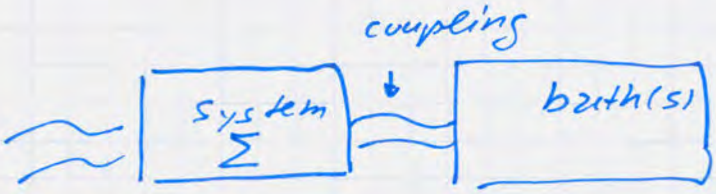
Fluctuation Theorems

1. Response Theory & Fluctuations
2. A Primer on the 2-nd Law
3. Work-Theorems (mostly classical) & Relation to the Second Law



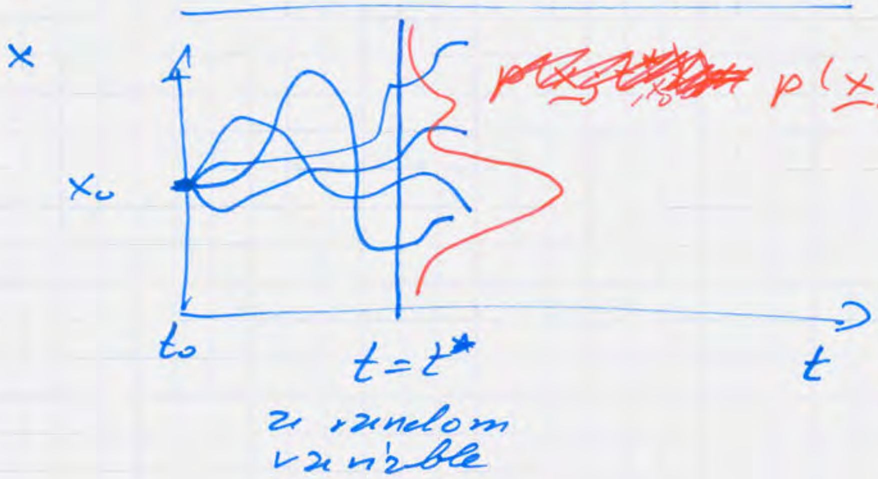
$\underset{\sim}{x}$: state variables

those are subject to

(1) Fluctuations from baths

(2) external forces acting on the system.

$\underset{\sim}{x}(t)$: a stochastic process



$p(\underset{\sim}{x}, t^* | \underset{\sim}{x}_0, t = t_0)$

can be chosen randomly $\rho(\underset{\sim}{x}_0)$

$p(x, t = t^*)$

$= \int d\underset{\sim}{x}_0 \, \rho(\underset{\sim}{x}_0) \, p(\underset{\sim}{x} t^* | \underset{\sim}{x}_0 t_0)$

$p(\underset{\sim}{x}\, t_0) \to p(\underset{\sim}{x}, t^*) \to p(\underset{\sim}{x}; t)$

Undergoes a time evolution!

$$\dot{p}(\underset{\sim}{x}, t) = \Gamma \, p(\underset{\sim}{x}, t) \quad : \text{master operator}$$

(Markov-processes!)

Markov:

Propagator

$$p^{(n)}(\underset{\sim}{x}_n t_n, \ldots, \underset{\sim}{x}_0 t_0) = R(\underset{\sim}{x} t_n | \underset{\sim}{x}_{n-1} t_{n-1}) \, R(x_{n-1} t_{n-1} | x_{n-2} t_{n-2}) \times \ldots R(\underset{\sim}{x}_1 t_1 | \underset{\sim}{x}_0 t_0) \, p(\underset{\sim}{x}_0, t_0)$$

non-Markov:

$$p(t) = R(t|t_0) \, p(t_0)$$

$$\dot{p}(t) = \underbrace{\dot{R}(t|t_0) \, R^{-1}(t|t_0)} \, p(t) = \Gamma_{t_0}(t) \, p(t)$$

examples

I. Focker-Planck-eq.:

$$\dot p(\underline{x},t) = -\frac{\partial}{\partial \underline{x}}\, \underline{j}(x,t) \Leftrightarrow \dot p + \mathrm{div}\, \underline{j} = 0$$

conservation of probability

$$= -\frac{\partial}{\partial \underline{x}}\left\{ \underline{f}(\underline{x})\, p(\underline{x},t) - \underline{\underline{D}}(\underline{x}) \frac{\partial}{\partial \underline{x}} p(\underline{x},t)\right\}$$

$\Updownarrow$ relation to a stochastic diff. eq.

$\underline{\underline{D}}(\ldots) = \underline{\underline{g}}(\ldots)\,\underline{\underline{g}}^t(\ldots)$ $\quad \dot{\underline{x}} = \underline{f}(\underline{x}) + \underline{\underline{g}}(\underline{x}) : \frac{d\underline{w}(t)}{dt}$

stoch. calculus

Ito $\rightarrow \underline{\underline{D}}(\underline{x}) \frac{\partial^2}{\partial \underline{x}^2} p(\underline{x},t)$

Stratonovich $\rightarrow \frac{\partial}{\partial \underline{x}} \underline{\underline{g}}(x) \frac{\partial}{\partial x}\underline{\underline{g}}(x)\, p(\underline{x},t)$

Hänggi (postpoint) $\frac{\partial}{\partial \underline{x}} \underline{\underline{D}}(\underline{x}) \frac{\partial}{\partial \underline{x}} p(\underline{x},t)$ (transport form)

II. Liouville eq. $\underline{X} \rightarrow$ phase space $(q_1, p_1, q_2, p_2, \ldots q_N, p_N)$

Poisson bracket: $\{f,g\} = \sum_i \left\{ \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i} - \frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} \right\}$

$$\dot p(\underline{X},t) = \{\mathcal{H}(\underline{X}), p(\underline{X},t)\}$$

Now: perturbation acting on system only

$$\mathcal{H}_0 \rightarrow \mathcal{H}_0 - \lambda(t)\, Q(\underline{X}) \quad ; \quad H_0 = \frac{p^2}{2m} + U(x)$$

$$m\ddot x = -\frac{\partial U}{\partial x} + \lambda(t) + \sqrt{2D(x)} : \frac{dw}{dt}$$

$$\Leftrightarrow \Gamma(t) = \Gamma_0 - \lambda(t)\frac{\partial}{\partial x} \;;\; \dot p(\underline{x},t) = \Gamma_0\, p(\underline{x},t) - \lambda(t)\frac{\partial}{\partial x} p(\underline{x},t)$$

Linear Response Theory

$$\Gamma_{total} = \underset{\text{no perturbation}}{\Gamma_0} + \underset{\text{imposed perturbation}}{\Gamma_{ext}(t)}$$

we set: $\Gamma_{ext}(t) \equiv \lambda(t)\,\Omega$

$$\dot{p}(x,t) = \int \Gamma_{total}(x,y;t)\, p(y,t)\, dy$$

$$= \int \{\Gamma_0(x,y) + \lambda(t)\Omega(x,y)\}\, p(y,t)\, dy$$

conservation of probability

$$\Rightarrow \int \Gamma(x,y;t)\,dx = 0 \Leftrightarrow \int \Gamma_0(x,y)\,dx = 0 \;\&\; \int \Omega(x,y)\,dx = 0$$

Dyson-Eq.

$$\dot{p} = (\Gamma + \Gamma_{ext})\, p$$

$p(t) = R(t|s)\,p(s)$; $R(t|s)$: Propagator

$$\Rightarrow \dot{p}(t) = \dot{R}(t|s)\,p(s)$$

$$= \Gamma(t)\underbrace{R(t|s)\,p(s)}_{p(t)} = \Gamma(t)\,p(t)$$

$$\boxed{\dot{R}(t|s) = (\Gamma_0 + \Gamma_{ext}(t))\, R(t|s)}\,; \quad R(t|t) = R(t_0|t_0) = 1$$

$$\langle x|R(t_0|t_0)|y\rangle = \delta(x-y)$$

solution: $t \geq t_0$; $s \geq t_0$; $t \geq s$

EXACT: $R(t|t_0) = R_0(t|t_0) + \int_{t_0}^{t} R_0(t|s)\,\Gamma_{ext}(s)\,R(s|t_0)\,ds$

$$\dot{R}(t|t_0) = \underbrace{\Gamma_0 R_0(t|t_0) + \Gamma_0 \int_{t_0}^{t} R_0(t|s)\,\Gamma_{ext}(s)\,R(s|t_0)\,ds}_{\Gamma_0 R(t|t_0)}$$

$$+ \underbrace{R_0(t|t)}_{1}\,\Gamma_{ext}(t)\,R(t|t_0)$$

$$= (\Gamma_0 + \Gamma_{ext}(t))\, R(t|t_0) \quad \text{q.e.d.}$$

Linear Response

replace $R(t|s)$ with unperturbed solution

$$R(t|s) \Rightarrow R_0(t|s) = \exp \Gamma_0 (t-s)$$

$$p(t) = p_0(t) + \int_{t_0}^{t} R_0(t|s) \lambda(s) \Omega\, p_0(s)$$

from now on $p_0 = \bar{p}$: stationary solution $\Gamma_0 \bar{p} = 0$

consider an observable $x(t)$

Linear response $\langle \delta x(t) \rangle = \langle x(t) \rangle_{p(t)} - \langle x(t) \rangle_{\bar{p}}$

$$:= \int_{t_0}^{t} \chi(t-s)\, \lambda(s)\, ds$$

where $\chi(t-s) = \underset{\substack{\Uparrow \\ \text{causality}}}{\Theta(t-s)} \iint dx\,dy\; x \{\Omega \bar{p}\}(y)\, R_0(x;t-s|y)$

Fluctuation-Theorem (Linear Response)

P. H.; Helv. Phys. Acta **51**, 202 (1978); Phys. Rep. **88**: 207 (1982)

Define: $\varphi(x)\bar{p}(x) = (\Omega \bar{p})(x)$; $\int \varphi(x)\bar{p}(x) = \int [\Omega \bar{p}](x)\,dx$

$$\Rightarrow \langle \varphi(x) \rangle_{\bar{p}} = \underbrace{\int dx}_{0} \underbrace{\left(\int \Omega(x,y)\bar{p}(y)\,dy \right)}_{[\Omega \bar{p}](x)} \doteq 0$$

a stationary correlation!

$$\Rightarrow \chi(t-s) = \chi(\tau) = \Theta(t-s) \langle x(\tau)\, \delta\varphi(0) \rangle_{\bar{p}}$$

$$= \cancel{\Theta(t-s) \langle \delta x(\tau)\, \delta(\ldots) \rangle_{\bar{p}}}$$

$$:= \Theta(t-s) \langle \delta x_\tau\, \varphi(x(0)) \rangle_{\bar{p}}$$

"Linear Response measures the stationary correlation between $\delta x = x(t) - \langle x \rangle_{\bar{p}}$ & $\varphi(x(0))$"

Alternative Result for $\chi(\tau)$

$$\Gamma(t) = \left[\Gamma_0 + \lambda(t)\,\Omega\right] \quad p_{\text{accompanying frozen}} = 0$$

linear response δp_a:

$$\Gamma_0\, \delta p_a + (\Omega \bar{p})\, \lambda(t) = 0$$

define: $\delta p_a(x; \lambda(t)) := \Psi(x)\, \bar{p}(x)\, \lambda(t)$

$$\Rightarrow \quad [\Omega \bar{p}](x) = -\int \Gamma_0(x, z)\, \Psi(z)\, \bar{p}(z)\, dz$$

again one can show $\langle \Psi(x) \rangle_{\bar{p}} = 0$

$$\Rightarrow \chi(\tau) = -\Theta(\tau) \iiint x\, R_0(x; \tau | y)\, \Gamma_0(y, z)\, \Psi(z)\, \bar{p}(z)\, dx\, dy\, dz$$

$R_0 = \exp(\Gamma_0 \tau)$ with $\frac{dR_0}{d\tau} = \Gamma_0 R_0(\tau) = R_0(\tau)\Gamma_0$

$$= -\Theta(\tau) \frac{d}{d\tau} \iint dx\, dz\; \delta x\; R_0(x; \tau | z)\, \Psi(z)\, \bar{p}(z)$$

$$\boxed{\chi(\tau) \doteq -\Theta(\tau) \frac{d}{d\tau} \langle \delta x(\tau)\, \Psi(x(0)) \rangle_{\bar{p}}}$$

2-nd Fluctuation-Theorem

Examples

Isolated system $\dot{\rho}(X,t) = \{(H_0 + H_{ext}), \rho\}$

Liouville eq.

$$H_{ext}(t) = -\lambda(t)x$$

$$\Rightarrow \Omega = -\{x, ..\} \quad \& \quad \bar{\rho}(X) = Z^{-1}\exp(-\beta H_0(X))$$

canonical Gibbs!

$$\varphi(X)\bar{\rho}(X) \equiv [\Omega\bar{\rho}]_X \Rightarrow \varphi(X) = \{x, H_0(X)\}\beta = \beta\dot{x}$$

likewise: $\psi(x) = \beta x$

Therefore: $\chi(\tau) = \Theta(\tau)\beta\langle\delta x(\tau)\dot{x}(0)\rangle_{\bar{\rho}=\rho_{eq.}}$

$$= -\Theta(\tau)\beta\cdot\frac{d}{d\tau}\langle\delta x(\tau)\delta x(0)\rangle_{\bar{\rho}=\rho_{eq}}$$

$$= -\Theta(\tau)\frac{1}{k_B T}\frac{d}{d\tau}\langle\delta x(\tau)\delta x(0)\rangle$$

Kubo - classical Fluctuation - Dissipation Theorem (1960)

Quantum Generalization Callen-Welton (1951)

$$\chi_{xx}(\tau) = \frac{i\,\Theta(\tau)}{\hbar} \langle [x(\tau), x(0)] \rangle_\beta$$
$$= -\Theta(\tau) \int_0^\beta \langle x(-i\hbar\lambda)\, \dot{x}(\tau) \rangle_\beta \, d\lambda$$
$$\left(-\Theta(\tau)\, \beta \langle \delta\dot{x}(\tau)\, \delta x(0) \rangle \right)$$

$$\chi''(\omega) = \frac{1}{\hbar} \tanh(\hbar\omega\beta/2)\, S_{xx}(\omega)$$

$\frac{1}{2} \langle (\delta x(\tau)\delta x(0) + \delta x(0)\delta x(\tau)) \rangle_\beta$

symmetrized

Therefore: ~~$S_{xx}(\omega) = \hbar \coth \hbar\beta\omega/2$~~

$$S_{xx}(\omega) = \hbar \coth(\hbar\omega\beta/2)\, \chi''(\omega)$$

one measures the response to the single-time observable:

$$\delta x(t) = \langle x(t) \rangle - \langle x(t) \rangle_{\beta_{eq}}$$

One does not do a two-time measurement of a quantum correlation!

Work-Theorems -

Nonlinear Fluctuation-Theorems

$\boxed{\text{Thermodynamics}}$ a brief primer

$$dE = \delta Q + \delta W = TdS - pdV - \mu dN \dots$$

state functions: Legendre-Transforms of internal energy $E = E(S, V, N; \dots)$

Enthalpy: $H = E + pV = H(S, p; \dots)$

Helmholtz free energy $F = E - TS = F(T, V, \dots)$

Gibbs free energy $G = H - TS = E + pV - TS = G(p; T; N, \dots)$

$$\Delta F = \Delta E - T\Delta S - \underbrace{S\Delta T}_{0} = \Delta Q + \Delta W - T\Delta S$$

in thermal equilibrium isothermal $\Delta Q = T\Delta S$

$$\Rightarrow \Delta F = \Delta W_{reversible}$$

2-nd Law; canonical ensemble - heat exchange with the bath is allowed but no ΔN

BTW: Isolated: $\Delta Q = 0$; $\Delta N = 0$

closed : $\Delta Q \neq 0$; $\Delta N = 0$

"open" : $\Delta Q \neq 0$; $\Delta N \neq 0$

2-nd Law: $\Delta S = \frac{\delta Q^{irr}}{T} + \Sigma$; Σ: Entropie-Produktion

& $T \geq 0$ $\quad\quad \Sigma \geq 0$, $\Sigma = 0$: reversible

$$T\Delta S = \delta Q^{reversible} \geq \delta Q^{irr} + \underbrace{T(\geq 0)\,\Sigma}_{W_{diss}}$$

Set: $T\Delta S - \Delta Q = W_{diss} \geq 0$

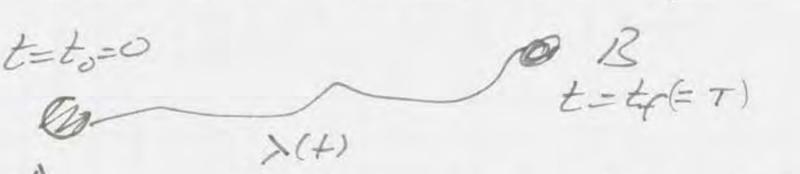
$$\Rightarrow \Delta F = \Delta Q + \Delta W - T\Delta S = T\Delta S - W_{diss} + \Delta W - T\Delta S = \Delta W - W_{diss}$$

$$\Delta F \leq \Delta W = \langle \Delta W \rangle_{\text{if } W \text{ fluctuates}}$$

Fluctuation-(Work)-Relations

Rev. M. Campisi, P. Hänggi, P. Talkner Rev. Mod. Phys.
classical & quantum! $\underline{83}$: 771–791 (2011)
C. Jarzynski, Ann. Rev. Cond. Matter Phys. $\underline{2}$, 329 (2011)
(classical)

also known under noneq. Work-Fluctuation-Theorems



work parameter; $\lambda(t)$: a protocol for external "force" values acting on SYSTEM

$A;\ \lambda = \lambda_0$

prepared in canonical thermal equilibrium

$\underline{A}$: $\lambda(t=0) = \lambda_0$; thermal eq. $\rho_A = \frac{1}{Z_A}\exp -\beta \mathcal{H}(\underline{X};\lambda_A)$

Its free energy is $\underline{\underline{F_A}}$

hypothetical equilibrium with $\mathcal{H}(X_B; \lambda = \lambda_f) \Rightarrow \underline{\underline{F_B}}$

$$\mathcal{H}(X; \lambda(t)) = \overset{S}{\mathbf{H}}(x_{System}; \lambda(t)) + \overset{E}{\mathbf{H}}_{\underset{(bath)}{Environment}} + H_{Int.}$$

form $\overset{S}{H}(x_{t_f}; \lambda_f) - \overset{S}{H}(x_{t_0}; \lambda_0)$

$$= \underbrace{\int_0^{t_f} dt\, \frac{\partial H^S}{\partial \lambda}(x_t; \lambda_t)\dot{\lambda}(t)}_{\text{external Work on the system}} + \underbrace{\int_0^{t_f} dt\, \dot{\underline{x}}\, \frac{\partial H^S}{\partial \underline{x}}}_{\text{"formally" heat "Q" absorbed by the system}}$$

note: $\underline{x}_t$: is a stochastic process; a noisy trajectory!
(not given by Hamiltonian when interacting with a bath!

main result (Jarzynski, PRL 1997)

$$\langle \exp -\beta W \rangle \stackrel{!}{=} \exp(-\beta \Delta F)$$

W: a non eq.-fluctuating quantity, $\Delta F \doteq F_B - F_A$

but no thermal equilibrium at time $t = t_f$ with $F = F_B$

Proof: here for an isolated system ($\Delta Q = 0$)

$$\underline{q} = (q_1, \ldots, q_D)\ ;\ \underline{p} = (p_1, \ldots, p_D)\ ;\ \underline{z} = (\underline{q}, \underline{p})$$

phase-space

Protocol: $\lambda(t)$

$$H = H_0(\underline{z}_t) - \lambda(t)\, Q(\underline{z}_t)\ ;\quad -\frac{\partial H(\underline{z}; \lambda(t))}{\partial Q_t} = \lambda(t)$$

full H ; bare H

$$t = t_0 = 0 \quad p_{eq}(z_0, \lambda_0) = \frac{1}{Z(\lambda_0)} \exp\left(-\beta H(z_0, \lambda_0)\right)$$

$$F(\lambda) = kT \ln Z(\lambda)\ ;\quad Z(\lambda) = \int dz \exp(-\beta H)$$
$$= \beta^{-1} \ln Z(\lambda)$$

$$\Delta F := F(\lambda_{t_f}) - F(\lambda_0) = -\beta^{-1} \ln\left(\frac{Z(\lambda_f)}{Z(\lambda_0)}\right)$$

$t = t_0 = 0$ $\underline{z}_0 \rightsquigarrow \underline{z}_t \rightsquigarrow z_{t_f}$ realizations; that were prepared statistically with Boltzmann weight $p_{eq}^{\text{canonical}}(\underline{z}_0, \lambda_0)$

Given such a realization $0 \sim\!\sim t_f$

we define

Exclusive work: $$W_0 \stackrel{!}{=} \int_0^{t_f} dt\, \lambda(t)\, \dot{Q}(\underline{z}_t) \qquad (*)$$

$Q = \text{"}x\text{"} \Rightarrow \int \text{force}\, dx$

Inclusive work: $$W \stackrel{!}{=} -\int_0^{t_f} dt\, \dot{\lambda}(t)\, Q(\underline{z}_t) = \int_{\lambda_0}^{\lambda_f} d\lambda_t \left(\frac{\partial H}{\partial \lambda}\right) \quad (**)$$

$\left(\stackrel{\text{i. gen.}}{\neq} \int \text{force}\, dx\right)$

Important $\frac{\partial H}{\partial \underline{z}} \cdot \frac{\partial \underline{z}}{\partial t} = \left(\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p} \right) \begin{pmatrix} \dot{q} = \frac{\partial H}{\partial p} \\ \dot{p} = -\frac{\partial H}{\partial q} \end{pmatrix}$

$$= \left(\frac{\partial H}{\partial q}\right)\left(\frac{\partial H}{\partial p}\right) - \left(\frac{\partial H}{\partial p}\right)\left(\frac{\partial H}{\partial q}\right) \doteq 0$$

$$= -\dot{p} \cdot \dot{q} - \dot{q} \cdot (-\dot{p}) = 0$$

Thus: $\frac{dH(z_t, \lambda_t)}{dt} = \underbrace{\frac{\partial H}{\partial \underline{z}} \cdot \frac{d\underline{z}}{dt}}_{0} + \frac{\partial H}{\partial \lambda_t} \frac{\partial \lambda_t}{\partial t}$

$$= \dot{\lambda}(t) \frac{\partial H}{\partial \lambda_t} = -\dot{\lambda}_t \, Q(\underline{z}_t)$$

$$\frac{dH_0}{dt}(z_t) = \frac{d}{dt}\left(H(\underline{z}_t; \lambda_t) + \lambda_t Q(\underline{z}_t) \right)$$

$$= -\dot{\lambda}_t Q(\underline{z}_t) + \dot{\lambda}_t Q + \lambda_t \dot{Q}$$

$$= \lambda(t) \dot{Q}(\underline{z}_t) = \lambda_t \dot{Q}(\underline{z}_t)$$

(z_t) evolves under full Hamiltonian

$\Rightarrow W_0 = \underset{\text{with } (*)}{\int_0^{t_f} dt \frac{dH_0}{dt}} = H_0(\underline{z}_{t_f}) - H_0(\underline{z}_0)$

exclusive work (point of view)

$W = \underset{\text{with } (**)}{\int_0^{t_f} dt \frac{dH}{dt}} = H(\underline{z}_f; \lambda_f) - H(\underline{z}_0; \lambda_0)$

inclusive work (point of view)

$$\Rightarrow W_0 - W = \lambda_f \, Q(\underline{z}_f) - \lambda_0 \, Q(\underline{z}_0)$$

If $\lambda_f = \lambda_0 \overset{!}{=} 0 \iff \boxed{W_0 = W}$

Note: In general "Statistics" of $W_0 \Rightarrow P(W_0)$

is not the same as $P(W) \Rightarrow W$

Proof Inclusive case

$$\langle \exp(-\beta W) \rangle = \int dz_0 \, p_{eq}(\underline{z}_0, \lambda_0) \exp -\beta W(\underline{z}_0)$$

$$= \frac{1}{Z_A(\lambda_0)} \int dz_0 \exp -\beta H(\underline{z}_0, \lambda_0) \times \exp -\beta [H(\underline{z}_f, \lambda_f) - H(\underline{z}_0, \lambda_0)]$$

$$= \frac{1}{Z_A(\lambda_0)} \int dz_0 \exp -\beta H(\underline{z}_f(\underline{z}_0); \lambda_f)$$

with $\left| \partial \underline{z}_f / \partial \underline{z}_0 \right| = 1$ (Liouville eq. preserves areas)

Jacobian

$$= \frac{1}{Z_A(\lambda_0)} \int dz_f \exp -\beta H(\underline{z}_f; \lambda_f) \cdot \underbrace{\left| \frac{\partial z_f}{\partial z_0} \right|^{-1}}_{1}$$

$$\stackrel{!}{=} \frac{Z_B(\lambda_f)}{Z_A(\lambda_0)} = \exp(-\beta \Delta F) \quad \text{q.e.d.}$$

Jarzynski (1997)

$$\boxed{\lambda_0 = 0;} \quad p_{eq}(z_0; \lambda_0 = 0) = \frac{1}{Z_0} \exp(-\beta H_0(\underline{z}_0)) \Leftarrow \lambda_0 = 0$$

$$\text{with } W_0 = H_0(\underline{z}_f) - H_0(\underline{z}_0)$$

$$\langle \exp(-\beta W_0) \rangle = \int dz_0 \, p_{eq}(\underline{z}_0) \exp(-\beta W_0(\underline{z}_0))$$

$$= \frac{1}{Z_0} \int dz_f \exp -\beta H_0(\underline{z}_f) \underbrace{\left| \frac{\partial z_0}{\partial z_f} \right|}_{1}$$

$$= \frac{Z_0}{Z_0} = 1$$

Note: It has nothing to do with cyclic!

Connection with 2-nd Law

$$\langle \exp -\beta W \rangle = \exp(-\beta \Delta F)$$

protocol ends at $t = t_f$ $\quad \underset{t > t_f}{\lambda = \lambda_f} \Rightarrow \dot{\lambda} = 0$

no additional work is done during relaxation towards equilibrium

$\Rightarrow$ W inclusive IS the work between two equilibrium states

$F(\lambda_f)$; $p_{eq}(\dots;\lambda_f)$ & $F(\lambda_0)$; $p_{eq}(\dots,\lambda_0)$

This is not so for W_0 (inclusive work!)

$\rightsquigarrow$ no rigorous connection to 2-nd Law
(although also ineq. follows)!!

Jensen-inequality

$$\langle \exp x \rangle \geq \exp \langle x \rangle$$

$$\langle \exp -\beta W \rangle \geq \exp(-\beta \langle W \rangle)$$

$$\overset{\shortparallel}{\exp(-\beta \Delta F)}$$

ln.) $\quad +\beta \Delta F \overset{\leq}{\geq} +\beta \langle W \rangle$

$$\boxed{\Delta F \leq \langle W \rangle}$$

in eq. $\Delta F \overset{!}{=} \langle W^{eq} \rangle$

note that a fluctuation W can obey

$W < \Delta F$; thus violating (as a fluctuation) the 2nd Law

Set for a W-violution

$$W = \Delta F - \varepsilon; \quad \varepsilon > 0 ! \quad (W_{fluct.} < \Delta F)$$

$$\underline{\underline{\mathrm{Prob}\,(W \leq \Delta F - \varepsilon)}} = \int_{-\infty}^{\Delta F - \varepsilon} \rho_{noneq.}(W)\, dW$$

= probability to observe a work value which is $\underline{\text{LESS}}$ than $(\Delta F - \varepsilon)$!

$$\leq \int_{-\infty}^{\Delta F - \varepsilon} dW \rho(W) \exp \beta [\underbrace{\underline{\Delta F - \varepsilon} - W}_{\geq 0}]$$

$$\leq \exp \beta [\Delta F - \varepsilon] \underbrace{\int_{-\infty}^{+\infty} dW \rho(W) e^{-\beta W}}_{\exp(-\beta \Delta F)}$$

$$= \underline{\underline{\exp(-\beta \varepsilon)}}$$

for macroscopic changes $\varepsilon \gg kT \rightarrow$ Prob. fantastically $\underline{\underline{\text{small}}}$!