Fluctuation theorems / relations and Jarzynski equality

General "exact" results for non-equilibrium systems (not only linear response theory)

- Crook's FT : (canonical ensemble)

$$\frac{P_F(W_{diss})}{P_R(-W_{diss})} = \exp\left(\frac{W_{diss}}{T}\right)$$

$A \to B$ — Forward trajectory

$B \to A$ Reverse trajectory

$\Delta F = F_B - F_A$ equilibr. free energy difference

- J.E.

$$\left\langle \exp\left(-\frac{W}{T}\right)\right\rangle = \exp\left(-\frac{\Delta F}{T}\right)$$

work exerted ON the system

out-of-equilibr. average

F.T. proved in different context

- deterministic dynamics (Gallavotti-Cohen ; Evans-Searles)
- stochastic dynamics

Langevin

Markov Chain

Crooks

- Non-equil. transient states
- Non-equilibr. STEADY STATES (NESS)

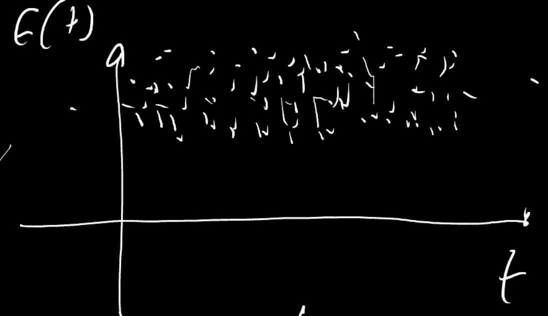
Stochastic fluctuations $\longrightarrow$ decrease with system size

(evident for SMALL SYSTEMS

$\longrightarrow$ STOCHASTIC THERMODYNAMICS

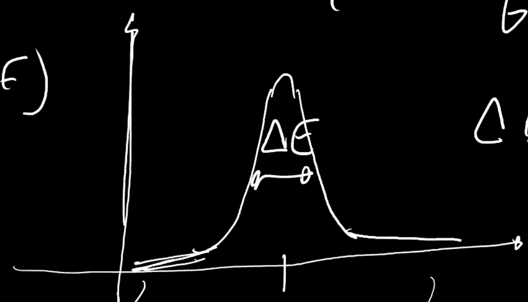
Extensive quantity (energy, work, entropy)

Energy measure in MD simul. or exp. (eq. at T)



$\langle E \rangle$

$p^{eq}(E)$



Gaussian with s.d.

$\Delta E \sim 1/\sqrt{N}$

from L.D. theory

exponential tails for $E - \langle E \rangle$ (non Gaussian) $\gg \frac{1}{\sqrt{N}}$

$\langle E \rangle$

Central Limit Th.

$\Delta E \xrightarrow[N \to \infty]{} 0$

Thermodynamics: macroscopic potentials, state functions

Canonical ensemble: $U(N,V,T)$; $S(N,V,T)$; $F(N,V,T)$

$$F = U - TS$$

Helmholtz free energy

Thermodyn. Transform. from an initial to a final macroscopic state $(V_i \to V_f)$

1st LAW: $\Delta U = \underbrace{\Delta Q}_{\text{heat absorbed by the system}} + \overbrace{W}^{\text{work exerted on the system}}$

$(W = -P\,\Delta V)$

pressure

2^{nd} LAW: $\Delta Q \leq T\Delta S$ (= only for reversible transformation)

$$W_{diss} \equiv T\Delta S - \underbrace{\Delta q}_{T\Delta S_B} = T\Delta S_{TOT} \geq 0$$

(canonical ensemble)

entropy change in the reservoir

$W_{diss} \to$ entropy production

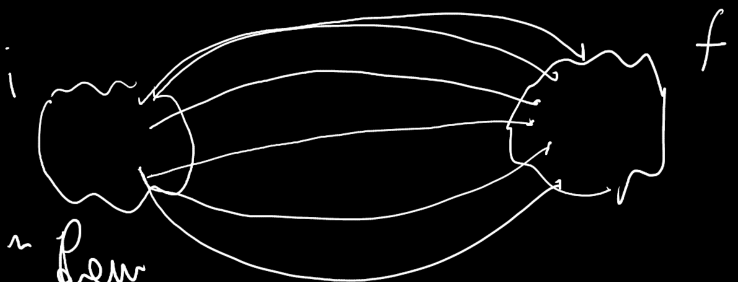
$$\Delta F = \Delta U - T\Delta S \underset{\text{1st law}}{=} \Delta Q + W - T\Delta S = W - W_{diss}$$

$W = W_{diss} + W_{rev}$

$\Delta F = W_{rev}$ $\qquad W_{diss} \geq 0 \to \Delta F = W_{rev} \leq W$

So far macrosc. thermodynamics

Stoch. thermodyn. $\to$ individual trajectories



2^{nd} law is violated for individual trajectories

2^{n} law violations $\to$ stochastic fluctuations $\xrightarrow[N\to\infty]{}$ macroscopic 2^{nd} law

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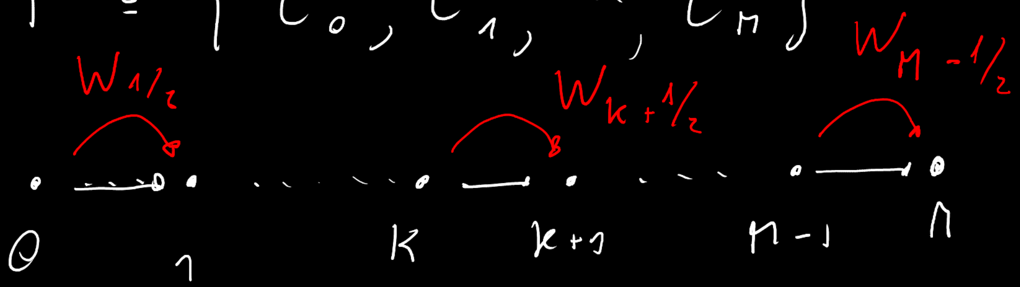
Markov Chain dynamics $\to$ discrete time

discrete state space $\qquad t_k = k\Delta t \quad k = 0, 1, \dots, M$

$\mathcal{C}$ = system state

Trajectory (path) $\Gamma = \{ \mathcal{C}_0, \mathcal{C}_1, \dots, \mathcal{C}_M \}$



Markov update rule: $P_{k+1}(\mathcal{C}) = \sum_{\mathcal{C}'} W_{k+1/2}(\mathcal{C}' \to \mathcal{C}) P_k(\mathcal{C}')$

non-homogeneous MC — $W_{k+1/2}$ depend on time

$$\sum_{\mathcal{C}'} W_{k+1/2}(\mathcal{C} \to \mathcal{C}') = 1 \quad \text{(normalization)}$$

Time-dependence driven by control parameter λ

$$\lambda : \underbrace{\lambda_0, \lambda_{1/2}, \dots, \lambda_{M-1/2}, \lambda_M}_{\text{exp. protocol}}$$

$$W_{\lambda_{k+1/2}} \equiv W_{k+1/2}$$ (λ DOES NOT FLUCTUATE)

Generic observable $A(\Gamma)$

$$\langle A \rangle = \sum_{\Gamma} A(\Gamma) P(\Gamma)$$

non-equilibrium average

$P(\Gamma)$ = prob. of path Γ

$$P(\Gamma) = \underbrace{P_{\lambda_0}(\mathcal{C}_0)}_{\text{choice of initial conditions}} \prod_{k=0}^{M-1} W_{k+1/2}(\mathcal{C}_k \to \mathcal{C}_{k+1})$$

$$A(\Gamma) \equiv \exp\left(-S(\Gamma)\right) \equiv \frac{\rho_{\lambda_M}(\varphi_M)}{\rho_{\lambda_0}(\varphi_0)} \prod_{k=0}^{M-1} \frac{W_{k+1/2}(\varphi_{k+1}\to\varphi_k)}{W_{k+1/2}(\varphi_k\to\varphi_{k+1})}$$

$\rho_{\lambda_M}(\varphi)$ — generic PDF — normalized

$\rightarrow \quad \sum_{\varphi} \rho_{\lambda_M}(\varphi) = 1 \qquad W_{k+1/2}(\varphi_k\to\varphi_{k+1}) > 0 \quad \forall\, \varphi_k, \varphi_{k+1}$

$\rho_{\lambda_0}(\varphi) > 0 \quad \forall\, \varphi$

$$\langle A\rangle = \langle \exp(-S)\rangle \overset{!}{=} \sum_{\Gamma} A(\Gamma)\,\rho(\Gamma) = \sum_{\Gamma} \rho_{\lambda_M}(\varphi_M) \prod_{k=0}^{M-1} W_{k+1/2}(\varphi_{k+1}\to\varphi_k)$$

$$\sum_{\Gamma} = \sum_{\varphi_0,\varphi_1,\dots,\varphi_M}$$

$$= \overbrace{\sum_{\varphi_0} W_{1/2}(\varphi_1\to\varphi_0)}^{1 =} \overbrace{\sum_{\varphi_1} W_{3/2}(\varphi_2\to\varphi_1)}^{1 =} \cdots\cdots \overbrace{\sum_{\varphi_{M-1}} W_{M-1/2}(\varphi_M\to\varphi_{M-1})}^{1 =} \cdot \underbrace{\sum_{\varphi_M} \rho_{\lambda_M}(\varphi_M)}_{= 1}$$

$$\boxed{\langle A\rangle = \langle \exp(-S)\rangle = 1}$$

$$S(\Gamma) = -\ln\left(A(\Gamma)\right) = \ln\left[\frac{\rho_{\lambda_0}(\varphi_0)}{\rho_{\lambda_M}(\varphi_M)}\right] + \sum_{k=0}^{M-1} \ln\left[\frac{W_{k+1/2}(\varphi_k\to\varphi_{k+1})}{W_{k+1/2}(\varphi_{k+1}\to\varphi_k)}\right]$$

$\langle \exp(-S)\rangle = 1 \longrightarrow$ KAWASAKI identity

(Equivalent to J.E.)

$S(\Gamma) \longrightarrow$ total entropy produced along Γ
(dissipated work W_{diss} in the canonical ensemble)

Jensen inequality ($-\ln$ is a convex function)

$$\langle -\log[\exp(-S)] \rangle \geq -\log[\langle \exp(-S) \rangle]$$

$$\boxed{\langle S \rangle \geq 0}$$ – stochastic formulation of 2^{nd} law

$\Rightarrow$ individual trajectories exist for which

$S(\Gamma) < 0$ – more and more probable for smaller and smaller systems

Reconcile with Loschmidt paradox!

(It can be shown that $S(\Gamma) > 0 \ \forall \Gamma$
$\Rightarrow \langle \exp(-S) \rangle < 1$)