\mathbf{v}$ under time-rev. op.)

$\mathbf{x}$: even-parity variable

¶ underdamped dynamics with general NEQ forces

$$\dot{\mathbf{v}} = -\gamma \mathbf{v} + \boldsymbol{\xi} - \nabla \mathbf{V}(\mathbf{x}; \lambda(t)) + \mathbf{f}_{nc}(\mathbf{x}) + \mathbf{g}(\mathbf{x}, \mathbf{v})$$

$\lambda(t)$: time-dep. protocol

$\mathbf{f}_{nc}(\mathbf{x})$: non-conserv. force like swirling force, nano-heat engine

$\mathbf{g}(\mathbf{x}, \mathbf{v})$: velocity-dep. force in active matter dynamics, feedback control, magnetic force, molecular refrigerator, ...

If odd-parity variables are introduced ???

[A] $\Delta S_{\rm env} = \Delta S_{\rm res}$?? NO !!

$\Delta S_{\rm env} = \Delta S_{\rm res} + \Delta S_{\rm odd}$ (deterministic irreversibility)

In the steady state, $\langle \Delta S_{\rm env} \rangle \geq 0$ $\langle \Delta S_{\rm res} \rangle \not\geq 0$

$\mathbf{g}(\mathbf{v})$: velocity-dep. force

[CKwon/JYeo/HKLee/HP(2013?)]

[B] $\Delta S_{\rm ex}, \Delta S_{\rm hk}$: FT variables ?? Yes & No !!

$\Delta S_{\rm ex}$: FT $\Delta S_{\rm hk}$: not FT in general $(\ p_x^s \neq p_{\epsilon x}^s)$

$\Delta S_{\rm hk} = \Delta S_{\rm bDB} + \Delta S_{\rm as}$ $\langle \Delta S_{\rm hk} \rangle$ can be negative.

$\Delta S_{\rm bDB}$: FT $\Delta S_{\rm as}$: not FT

[HKLee/CKwon/HP(2013)]

Ending

- Remarkable equality in non-equilibrium (NEQ) dynamic processes, including Entropy production, NEQ work and EQ free energy.
- Turns out quite robust, ranging over non-conservative deterministic system, stochastic Langevin system, Brownian motion, discrete Markov processes, and so on.
- Still source of NEQ are so diverse such as global driving force, non-adiabatic volume change, multiple heat reservoirs, multiplicative noises, nonlinear drag force (odd variables), and so on.
- Validity and applicability of these equalities and their possible modification (generalized FT) for general NEQ processes.
- More fluctuation theorems for classical and also quantum systems
- Still need to calculate P(W), P(Q), ··· for a given NEQ process.
- Effective measurements of free energy diff., driving force (torque), ..