Lecture #9

github.com/gecrooks/LectureNotes220b

(1) Microscopic FT

$$\frac{P_\Lambda(x)}{P_{\tilde\Lambda}(\tilde x)} = e^{+\beta W - \beta\Delta F}$$

general

$$\frac{P_\Lambda(x)}{P_{\tilde\Lambda}(\tilde x)} = e^{+\Sigma}$$

$\Sigma \equiv$ entropy production

Detailed FT

$$\frac{P_\Lambda(+W)}{P_{\tilde\Lambda}(-W)} = e^{+\beta W - \beta\Delta F}$$ (2)

$$\frac{P_\Lambda(+\Sigma)}{P_{\tilde\Lambda}(-\Sigma)} = e^{+\Sigma}$$

(2)

Integrated FT
Jarzynski identity

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

$$\langle e^{+\Sigma}\rangle = 1$$

$$\beta\langle W\rangle \geqslant \beta\Delta F$$

$$\langle\Sigma\rangle \geqslant 0$$

[After (3)]

(3)

$$D(x\,\|\,\tilde x) = \beta\langle W\rangle - \beta\Delta F$$

$$= \langle\Sigma\rangle$$

Detailed FT

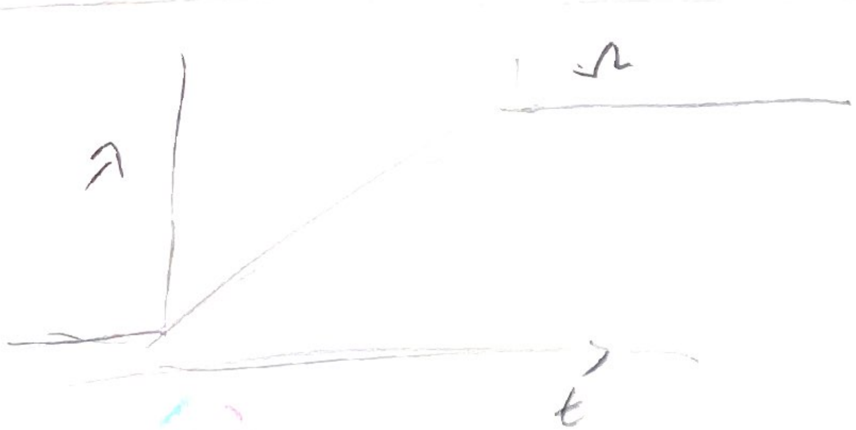
$$P_\Omega(+W) \stackrel{?}{=} \sum_X P_\Omega(X)\,\delta(W[X]-W) = \sum_{\tilde X} P_{\tilde\Omega}(\tilde X)\, e^{+\beta W[X]-\beta\Delta F}\,\delta(-\tilde W[\tilde X]-W)$$

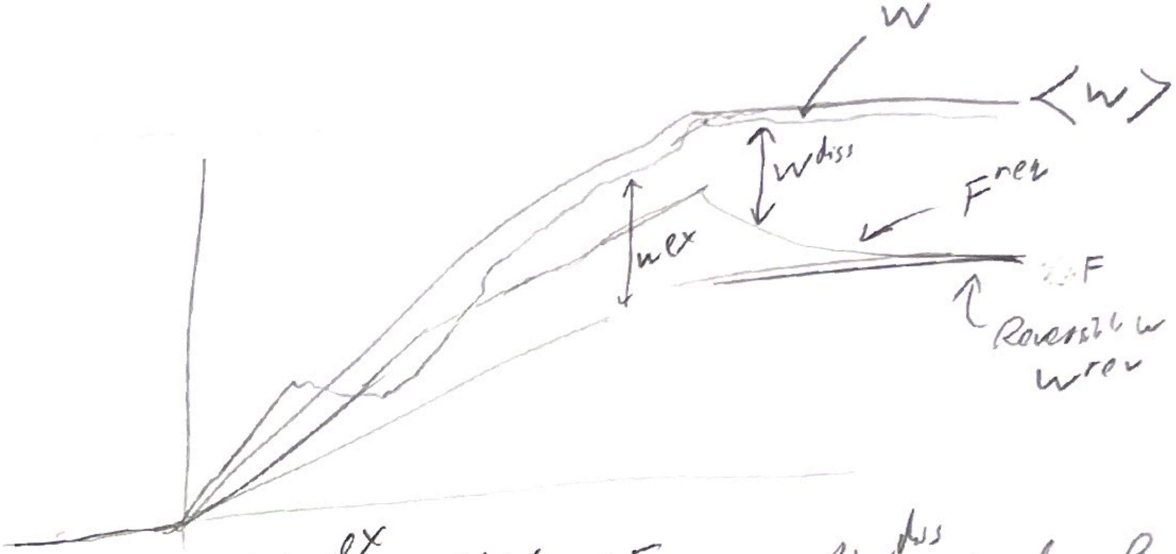
$$= e^{+\beta W-\beta\Delta F} \underbrace{\sum_{\tilde X} P(\tilde X)\,\delta(-\tilde W[\tilde X]-W)}_{P_{\tilde\Omega}(-W)}$$

$$\boxed{\frac{P_\Omega(+W)}{P_{\tilde\Omega}(-W)} = e^{-\beta W-\beta\Delta F}}$$

$\to$ on BI

Dissipation





$$\beta W^{ex} = \beta W - \beta F = \beta W^{diss} \text{ in lon. Run}$$
$$= \Sigma$$

$$D(X \| \tilde{X}) = \sum_{\tilde{X}} P(X) \ln \frac{P(\tilde{X})}{P(X)}$$
$$= \beta\langle W \rangle - \beta \Delta F = \langle \Sigma \rangle$$

$$\beta W^{ex} = \beta W - \beta \Delta F$$
$$= \beta W - \beta \Delta E + \Delta S^{sys}$$
$$= -\beta Q + \Delta S^{sys}$$
$$= \Delta S^{env} + \Delta S^{sys} = \Sigma \text{, entropy production}$$

$\boxed{\text{Kawai 2007}}$

[written on Board #1)

[Dissipation, entropy increase is a quantitative measure of the breaking of time Reversal Symmetry]

What is dissipation? Breaking of T.R.S.

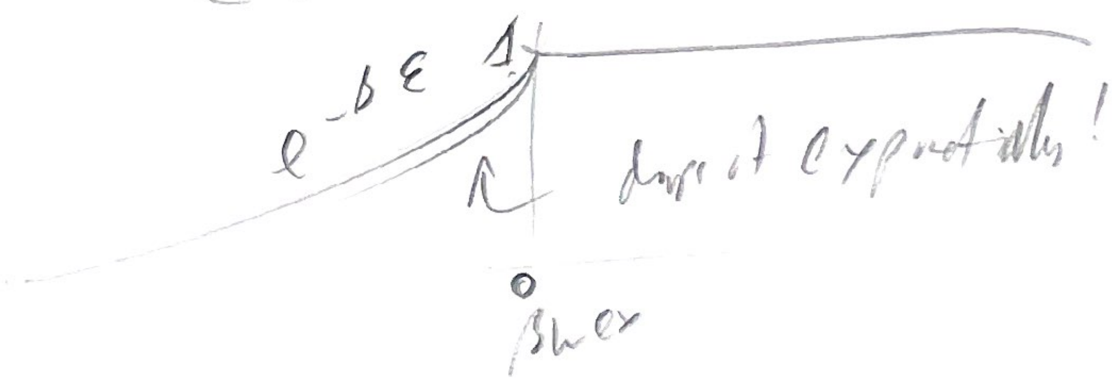
JE Resultats

$$P(w^{ex} \leq -\varepsilon) = \int_{-\infty}^{-\varepsilon} dw\, P(w)\, e^{-\beta\varepsilon - \beta w^{ex}}$$

$$\leq \int_{-\infty}^{\infty} dw\, P(w)\, e^{-\beta\varepsilon - \beta w^{ex}}$$

$$\leq e^{-\beta\varepsilon} \underbrace{\left\langle e^{-\beta w^{ex}} \right\rangle}_{=1}$$

$$\leq e^{-\beta\varepsilon}$$



History of FTs

A1

Bochkov 1977

Evans, Cohen, Morriss 1993

simulation

deterministic

steady state

Evans Searles 1994

Gallavotti, Cohen 1996 (coined FT)

Jarzynski 1997

Kurchan 1998 (stochastic)

Crooks 1998/99

Lebowitz & Spohn 1999

RADFORD Neal 2001

Annealed Importance sampling

⇓

experiments & more.

C1

n	Moments	Central Moments μ_n			Cumulants κ_n
1	$\langle x \rangle$				$\langle x \rangle$
2	$\langle x^2 \rangle$	$\langle (x - \langle x \rangle)^2 \rangle$	σ^2	variance	σ^2
3	$\langle x^3 \rangle$	$\langle (x - \langle x \rangle)^3 \rangle$	$\frac{\mu_3}{\sigma^{3/2}}$	skew	μ_3
4	$\langle x^4 \rangle$	$\langle (x - \langle x \rangle)^4 \rangle$	$\frac{\mu_4}{\sigma^4}$	Kurtosis	$\mu_4 - 3\sigma^4$

ex. Kurtosis $= \frac{\mu_4}{\sigma^4} - 3$

$$M(t) = \langle e^{tx} \rangle = 1 + \langle x \rangle t + \frac{1}{2!}\langle x^2 \rangle t^2 \ldots \qquad \left.\frac{d^n M}{dt^n}\right|_{t=0} = \langle x^n \rangle$$

$$K(t) = \ln \langle e^{tx} \rangle = t\kappa_1 + \frac{\kappa_2}{2!}t^2 + \frac{\kappa_3}{3!}t^3 \ldots$$

$Z = X + Y$ independent Random Variables

$$K_Z(t) = \ln \langle e^{t(x+y)} \rangle = \ln \langle e^{tx} \rangle + \ln \langle e^{ty} \rangle = K_X(t) + K_Y(t)$$

[cumulant accumulate!]

Normal $= \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$ $\qquad K(t) = \mu t + \sigma^2 t/2$ [all higher cumulants are zero!]

$\bigcirc$ 5

Jarzynski

$$\langle e^{-\Sigma} \rangle = 1$$

$t = 0$

$$K_\Sigma = \ln \langle e^{-t\Sigma} \rangle \quad \text{for Normal } 0 = -\mu + \frac{\sigma^2}{2}$$

$$\Delta F = \langle W \rangle - \frac{\sigma_W^2}{2}$$

$$\boxed{\mu_\Sigma = \frac{\sigma_\Sigma^2}{2}}$$

$$K_\Sigma(t) \geq \ln \frac{\cosh\left[(\alpha + \frac{1}{2})\, g(\langle \Sigma \rangle)\right]}{\cosh\left[\frac{1}{2}\, g(\langle \Sigma \rangle)\right]}$$

$$g^{-1}(x) = x \tanh \frac{x}{2}$$

Salazar 2023

Central limit Theorem   Normal

<3

$\cancel{\mu} = K_1 = 0$

$$T = \frac{1}{N}\sum_{i=1}^{N} X_i$$

$$K_X(t) = K_1 + \frac{K_2^X t^2}{2!} + \frac{K_3^X t^3}{3!} + \frac{K_4^X t^4}{4!} \ldots$$

$$K_T(t) = \frac{N}{N} K_1 t + \frac{N}{N^2}\frac{K_2^X t^2}{2!} + \frac{N}{N^3} K_3^X t^3 + \frac{N}{N^4} K_4^X t^4$$

$$K_n^T = \frac{1}{N^{n-1}} K^X$$

μ

var $\sim \frac{1}{N}$

~~all other~~ higher order cumulants scale to zero

$\Longrightarrow$ Normal

Partition function

$$f(x) = \frac{u(x)}{v(x)}$$

$$= \frac{u'(x)}{v(x)} - \frac{u(x)v'(x)}{v^2(x)}$$

C4

Kernel for Canonical Distribution

$$K_x(t) \equiv \ln\langle e^{tE}\rangle = \ln \sum \frac{1}{Z(\beta)} e^{-\beta E_i + tE} = \ln \frac{Z(\beta - t)}{Z(\beta)}$$

$$K_x^{(1)}(t)\Big|_{t=0} = -\frac{Z'(\beta)}{Z(\beta)} = \langle E\rangle = \frac{d}{d\beta} \ln Z(\beta)$$

$$K_x^{(2)}(t)\Big|_{t=0} = \frac{Z''(\beta)}{Z(\beta)} - \frac{Z'(\beta)^2}{Z(\beta)^2} = \langle (E - \langle E\rangle)^2\rangle^2$$

$$\frac{\partial^n}{\partial \beta^n} \ln Z(\beta) = K_n \quad \text{cumulants of energy}$$