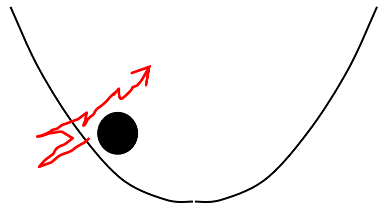
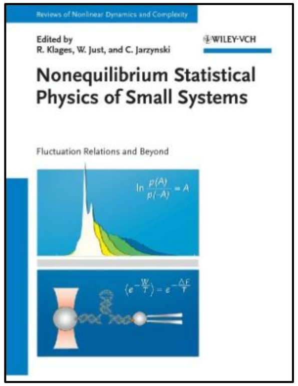
A rough guide to fluctuation relations

Ian Ford

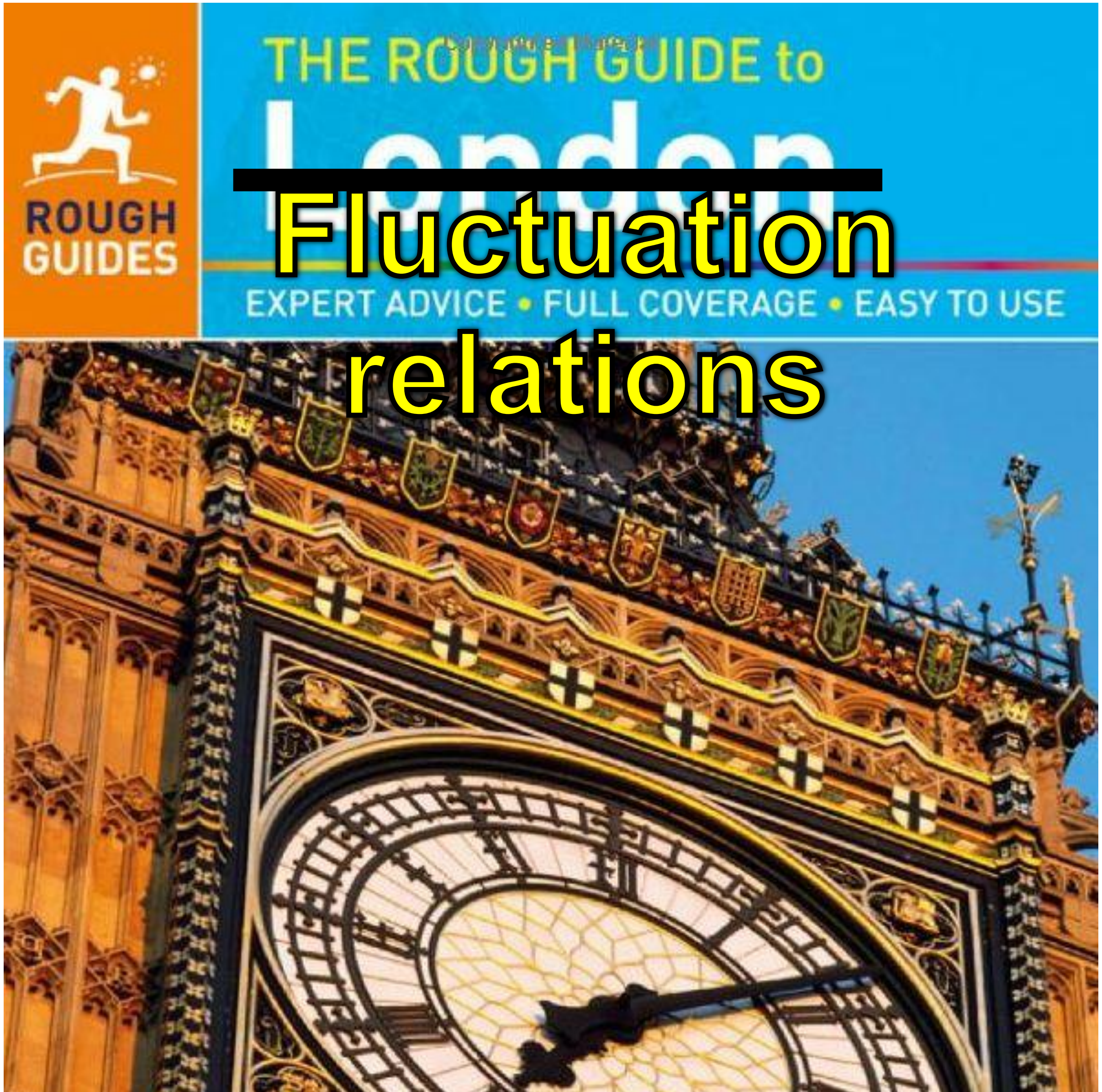
Department of Physics and Astronomy
and
London Centre for Nanotechnology
University College London, UK



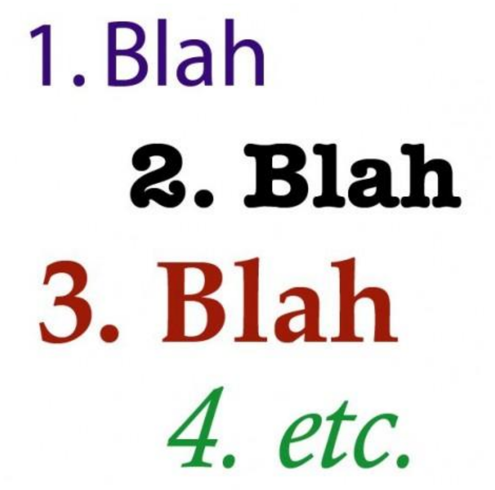
Fluctuation relations: a pedagogical overview
with Richard Spinney, in
Also http://arxiv.org/abs/1201.6381



Fluctuation relations

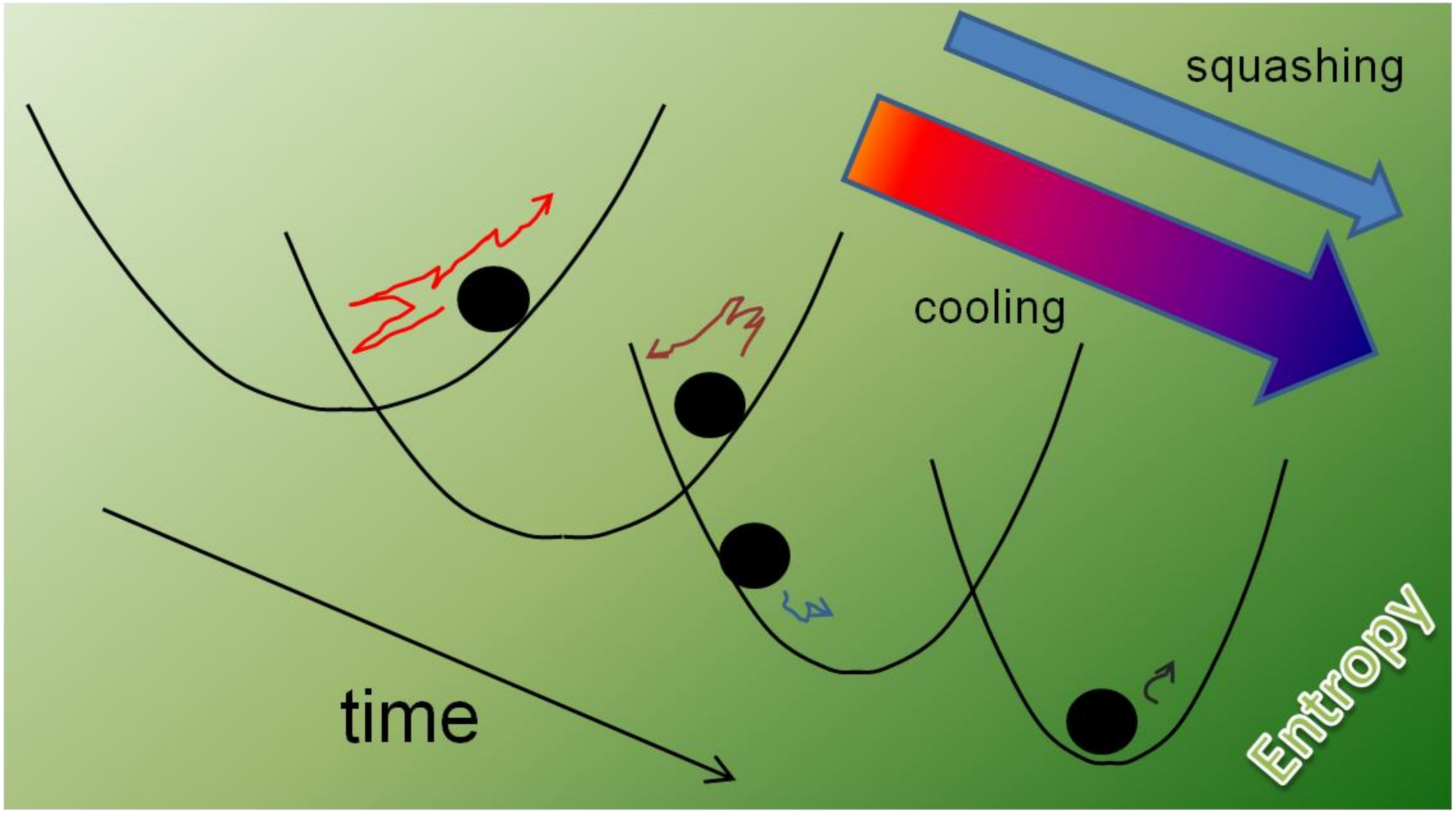


Summary



- What are fluctuation relations?
- Stochastic thermodynamics of small systems
- Defining a path-dependent entropy production
- Simple demonstrations of fluctuation relations
- Measurement, information and entropy

Thermodynamic process driven by changes in Hamiltonian and external temperature



Jarzynski equality

$$\langle \exp\left(-\Delta W_0 / k_B T\right)\rangle = \exp\left(-\Delta F / k_B T\right)$$

$$\Delta W_0 = \int_0^\tau \frac{\partial \phi(x(t), \lambda_0(t))}{\partial \lambda_0} \frac{d\lambda_0(t)}{dt} dt$$

e.g. $$\phi(x,t) = \frac{1}{2}\lambda_0(t) x^2$$

External work performed by a change to the Hamiltonian.
Start in canonical equilibrium; average over paths.

Bochkov-Kuzovlev work relation

$$\langle \exp\left(-\Delta W_1 / k_B T\right)\rangle = 1$$

$$\Delta W_1 = \int_0^\tau f(x(t), \lambda_1(t)) \circ dx$$

Work performed by externally imposed force: not part of H
again start in equilibrium, average over paths.

Crooks relation

$$\frac{P^F(\Delta W_0)}{P^R(-\Delta W_0)} = \exp\left[\frac{\Delta W_0 - \Delta F}{k_B T}\right]$$

Must start in equilibrium

- Compress system and do work
- Expand and receive work back
- Probabilities of same work in and out are typically not equal

Equivalent for Bochkov-Kuzovlev case

$$\frac{\mathcal{P}^F(\Delta W_1)}{\mathcal{P}^R(-\Delta W_1)} = \exp\left[\frac{\Delta W_1}{k_B T}\right]$$

- for non-Hamiltonian work
- must start in equilibrium

Consequence of Jarzynski/Bochkov & Kuzovlev

$$\langle \exp(-(\Delta W_0 - \Delta F)/k_B T) \rangle = 1 \qquad \langle \exp(-\Delta W_1 / k_B T) \rangle = 1$$

Jensen's inequality

$$1 = \langle \exp(X) \rangle \geq \exp\langle X \rangle \Rightarrow \langle X \rangle \leq 0$$

$$\Rightarrow \quad \Delta W_d = \langle \Delta W_0 \rangle - \Delta F \geq 0$$

Hamiltonian dissipative work

and

$$\Delta W_d = \langle \Delta W_1 \rangle \geq 0$$

Non-Hamiltonian dissipative work

Average dissipative work ΔW_d, starting from canonical equilibrium, is never negative.

Integral fluctuation theorem: introducing Δs_{tot}

$$\left\langle \exp(-\Delta s_{\text{tot}} / k_B) \right\rangle = 1$$

Detailed fluctuation theorem

$$P^F(\Delta s_{\text{tot}}) = \exp(\Delta s_{\text{tot}} / k_B)\, P^R(-\Delta s_{\text{tot}})$$

Holds for particular circumstances

$$\left\langle \Delta s_{\text{tot}} \right\rangle \geq 0$$

Any initial condition: average Δs_{tot} never negative.
We claim $\left\langle \Delta s_{\text{tot}} \right\rangle$ is the thermodynamic entropy production in the process.

Thermodynamic entropy change

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{med}}$$

- Relaxation
  - towards a stationary state
  - transient
- Driving
  - Due to ‘nonequilibrium constraint’
  - could be stationary

$$\Delta S_{\text{sys}} + \frac{\langle \Delta Q_{\text{ex}} \rangle}{T_{\text{med}}}$$

$$\frac{\langle \Delta Q_{\text{hk}} \rangle}{T_{\text{med}}}$$

$$\Delta S_{\text{sys}} = \langle \Delta s_{\text{sys}} \rangle \qquad \Delta S_{\text{med}} = \langle \Delta s_{\text{med}} \rangle = \frac{\langle \Delta Q_{\text{ex}} \rangle}{T_{\text{med}}} + \frac{\langle \Delta Q_{\text{hk}} \rangle}{T_{\text{med}}}$$

Other fluctuation relations

- Gallavotti-Cohen

$$P(\Delta s_{\text{med}}) \approx \exp(\Delta s_{\text{med}} / k_B) P(-\Delta s_{\text{med}})$$

- Speck-Seifert $\langle \exp\left[-\Delta Q_{\text{hk}}/k_B T\right] \rangle = 1$

- Hatano-Sasa

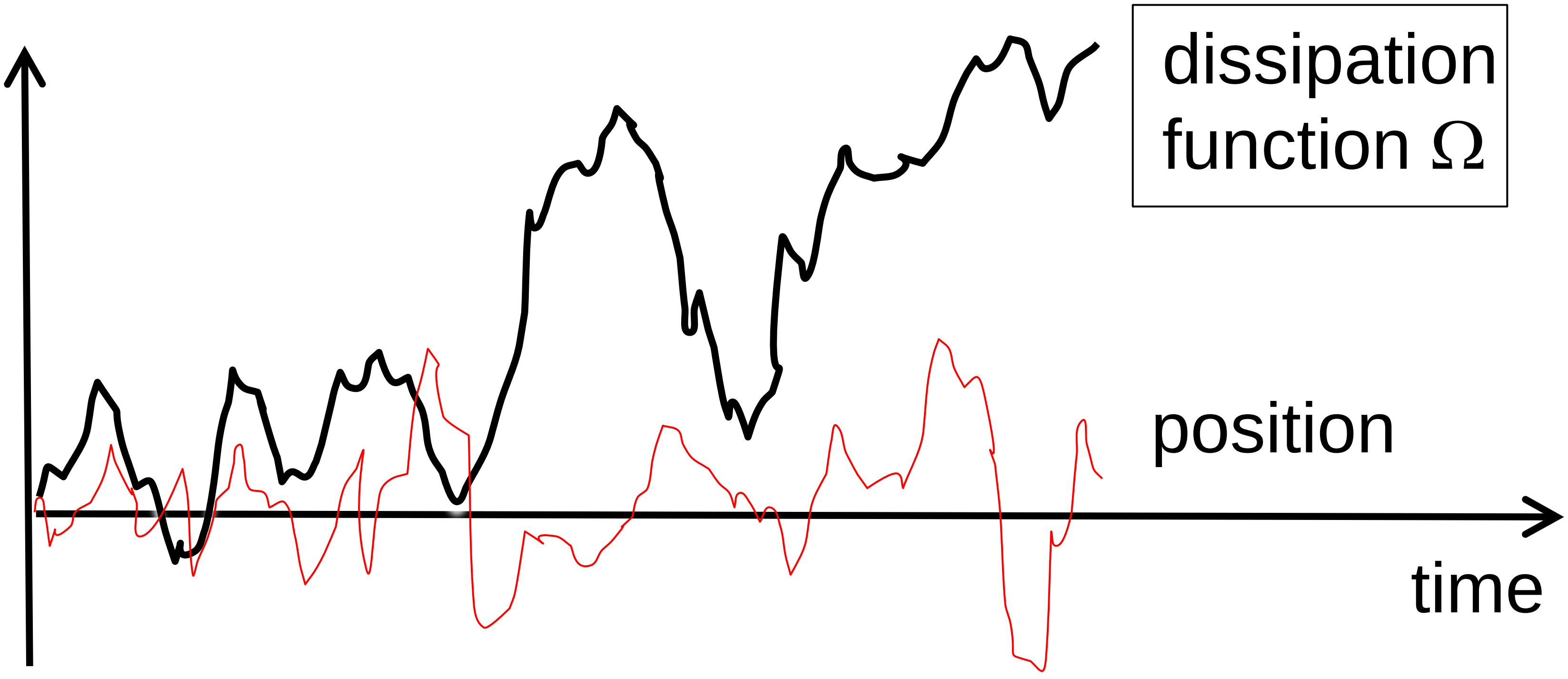
$$\left\langle \exp(-\Delta Q_{\text{ex}} / k_B T - \Delta s_{\text{sys}} / k_B \right\rangle = 1$$

Derivation of fluctuation relations?

- Deterministic mechanics
  - Jarzynski, Evans,Gallavotti-Cohen, etc
- Stochastic dynamics
  - Sekimoto, Seifert, Crooks, etc

Deterministic thermodynamics (Evans)

- Non-linear dynamics of a thermally open system
- Identify a quantity that increases with time when averaged over initial state



Evans-Searles fluctuation theorem

Phase-space contracting dynamics under a ‘deterministic thermostat’

$$P(\Gamma_0, 0) \rightarrow P(\Gamma_t, t)$$ by Liouville

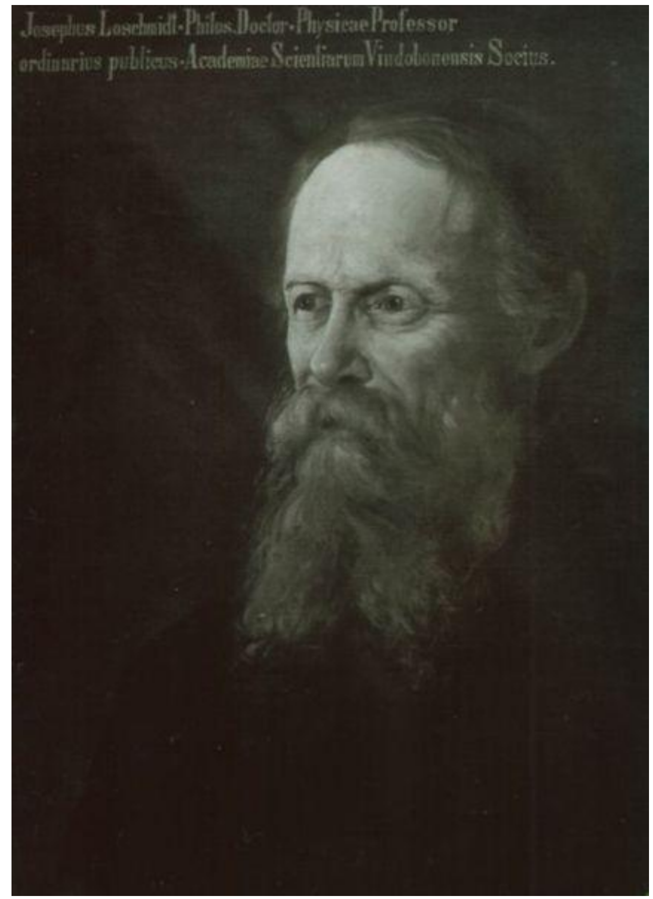
Define $$\bar{\Omega}_t(\Gamma_0)t = \ln\left(\frac{P(\Gamma_t, t)}{P(\Gamma_t, 0)}\right)$$

$$\Rightarrow \quad P(\bar{\Omega}_t) = \exp\left(\bar{\Omega}_t t\right) P(-\bar{\Omega}_t)$$

Average dissipation function over time t is never negative $\left\langle \overline{\Omega}_t \right\rangle \geq 0$

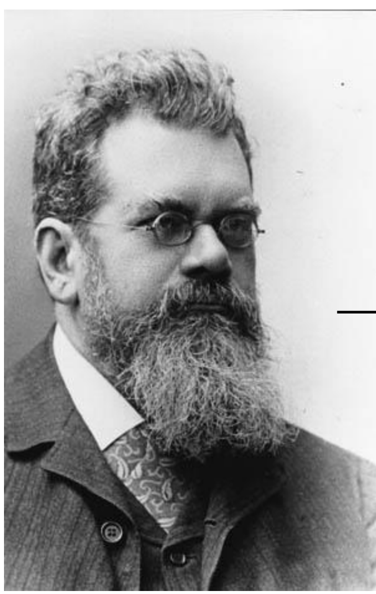
Loschmidt's reversibility paradox

- mechanics is time-reversal invariant
- average dissipation function increases both ways in time
- So what is this entropy function that always increases in forward time?



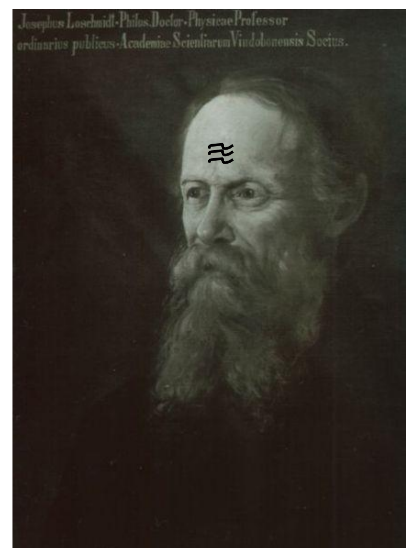
Stochastic thermodynamics provides such

- Breaks time-reversal invariance in the model dynamics
- Entropy change is evidence of the failure to respect time reversal invariance during a process



Loschmidt, I've derived the H-theorem!

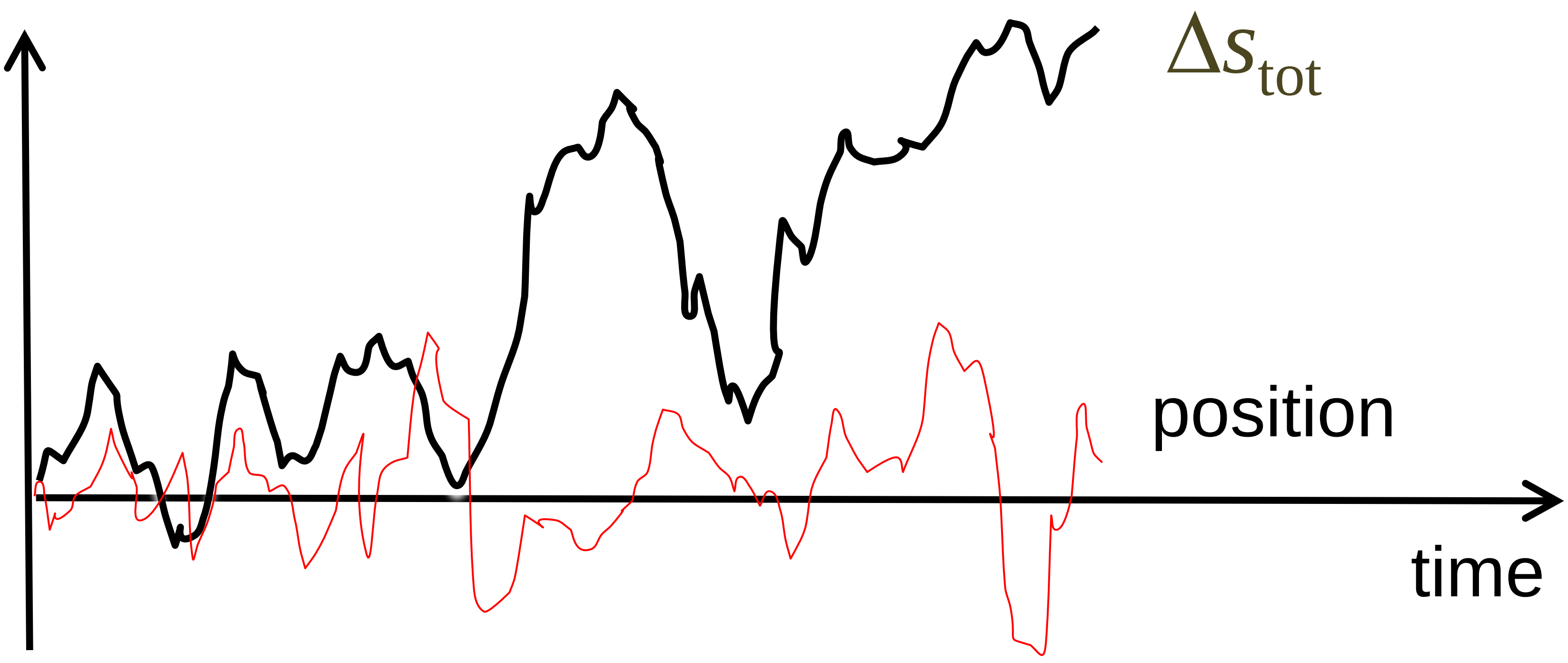
(not stochastic thermodynamics, but nevertheless a model that breaks time reversal symmetry)



Not happy

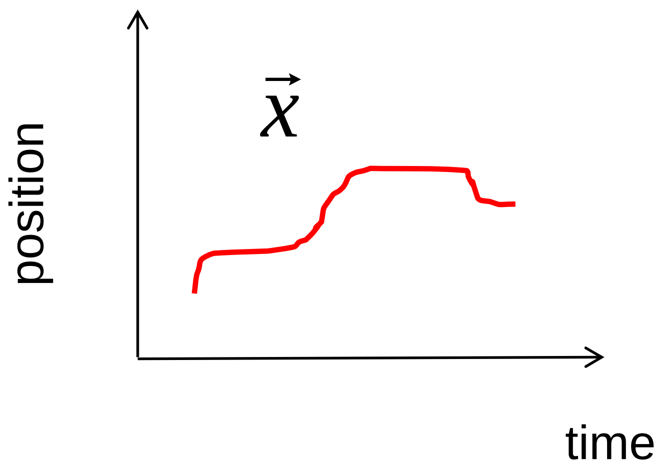
Stochastic thermodynamics (Sekimoto,Seifert)

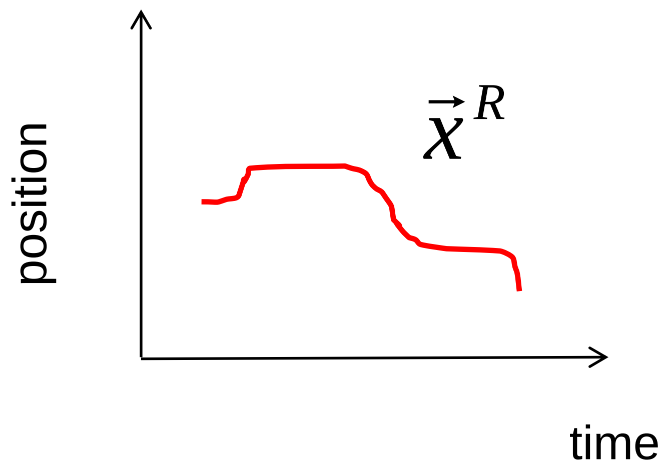
- Centrepiece: total microscopic entropy production Δs_{tot} linked to irreversibility



Entropy production in stochastic dynamics

The relative likelihood of observing the reversed behaviour





under forward protocol λ(t)

under reversed protocol λ(τ-t)

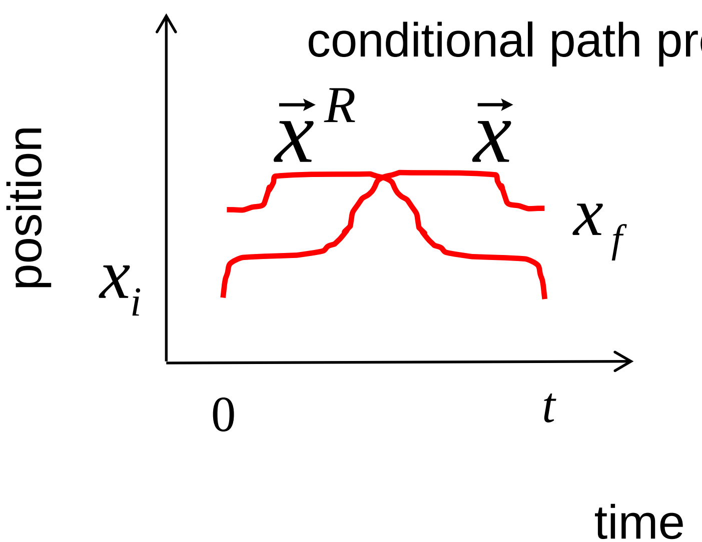
Entropy production in stochastic dynamics 2

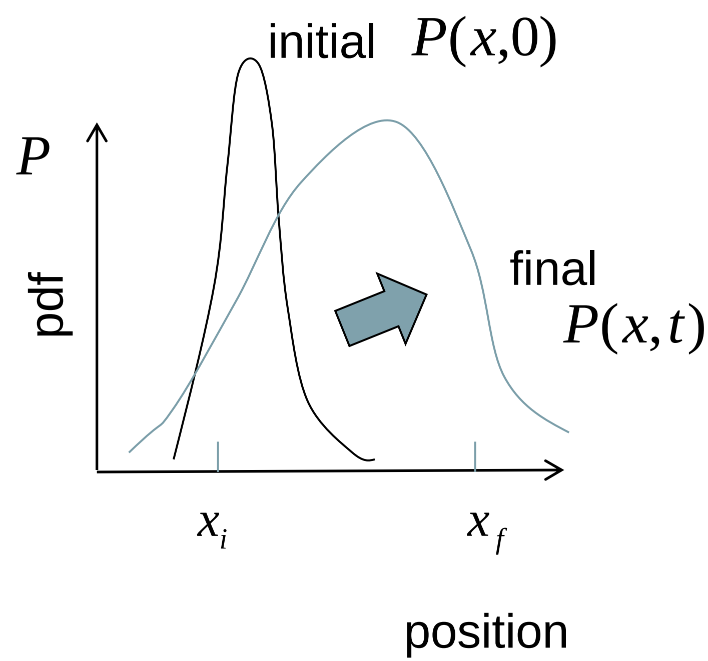
- Define total entropy change

state probabilities

$$\Delta s_{\mathrm{tot}} = \ln\left(\frac{\mathrm{P}(\vec{x})}{\mathrm{P}^{R}(\vec{x}^{R})}\right) = \ln\left(\frac{T^{F}(x_f \mid x_i)P(x_i,0)}{T^{R}(x_i \mid x_f)P(x_f,t)}\right)$$

conditional path probabilities





Entropy production in stochastic dynamics 3

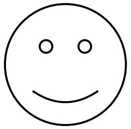
$$\Delta s_{\text{tot}} = \boxed{-\ln\left(\frac{P(x_f,t)}{P(x_i,0)}\right)} + \boxed{\ln\left(\frac{T^F(x_f \mid x_i)}{T^R(x_i \mid x_f)}\right)}$$

$$= \Delta s_{\text{sys}} + \Delta s_{\text{med}}$$

path-dependent change in medium entropy

path-dependent change in system entropy, and

$$\langle s_{\text{sys}} \rangle = -\int dx\, P(x,t) \ln P(x,t) = S_{\text{Shannon}}$$



Average Δs_{tot} ?

$$\Delta s_{\mathrm{tot}} = \ln\left(\frac{\mathrm{P}(\vec{x})}{\mathrm{P}^R(\vec{x}^R)}\right) = \ln\left(\frac{T^F(x_f \,|\, x_i)P(x_i,0)}{T^R(x_i \,|\, x_f)P(x_f,t)}\right)$$

Would be nice if $\langle \Delta s_{\mathrm{tot}} \rangle = \Delta S_{\mathrm{tot}}$

- Really the change in thermodynamic entropy?
  - Test 1. Never negative?
  - Test 2. Related to heat transfers?

Integral fluctuation relation proves Test 1

For any two dynamical schemes that generate paths $\vec{x}$ and $\vec{x}^*$ in a 1:1 correspondence with given probabilities we define

$$\mathcal{A}[\vec{\boldsymbol{x}}] = \ln\left[\mathcal{P}[\vec{\boldsymbol{x}}]/\mathcal{P}^*[\vec{\boldsymbol{x}}^*]\right]$$

Such that
$$\begin{aligned}\langle\exp\left[-\mathcal{A}[\vec{\boldsymbol{x}}]\right]\rangle &= \int d\vec{\boldsymbol{x}}\;\mathcal{P}[\vec{\boldsymbol{x}}]\exp\left[-\mathcal{A}[\vec{\boldsymbol{x}}]\right] \\ &= \int d\vec{\boldsymbol{x}}\;\mathcal{P}[\vec{\boldsymbol{x}}]\frac{\mathcal{P}^*[\vec{\boldsymbol{x}}^*]}{\mathcal{P}[\vec{\boldsymbol{x}}]} \\ &= \int d\vec{\boldsymbol{x}}^*\;\mathcal{P}^*[\vec{\boldsymbol{x}}^*] = 1.\end{aligned}$$

Δs_{tot} has this form:

Jensen's inequality then implies $\langle \Delta s_{\text{tot}} \rangle \geq 0$

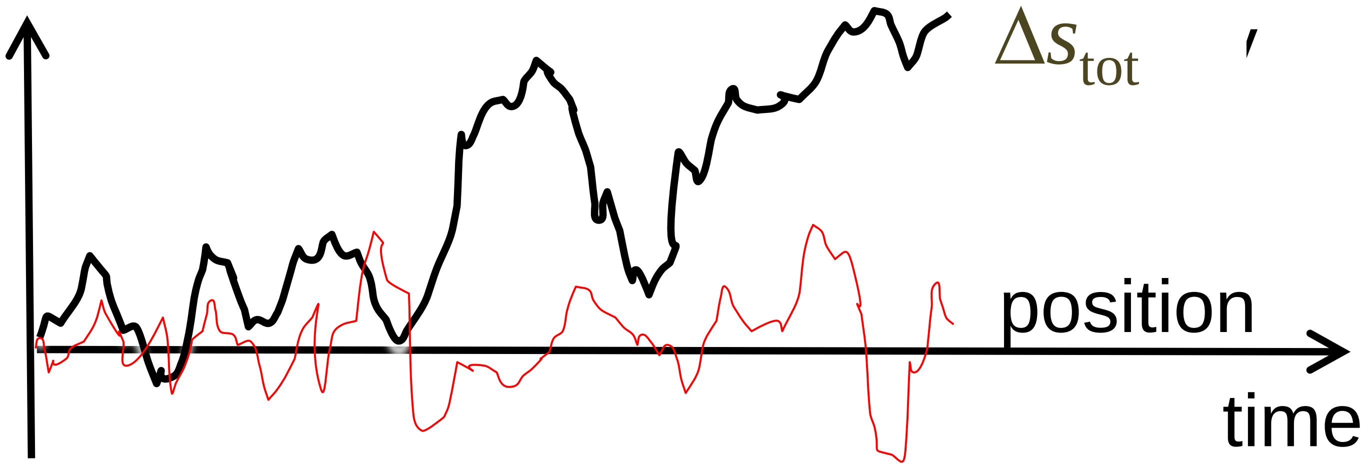
Test 2: connection with heat transfer
- for overdamped Brownian motion:

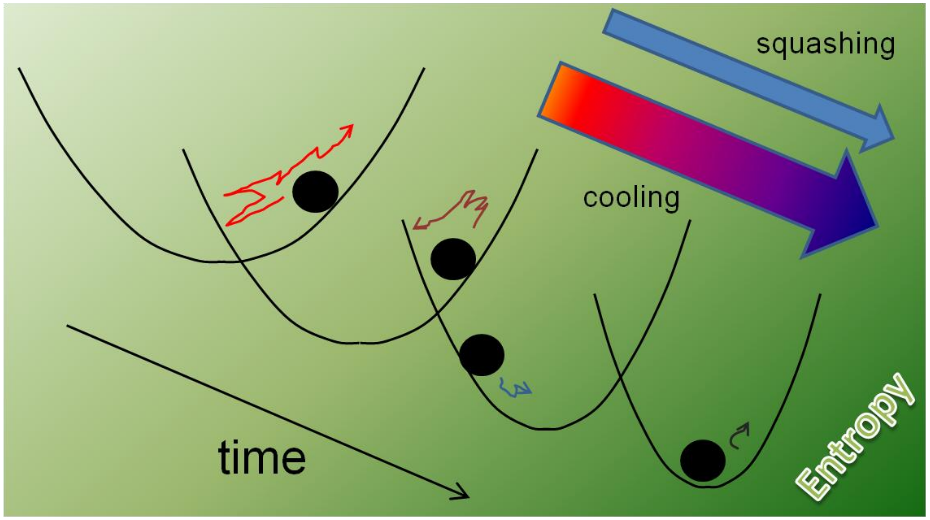
$$dx = \frac{F(x)}{m\gamma}dt + \sqrt{\frac{2k_B T(x)}{m\gamma}}dW$$

$$T(x'|x) \propto \exp\left[-\frac{m\gamma}{4k_B T dt}\left(x' - x - \frac{F(x)}{m\gamma}dt\right)^2\right]$$

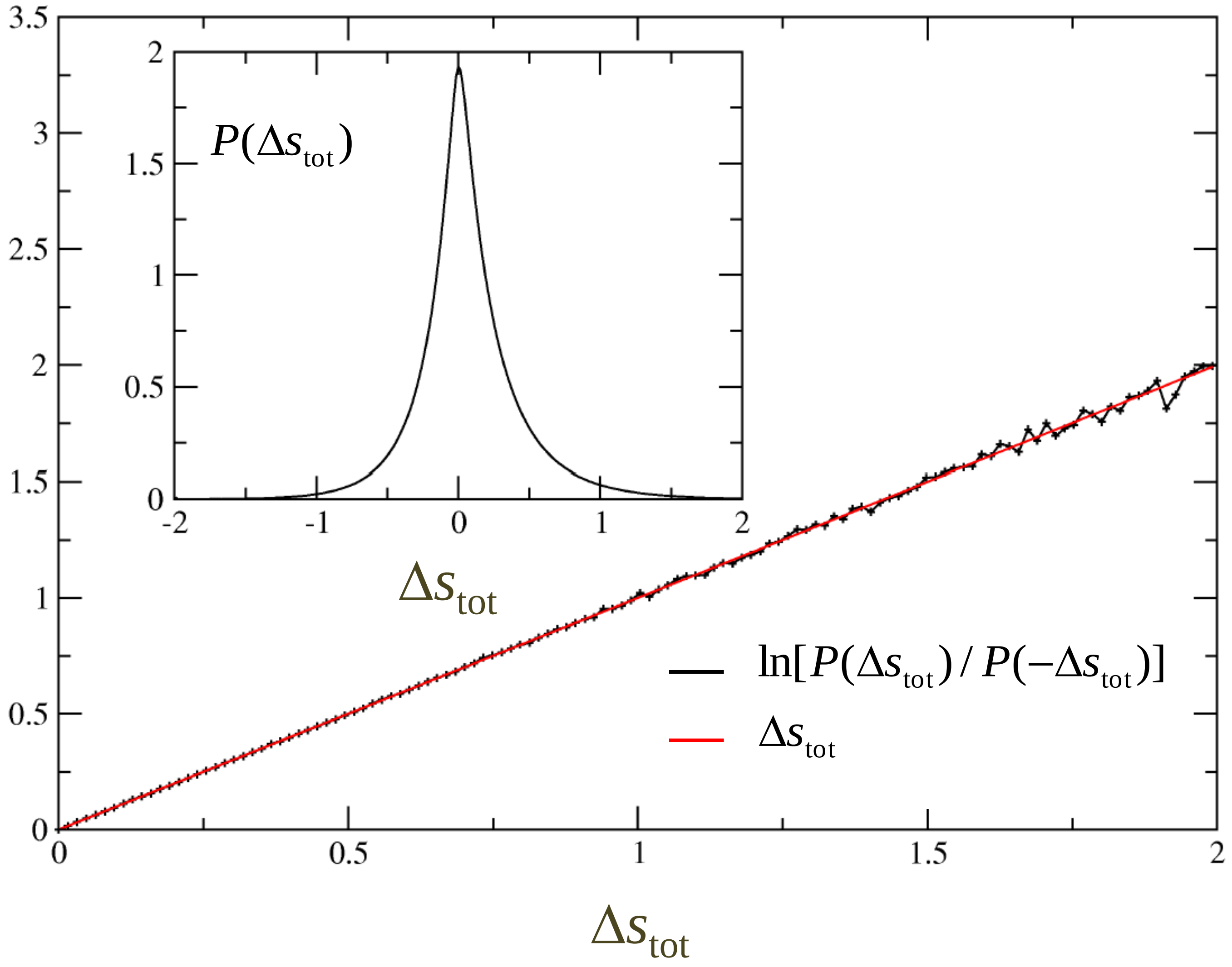
$$\frac{\Delta s_{\mathrm{med}}}{k_B T} = \ln\left[\frac{T(x'|x)}{T(x|x')}\right] = \frac{F(x)}{k_B T} \circ dx = -\frac{dQ}{k_B T}$$

Furthermore: $$d\Delta s_{\text{tot}} = Xdt + YdW$$

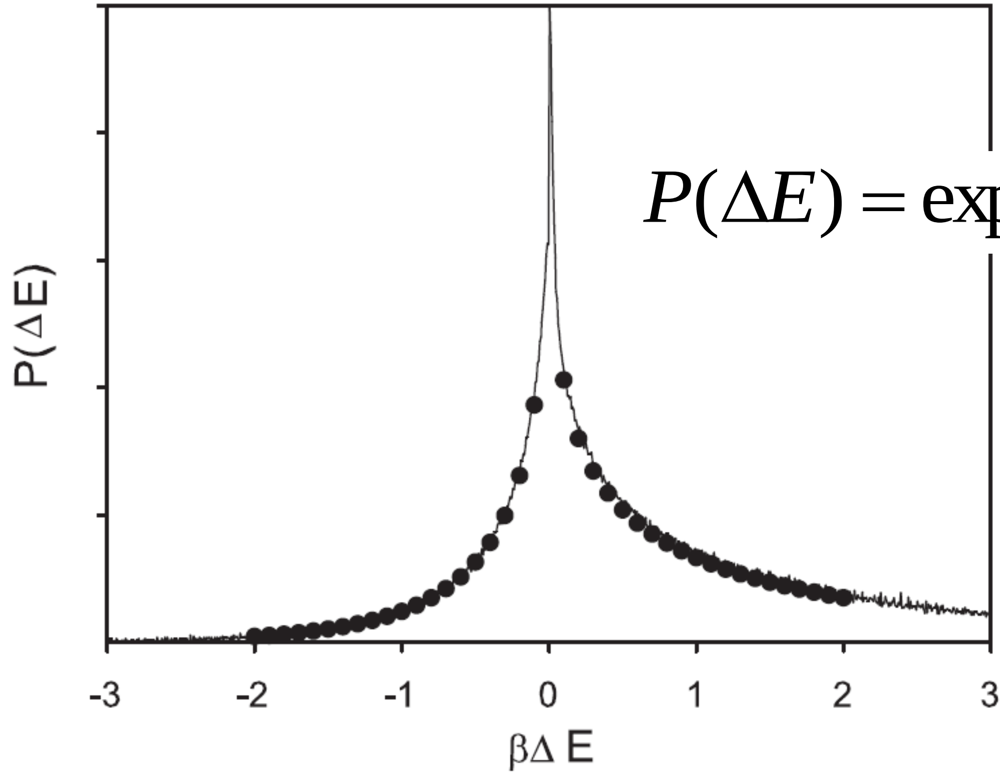




Example: cyclically compressed/expamded isothermal harmonic oscillator



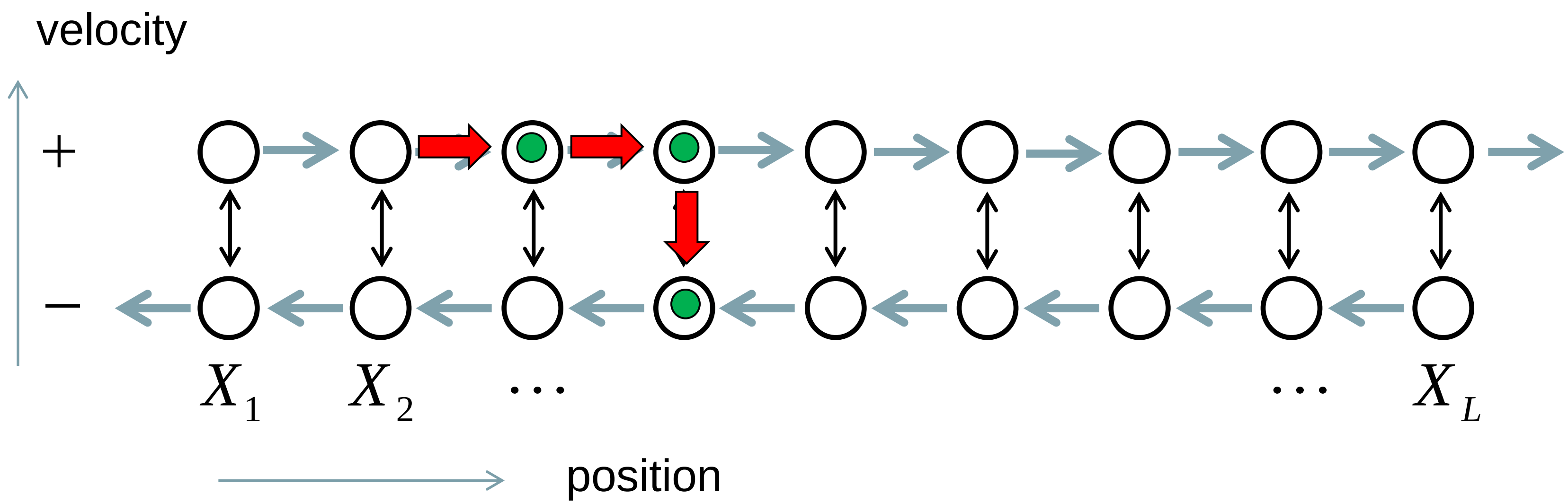
Cyclically compressed adiabatic oscillator



$$P(\Delta E) = \exp(\beta \Delta E) P(-\Delta E)$$

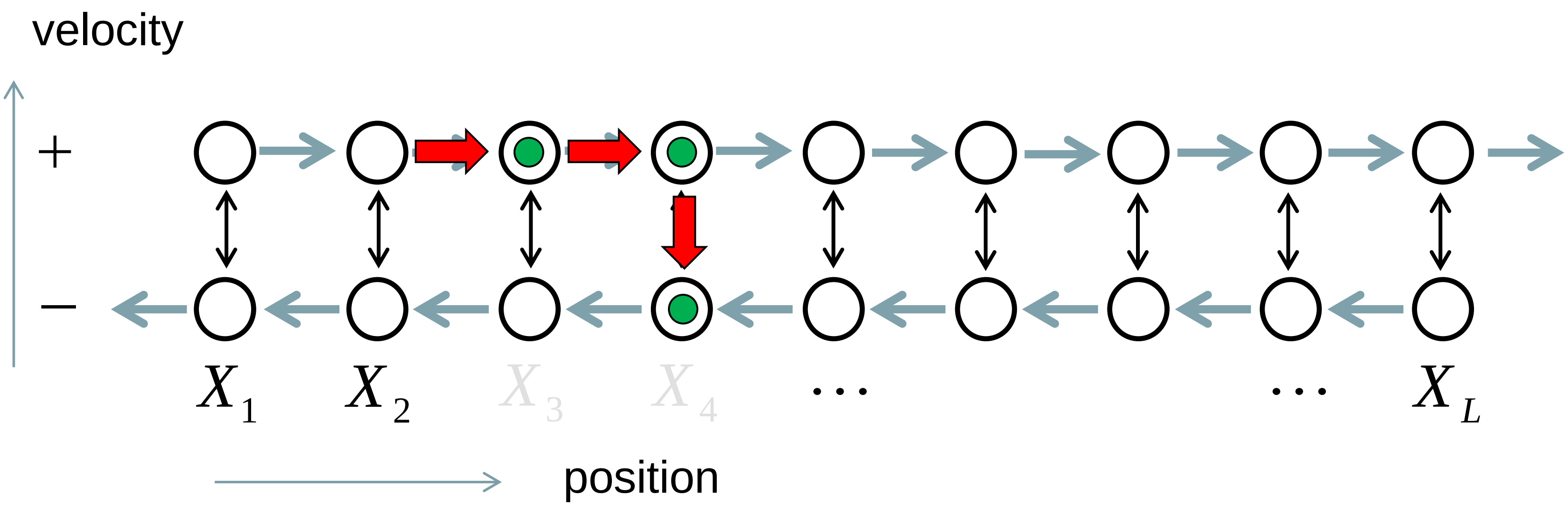
$$P(\Delta E) = \frac{\beta \exp(\beta \Delta E/2)}{\pi \sqrt{2\beta \langle \Delta E \rangle}} K_0 \left(\frac{\beta |\Delta E|}{2} \sqrt{1 + \frac{2}{\beta \langle \Delta E \rangle}} \right)$$

Discrete phase spaces:
particle motion on 1-d lattice with two velocities



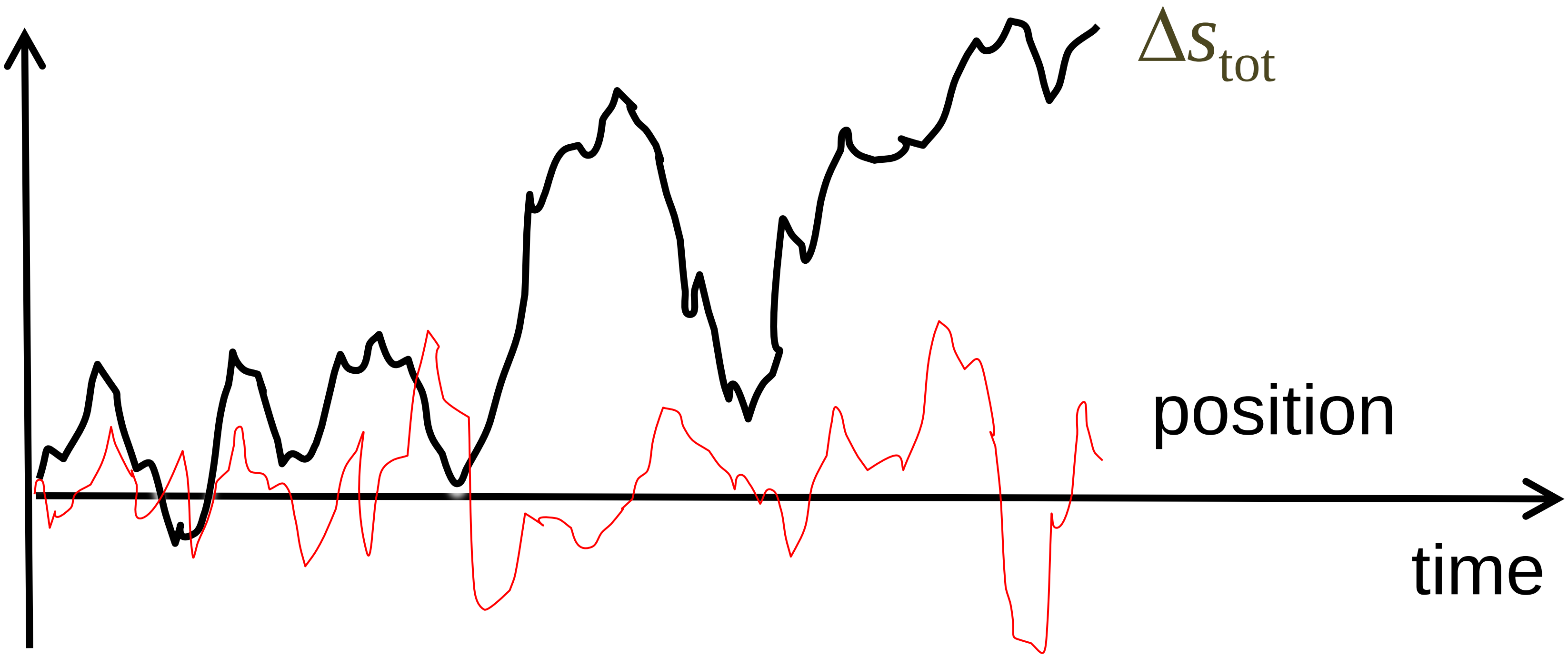
Stochastic dynamics generates a path of residence and transitions between points

A string of entropy increments for a path

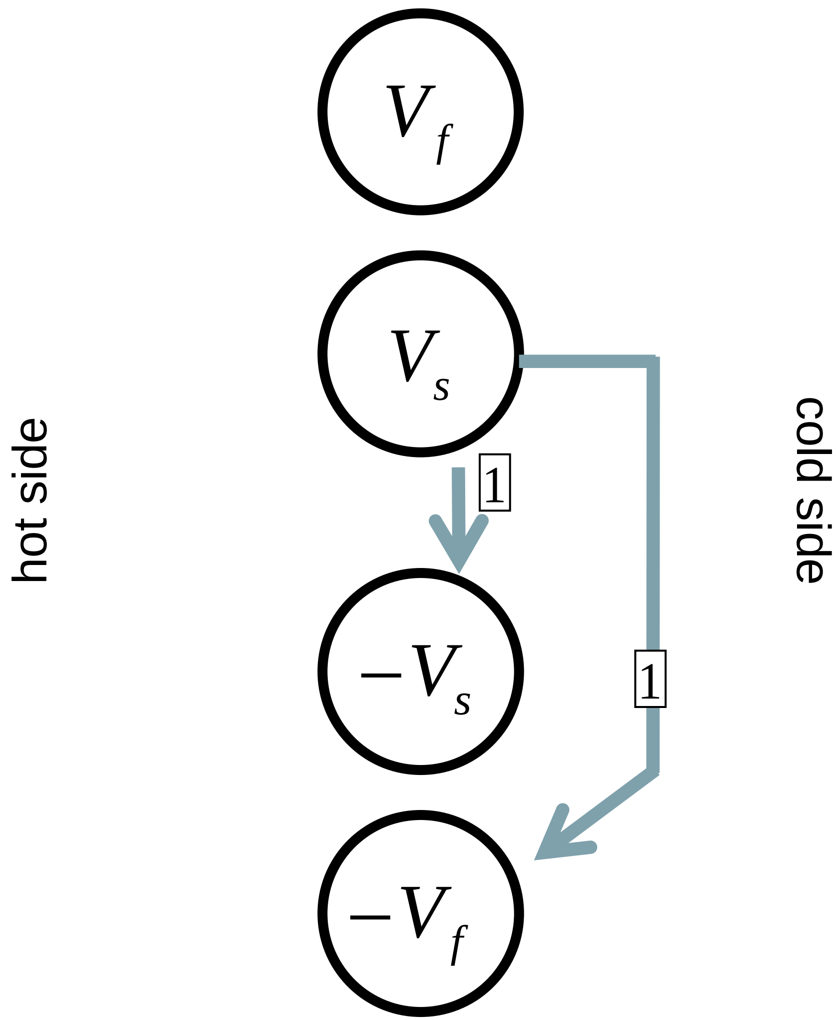


$$\Delta s_{\text{tot}} = \Delta s_{\text{tot}}(X_2^+ \to X_3^+) + \Delta s_{\text{tot}}(X_3^+, \Delta t') + \Delta s_{\text{tot}}(X_3^+ \to X_4^+)$$
$$+ \Delta s_{\text{tot}}(X_4^+, \Delta t'') + \Delta s_{\text{tot}}(X_4^+ \to X_4^-) + \Delta s_{\text{tot}}(X_4^-, \Delta t''')$$

Discrete version of:



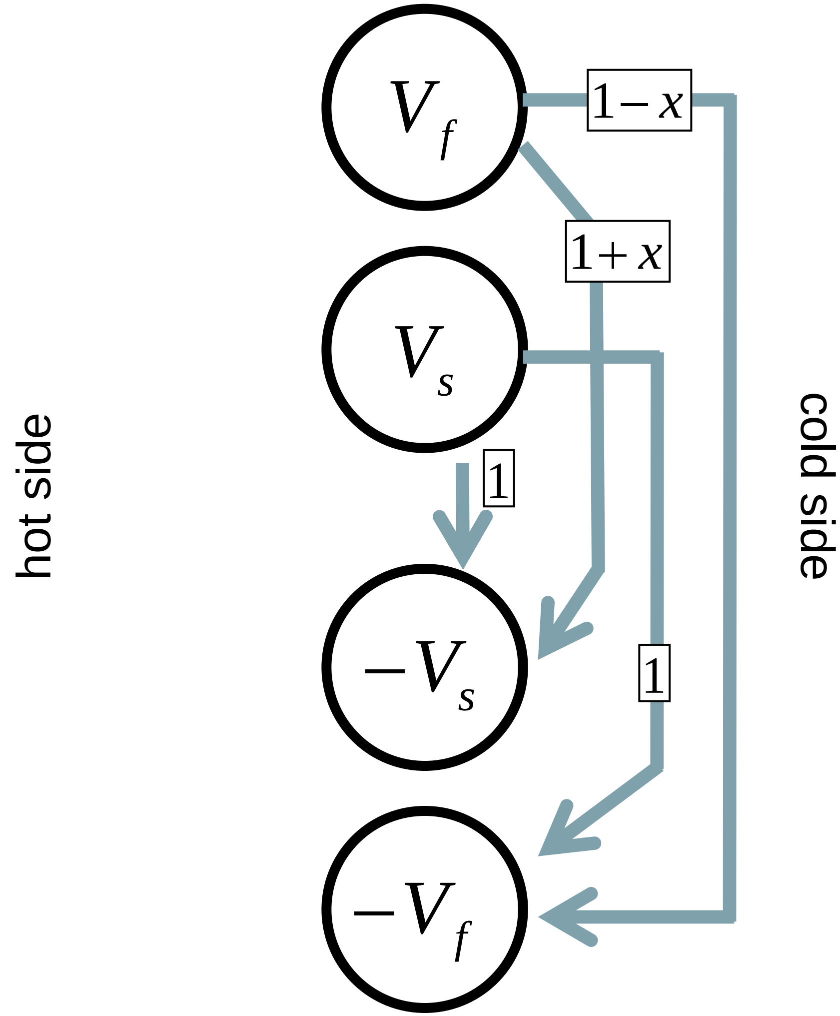
Simple model of thermal conduction



Slow and fast velocity states in each direction

Ford and Spinney, submitted

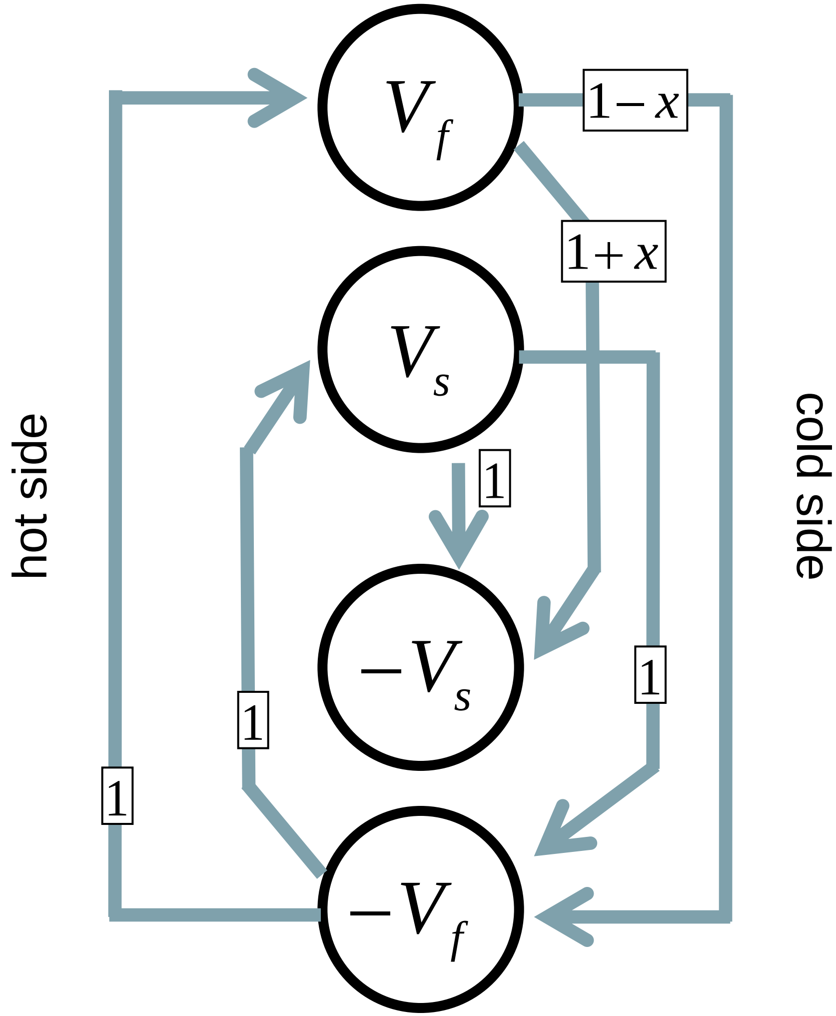
Simple model of thermal conduction



Slow and fast velocity states in each direction

Cold side preferentially slows down fast particles

Simple model of thermal conduction



Slow and fast velocity states in each direction

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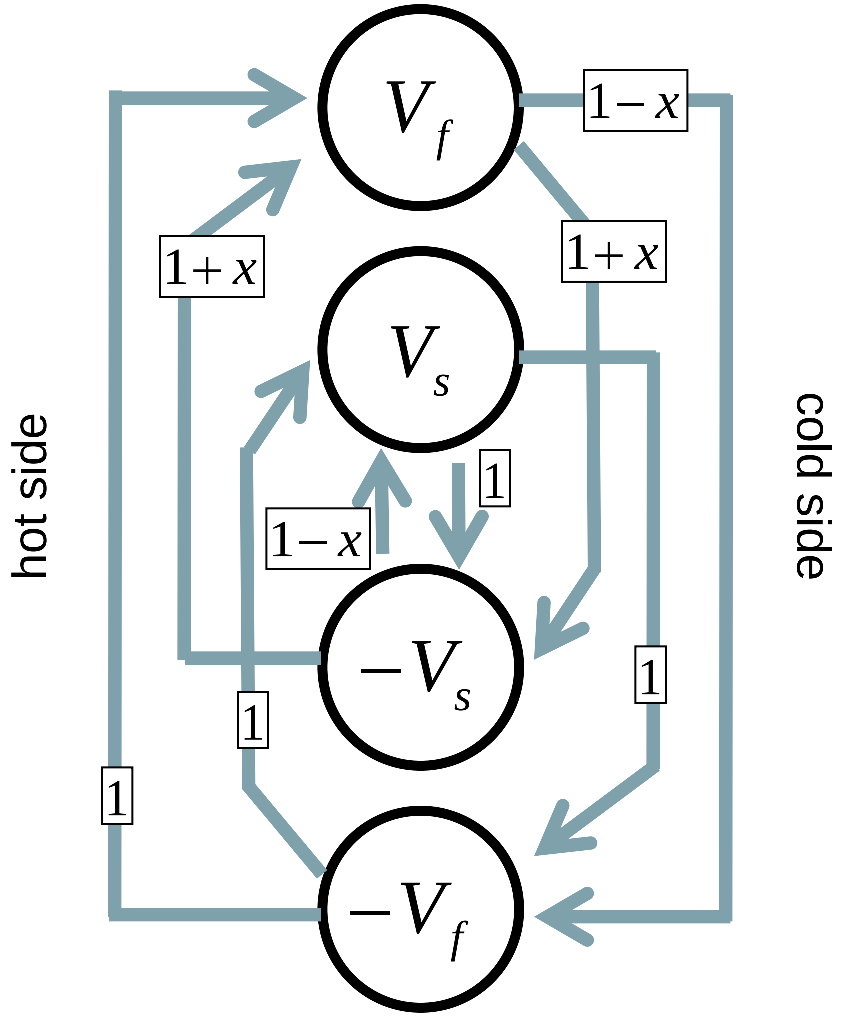
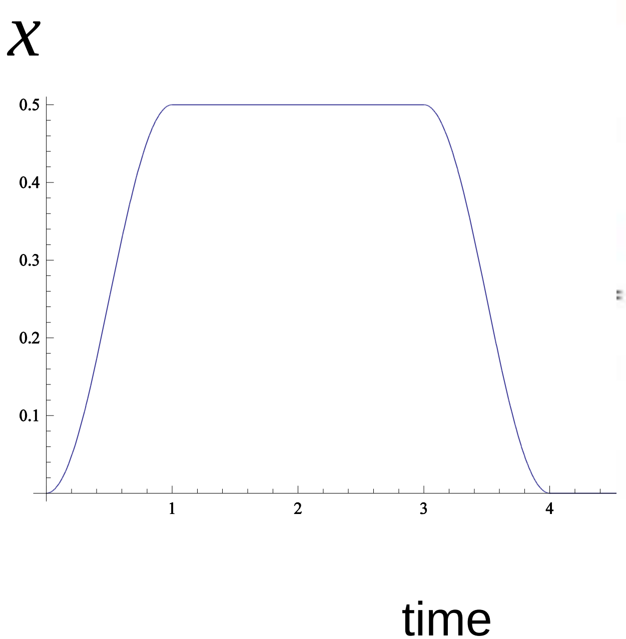


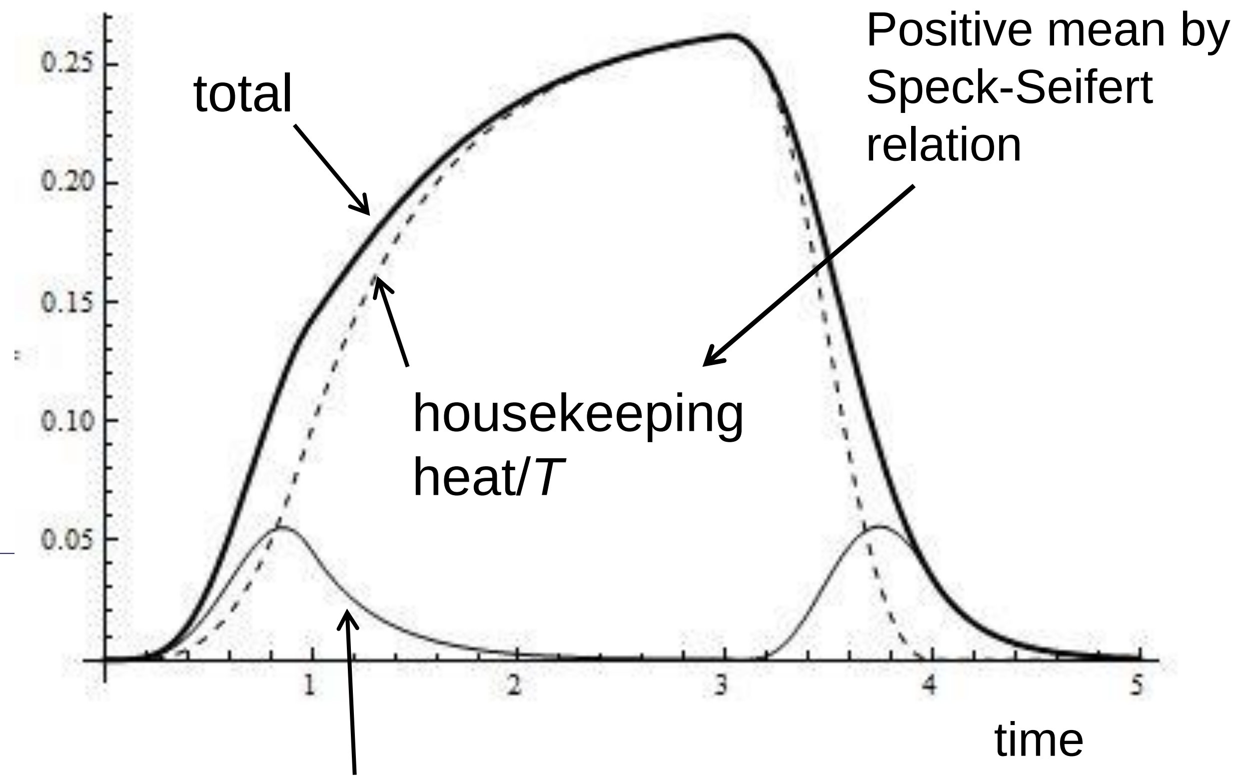
Slow and fast velocity states in each direction

Cold side preferentially slows down fast particles

Hot side preferentially speeds up slow particles

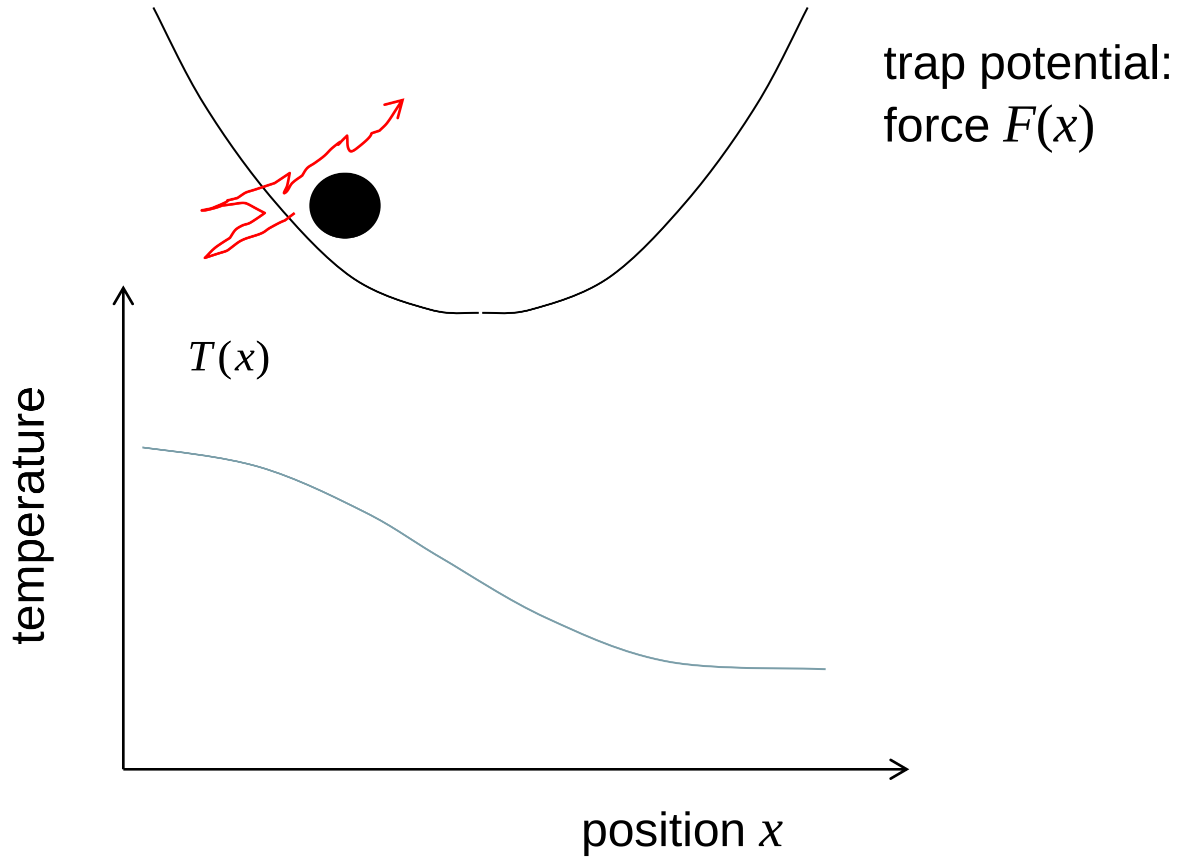
Mean entropy production rates for a time-dependent temperature difference *x*





Positive mean value by Hatano-Sasa relation → excess heat/T+d(system entropy)/dt

Thermal conduction in the continuum: trapped particle in a temperature gradient



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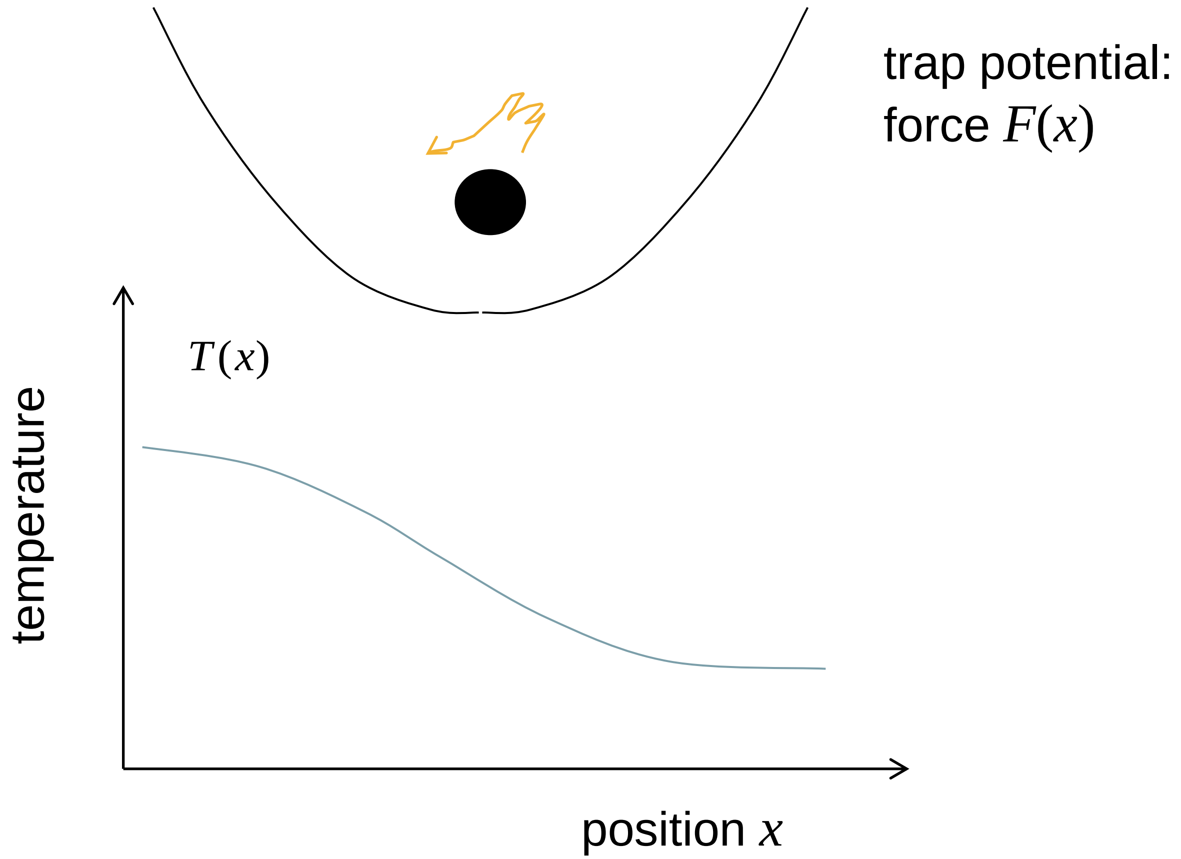
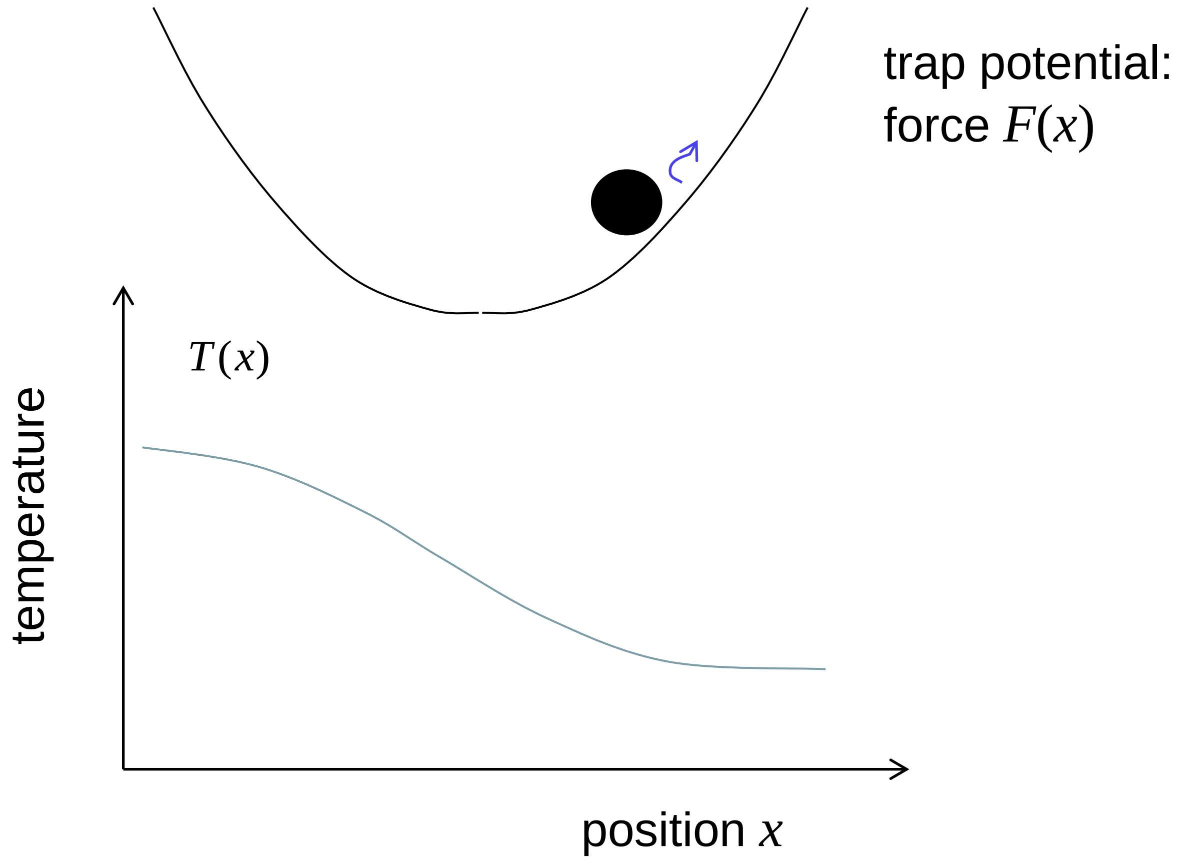


Thermal conduction in the continuum: trapped particle in a temperature gradient



Dynamics of thermal conduction:

- Stochastic differential equations for position and velocity:

$$dx = v\,dt$$

$$dv = -\gamma v\,dt + \frac{F(x)}{m}dt + \sqrt{\frac{2k_B T(x)\gamma}{m}}dW$$

Entropy production in thermal conduction:

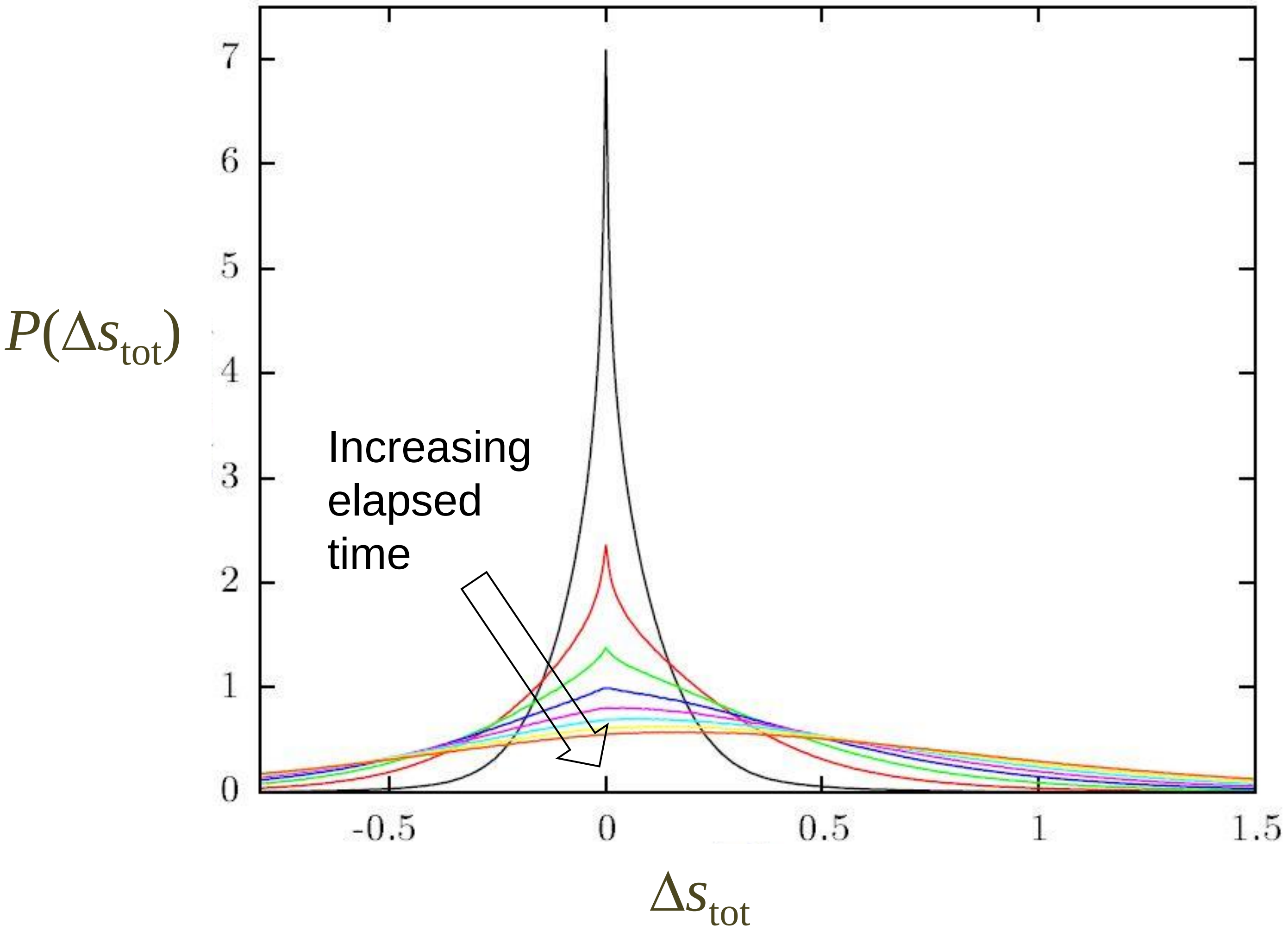
- Determine the transition probabilities $T(x+dx|x)$ and get

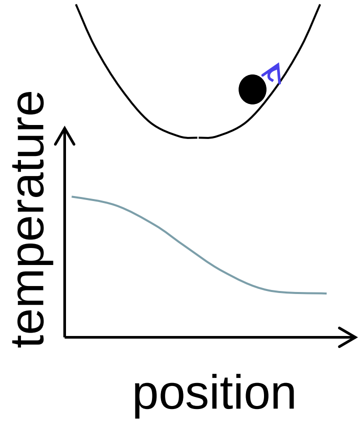
$$d\Delta s_{\text{tot}} = d\Delta s_{\text{sys}} - \frac{1}{k_B T(x)} d\left(\frac{mv^2}{2}\right) + \frac{F}{k_B T(x)} dx$$

$$-\frac{dE_{\text{KE}}}{k_B T(x)} - \frac{dE_{PE}}{k_B T(x)} = \frac{d\Delta Q_{\text{med}}}{k_B T(x)} = d\Delta s_{\text{med}}$$

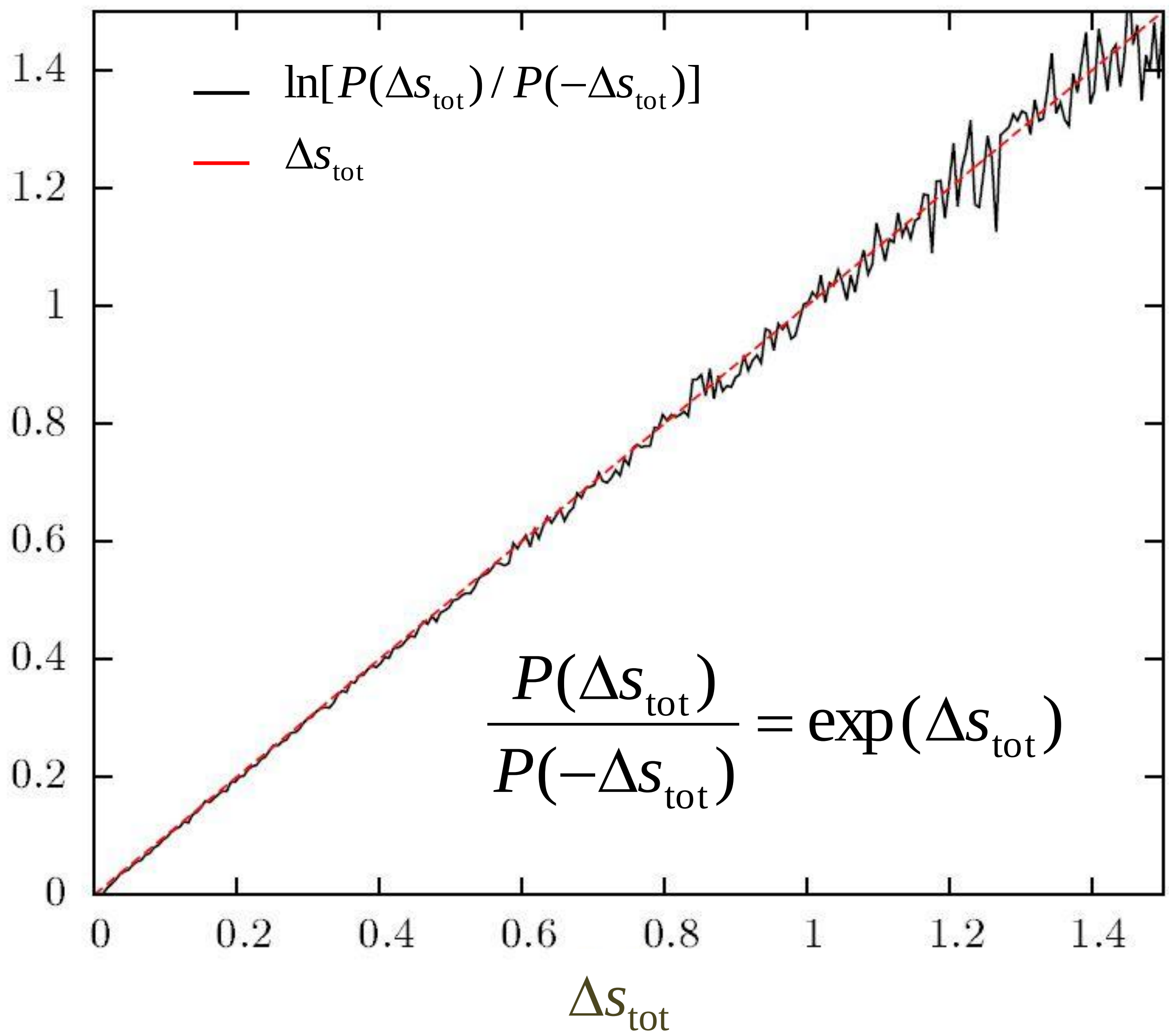
Spinney and Ford PRE85, 051113 (2012)

Distributions of total path-dependent entropy production for stationary thermal conduction





Δs_{tot} satisfies a detailed fluctuation relation



Jarzynski-Sagawa-Ueda equality

$$\left\langle \exp(-(\Delta W_0 - \Delta F)/k_B T - \boxed{I_{xy}}) \right\rangle = 1$$

- Jarzynski holds for initial equilibrium state
- Make measurement *y* of system variable *x* to gain information: distribution of *x* is changed

$$P(x) \rightarrow P(x \mid y)$$

$$I_{xy} = \ln\left[P(x \mid y) / P(x) \right]$$

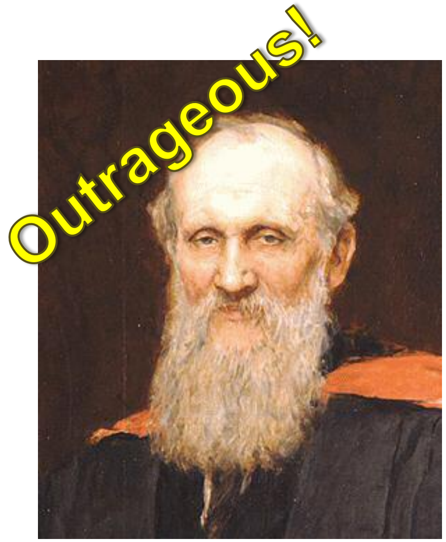
Dissipative work and mutual information I_m

$$\Delta W_d = \langle \Delta W_0 \rangle - \Delta F \geq -k_B T \, \bar{I}_{xy}$$

by Jensen

$$\bar{I}_{xy} = I_m = \int dxdy \; P(x \mid y) P(y) \ln\left(\frac{P(x \mid y)}{P(x)} \right) \geq 0$$

- Acquisition of information allows breakage of Kelvin’s statement of the second law
  - cyclic extraction of work from a single heat bath



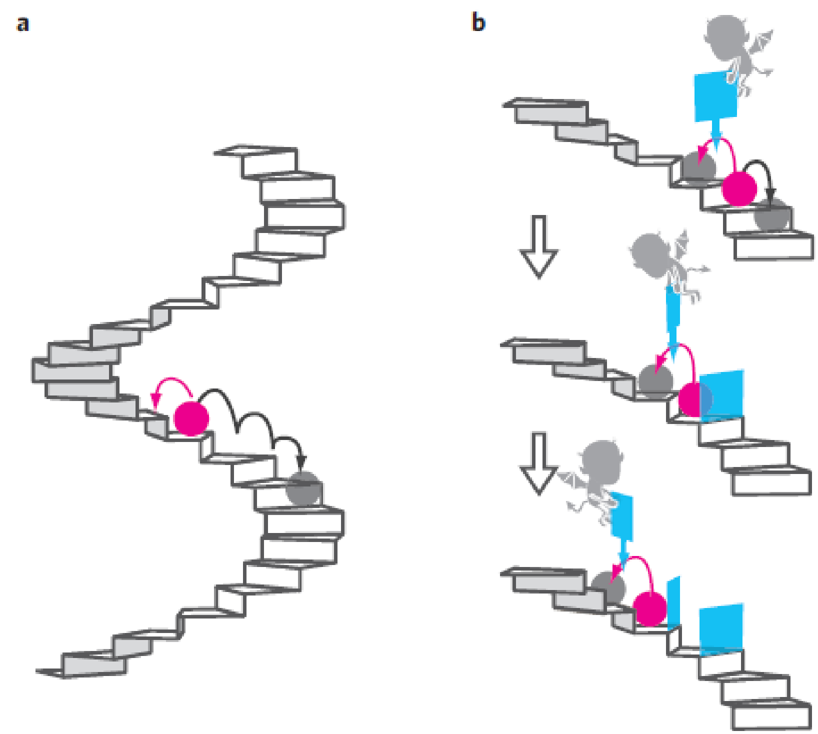
LETTERS
PUBLISHED ONLINE: 14 NOVEMBER 2010 | DOI: 10.1038/NPHYS1821
nature physics

Experimental demonstration of information-to-~~energy~~ free energy conversion and validation of the generalized Jarzynski equality

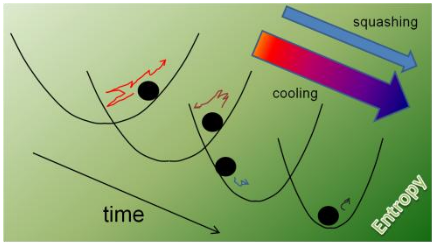
Shoichi Toyabe[1], Takahiro Sagawa[2], Masahito Ueda[2,3], Eiro Muneyuki[1]* and Masaki Sano[2]*

In 1929, Leó Szilárd invented a feedback protocol[1] in which a hypothetical intelligence—dubbed Maxwell's demon—pumps heat from an isothermal environment and transforms it into work. After a long-lasting and intense controversy it was finally clarified that the demon's role does not contradict the second law of thermodynamics, implying that we can, in principle, convert information to free energy[2–6]. An experimental demonstration of this information-to-energy conversion, however, has been elusive. Here we demonstrate that a non-equilibrium feedback manipulation of a Brownian particle on the basis of information about its location achieves a Szilárd-type information-to-energy conversion. Using real-time feedback control, the particle is made to climb up a spiral-staircase-like potential exerted by an electric field and gains free energy larger than the amount of work done on it. This enables us to verify the generalized Jarzynski equality[7], and suggests a new fundamental principle of an 'information-to-heat engine' that converts information into energy by feedback control.

To illustrate the basic idea of our feedback protocol, let us



A rough summary



- A plethora of fluctuation relations
  - integral, detailed, Jarzynski, Crooks, Evans-Searles, Bochkov-Kuzovlev, Gallavotti-Cohen, Speck-Seifert, Hatano-Sasa, Jarzynski-Sagawa-Ueda, etc
  - Statements about the likely thermodynamic behaviour of a small system
- Stochastic thermodynamics is (arguably) the simplest framework
- Key quantity: Δs_{tot} - a measure of path irreversibility
  - when path-averaged equals thermodynamic entropy production ΔS_{tot}
- Components of total entropy production:
  - system, medium, excess, housekeeping heat(s) ...
  - mutual information of measurement and Maxwell's demon ...

- Examples for discrete and continuous stochastic dynamics
- Thanks for listening!