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KIAS KOREA INSTITUTE FOR ADVANCED STUDY

Entropy and Fluctuation Theorem

1. Prelude & Brief History of Fluctuation theorems
2. Thermodynamics & Jarzynski/Crooks FT
3. Experiments & Applications
4. Stochastic thermodynamics & FTs
5. Detailed balance & Fluctuation-dissipation theorem
6. Summary & Outlook

KIAS-SNU physics winter camp 2018 (12.26-01.04)

Prelude

자연 현상을 지배하는 물리학 법칙 중에 가장 신비스러운 법칙이 엔트로피 증가 법칙이라고 불리우는 열역학 제2법칙이다. 이 법칙에 따르면, 수 많은 입자들이 모인 고립된 거시계의 동력학은 엔트로피라는 물리량이 증가하는 방향으로만 움직이게 하며, 미시적 물리법칙인 양자역학과 상대론이 보장하는 시간의 대칭성을 지키지 않는다. 이 엔트로피 법칙을 통해 엔트로피가 극대화된 상태(평형상태)에 대한 물리적인 이해가 가능해 졌으나, 평형 상태로 가는 중간과정 또는 일반적인 비고립계에 대한 직접적이고 정량적인 이해는 거의 없었다.

최근 이러한 비평형과정에 대한 매우 일반적이고 기초적인 정리들이 발견되었으며, 이를 비평형 요동정리(nonequilibrium fluctuation theorems)라고 부른다. 이 정리들은 열역학 제2법칙처럼 부등식 법칙이 아니라, 등식법칙이며, 열역학 제2법칙이 자연스레 유도된다. 또한 한 특별한 예가 소위 Jarzynski 동등성(equality)이며, 이를 이용하면, 근본적으로 비평형 물리량인 일(work)과 평형 물리량인 자유에너지(free energy)을 직접 연결한다. 이는 비평형 과정을 이해하기 위한 중요한 첫 걸음으로 평가된다.

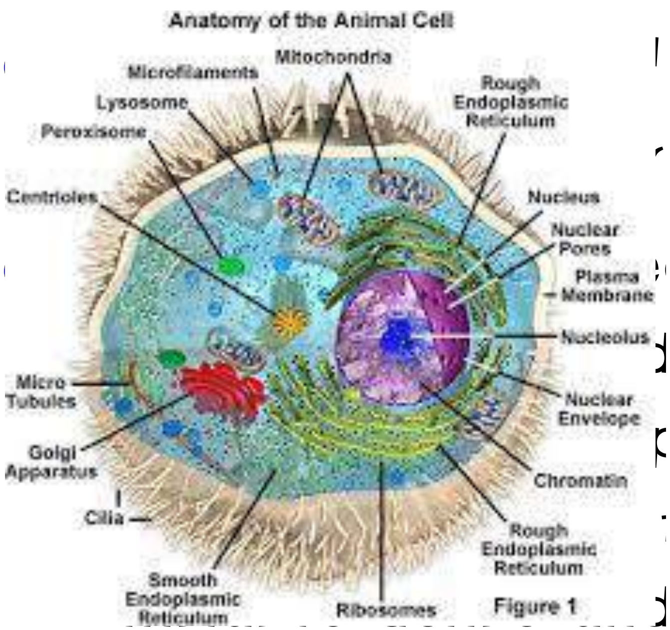
이 강연에서는 열역학 제2법칙을 돌아보고, 비평형 요동정리를 소개하며, 간단히 유도해 보고자 한다. 또한 이 정리가 내포하고 있는 함의(triviality & generality)에 대해 논의한다.

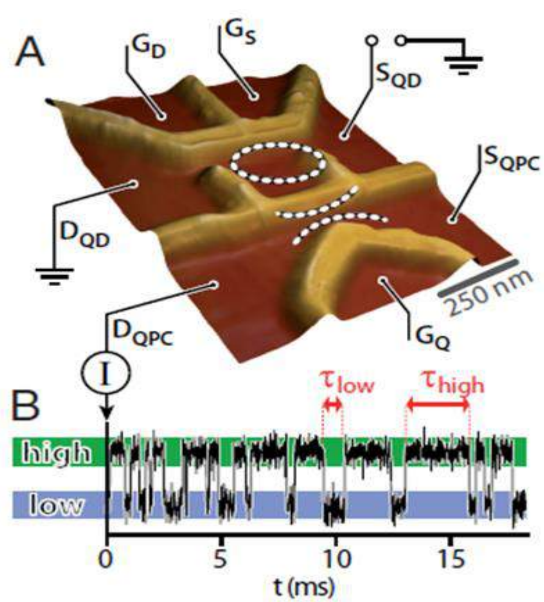
Nonequilibrium processes

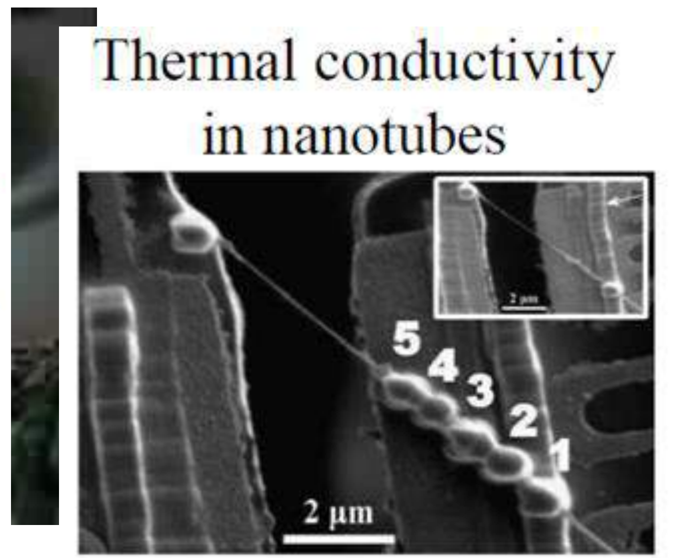
- Why NEQ processes?

active matter

- 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)

- Carnot (1824)
  Clausius (1862)

- Evans, Cohen, Morris (1993)

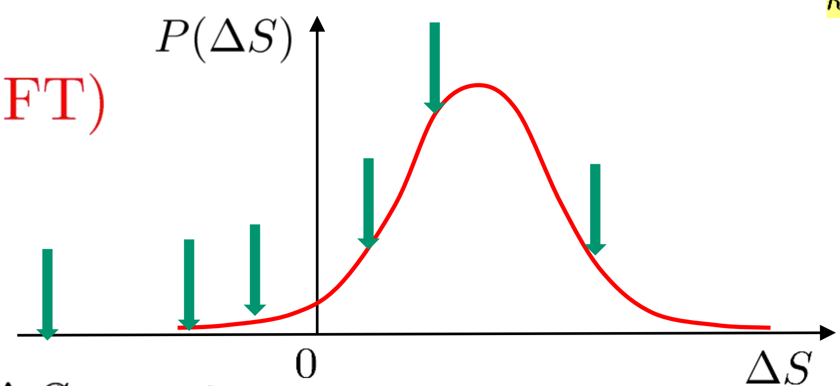
observation of FT in molecular dynamics simulations on fluid systems

- Gallavotti and Cohen (1995)

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

$k_B \equiv 1$

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



Gallavotti-Cohen symmetry

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

(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)

FT in Hamiltonian systems (work-free energy relation)

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

$\beta = 1/T$

- 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 ⋆ Kawasaki (1967)

- Crooks (1999)

DFT for stochastic systems

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

- Hatano and Sasa (2001)

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

- Speck/Seifert/vdBroeck (2005)
- Speck/Seifert (2007)

non-Markovian, non-Gaussian ??

- Sagawa/.... (2008)

Information entropy

Information thermodynamics

- Our group/Spinney/Ford (2012)

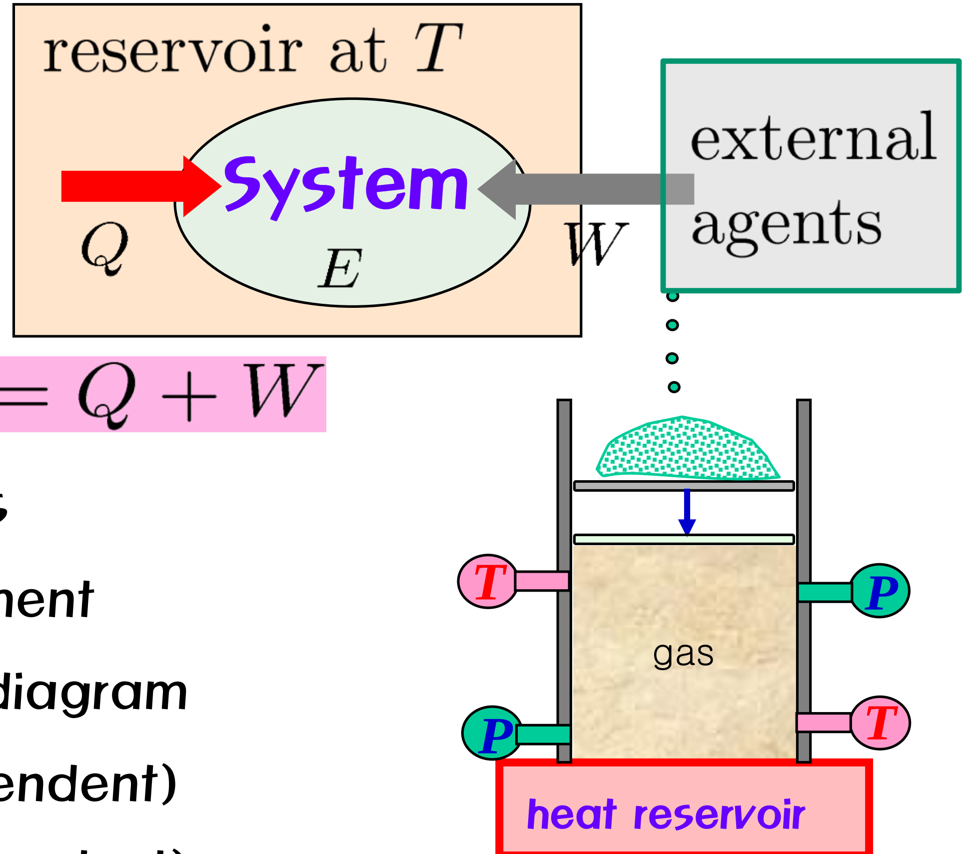
odd parity

- Experiments: Bustamante, Ciliberto (2002,2005), ...
- Kurchan/Tasaki (2000), Hänggi (2007)

Quantum FT

Thermodynamics

- Q: heat absorbed by the system
- W: work done on the system
- E: internal energy of the system



Themodyn. 1st law

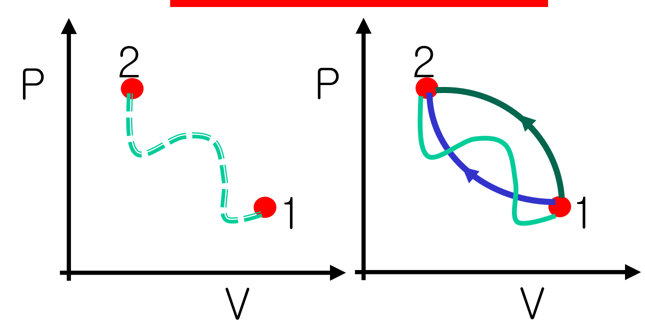
$$\Delta E = Q + W$$

Quasi-static (reversible) process

- almost equilibrium at every moment
- path is well defined in the P-V diagram
- work : $W = \int PdV$ (path-dependent)
- heat : $Q = \Delta E - W$ (path-dependent)

Irreversible process

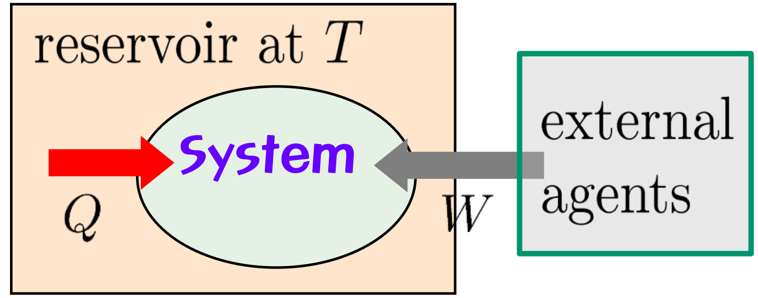
- path can not be defined in the P-V diagram
- cannot calculate W with P and V (NEQ)



Thermodynamics

Thermodyn. 1st law

$$\Delta E = Q + W$$



Thermodyn. 2nd law

S: entropy

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

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

Phenomenological law

$$dS \neq \frac{dQ}{T}$$

$$\langle W \rangle \geq \Delta F$$

$$dS_r = \frac{dQ}{T}$$

Total entropy does not change during reversible processes.

Total entropy increases during irreversible (NEQ) processes.

▶ Work and Free energy $(F = E - TS)$

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

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

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

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

Jarzynski equality (IFT)

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

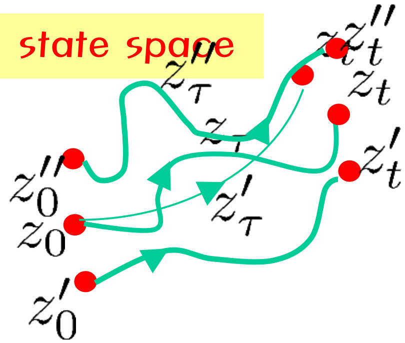
Crooks relation (DFT)

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

Jarzynski equality

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 $T = 1/\beta$

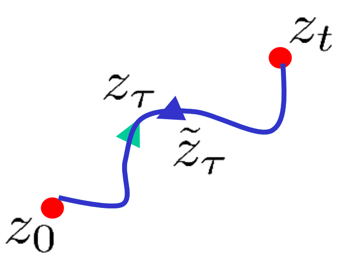
- $W[z_\tau] = H_{\lambda_t}(z_t) - H_{\lambda_0}(z_0)$ (no heat reservoir $Q = 0 \rightarrow W = \Delta E$)
- $\langle e^{-\beta W}\rangle = \int \mathcal{D}z_\tau \mathcal{P}_F(z_\tau) e^{-\beta W[z_\tau]} = \int dz_0 p(z_0, 0) e^{-\beta W}$ ($\mathcal{P}_F(z_\tau) = p(z_0, 0)$)
  - $p(z_0, 0) = e^{-\beta H_{\lambda_0}(z_0)}/Z_{\lambda_0}$ ($Z_{\lambda_0} = \int dz_0 e^{-\beta H_{\lambda_0}(z_0)}$: 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

Crooks 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: $\tilde{\lambda}_\tau = \lambda_{t-\tau}$
- ¶ EQ initial ensemble for both F(B)-paths.

odd variable

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

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

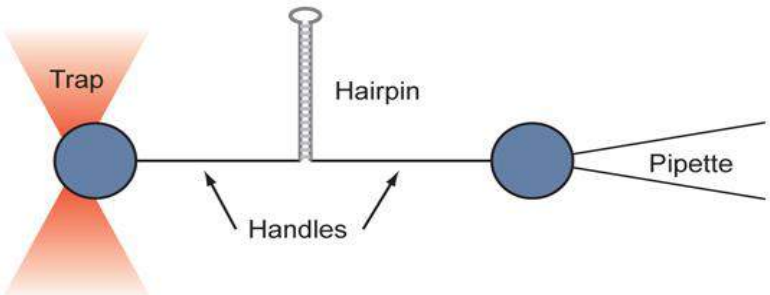
$$\to \frac{P_F(W)}{P_R(-W)} = e^{\beta W - \beta \Delta F}$$

Crooks detailed FT for PDF of Work

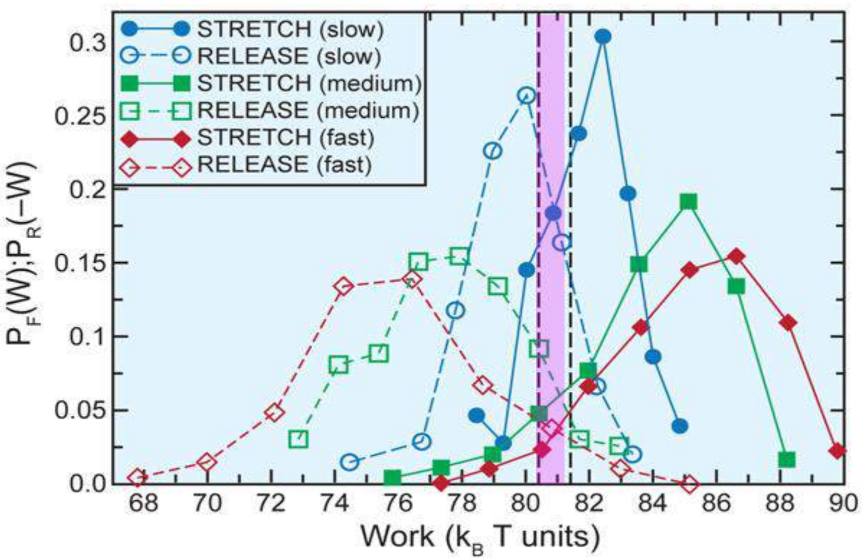
- For $\mathcal{O}[z] = e^{-\beta W[z]}$, $\langle e^{-\beta W} \rangle_F = e^{-\beta \Delta F}$ (Jarzinsky equality) "Integral" FT

Experiments & Applications

DNA hairpin mechanically unfolded by optical tweezers

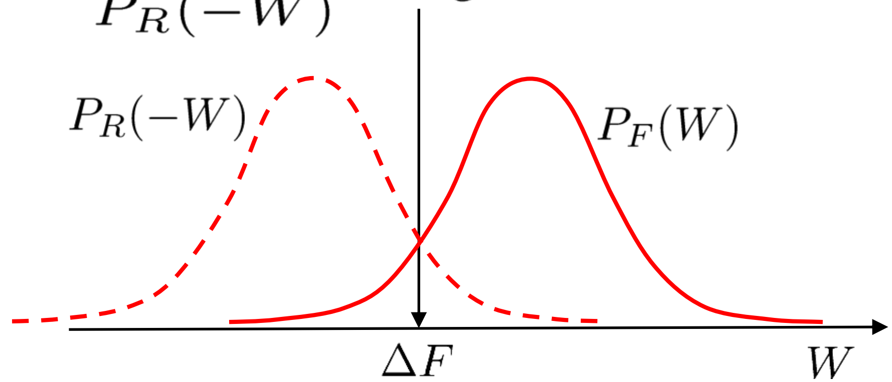


Collin/Ritort/Jarzynski/Smith/Tinoco/Bustamante, Nature, 437, 8 (2005)



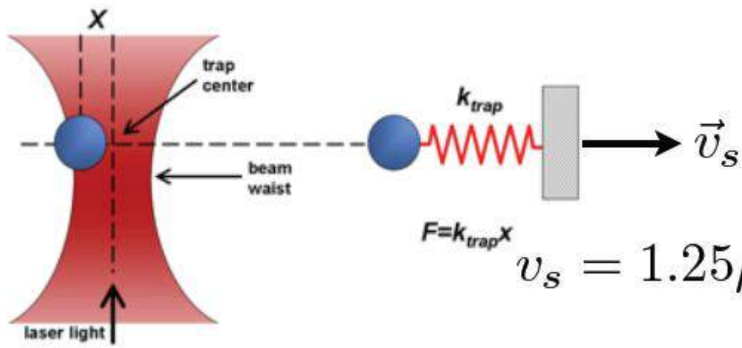
Detailed fluctuation theorem

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



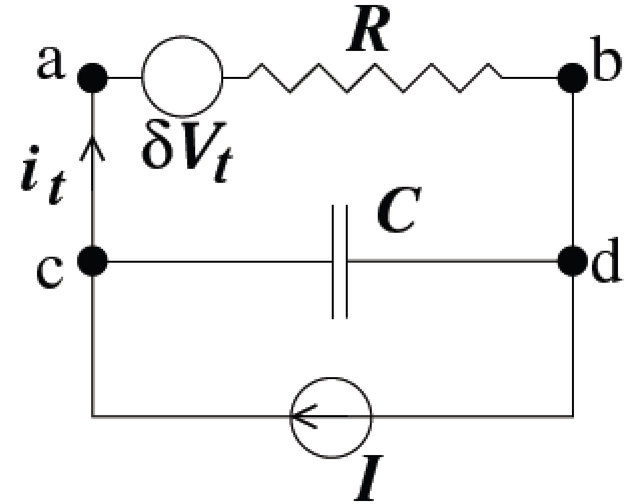
- At $P_F(W) = P_R(-W)$, W must be the same as ΔF, independent of intermediate processes.

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



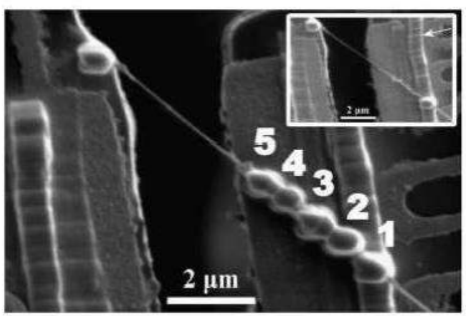
$v_s = 1.25\mu\text{m/s}$

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



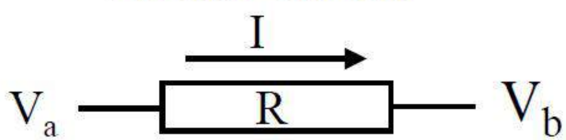
[Garnier&Ciliberto `05]

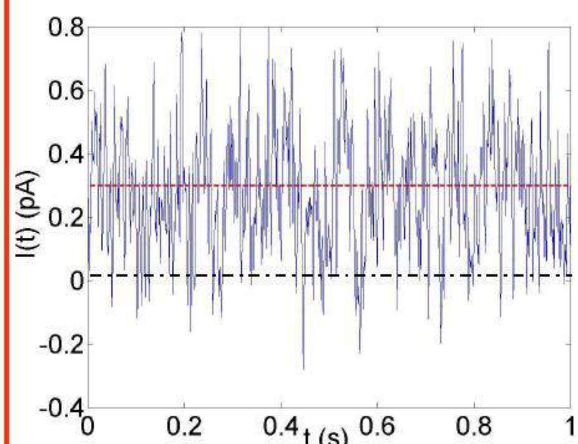
Thermal conductivity in nanotubes



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

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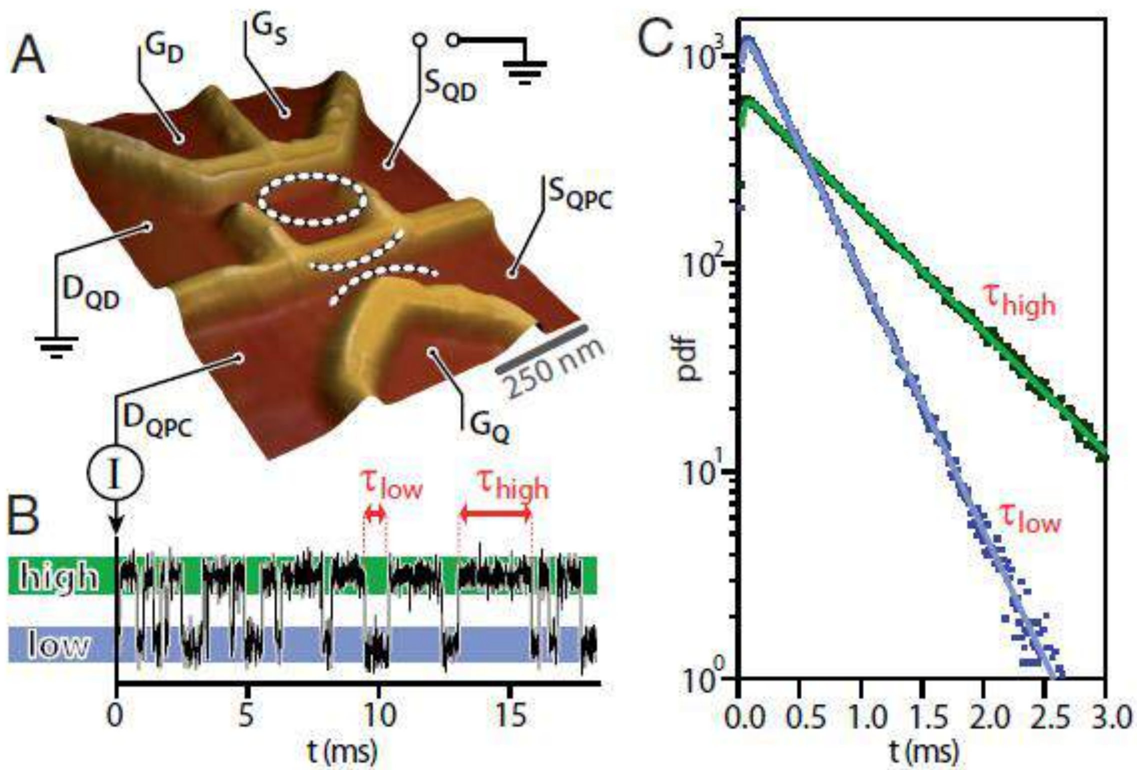

Fig. 1. Real-time counting of electrons tunneling through a quantum dot.

VOLUME 92, NUMBER 16 PHYSICAL REVIEW LETTERS week ending 23 APRIL 2004

Fluidized Granular Medium as an Instance of the Fluctuation Theorem

Klebert Feitosa* and Narayanan Menon†
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(Received 14 August 2003; published 21 April 2004)

We study the statistics of the power flux into a collection of inelastic beads maintained in a fluidized steady state by external mechanical driving. The power shows large fluctuations, including frequent large negative fluctuations, about its average value. The relative probabilities of positive and negative fluctuations in the power flux are in close accord with the fluctuation theorem of Gallavotti and Cohen, even at time scales shorter than those required by the theorem. We also compare an effective temperature that emerges from this analysis to the kinetic granular temperature.

DOI: 10.1103/PhysRevLett.92.164301 PACS numbers: 45.70.Mg, 05.40.–a

Take a fistful of marbles in your hand and shake them vigorously. In order to maintain the motions of the mar-

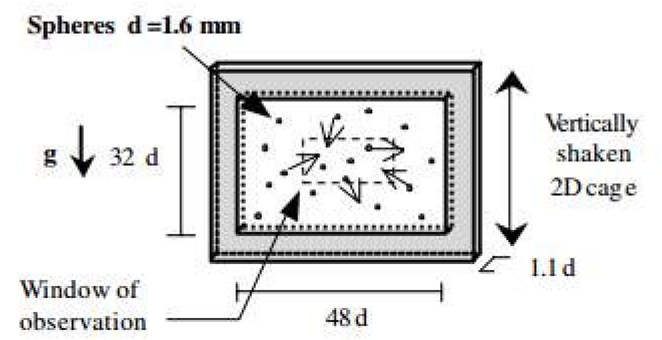

FIG. 1. Sketch of the experimental cell. The dashed rectangle is a window measuring $10d \times 21d$, fixed in the laboratory frame, in which we study the flux of kinetic energy.

an observation made in a simulation of a sheared hard-sphere fluid [3], they proved a very general result regarding the entropy flux into a system maintained in a nonequilibrium steady state by a time-reversible thermostat. If dynamics in the system are chaotic [4], then

$$\Pi(\sigma_\tau)/\Pi(-\sigma_\tau) = \exp(\sigma_\tau \tau), \quad (1)$$

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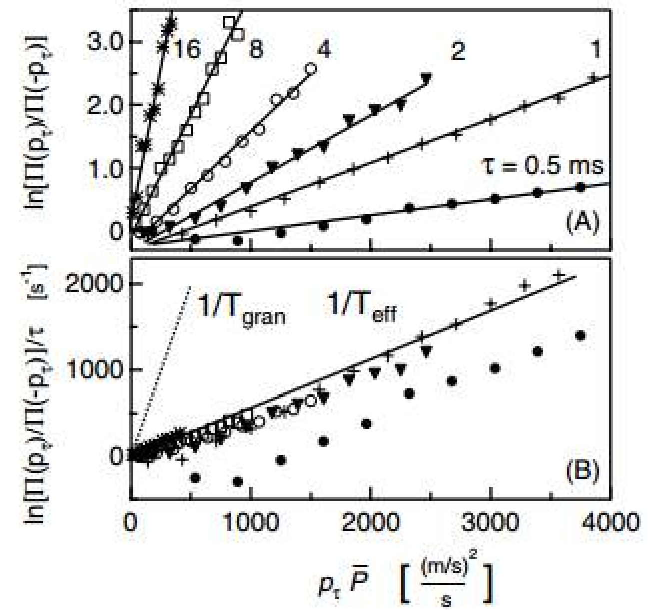

FIG. 4. (a) $\ln[\Pi(p_\tau)/\Pi(-p_\tau)]$ versus $p_\tau \overline{P}$ for τ ranging from 0.5 to 16 ms. (b) $\ln[\Pi(p_\tau)/\Pi(-p_\tau)]/\tau$ versus $p_\tau \overline{P}$ ($\overline{P} = 356\ \mathrm{m}^2\,\mathrm{s}^{-3}$). The solid line shows the slope of the collapsed curves. A dashed line of slope $1/T_{gran}$ is drawn for comparison.

NATURE PHYSICS | ARTICLE

Experimental test of the quantum Jarzynski equality with a trapped-ion system

Shuoming An, Jing-Ning Zhang, Mark Um, Dingshun Lv, Yao Lu, Junhua Zhang, Zhang-Qi Yin, H. T. Quan & Kihwan Kim

Affiliations | Contributions | Corresponding authors

Nature Physics **11**, 193–199 (2015) | doi:10.1038/nphys3197
Received 16 April 2014 | Accepted 14 November 2014 | Published online 22 December 2014

Abstract

The Jarzynski equality relates the free-energy difference between two equilibrium states to the work done on a system through far-from-equilibrium processes—a milestone that builds on the pioneering work of Clausius and Kelvin. Although experimental tests of the equality have been performed in the classical regime, the quantum Jarzynski equality has not yet been fully verified owing to experimental challenges in measuring work and work distributions in a quantum system. Here, we report an experimental test of the quantum Jarzynski equality with a single $^{171}Yb^{+}$ ion trapped in a harmonic potential. We perform projective measurements to obtain phonon distributions of the initial thermal state. We then apply a laser-induced force to the projected energy eigenstate and find transition probabilities to final energy eigenstates after the work is done. By varying the speed with which we apply the force from the equilibrium to the far-from-equilibrium regime, we verify the quantum Jarzynski equality in an isolated system.

arXiv: 1008.1184

KEK-T

Non-Equilibrium Fluctuations of Black Hole Horizons

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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.

arXiv: 1301.6368

27 Jan 2013

ON NON-EQUILIBRIUM PHYSICS AND STRING THEORY

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In this article we review the relation between string theory and non-equilibrium physics based on our previously published work. First we explain why a theory of quantum gravity and non-equilibrium statistical physics should be related in the first place. Then we present the necessary background from the recent research in non-equilibrium physics. The review discusses the relationship of string theory and aging phenomena, as well as the connection between AdS/CFT correspondence and the Jarzynski identity. We also discuss the emergent symmetries in fully developed turbulence and the corresponding non-equilibrium stationary states. Finally we outline a larger picture regarding the relationship between non-perturbative quantum gravity and non-equilibrium statistical physics. This relationship can be understood as a natural generalization of the well-known Wilsonian relation between local quantum field theory and equilibrium statistical physics of critical phenomena. According to this picture the AdS/CFT duality is just an example of a more general connection between non-perturbative quantum gravity and non-equilibrium physics. In the appendix of this review we discuss a new kind of complementarity between thermodynamics and statistical physics which should be important in the context of black hole complementarity.

Summary of Part I

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

(Detailed FT) Gallavotti-Cohen symmetry

$$\langle e^{-\Delta S} \rangle = 1$$

(Integral FT)

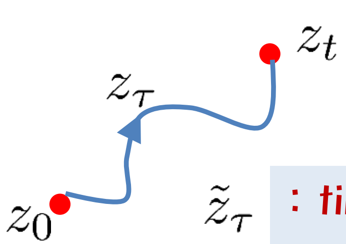
$$\frac{P_F(W)}{P_R(-W)} = e^{\beta W - \beta \Delta F}$$

(Detailed FT) **Crooks relation**

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

(Integral FT) **Jarzynski equality**

¶ EQ initial ensemble



$\tilde{z}_\tau$: time-reverse path

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

$$= e^{\beta (W - \Delta F)_F}$$

Stochastic thermodynamics

[Sekimoto(1998),Seifert(2005)]

Microscopic deterministic dynamics

- Hamilton equation
- TR symmetry

coarse-graining, truncation

Stochastic dynamics

- Langevin equation
- Master equation
- TR symmetry broken

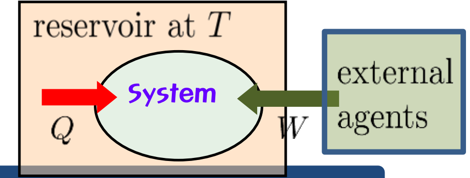
stochastic thermodynamics
trajectory level
energetics? entropy production?

equilibrium SM

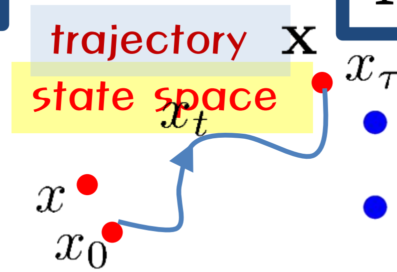
Macroscopic thermodynamics

- NOT really dynamics
- TR symmetry broken

Stochastic thermodynamics



Equilibrium



- state ensemble: $\{x\}$
- state probability: $p(x)$
  - microcanonical: $p(x) = 1/\Omega$
  - canonical: $p(x) = \exp[(F - E(x))/T]$
- observable: $A(x)$
  - average: $\langle A \rangle = \sum_x p(x) A(x)$
  - energy: $E(x) = \frac{\vec{p}^2}{2m} + V(\vec{x})$
  - entropy: $S(x) \equiv -\ln p(x)$

(Shannon) $\langle S \rangle = -\sum_x p(x) \ln p(x)$

⋆ micro: $\langle S \rangle = \ln \Omega$ (Boltzmann)

⋆ canon: $\langle S \rangle = -(F - \langle E \rangle)/T$

Nonequilibrium Process

- trajetory ensemble: $\{\mathbf{x}\}$
- trajectory probability: $\mathcal{P}(\mathbf{x})$
  - $\mathcal{P}(\mathbf{x}) = p(x_0)\Pi(\mathbf{x})$

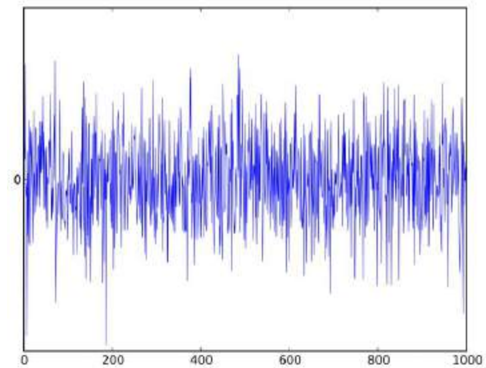
    (conditional path prob.)
- observable: $A(\mathbf{x})$
  - average: $\langle A \rangle = \sum_{\mathbf{x}} \mathcal{P}(\mathbf{x}) A(\mathbf{x})$
  - work and heat: $W(\mathbf{x})$, $Q(\mathbf{x})$
  - $\Delta E = W(\mathbf{x}) + Q(\mathbf{x})$
  - $\Delta S_{\rm res} = -\frac{Q(\mathbf{x})}{T}$
  - $\Delta S_{\rm sys} = -\ln(p(x_\tau)/p(x_0))$?? (NEQ entropy)
  - $\langle \Delta S_{\rm tot} \rangle = \langle \Delta S_{\rm sys} \rangle + \langle \Delta S_{\rm res} \rangle \geq 0$

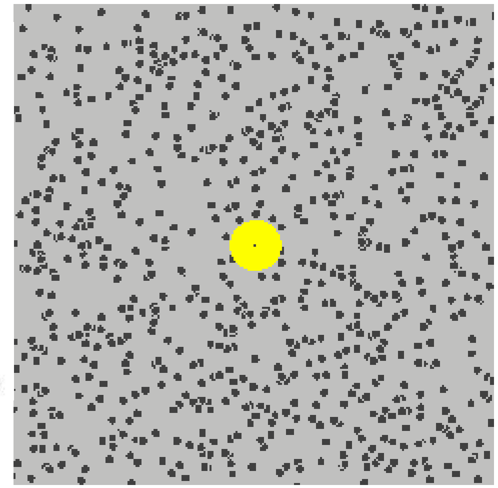
Langevin systems in contact with a heat reservoir

¶ Hamiltonian dynamics $\quad H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})$

$$\dot{\mathbf{x}} = \nabla_{\mathbf{p}} H = \frac{\mathbf{p}}{m}$$

$$\dot{\mathbf{p}} = -\nabla_{\mathbf{x}} H = -\nabla_{\mathbf{x}} V$$





¶ Langevin dynamics

$$\dot{\mathbf{x}} = \mathbf{v} \qquad m\dot{\mathbf{v}} = -\nabla_{\mathbf{x}} V \; -\gamma\mathbf{v} + \boldsymbol{\xi}$$

$$\langle \boldsymbol{\xi}(t) \rangle = 0 \;\; \langle \boldsymbol{\xi}(t)\boldsymbol{\xi}^T(t') \rangle = 2D\mathsf{I}\delta(t-t') \qquad \gamma = D/T \text{ (Einstein-Smoluchowski)}$$

⋆ $\mathbf{f}_{\rm res} = -\gamma\mathbf{v} + \boldsymbol{\xi}$: thermal force exerted by heat reservoir

⋆ mechanical forces

- conservative force: $-\nabla V$ Equilibrium (steady state)
- time-dependent protocol $\lambda(t)$: $V = V(\mathbf{x}, \lambda)$
- non-conservative force: $\mathbf{f}_{\rm nc}(\mathbf{x}), \mathbf{f}_{\rm nc}(\mathbf{x}, \mathbf{v}), \mathbf{f}_{\rm nc}(\mathbf{x}, \lambda), \ldots$

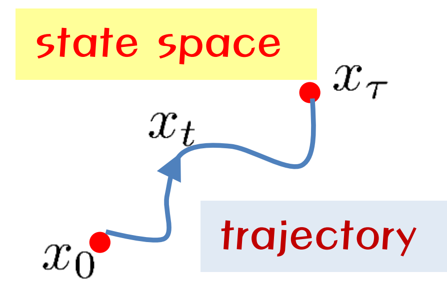
Langevin (stochastic) dynamics

¶ Brownian particle in a potential V with time-dependent protocol $\lambda(t)$

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

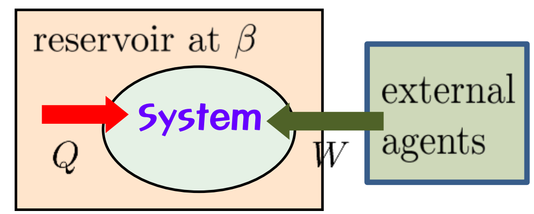


$$\dot{K} = \frac{d}{dt}\left[\frac{1}{2}v^2\right] = v \circ \dot{v} = -v\partial_x V + v \circ (-\gamma v + \xi)$$

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

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

[Sekimoto(1998)]



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

$$\dot{Q} \equiv v \circ (-\gamma v + \xi) = v \circ f_{\rm res} \quad \text{and} \quad \dot{W} \equiv \dot{\lambda}(\partial_\lambda V)$$ (Jarzynski work)

[Jarzynski(1997)]

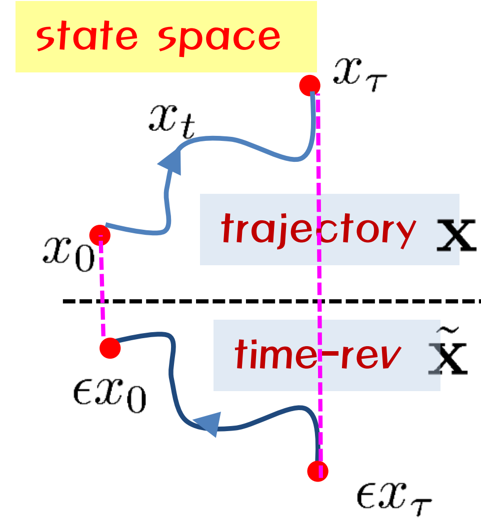
$*$ with NEQ force $f_{\rm neq}(x,v)$, $\quad \dot{W} \equiv \dot{\lambda}(\partial_\lambda V) + v f_{\rm neq}$

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

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

[Seifert(2005)]

Stochastic process, Irreversibility & Total entropy production



¶ Dynamic trajectory in state space $(0 < t < \tau)$
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 for a trajectory $\mathbf{x}$ (total entropy production)

$$\Delta S_{\mathrm{tot}}^{\mathrm{Irr}}[\mathbf{x}] \equiv \ln \frac{\mathcal{P}[\mathbf{x}]}{\mathcal{P}[\tilde{\mathbf{x}}]}$$

$\mathcal{P}[\mathbf{x}]$:probability of traj. $\mathbf{x}$
$\tilde{\mathbf{x}}$: time-reversed traj.
$[\tilde{\mathbf{x}}(t) = \epsilon \mathbf{x}(\tau - t)]$

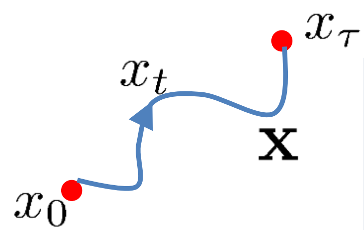
Time-reversed dynamics ??
[Sekimoto(1998)/Seifert(2005)]

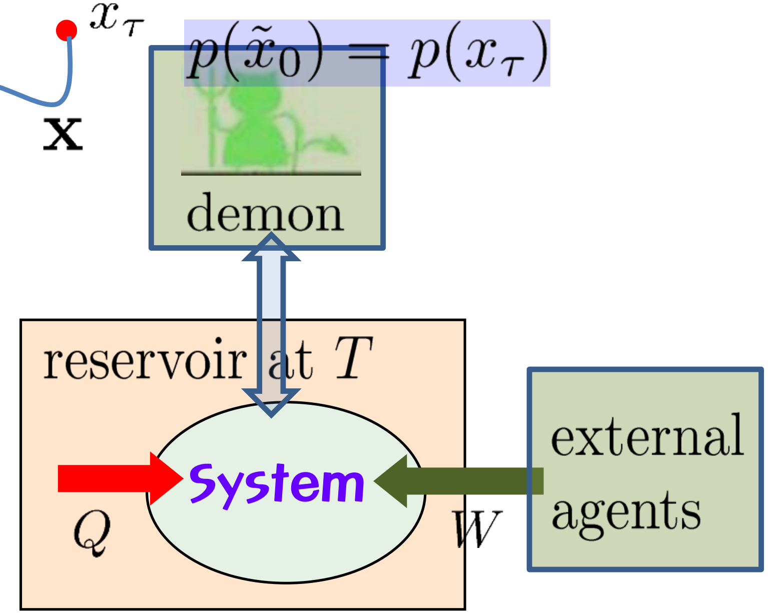
- *integral* fluctuation theorem (FT) : automatic
  $\langle e^{-\Delta S_{\mathrm{tot}}} \rangle = \sum_{\mathbf{x}} \mathcal{P}[\mathbf{x}] e^{-\Delta S_{\mathrm{tot}}[\mathbf{x}]} = \sum_{\tilde{\mathbf{x}}} \mathcal{P}[\tilde{\mathbf{x}}] = 1$ (Jacobian $|\partial \tilde{\mathbf{x}} / \partial \mathbf{x}|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

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

Total entropy production and its components

$$\Delta S_{\rm tot}[\mathbf{x}] = \ln \frac{\mathcal{P}[\mathbf{x}]}{\mathcal{P}[\tilde{\mathbf{x}}]} = \ln \frac{p(x_0)\Pi[\mathbf{x}]}{p(\tilde{x}_0)\Pi[\tilde{\mathbf{x}}]}$$





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

- $\Delta S_{\rm sys} = -\ln[p(x_\tau)/p(x_0)]$
- $\Delta S_{\rm env} = \ln[\Pi(\mathbf{x})/\Pi(\tilde{\mathbf{x}})] = -\beta Q = \Delta S_{\rm res}$

(Schnakenberg, 1976)

- $\Delta S_{\rm sys}$, $\Delta S_{\rm res}$: not FT variables

† steady state $\langle \Delta S_{\rm sys} \rangle = 0$, $-\langle Q \rangle \geq 0$ or $-\langle W \rangle \leq 0$ (cannot do work outside)

⋆ Maxwell's demon (1867) measurement & feedback control

do work outside with a single reservoir

Joint system (system+demon)

- Demons are exorcised !!

- $\Delta S_{\rm joint} = \Delta S_{\rm sys} + \Delta S_{\rm dem} - \Delta I$ ($I \geq 0$: mutual information)

† steady state $-\langle Q \rangle \geq T\Delta I$ or $-\langle W \rangle \leq -T\Delta I$ (ΔI usually negative)

- Information thermodynamics
- Information engines

Total entropy production and its components

[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 $\langle e^{-\Delta S_{\rm ex}}\rangle = 1, \langle e^{-\Delta S_{\rm hk}}\rangle = 1$
- $2^{\rm nd}$ laws
- $\Delta S_{\rm hk}$: adiabatic, $\Delta S_{\rm ex}$: non-adiabatic ($\Delta S_{\rm ex}$ vanishes in $\dot{\lambda} \to 0$ limit)

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

★★ odd-parity problems

$\Delta S_{\rm env} = \ln[\Pi(\mathbf{x})/\Pi(\tilde{\mathbf{x}})] = \Delta S_{\rm res} + \Delta S_{\rm unc}$

$\Delta S_{\rm hk}$: not FT in general

★★ quantum FT

Hamiltonian systems (work-free energy relation)

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

Not much about systems in contact with heat reservoirs

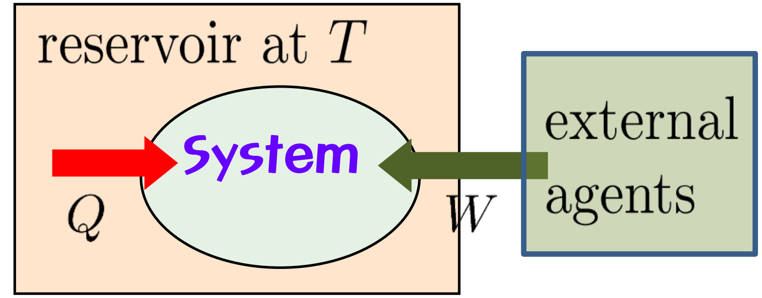
Probability theory viewpoint

on Fluctuation theorems

Seifert, PRL 95, 040602 (2005)

Esposito/VdBroeck, PRL 104, 090601 (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 $\langle R \rangle \geq 0$.

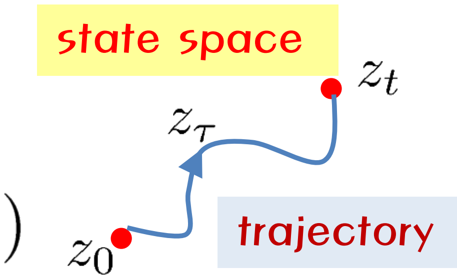
Thermodynamic 2nd laws

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"

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

$$R(z_\tau) \equiv \ln \frac{\mathcal{P}(z_\tau)}{\tilde{\mathcal{P}}(\tilde{z}_\tau)} \Rightarrow \langle e^{-R} \rangle_{\mathcal{P}} = \sum_{z_\tau} e^{-R(z_\tau)} \mathcal{P}(z_\tau) = \sum_{\tilde{z}_\tau} \tilde{\mathcal{P}}(\tilde{z}_\tau) = 1$$

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

Integral fluctuation theorem

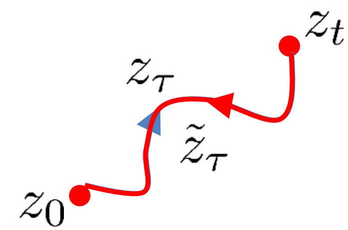
$$\langle e^{-R} \rangle_{\mathcal{P}} = 1$$

$$\langle R \rangle_{\mathcal{P}} \geq 0$$

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

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

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

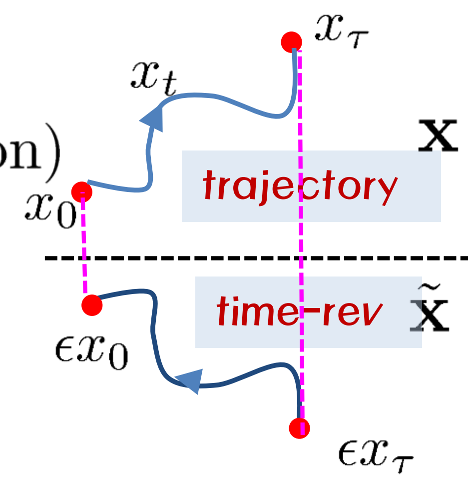
$$\langle \mathcal{O}(z_\tau) \rangle_{\mathcal{P}} = \langle \tilde{\mathcal{O}}(\tilde{z}_\tau) e^{-\tilde{R}(\tilde{z}_\tau)} \rangle_{\tilde{\mathcal{P}}}$$ with $\mathcal{O}(z_\tau) = \tilde{\mathcal{O}}(\tilde{z}_\tau)$

(Generalized Crooks' relation)

HW#1(a)

Summary of Part II

¶ Irreversibility for a trajectory $\mathbf{x}$ (total entropy production)



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

$\mathcal{P}[\mathbf{x}]$:probability of traj. $\mathbf{x}$

$\tilde{\mathbf{x}}$: time-reversed traj.

$[\tilde{\mathbf{x}}(t) = \epsilon\mathbf{x}(\tau - t)]$

- *integral* fluctuation theorem (FT) : automatic

  $\langle e^{-\Delta S_{\rm tot}} \rangle = \sum_{\mathbf{x}} \mathcal{P}[\mathbf{x}] e^{-\Delta S_{\rm tot}[\mathbf{x}]} = \sum_{\tilde{\mathbf{x}}} \mathcal{P}[\tilde{\mathbf{x}}] = 1$ (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

  $P(\Delta S_{\rm tot})/P(-\Delta S_{\rm tot}) = e^{\Delta S_{\rm tot}}$ $\quad \mathcal{P}(\tilde{\mathbf{x}}) = f \circ \mathcal{P}(\mathbf{x})$ $\quad f^2 = I$

- $R[\mathbf{x}] \equiv \ln \dfrac{\mathcal{P}[\mathbf{x}]}{\tilde{\mathcal{P}}[\tilde{\mathbf{x}}]}$ (relative entropy)

¶ Brownian particle in a potential V with time-dependent protocol $\lambda(t)$

$\dot{v} = -\partial_x V(x;\lambda) + f_{\rm neq}(x,v) - \gamma v + \xi \quad (v = \dot{x}$ & $m = 1)$

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

- Heat Q and Work W : $\dot{Q} \equiv v \circ (-\gamma v + \xi) = v \circ f_{\rm res}$, $\dot{W} \equiv \dot{\lambda}(\partial_\lambda V) + v f_{\rm neq}$

- Entropy production : $\Delta S_{\rm tot} = -\ln(p_{x_\tau}/p_{x_0}) - \beta Q[\mathbf{x}]$

  with Schnakenberg formula $-\beta Q[\mathbf{x}] = \ln[\Pi(\mathbf{x})/\Pi(\tilde{\mathbf{x}})]$

Dynamic processes & Path probability ratio

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

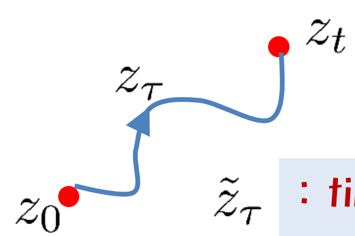
$H = \frac{p^2}{2m} + \frac{1}{2}\lambda_\tau x^2$ with $\lambda_\tau = \lambda(\tau)$

¶ 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:

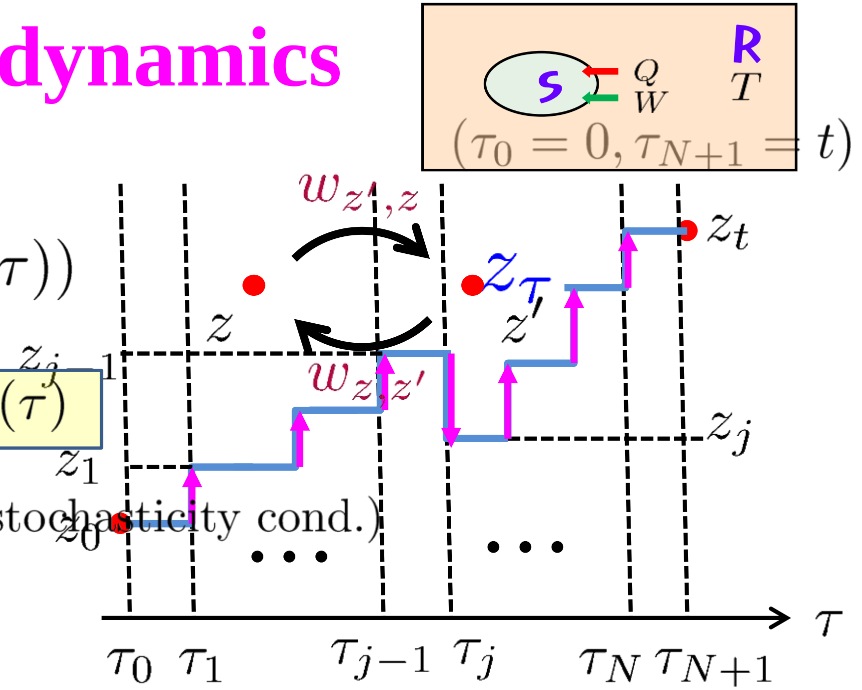


$\tilde{z}_\tau$: time-reverse path

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

($\Pi(z_\tau)$: 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:

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

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

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

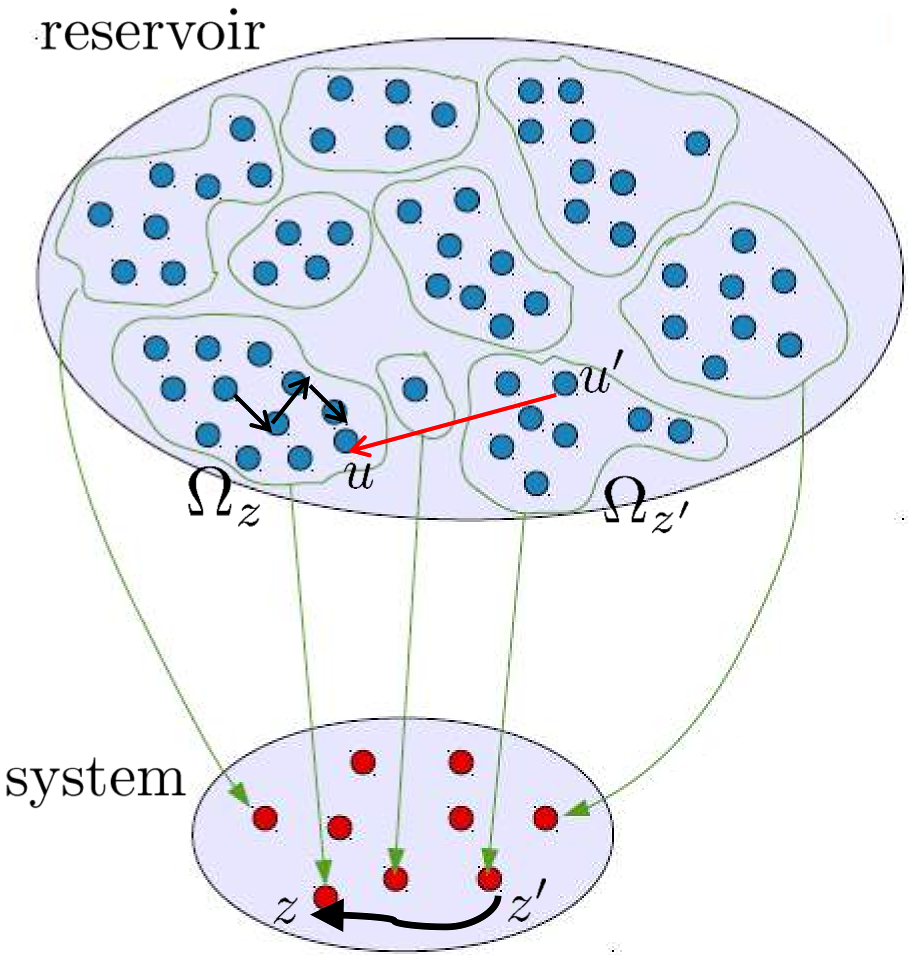
$$\tilde\Pi(\tilde z_\tau) \sim \prod_{j=1}^{N} e^{\int_{\tau_{j-1}}^{\tau_j} d\tau' W_{z_{j-1},z_{j-1}}(\lambda_{\tau'})} W_{z_{j-1},z_j}(\lambda_{\tau_j}) \cdot e^{\int_{\tau_N}^{t} d\tau' W_{z_N,z_N}(\lambda_{\tau'})}$$

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

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

Reservoir entropy change

Schnakenberg/Hinrichsen/Park



total isolated system $y=(z,u)$

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

Assumption (reservoir) :

instantaneous relaxation into a sector

Micro-reversibility :(isolated system)

$$w_{y,y'} = w_{y',y}$$

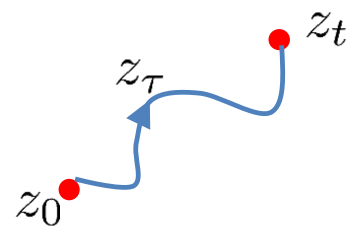
→ steady state : equally likely

$$w_{y,y'} p^s_{y'} = w_{y',y} p^s_y$$ (detailed balance)

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

More transparent in Langevin dynamics description

Langevin dynamics



¶ Brownian particle with (cons.+noncons.) force $f(x)$

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

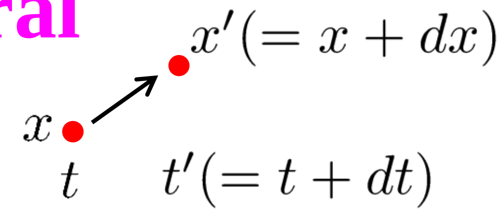
with $\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$ and $\gamma = \beta D$ (Einstein relation)

- $\Pi[z_\tau]$: conditional probability for path z_τ

$$\Pi[z_\tau] \sim e^{-\int_0^t d\tau \frac{\xi^2}{4D}} = e^{-\int_0^t d\tau \frac{1}{4D}(\dot{v}+\gamma v - f)^2} \quad \text{(Onsager-Machlup)}$$

$$= \mathcal{J} e^{-\int_0^t d\tau \left[\frac{1}{4D}(\dot{v}+\gamma v - f)^2 \ [\text{illegible}] \right]} \quad \text{(Stratonovich)}$$

Discretization scheme for a path integral



$$\dot{x} = f(x) + \xi \qquad \text{(infinitesimal path)}$$

$$dx = x' - x = \int_t^{t'} ds\ [f(x(s)) + \xi(s)]$$

$$\simeq f(x_\alpha)dt + \int_t^{t'} ds\ \xi(s) \quad [x_\alpha = x + \alpha dx = \alpha x' + (1-\alpha)x]$$

$$\langle dx \rangle = f(x_\alpha)dt \simeq f(x)dt + \alpha(\partial_x f)dxdt$$

$$\langle (dx)^2 \rangle \simeq \int_t^{t'} \int_t^{t'} dsds' \ \langle \xi(s)\xi(s') \rangle = 2Ddt \qquad \langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$$

$$\Pi[dx]_t^{t'} = \langle \delta(x' - x - \int_t^{t'} ds\,[f(x(s)) + \xi(s)]) \rangle \qquad \int dx' \Pi[dx]_t^{t'} = 1$$

$$\simeq \langle \delta(x' - x - f(x_\alpha)dt - \int_t^{t'} ds\ \xi(s)) \rangle * \mathcal{J}$$

?

$$\mathcal{J} = 1 - \alpha dt \partial_x f|_{x_\alpha}$$

$$\simeq \frac{1}{\sqrt{4\pi D dt}} e^{-\frac{dt}{4D}(\dot{x} - f(x_\alpha))^2 - \alpha dt \partial_x f|_{x_\alpha}} \qquad \simeq e^{-\alpha dt \partial_x f|_{x_\alpha}}$$

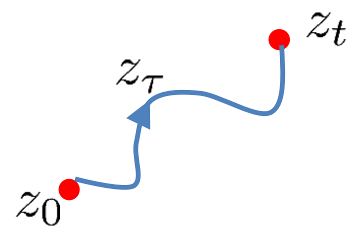
$\alpha = 0$ (Ito), $1/2$ (Stratonovich), 1 (anti-Ito)

HW#1(b)

HW#1(c) $\langle \xi(t)\xi(t') \rangle = 2D(x)\delta(t-t')$

(Propagator & Fokker-Planck eq.)

Langevin dynamics



¶ Brownian particle with (cons.+noncons.) force $f(x)$

$$\dot{v} = f(x) - \gamma v + \xi \quad (v = \dot{x} \ \& \ m = 1)$$
with $\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')$ and $\gamma = \beta D$ (Einstein relation)

$\tilde{z}_\tau$: *time-reverse path*

- $\Pi[z_\tau]$: conditional probability for path z_τ

$$\Pi[z_\tau] \sim e^{-\int_0^t d\tau \frac{\xi^2}{4D}} = \mathcal{J} e^{-\int_0^t d\tau \frac{1}{4D}(\dot{v}+\gamma v - f)^2} \sim e^{-\int_0^t d\tau \left[\frac{1}{4D}(\dot{v}+\gamma v - f)^2 - \frac{1}{2}\gamma\right]}$$

(Onsager-Machlup)
(Stratonovich)

$$\Pi[\tilde{z}_\tau] \sim e^{-\int_0^t d\tau \left[\frac{1}{4D}(\dot{v}-\gamma v - f)^2 - \frac{1}{2}\gamma\right]}$$

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

(Schnakenberg formula !)

- $$\ln \frac{\Pi(z_\tau)}{\Pi(\tilde{z}_\tau)} = -\frac{\gamma}{D}\int_0^t d\tau \ v(\dot{v} - f) = -\beta \int_0^t d\tau \ v(-\gamma v + \xi) = -\beta Q(z_\tau) = \Delta S_{\mathrm{res}}(z_\tau)$$

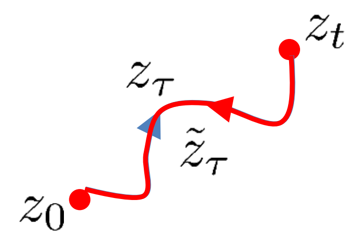
HW#2(a) $\dot{v} = f(x, v) - \gamma v + \xi$

HW#2(b) $f(x, v) = -\gamma' v$: Calculate $\langle Q\rangle$ and $\langle \Delta S_{\mathrm{env}}\rangle$ in the SS

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

$\langle e^{-\Delta S_{\rm tot}} \rangle = 1$ but $\langle e^{-\Delta S_r} \rangle \neq 1$ 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.

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

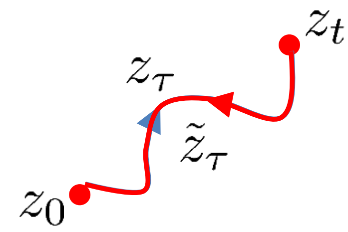
$\star$ Choose $p_0(z_0) = \tilde{p}_0(\tilde{z}_0) = c$ (uniform: $T = \infty$)

➡ Q satisfies IFT & DFT exactly at any t like $\langle e^{\beta Q} \rangle = 1$.

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

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.]

- $$R(z_\tau) = \ln \frac{\Pi(z_\tau) p^0_{z_0}}{\Pi(\tilde{z}_\tau) \tilde{p}^0_{\tilde{z}_0}} = \Delta S_r(z_\tau) - \beta \Delta F + \beta \Delta E(z_\tau)$$
  $$= -\beta Q(z_\tau) + \beta \Delta E(z_\tau) - \beta \Delta F = \beta(W(z_\tau) - \Delta F) = \beta W_d(z_\tau)$$

- $f^2 = I$ $\quad \star\ \langle e^{-\beta W_d} \rangle = 1$ or $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$ and $\frac{P(W)}{\tilde{P}(-W)} = e^{\beta(W-\Delta F)}$.

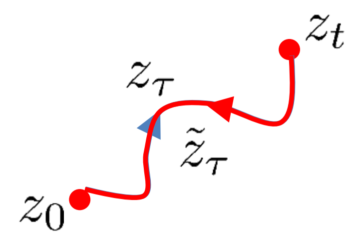
- Other arbitrary initial conditions? $\langle \Delta S_{\mathrm{tot}} \rangle \geq 0$
  $\Delta S_{\mathrm{tot}} = \Delta S - \beta Q = \beta W - \Delta E + \Delta S \approx \beta W_d$ (large t)
  $\star$ FT approx. valid only for large t.
  ➡ $\langle \Delta W_d \rangle$ does not increase monotonically in time.
  $\star$ not for rare events with exponentially small probability (unbounded E)
  (Initial memory does not go away forever !) Same happens to Q.

HW#2(c)

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

- $\Delta S_{\text{tot}}(z_\tau) = \Delta S_{hk}(z_\tau) + \Delta S_{ex}(z_\tau)$

$$\tilde{p}^0_{\tilde{z}_0} = p_{z_t}(t)$$

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

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

$$W^+_{z,z'}(\lambda_\tau) \equiv \frac{W_{z',z}(\lambda_\tau)p^s_z(\lambda_\tau)}{p^s_{z'}(\lambda_\tau)} \qquad \sum_z W^+_{z,z'} = 0$$

$$\langle e^{-\Delta S_{hk}} \rangle = 1 \text{ and } \langle e^{-\Delta S_{ex}} \rangle = 1$$

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

Summary and Outlook

- 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), information reservoir, 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
- Nonequilibrium fluctuation-dissipation relation (FDR) : Alternative measure (instead of EP) for NEQ processes?
- Usefulness of FT? Efficiency of information (heat) engine, effective measurements of free energy diff., driving force (torque), ..
- Strong couplings, entropy & 2nd law for quantum systems, quantum thermalization, quantum engines, black-hole physics, ···