Lecture

II

work-theorems

Work - Theorems -

Nonlinear Fluctuation - Theorems

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

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

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

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

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

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

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

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

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

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

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

$$\Rightarrow \Delta F = \Delta Q + \Delta W - T\Delta S = \overbrace{T\Delta S - W_{diss}}^{\Delta Q} + \Delta W - T\Delta S = \Delta W - \underbrace{W_{diss}}_{\geq 0}$$

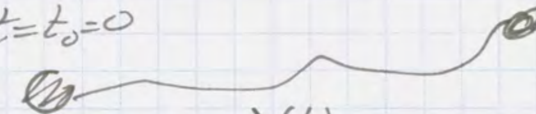
$$\Delta F \leq \Delta W \equiv \langle \Delta W \rangle_{\text{if } W \text{ fluctuates}}$$

Fluctuation-(Work)-Relations

Rev. M. Campisi, P. Hänggi, P. Talkner Rev. Mod. Phys. classical & quantum! 83: 771-791 (2011)

C. Jarzynski, Ann. Rev. Cond. Matter Phys. 2, 329 (2011) (classical)

also known under noneq. Work-Fluctuation-Theorems

$t = t_0 = 0$  B $t = t_f (= \tau)$

$\lambda(t)$

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

A; $\lambda = \lambda_0$

prepared in canonical thermal equilibrium

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

$$\mathcal{H}(X; \lambda(t)) = H^S(x_{System}; \lambda(t)) + H^E_{\substack{Environment \\ (bath)}} + H_{Int.}$$

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

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

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

correct when?!

(i) Isolated system

main result (Jarzynski, PRL 1997)

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

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 ($\Delta G = 0$)

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

phase-space

Protocol: $\lambda(t)$

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

full H bare H

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

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

$$= -\beta^{-1} \ln Z(\lambda)$$

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

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

Given such a realization

we define

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

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

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

$(\overset{\text{i. gen.}}{\neq} \int \text{force}\, dx)$

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

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

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

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

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

$$\frac{d H_0}{dt}(z_t) = \frac{d}{dt}\Big(H(\underline{z}_t; \lambda_t) + \lambda_t Q(\underline{z}_t) \Big)$$

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

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

$\underline{z}_t$ evolves under full Hamiltonian

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

exclusive work (point of view)

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

inclusive work (point of view)

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

If $\lambda_f = \lambda_0 \stackrel{!}{=} 0 \Leftrightarrow \boxed{W_0 = W}$

Note: In general "Statistics" of $W_0 \Leftrightarrow P(W_0)$ is not the same as $P(W) \Leftrightarrow W$

Proof Inclusive case

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

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

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

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

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

$$\doteq \frac{Z_B(\lambda_f)}{Z_A(\lambda_0)} = \underline{\underline{\exp(-\beta \Delta F)}} \qquad \text{q.e.d.}$$

Jarzynski (1997)

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

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

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

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

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

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 $t = t_f$ $\quad \lambda_{t > t_f} = \lambda_f \Rightarrow \dot{\lambda} = 0$

no additional work is done during relaxation towards equilibrium

$\Rightarrow$ W inclusive IS the work between two equilibrium states $F(\lambda_f)$; $p_{eq}(\ldots;\lambda_f)$ & $F(\lambda_0)$; $p_{eq}(\ldots,\lambda_0)$

This is not so for W_0 (inclusive work!)

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

Jensen-inequality

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

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

$\quad \| $

$\exp(-\beta \Delta F)$

note: $\langle \exp -\beta W \rangle \neq \exp -\beta \langle W \rangle$ for W NOT sharp

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

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

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

"=" only for macroscopic system (when W-fluctuations can be NEGLECTED)

note that a fluctuation W can obey

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

In general $\langle W^{rev} \rangle < \Delta F$ in reverse equilibrium as W^{rev} fluctuates for SMALL eq.-systems

Set for a W-violation

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

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

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

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

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

$$= \exp(-\beta \varepsilon)$$

For macroscopic changes $\varepsilon \gg kT \rightarrow$ Prob. fantastically small!