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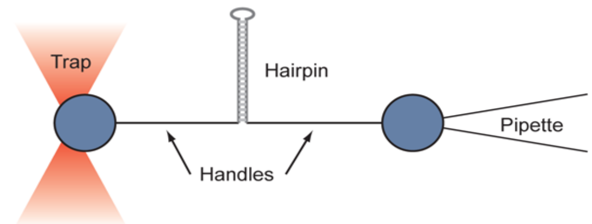
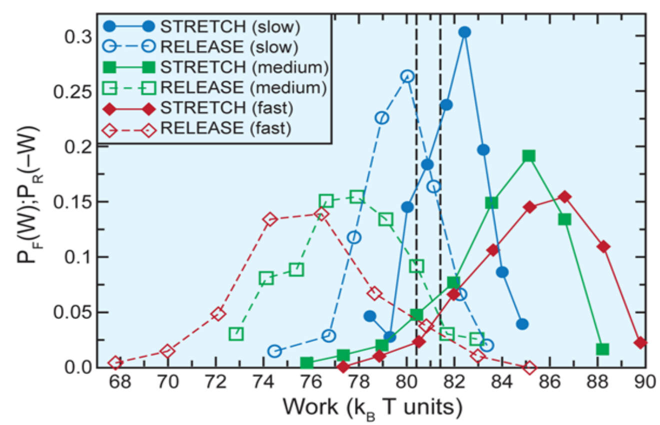
KIAS KOREA INSTITUTE FOR ADVANCED STUDY

Entropy and Thermodynamic 2nd laws : New Perspective

- Stochastic Thermodynamics and Fluctuation Theorems

1. Nonequilibrium processes
2. Brief History of Fluctuation theorems
3. Thermodynamics & Jarzynski/Crooks FTs
4. Experiments
5. Stochastic Thermodynamics
6. Ending

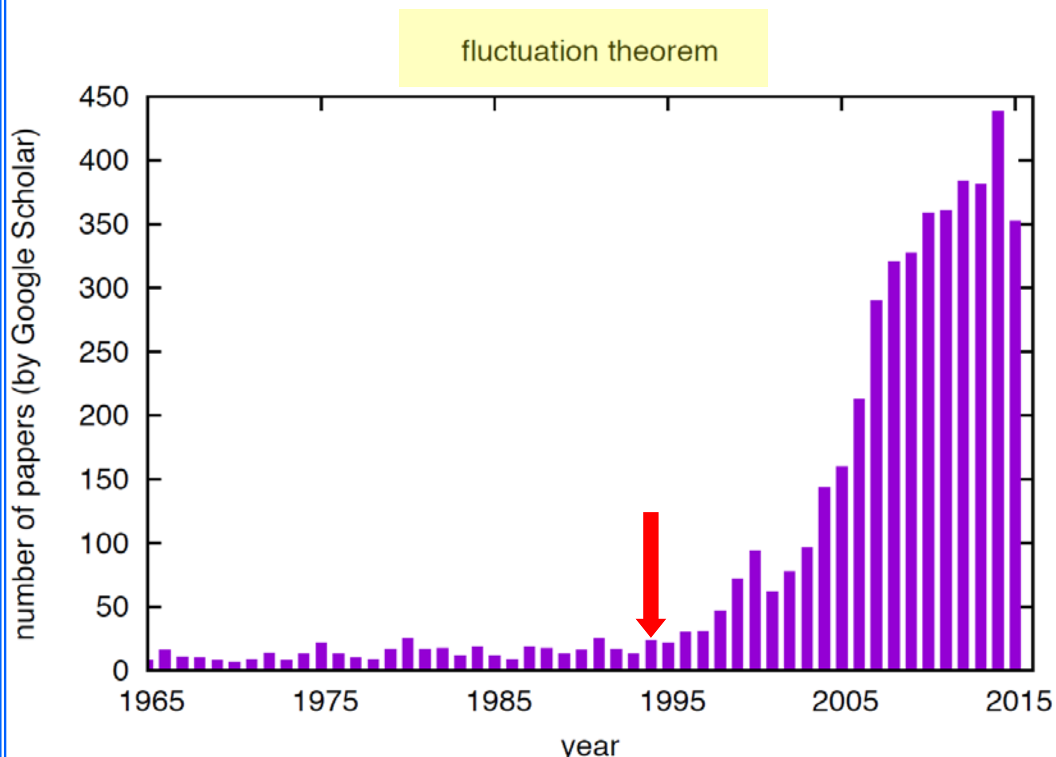


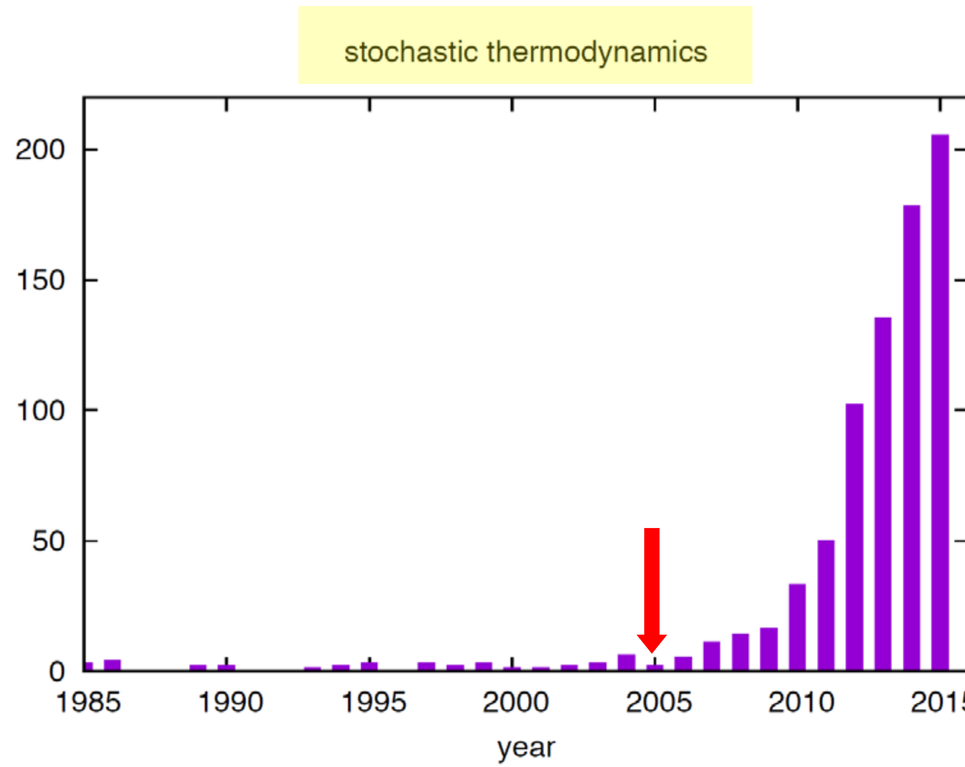


(Bustamante)

Colloquium at SNU, Seoul (Sept. 23, 2015)

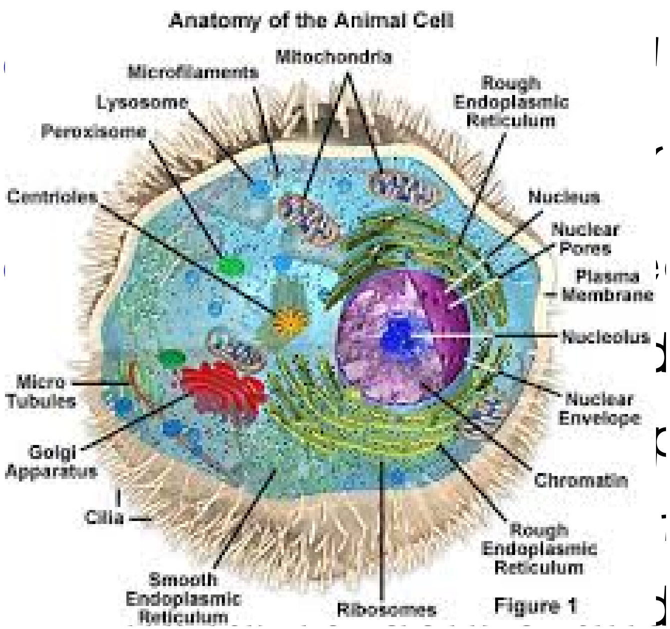
Outbursts of research activity

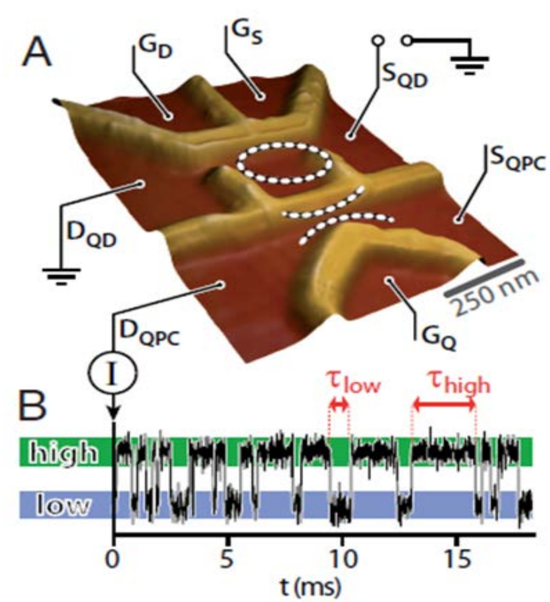


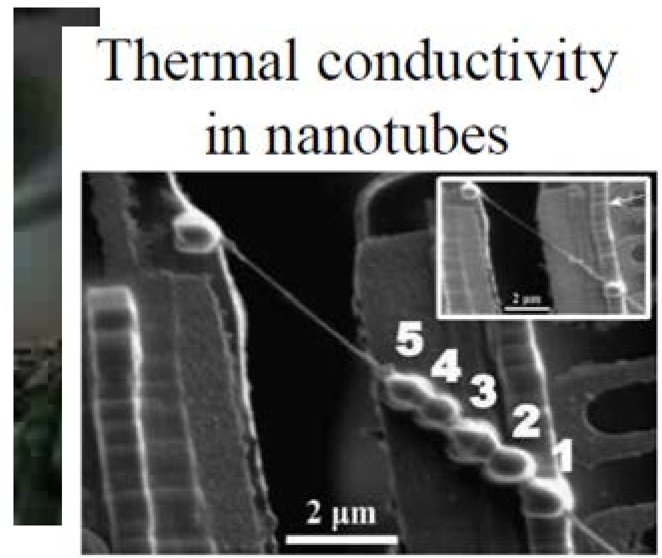


Nonequilibrium processes

- 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., ⋯







r general NEQ processes

Brief history of FT (I)

- Evans, Cohen, Morris (1993)

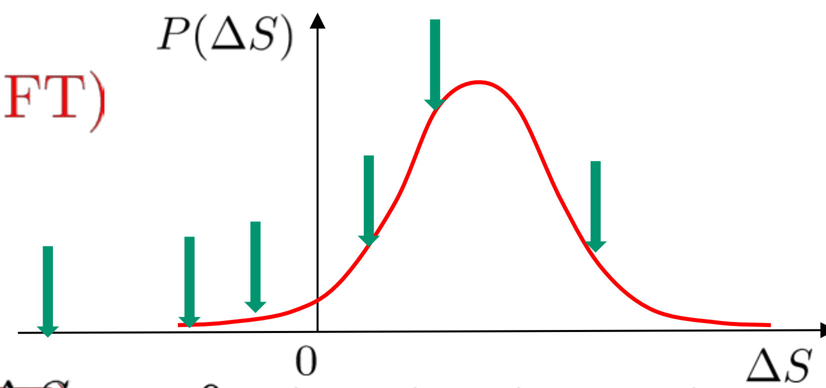
observation of FT in molecular dynamics simulations on fluid systems

- Gallavotti and Cohen (1995)

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

$k_B \equiv 1$

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

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

FT in Hamiltonian systems (work-free energy relation) $\beta = 1/T$

- 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)

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

DFT for stochastic systems

- Hatano and Sasa (2001)
- Speck/Seifert/vdBroeck (2005)
- Speck/Seifert (2007)
- Sagawa/.... (2008)
- Our group/Spinney/Ford (2012)

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

non-Markovian, non-Gaussian ??

Information entropy

Information thermodynamics

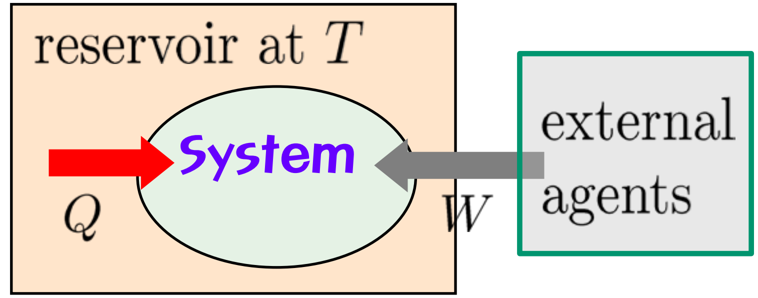
odd parity

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

Thermodynamics & Jarzynski/Crooks FT

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

$$dS \neq \frac{dQ}{T} \qquad \langle W \rangle \geq \Delta F \qquad dS_r = \frac{dQ}{T}$$

Total entropy does not change during reversible processes.

Total entropy increases during irreversible (NEQ) processes.

▶ Work and Free energy $(F = E - TS)$

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

$$\langle e^{-\Delta S_{\rm tot}} \rangle = 1 \qquad \Delta S_r = -\frac{Q}{T}$$

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

Jarzynski equality (IFT)

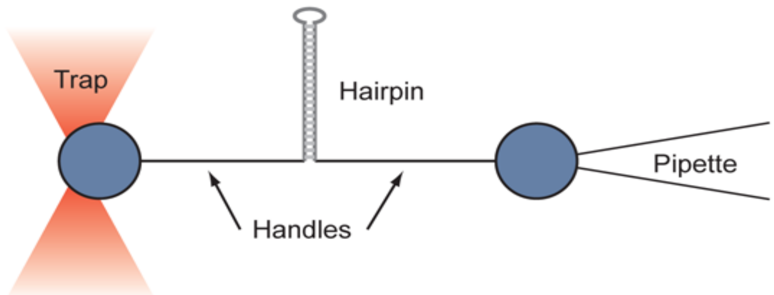
$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$

Crooks relation (DFT)

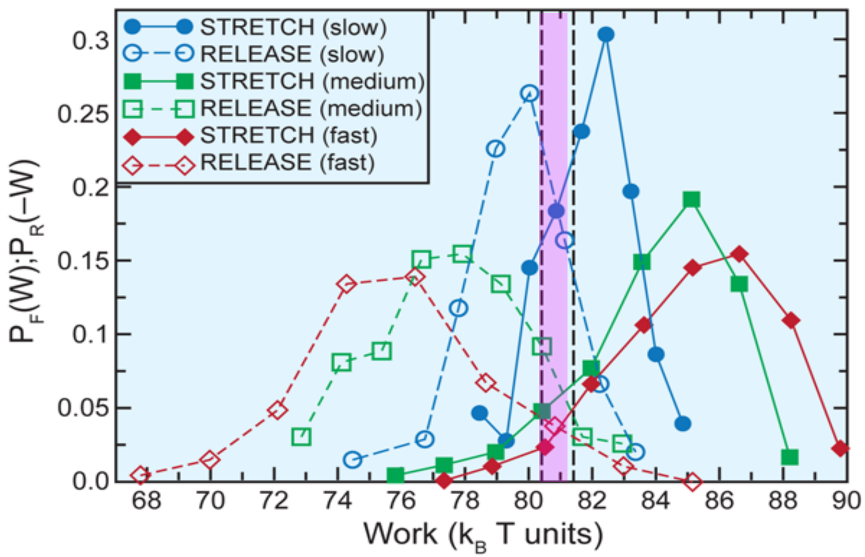
$$\frac{P_F(W)}{P_R(-W)} = e^{\beta W - \beta \Delta F}$$

Experiments & Applications

DNA hairpin mechanically unfolded by optical tweezers

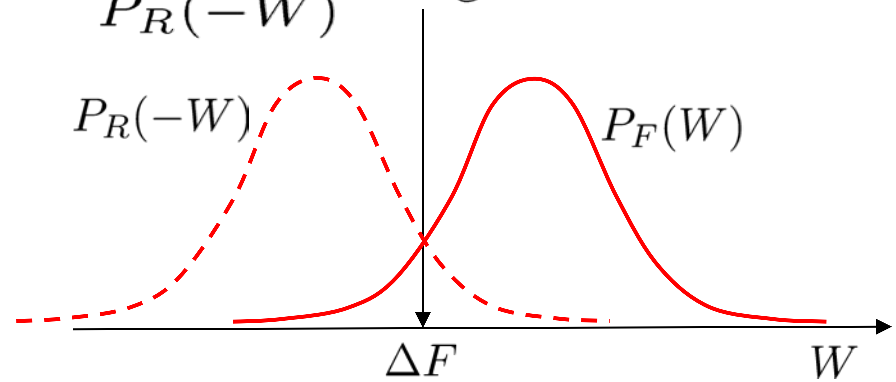


Collin/Ritort/Jarzynski/Smith/Tinoco/Bustamante, Nature, 437, 8 (2005)



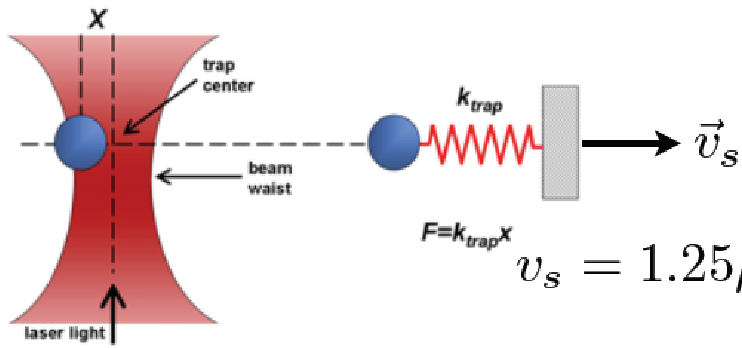
Detailed fluctuation theorem

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



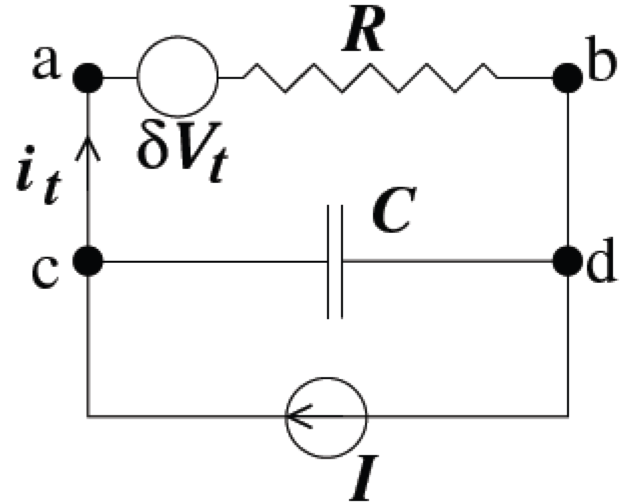
- At $P_F(W) = P_R(-W)$, W must be the same as ΔF, independent of intermediate processes.

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



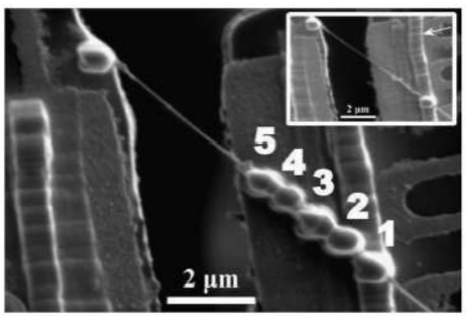
$$v_s = 1.25\mu\mathrm{m/s}$$

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



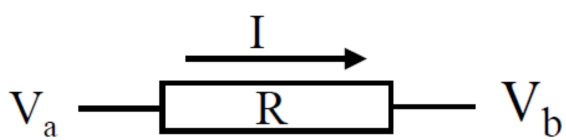
[Garnier&Ciliberto `05]

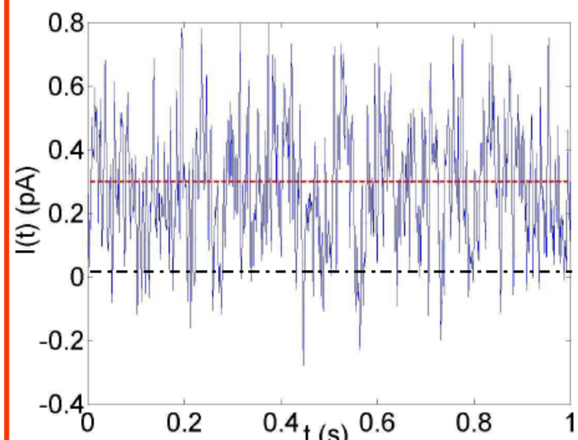
Thermal conductivity in nanotubes



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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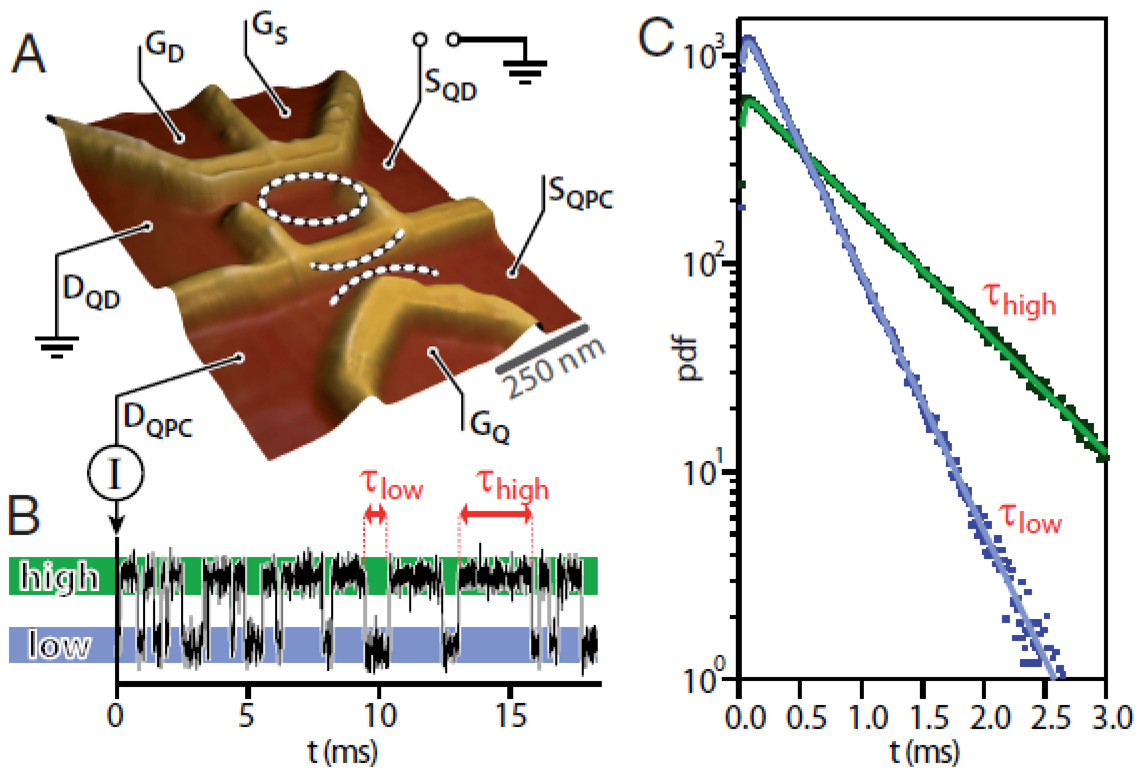

Fig. 1. Real-time counting of electrons tunneling through a quantum dot.

Fluidized Granular Medium as an Instance of the Fluctuation Theorem

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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-

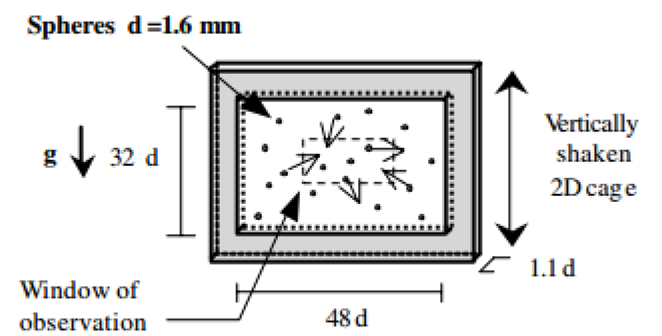

FIG. 1. Sketch of the experimental cell. The dashed rectangle is a window measuring $10d \times 21d$, fixed in the laboratory frame, in which we study the flux of kinetic energy.

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

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

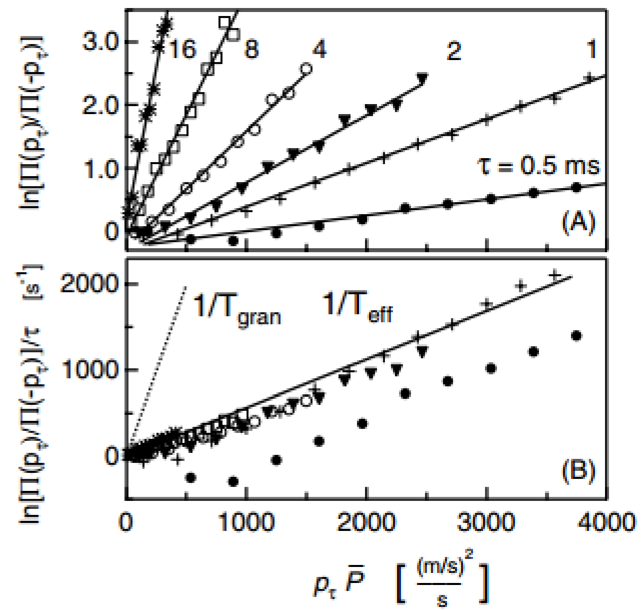

FIG. 4. (a) $\ln[\Pi(p_\tau)/\Pi(-p_\tau)]$ versus $p_\tau\overline{P}$ for τ ranging from 0.5 to 16 ms. (b) $\ln[\Pi(p_\tau)/\Pi(-p_\tau)]/\tau$ versus $p_\tau\overline{P}$ ($\overline{P} = 356\ \mathrm{m^2\,s^{-3}}$). The solid line shows the slope of the collapsed curves. A dashed line of slope $1/T_{gran}$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

arXiv: 1008.1184

KEK-T

Non-Equilibrium Fluctuations of Black Hole Horizons

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(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)]

Microscopic deterministic dynamics

- Hamilton equation
- TR symmetry

coarse-graining, truncation

Stochastic dynamics

- Langevin equation
- Master equation
- TR symmetry broken

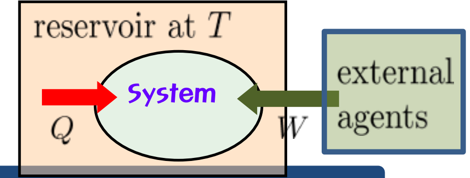
stochastic thermodynamics
trajectory level
energetics? entropy production?

equilibrium SM

Macroscopic thermodynamics

- NOT really dynamics
- TR symmetry broken

Stochastic thermodynamics



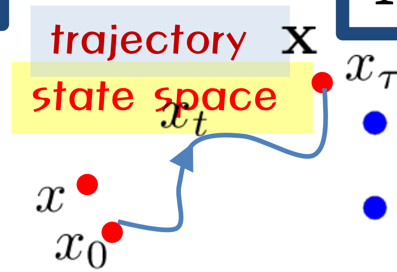
Equilibrium

- 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: $E(x) = \dfrac{\vec{p}^2}{2m} + V(\vec{x})$
  - entropy: $S(x) \equiv -\ln p(x)$

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

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

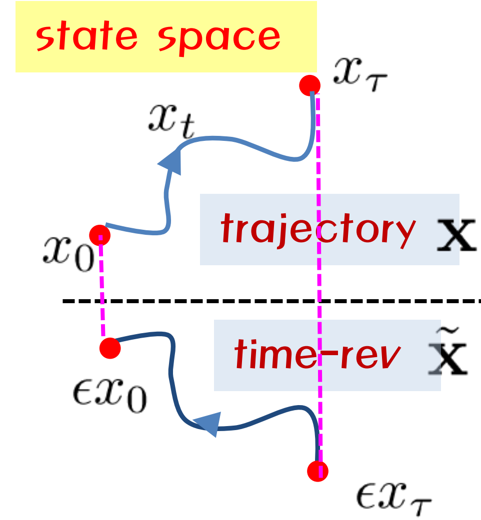
$\star$ canon: $\langle S \rangle = -(F - \langle E \rangle)/T$



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: $W(\mathbf{x})$, $Q(\mathbf{x})$
  - $\Delta E = W(\mathbf{x}) + Q(\mathbf{x})$
- $\Delta S_{\text{res}} = -\dfrac{Q(\mathbf{x})}{T}$
- $\Delta S_{\text{sys}} = -\ln p(x_\tau) + \ln p(x_0)$??(NEQ entropy)
- $\langle \Delta S_{\text{tot}} \rangle = \langle \Delta S_{\text{sys}} \rangle + \langle \Delta S_{\text{res}} \rangle \geq 0$

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)

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

$\mathcal{P}[\mathbf{x}]$:probability of traj. $\mathbf{x}$
$\tilde{\mathbf{x}}$: time-reversed traj.

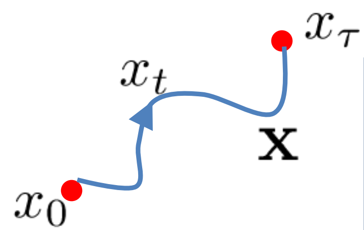
[Sekimoto(1998)/Seifert(2005)]

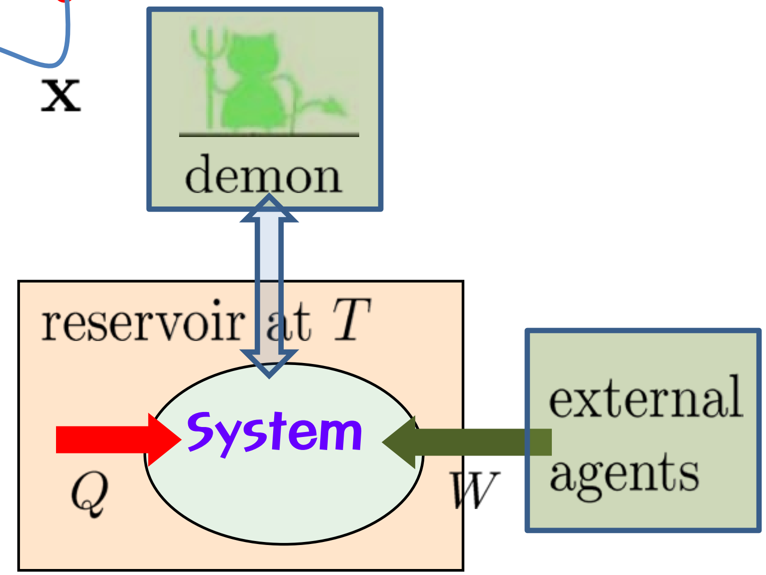
- *integral* fluctuation theorem (FT) : automatic
  $\langle e^{-\Delta S_{\rm tot}} \rangle = \sum_{\mathbf{x}} \mathcal{P}[\mathbf{x}] e^{-\Delta S_{\rm tot}[\mathbf{x}]} = \sum_{\tilde{\mathbf{x}}} \mathcal{P}[\tilde{\mathbf{x}}] = 1$ (Jacobian $|\partial \tilde{\mathbf{x}}/\partial \mathbf{x}| =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

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

Total entropy production and its components

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





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

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

(Schnakenberg, 1976)

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

† steady state $\langle \Delta S_{\rm sys} \rangle = 0$, $\langle Q \rangle \le 0$ or $\langle W \rangle \ge 0$ (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 !!

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

† steady state $\langle Q \rangle \le -T\Delta I$ or $\langle W \rangle \ge T\Delta I$ (ΔI can be 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

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 engine, effective measurements of free energy diff., driving force (torque), ..
- Need to calculate P(W), P(Q), ⋯ for a given NEQ process.