

## Lecture 8 Fluctuation Theorems, Intro

①

### JARZYNSKI IDENTITY

[We have discussed Probability, Transition Rates,  
Reversed paths of Thermodynamics, (Ruelle, ~~and~~ F.E)  
Dynamics]

→ Today Jarzynski Equation  
- Simplest, most precise estimate of S.M. Work not in [14]

"Integrated Fluctuation Theorem"

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

[Later]

Jarzynski PRL 1997

"25-year of Nano-scale Thermodynamics"

Nature 2022

Broedersz & Ronceray

~~Approx of~~  
Nature of physical world

# T.R. & Thermodynamic Equilibrium

Edington 1928

"The Nature of The Physical World" ②

ONLY Entropy determines arrow of time.

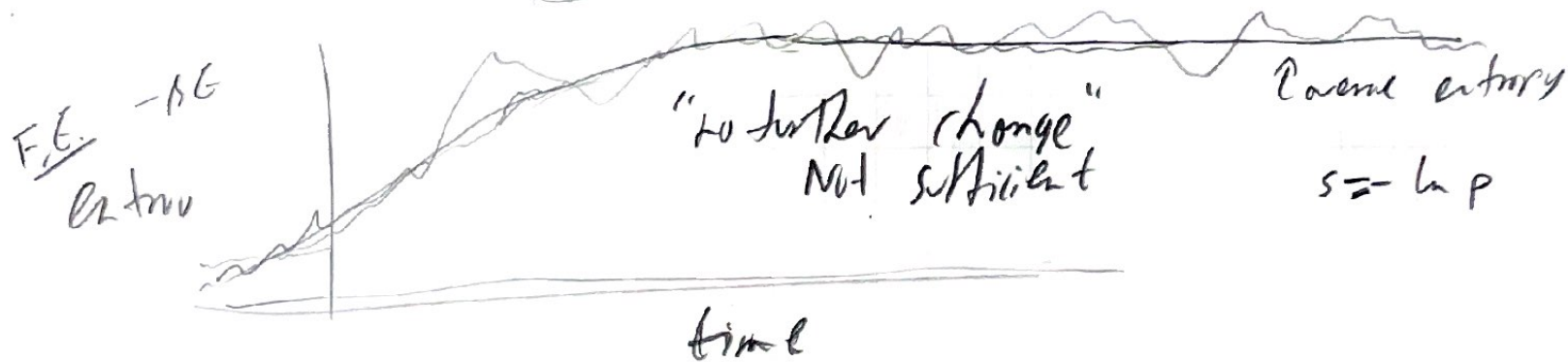
Thermodynamic Equilibrium - Statistically, time reversal ~~invariant~~ <sup>symmetric</sup>



~ 1 mol  $H_2O$

Time has no orientation nor origin

Homogeneous & isotropic



[clocks are fully not eq. devices]

[No clocks at Thermodynamic equilibrium]

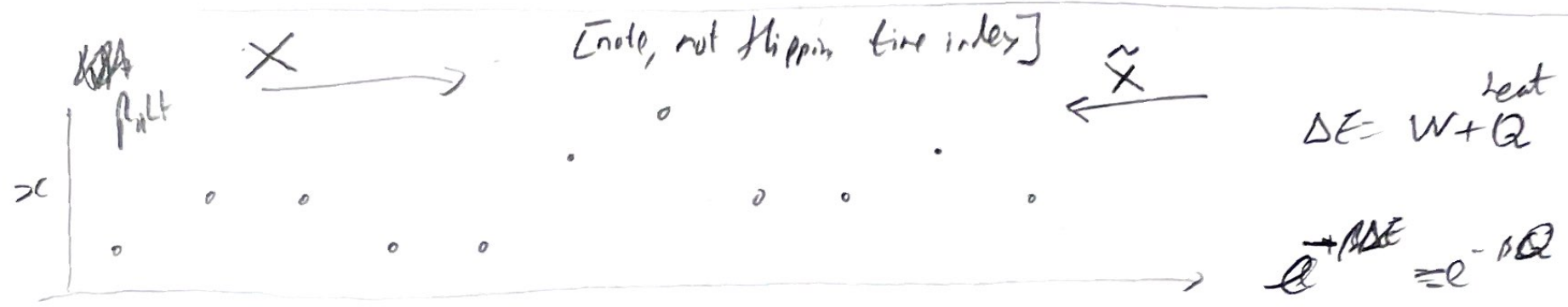
[Time has extant, but no orientation]

[This is very profound statement!]

(2)



DTMC



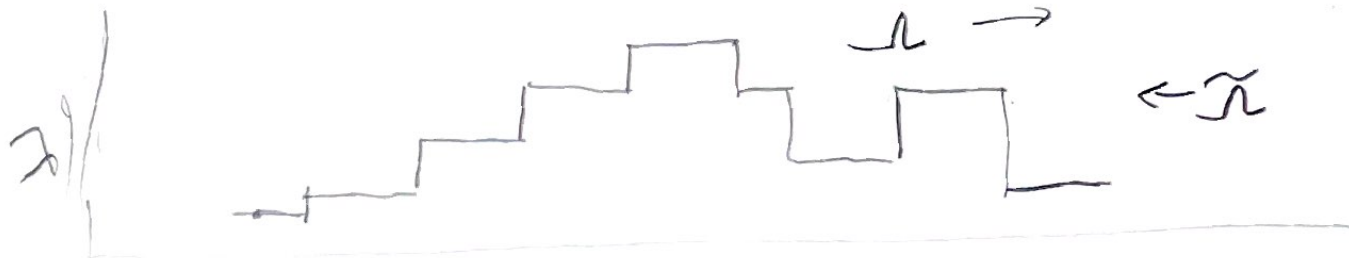
$$\left. \begin{aligned} \frac{P(x)}{P(\tilde{x})} &= 1 \\ \frac{P(x|x_0)}{P(\tilde{x}|x_0)} &= \frac{P(x_0)}{P(x_0)} = e^{-\beta[E(x_0) - \Delta E(x_0)]} \end{aligned} \right\} \begin{aligned} &\text{Port 3} \\ &= e^{-\beta Q} = e^{+\Delta S_{env}} \end{aligned}$$

[Crook 1998]

40

[Right]

Microscopic Fluctuation Theorem



$$\frac{P(x|x_0, \Lambda)}{P(\tilde{x}|x_t, \tilde{\Lambda})} = \prod_t \frac{P(x_{t+1}|x_t, \Lambda)}{\tilde{P}(x_t|x_{t+1}, \tilde{\Lambda})} = \prod_t e^{-\beta[E(x_{t+1}) - E(x_t)]}$$

$$= e^{-\beta Q} = e^{+\beta \Delta S^{en}}$$

(center)

[D.B. Property of the ensemble]

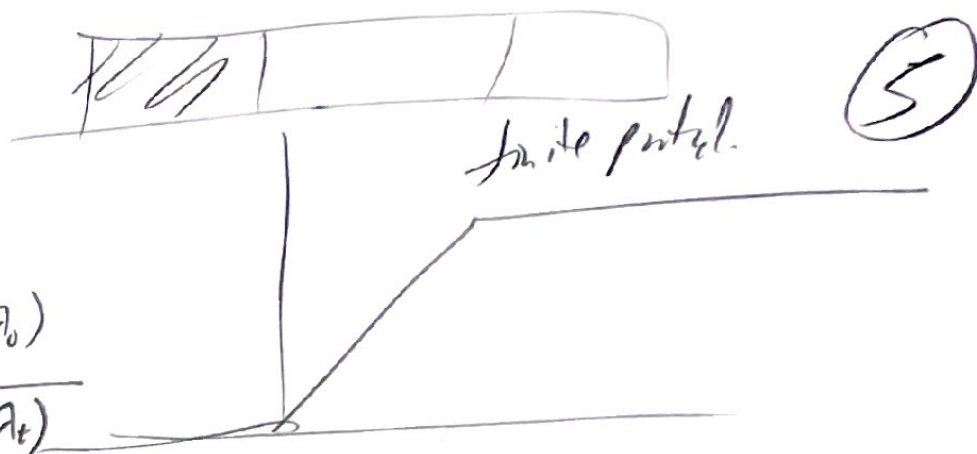
[center]



$$\frac{P(x)}{P(\tilde{x})} = \frac{P(x|x_0, \Lambda)}{P(x|x_t, \Lambda)} \frac{P(x_0|\lambda_0)}{P(x_t|\lambda_t)}$$

$$= e^{-\beta Q} \frac{e^{-\beta E(x_0, \lambda_0) + \beta F(\lambda_0)}}{e^{-\beta E(x_t, \lambda_t) + \beta F(\lambda_t)}}$$

$$= e^{+\beta \Delta E - \beta \Delta F} = e^{+\beta W^{ex}}$$



$$\Delta F = F(\lambda_t) - F(\lambda_0)$$

$$\Delta E = Q + W$$

$$\Delta E - Q = W$$

$$\langle e^{-\beta W[x, \Lambda]} \rangle = \sum_x P(x) e^{-\beta W[x, \Lambda]}$$

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

$$= e^{-\beta \Delta F}$$