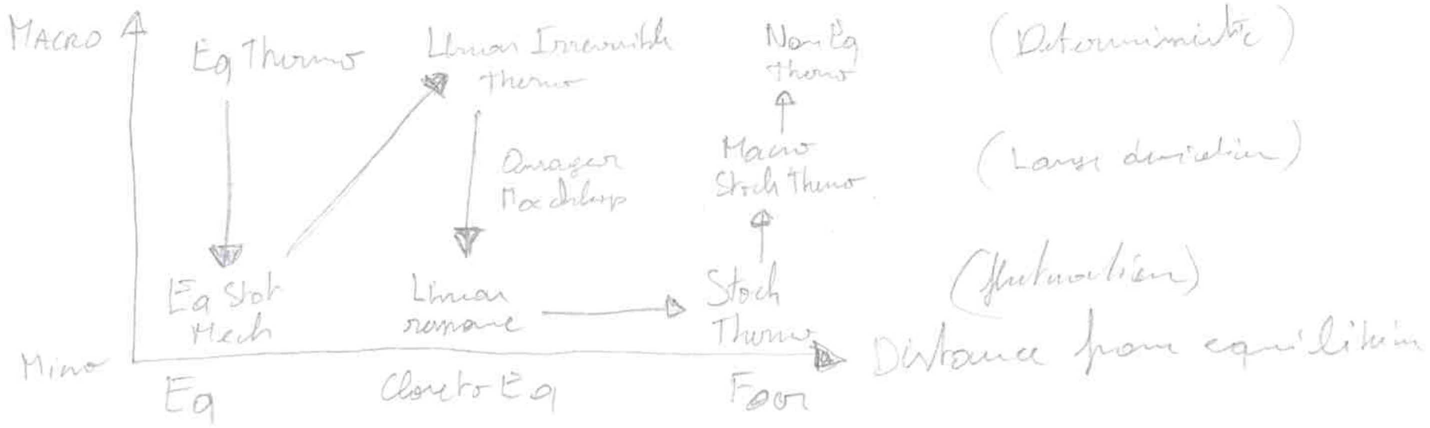
Stochastic Thermodynamics



Macroscopic thermodynamics : Falasco, ME arXiv 2307.12406

Plan :

Rao, ME NJP $\overline{20}$, 023007
(2018) Entropy $\overline{20}$, 635

I : General formulation of ST

II : Macro limit of ST

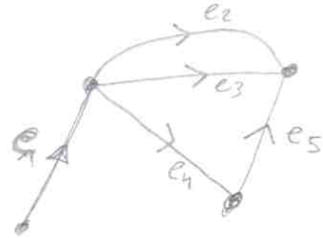
III : Applications + summary with slides of what I could not cover

Part I

- Dynamics

$$d_t P_i = \sum_j \overset{\text{can depend on time}}{W_{ij}} P_j = \sum_{j(\neq i)} W_{ij} P_j + W_{ii} P_i$$

$$\sum_i P_i = 1 \quad \sum_i d_t P_i = 0 \Rightarrow \sum_i W_{ij} = 0 \Rightarrow W_{ii} = -\sum_{j(\neq i)} W_{ji}$$



$$d_t P_i = \sum_{j(\neq i)} \left(W_{ij} P_j - W_{ji} P_i \right)$$

$$= \sum_j \left(W_{ij} P_j - W_{ji} P_i \right)$$

$$= \sum_{\substack{e>0 \\ \xleftarrow{\text{oriented edges}}}} D_e^i J_e$$

where $J_e \equiv W_e P_{o(e)} - W_{-s} P_{o(-e)} = -J_{-e}$

incidence matrix $D_e^i \equiv \delta_{io(e)} - \delta_{io(e)} = -D_{-e}^i$

Steady state $\sum_j W_{ij} P^{ss} = 0 \Rightarrow \sum_{e>0} D_e^i J_e^{ss} = 0$

Equilibrium $\forall e : J_e^{eq} = 0 \Rightarrow W_e P_{o(e)}^{eq} = W_{-e} P_{o(e)}^{eq}$

- Entropy balance

Shannon entropy : $S_{sh} = -\sum_i P_i \ln P_i$

$$d_t S_{sh} = -\sum_i d_t P_i \ln P_i - \underbrace{\sum_i P_i \frac{d_t P_i}{\cancel{P_i}}}_{=0}$$

$$= -\sum_{ij} W_{ij} P_j \ln P_i = -\sum_{ij} W_{ij} P_j \ln \frac{P_i}{P_j} \xrightarrow{} \text{adding zero}$$

$$= -\frac{1}{2}\sum_{ij} W_{ij} P_j \ln \frac{P_i}{P_j} \underbrace{- \frac{1}{2}\sum_{ij} W_{ij} P_j \ln \frac{P_i}{P_j}}_{-\frac{1}{2}\sum_{ji} W_{ji} P_i \ln \frac{P_j}{P_i}}$$

$$= -\frac{1}{2}\sum_{ij} \left(W_{ij} P_j - W_{ji} P_i \right) \ln \frac{P_i}{P_j} = \frac{1}{2}\sum_{ij} \left(W_{ij} P_j - W_{ji} P_i \right) \ln \frac{P_j}{P_i}$$

$$= \frac{1}{2}\sum_{\substack{e \\ \xleftarrow{\text{Sum over both directions}}}} \left(W_e P_{o(e)} - W_{-e} P_{o(-e)} \right) \frac{P_{o(e)}}{P_{o(-e)}}$$

If $A_e = -A_{-e}$

$$1)\ \frac{1}{2}\sum_e J_e A_e = \frac{1}{2}\sum_{e>0} J_e A_e + \frac{1}{2}\sum_{e>0} \overbrace{J_{-e} A_{-e}}^{J_e A_e}$$

$$= \sum_{e>0} J_e A_e$$

$$2)\ \frac{1}{2}\sum_e J_e A_e = \frac{1}{2}\sum_e W_e P_{o(e)} A_e - \frac{1}{2}\sum_e W_{-e} P_{o(-e)} \overset{-A_{-e}}{\overset{\parallel}{A_e}}$$

$$= \frac{1}{2}\sum_e W_e P_{o(e)} A_e + \frac{1}{2}\sum_e W_e P_{o(e)} A_e$$

$$= \sum_e W_e P_{o(e)} A_e$$

$$d_t S_{sh} = \sum_{e>0} J_e \ln \frac{P_{o(e)}}{P_{o(-e)}}$$

$$= \underbrace{\sum_{e>0} J_e \ln \frac{W_e P_{o(e)}}{W_{-e} P_{o(-e)}}}_{\equiv \dot{\Sigma} \geq 0} - \sum_{e>0} J_e \ln \frac{W_e}{W_{-e}}$$

Entropy production

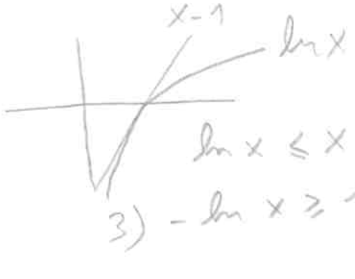
At equilibrium $\dot{\Sigma} = 0$

- Adiabatic - non adiabatic decomposition

$$\dot{\Sigma} = \underbrace{\sum_{e>0} J_e \ln \frac{W_e P^{ss}_{o(e)}}{W_{-e} P^{ss}_{o(-e)}}}_{\equiv \dot{\Sigma}_a} + \underbrace{\sum_{e>0} J_e \ln \frac{P_{o(e)}\, P^{ss}_{o(-e)}}{P_{o(-e)}\, P^{ss}_{o(e)}}}_{\equiv \dot{\Sigma}_{na}}$$

$$\dot{\Sigma}_a \overset{1+2}{=} \sum_e W_e P_{o(e)} \ln \frac{W_e P^{ss}_{o(e)}}{W_{-e} P^{ss}_{o(-e)}}$$

$$= \sum_e W_e P_{o(e)} \left(-\ln \frac{W_{-e} P^{ss}_{o(-e)}}{W_e P^{ss}_{o(e)}} \right)$$



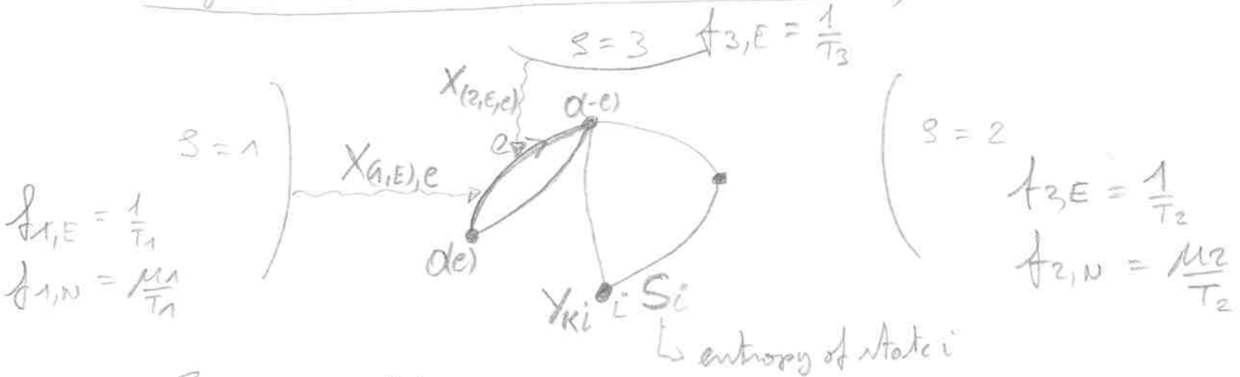
$\ln x \leq x - 1$

3) $-\ln x \geq 1 - x$

$$\overset{3}{\geq} \underbrace{\sum_e W_e P_{o(e)}}_{\underbrace{\sum_{ij} W_{ij} P_j}_{=0}} - \underbrace{\sum_e \cancel{W_e} P_{o(e)} \frac{W_{-e} P^{ss}_{o(-e)}}{\cancel{W_e} P^{ss}_{o(e)}}}_{\underbrace{\sum_{ij} W_{ji} P_i^{ss} \frac{P_j}{P_j^{ss}}}_{=0}} = 0$$

$\dot{\Sigma}_a \geq 0$ $\qquad$ $\dot{\Sigma}_a = 0$ if $\underbrace{P^{ss} \text{ is equilibrium } P^{eq}}_{\text{detailed balanced dynamics}}$: $W_e P^{eq}_{o(e)} = W_{-e} P^{eq}_{o(-e)}$

- Physics (local detailed balance):



ς reservoirs

K conserved quantities with amount Y_{Ki} ↳ state of the system

Each reservoir described by intensive field f_y $\quad y = (\varsigma, K)$

$$Y_{K\,o(-e)} - Y_{K\,o(e)} = \sum_i Y_{Ki} D_{ie} = \sum_\varsigma X_{(\varsigma,K)e}$$

change of conserved qty K
in the system when a
transition along e occurs

part of that change
that gets transferred
to reservoir ς

local detailed balance:

$$X_{ye} = -X_{y-e}$$

$$\ln \frac{W_e}{W_{-e}} = \underbrace{\bar{D}_e^T \bar{S}}_{\sum_i D_e^i S_i} - \underbrace{\bar{X}_e^T \bar{f}}_{\sum_y X_{ye} f_y} \rightarrow -\left(\frac{\delta E_1}{T_1} - \frac{\mu_1}{T_1}\delta N_1\right)$$

Ex $\varsigma = 1$ E

Entropy change in the system

Entropy change in the reservoir

f: $\frac{1}{T}$ $-\frac{\mu}{T}$ $\frac{P}{T}$ $-\frac{V}{T}$

K: E N Vol Q

System entropy : $S = \sum_i s_i p_i + S_{sh}$

$$d_t S = \sum_i s_i d_t p_i + \sum_i d_t s_i p_i + d_t S_{sh}$$

$$= \sum_{ij} W_{ij} p_j s_i + \sum_i d_t s_i p_i + d_t S_{sh}$$

$$= \sum_{ij} W_{ij} p_j (s_i - s_j) + \sum_i d_t s_i p_i + d_t S_{sh}$$

$$= \frac{1}{2} \sum_{ij} (W_{ij} p_j - W_{ji} p_i)(s_i - s_j) + \sum_i d_t s_i p_i + d_t S_{sh}$$

$$= \frac{1}{2} \sum_e J_e \bar{D}_e^T \bar{S} + \sum_i d_t s_i p_i + \mathring{\Sigma} - \sum_{e>0} J_e \ln \frac{w_e}{w_{-e}}$$

$$= \cancel{\sum_{e>0} J_e \bar{D}_e^T \bar{S}} + \sum_i d_t s_i p_i + \mathring{\Sigma} - \cancel{\sum_{e>0} J_e \bar{D}_e^T \bar{S}} + \sum_{e>0} J_e \bar{X}_e^T \bar{f}$$

$$= \mathring{\Sigma} + \sum_i d_t s_i p_i + \bar{I} \cdot \bar{f} \quad \text{where } \bar{I} = \sum_{e>0} J_e \bar{X}_e^T$$

$$\mathring{\Sigma} = \underbrace{d_t S}_{\text{entropy change in the system}} - \underbrace{\sum_i d_t s_i p_i}_{\text{remove the changes of internal entropy due to driving}} - \underbrace{\underset{\sum_y I^y f_y}{\underline{\bar{I} \cdot \bar{f}}}}_{\text{entropy changes in the reservoirs}} \geq 0$$

⑥b

Matrix A_{mn} :

$$A = \overbrace{\begin{pmatrix} | & | & | & | \\ | & | & | & | \end{pmatrix}}^{n \text{ columns}} \Big\} m \text{ rows}$$

Nullspace $N(A)$ all vectors $Ax = 0$ (kernel of A)

Column space $R(A)$ all lin comb of columns (image of A)

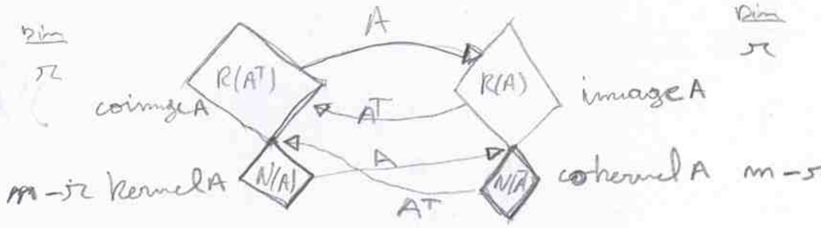
Row space $R(A^T)$ (coimage of A)

Nullspace $N(A^T)$ (cokernel of A)

$\dim R(A^T) = \dim R(A) = \text{rank} \equiv r$

$\dim N(A^T) = m - r$

$\dim N(A) = m - r$



$R(A^T) \perp N(A)$

$R(A) \perp N(A^T)$

$R(A^T)^\perp = N(A)$

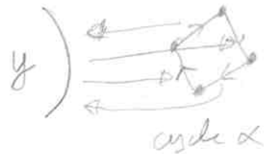
$R(A)^\perp = N(A^T)$

- Conservation laws :

$$\bar{\bar{M}} = \bar{\bar{X}}\,\bar{\bar{C}} \qquad\qquad \bar{l}_\lambda^T\,\bar{\bar{M}} = 0 \qquad \#\lambda = \#y - Rk(M)$$

$$M_{y\alpha} = \sum_e X_{ye} C_{e\alpha} \qquad\qquad \text{or } \sum_y l_\lambda^y M_{y\alpha} = 0$$

$$\text{or } \bar{l}_\lambda^T\,\bar{\bar{X}}\,\bar{\bar{C}} = 0$$



$$\downarrow$$

Since $N(D)$

$\bar{l}_\lambda^T\,\bar{X} \perp N(D)$: in $R(D^T)$

[coimage D]

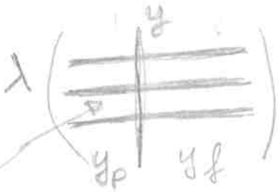
To each $\bar{l}^\lambda$ we can associate a conserved quantity $\bar{L}_\lambda$

such that $\bar{\bar{D}}^T\,\bar{L}^\lambda = \bar{\bar{X}}^T\,\bar{l}^\lambda$

change of L^λ along e : $\sum_i D_e^{\,i} L_i^\lambda = \sum_y X_{ye}\, l_\lambda^y$

$$\bar{\bar{D}}^T\,\bar{\bar{L}} = \bar{\bar{X}}^T\,\bar{\bar{l}}$$

$\bar{\bar{l}}$:



Square matrix

$\#y_p = \#\lambda$

$$\bar{\bar{D}}^T\bar{\bar{L}}\,\bar{\bar{l}}_p^{-1} = \bar{\bar{X}}_p^T\,\underbrace{\bar{\bar{l}}_p\,\bar{\bar{l}}_p^{-1}}_{=1} + \bar{\bar{X}}_f^T\,\bar{\bar{l}}_f\,\bar{\bar{l}}_p^{-1}$$

$$\bar{\bar{X}}^T\bar{f} = \bar{\bar{X}}_p^T\,\bar{f}_p + \bar{\bar{X}}_f^T\,\bar{f}_f$$

$$= \bar{\bar{D}}^T\bar{\bar{L}}\,\bar{\bar{l}}_p^{-1}\bar{f}_p - \bar{\bar{X}}_f^T\,\bar{\bar{l}}_f\,\bar{\bar{l}}_p^{-1}\,\bar{f}_p + \bar{\bar{X}}_f^T\,\bar{f}_f$$

$$= \bar{\bar{D}}^T\bar{\bar{L}}\,\bar{\bar{l}}_p^{-1}\bar{f}_p - \bar{\bar{X}}_f^T\,\underbrace{\left(\bar{\bar{l}}_f\,\bar{\bar{l}}_p^{-1}\bar{f}_p - \bar{f}_f\right)}_{\bar{F}}$$

$$\bar{F} \to \boxed{\#y_f = \#y - \#\lambda} \quad ⚠$$

non conservative forces

$$\ln \frac{w_e}{w_{-e}} = \bar{D}_e^{\dagger} \bar{S} - \bar{X}_e^{T} f$$

$$= \bar{D}_e^{\dagger} \underbrace{\left(\bar{S} - \bar{\bar{L}}\, \bar{l}_p^{-1} f_p \right)}_{-\bar{\Phi}} + \bar{X}_{fe}^{T} \bar{F}$$

$$\phi_i = -\left[S_i - \sum_{\lambda_{y_p}} L_i^{\lambda}\, l_{\lambda}^{y_p} f_{y_p} \right]$$ Thermodynamic potential

$$\mathring{\Sigma} = d_t S_{sh} + \sum_{e>0} J_e \ln \frac{w_e}{w_{-e}}$$

$$= d_t S_{sh} - \sum_{e>0} J_e \bar{D}_e^{T} \bar{\Phi} + \underbrace{\sum_{e>0} J_e \bar{X}_{fe}^{T}}_{= I_f} \cdot F$$

$$= d_t S_{sh} - \sum_i d_t P_i \phi_i + \bar{I}_f \cdot \bar{F}$$

$$= d_t S_{sh} - d_t \left(\sum_i P_i \phi_i \right) + \sum_i P_i \partial_t \phi_i + \bar{I}_f \cdot \bar{F}$$

$$= \bar{I}_f \cdot \bar{F} + \partial_t \Phi - d_t \Phi$$

where $\Phi = \sum_i P_i \left(\phi_i + \ln P_i \right)$

If $F = 0$: $\frac{w_e}{w_{-e}} = e^{-\phi_{o(-e)} + \phi_{o(e)}}$

At equilibrium $\frac{w_e}{w_{-e}} = \frac{P^{eq}_{o(-e)}}{P^{eq}_{o(e)}}$ $\longrightarrow$ $\frac{P_j^{eq}}{P_i^{eq}} = e^{-\phi_j + \phi_i}$

$$\sum_j P_j^{eq} = 1 = \sum_j e^{-\phi_j} P_i e^{\phi_i}$$

$$\Rightarrow P_i^{eq} = \frac{e^{-\phi_i}}{\sum_j e^{-\phi_j}}$$

$$\Rightarrow P_i^{eq} = e^{-\left[\phi_i - \Phi^{eq}\right]}$$

$$\Phi^{eq} = -\ln \sum_j e^{-\phi_j}$$

$$D(P|P^{eq}) = \sum_i P_i \ln P_i - \sum_i P_i \ln P_i^{eq}$$

$$= \sum_i P_i \left(\ln P_i + \phi_i \right) - \Phi^{eq}$$

$$= \Phi - \Phi^{eq} \geq 0$$

- $F = 0$ and no time dep driving

$P \to P^{eq}$ $\quad \Phi \to \Phi^{eq}$

$$\mathring{\Sigma} = -d_t D(P|P^{eq}) \geq 0$$

- NESS : $\mathring{\Sigma} = \overline{I}_f \cdot \overline{F} \geq 0$

- Reversible trsf : $F=0$ + slow driving.

$$\mathring{\Sigma} = -\sum_i d_t P_i \ln \frac{P_i}{P_i^{eq}} \qquad \left(\text{because } \mathring{\Sigma}_a = 0\right)$$

$$= -\sum_{ij} W_{ij} P_j \ln \frac{P_i}{P_i^{eq}}$$

$$P_i = P_i^{eq} + \delta P_i$$

$$\ln \frac{P_i}{P_i^{eq}} = \ln 1 + \frac{\delta P_i}{P_i^{eq}} \simeq \frac{\delta P_i}{P_i^{eq}} - \frac{1}{2}\left(\frac{\delta P_i}{P_i^{eq}}\right)^2 + O(\delta P_i^3)$$

$$\mathring{\Sigma} = -\sum_{ij} W_{ij} P_j^{eq} \left(1 - \frac{\delta P_j}{P_j^{eq}} + \dots\right)\left(\frac{\delta P_i}{P_i^{eq}} - \frac{1}{2}\left(\frac{\delta P_i}{P_i^{eq}}\right)^2 + \dots\right)$$

$$= \underbrace{-\sum_{ij} W_{ij} P_j^{eq} \frac{\delta P_i}{P_i^{eq}}}_{=0} + O(\delta P_i^2)$$

$$\underset{O(\delta P^2)}{\mathring{\Sigma}} = \underset{O(\delta P)}{\partial_t \Phi} - \underset{O(\delta P)}{d_t \Phi} \qquad \partial_t \Phi \simeq d_t \Phi$$

along a reversible trsf

Balance of conserved qties:

$$\sum_{e>0} J_e \overline{\overline{D}}_e^T \underbrace{\overline{\overline{L}}\,\overline{\overline{l}}_p^{-1}}_{\overline{\overline{\Pi}}_p} = \underbrace{\sum_{e>0} J_e \overline{\overline{X}}_{pe}^T}_{\overline{\overline{I}}_p} + \underbrace{\sum_{e>0} J_e \, {}^T\overline{\overline{X}}_{fe}^T}_{\overline{\overline{I}}_f} \overline{\overline{l}}_f \overline{\overline{l}}_p^{-1}$$

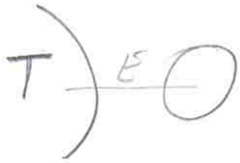
$$d_t \Big(\underbrace{\sum_i P_i \cdot M_{pi}}_{\langle M_p \rangle} \Big) = \sum_e J_e \overline{\overline{D}}_e^T \overline{\overline{\Pi}}_p + \partial_t \langle M_p \rangle$$

$$d_t \langle M_p \rangle = \overline{\overline{I}}_p + \overline{I}_f \overline{\overline{l}}_f \overline{\overline{l}}_p^{-1} + \partial_t \langle M_p \rangle$$

$$\# f = \# y - \# \lambda$$

$$\mathring{\Sigma} = \frac{d}{dt} S - \partial_t S - \sum_y I^y f^y$$

Ex 1



$$\mathring{\Sigma} = \frac{d}{dt} S - \partial_t S - I_E \frac{1}{T}$$

$$\frac{dE}{dt} = I_E + \partial_t E$$

$\# y = 1$
$\# \lambda = 1$
$\# f = 1$

$$\mathring{\Sigma} = \frac{d}{dt} S - \partial_t S - \frac{1}{T} \frac{dE}{dt} + \frac{1}{T} \partial_t E$$

$$\phi = \frac{E}{T} - S \qquad \frac{d\Phi}{dt} = \frac{1}{T} dE - dS + \left(\partial_t \frac{1}{T}\right) E$$

$$\mathring{\Sigma} = -\frac{d\Phi}{dt} + \left(\partial_t \frac{1}{T}\right) E - \partial_t S + \frac{1}{T} \partial_t E$$

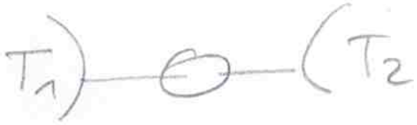
$$= \partial_t \Phi - \frac{d}{dt} \Phi$$

Quantum dot
Isothermal
$S_i = 0$

$$\mathring{\Sigma} = \frac{1}{T} \partial_t E - \frac{1}{T} d_t (E - TS)$$

$$T \dot{\Sigma} = \partial_t E - d_t F \qquad F = E - TS$$

Ex 2



$$\mathring{\Sigma} = d_t S - \partial_t S - \frac{1}{T_1} I_E^1 - \frac{1}{T_2} I_E^2$$

$$d_t E = I_E^1 + I_E^2 + \partial_t E$$

$\# y = 2 \quad \# \lambda = 1 \quad \# f = 1$

$$\mathring{\Sigma} = \underbrace{d_t S} - \partial_t S \underbrace{- \frac{1}{T_1} d_t E} + \frac{1}{T_1} I_E^2 + \frac{1}{T_1} \partial_t E - \frac{1}{T_2} I_E^2$$

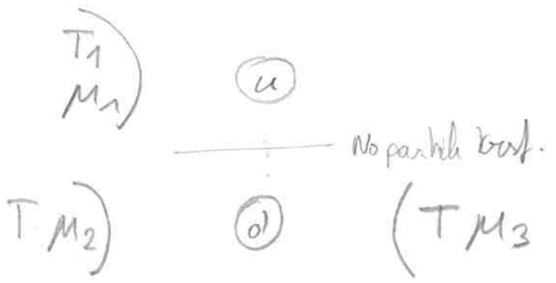
$$\Phi_1 = \frac{E}{T_1} - S \qquad d_t \Phi_1 = \frac{1}{T_1} d_t E - d_t S + \left(\partial_t \frac{1}{T_1}\right) E$$

$$\mathring{\Sigma} = -d_t \Phi_1 + \left(\partial_t \frac{1}{T_1}\right) E - \partial_t S + \frac{1}{T_1} \partial_t E + \left(\frac{1}{T_1} - \frac{1}{T_2}\right) I_E^2$$

$$= \partial_t \Phi_1 - d_t \Phi_1 + \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{\text{force}} I_E^2$$

Ex 3

No driving
Steady-State



$\# y = 5 \qquad 0 = d_t E = I_1^E + I_2^E + I_3^E$

$\# \lambda = 3 \qquad 0 = d_t N_u = I_1^N$

$\# f = 2 \qquad 0 = d_t N_d = I_2^N + I_3^N$

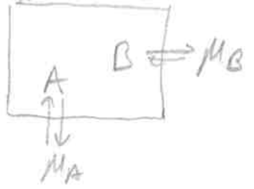
$$\dot{\Sigma} = -\frac{1}{T_1} I_1^E - \frac{1}{T} I_2^E - \frac{1}{T} I_3^E + \cancel{\frac{\mu_1}{T_1} I_1^N} - \frac{\mu_2}{T} I_2^N - \frac{\mu_3}{T} I_3^N$$

$$= \left(\frac{1}{T} - \frac{1}{T_1}\right) I_1^E + \left(\frac{\mu_3 - \mu_2}{T}\right) I_2^N$$

Ex 4

No driving
Isothermal
Steady-State

$\# y = 2$
$\# \lambda = 2 \quad \# f = 0$



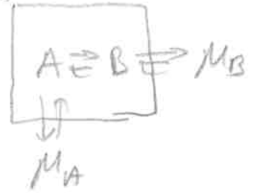
$0 = \frac{dN_A}{dt} = I_A$

$0 = \frac{dN_B}{dt} = I_B$

$T\dot{\Sigma} = \cancel{\mu_A I_A} + \cancel{\mu_B I_B} = 0$

eq

$\# y = 2$
$\# \lambda = 1 \quad \# f = 1$



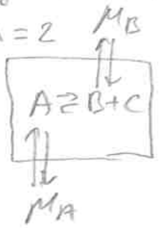
$0 = \frac{d(N_A + N_B)}{dt} = I_A + I_B$

$T\dot{\Sigma} = \mu_A I_A + \mu_B I_B$

$= (\mu_A - \mu_B) I_A$

NESS

$\# y = 2 \quad \# f = 0$
$\# \lambda = 2$



$0 = d_t(N_A + N_C) = I_A$

$0 = d_t(N_C - N_B) = I$

$T\dot{\Sigma} = \cancel{\mu_A I_A} + \cancel{\mu_B I_B}$

$= 0$

Eq

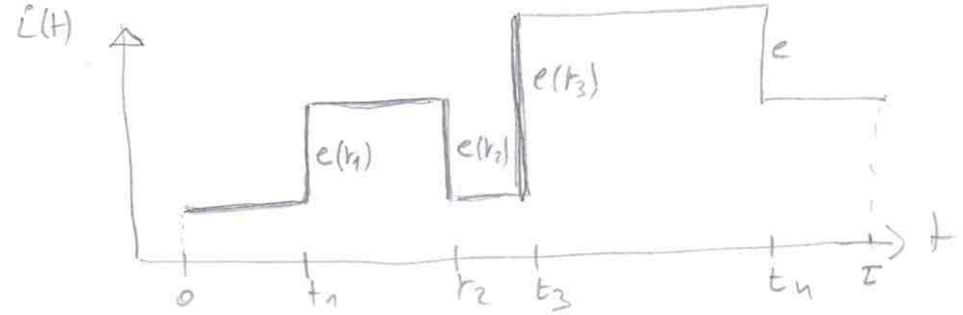
- Fluctuation level :

$W_{ij}(t)$: transition rate Prob that a jump at t : $\psi_i(t) = e^{-(-w_{ii})t}(-w_{ii})$

$W_{ii} = -\sum_{j(\neq i)} W_{ji} \Rightarrow -$ inverse average waiting time.

[Prob that being on i a jump happens after t : $\psi_i(t) = e^{w_{ii}t}(-w_{ii})$

Average waiting time before jump $\int_0^\infty d\tau\, \tau\, \psi_i(\tau) = -\frac{1}{w_{ii}}$]



$$P[x] = P_{i(0)}(0)\, e^{-\int_0^\tau dt\, W_e(t)\, \delta_{o(e)\, i(t)}} \prod_k W_{e(t_k)}(t_k)$$

time reversed driving $\rightarrow$

$$\tilde{P}[\bar{x}] = P_{i(\tau)}(\tau) \qquad \text{"} \qquad \prod_k W_{-e(t_k)}(t_k)$$

$$\Sigma(x) = \ln P[x]/\tilde{P}[\bar{x}]$$

$$\Sigma(x) = \sum_k \ln \frac{W_{e(t_k)}(t_k)}{W_{-e(t_k)}(t_k)} - \ln P_{i(\tau)}(\tau) + \ln P_{i(0)}(0)$$

$$= \sum_k \ln \frac{W_{e(t_k)}(t_k)\, P_{o(e(t_k))}(t_k)}{W_{-e(t_k)}(t_k)\, P_{o(-e(t_k))}(t_k)} - \int_0^\tau dt \frac{d}{dt} \ln P_{i(t)}$$

$$\frac{d}{dt}\langle \Sigma \rangle = \dot{\Sigma} \qquad \Sigma = D(\, P(X) \,\|\, \tilde{P}(\bar{X})\,) \geq 0$$

Integral FT

$$\langle e^{-\Sigma} \rangle = \sum_X P(X)\, e^{-\ln \frac{P(X)}{P(\bar{X})}} = \sum_X P(\bar{X}) = \sum_{\bar{X}} P(\bar{X}) = 1$$

$$P(\sigma) = \sum_x \delta(\sigma - \Sigma(x))\, P(x) = \sum_x \delta(\sigma - \Sigma(x))\, \tilde{P}(\bar{x})\, e^{\Sigma(x)}$$

$$= \sum_x \delta(\sigma - \Sigma(x))\, \tilde{P}(\bar{x})\, e^{\sigma}$$

$$= e^{\sigma} \sum_{\bar{x}} \delta(\sigma + \Sigma(\bar{x}))\, \tilde{P}(\bar{x})$$

$$= e^{\sigma} \sum_{\bar{x}} \delta(-\sigma - \Sigma(\bar{x}))\, \tilde{P}(\bar{x}) = \tilde{P}(-\sigma)$$

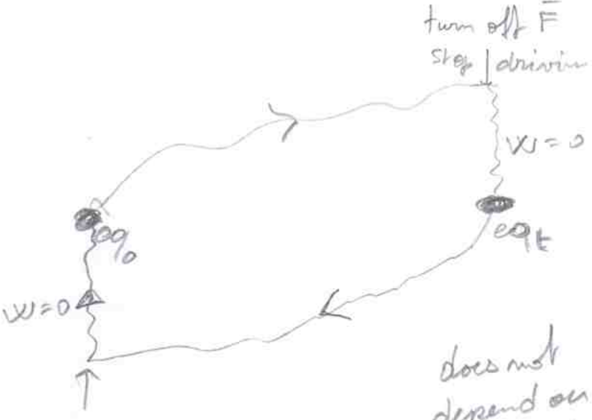
→ Assumption $\Sigma(-x) = -\Sigma(x)$ (involution)

Steady State : $P_m(t) = P_m(0) = P_m^{ss}$
(or periodic)

Equilibrium transitions :

$$\Sigma = \underbrace{\int_0^{t} \mathcal{I}_f \cdot \bar{F}\, d\tau + \int_0^{\tau} dt\, \partial_t \phi_i}_{w} - \underbrace{[\phi_{i(\tau)} + \ln P_{i(\tau)}]}_{\Phi^{eq}(\tau)} + \underbrace{[\phi_{i(0)} + \ln P_{i(0)}]}_{\Phi^{eq}(0)}$$

if eq



$$\frac{P(w)}{\tilde{P}(-w)} = e^{\left(w - \Delta\bar{\Phi}^{eq}\right)}$$

does not depend on where we stopped

$$\langle e^{-w} \rangle = e^{-\Delta\bar{\Phi}^{eq}}$$

NB: $\neq$ from $\left\langle e^{-(w - \Delta\phi)} \right\rangle = 1$

$$\langle w \rangle - \Delta\phi^{eq} \geq \langle w - \Delta\phi \rangle \geq 0$$

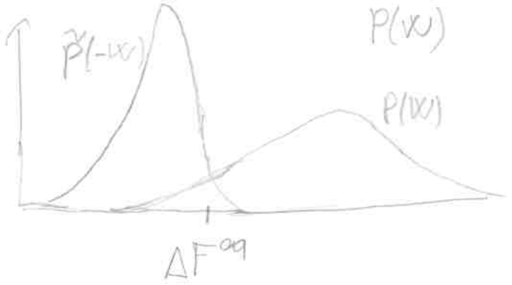
because $\underbrace{+\Delta\phi - \Delta\phi^{eq}}_{\geq 0}$

$$\langle e^{-\Sigma_a} \rangle = \langle e^{-\Sigma_{na}} \rangle = 1$$

Two experiments

1)

Bustamante [Science 2002
Nature 2005



2) Hiromaya Science (2006)
Garrard PRL (2006)

$$\frac{P(n)}{P(-n)} \overset{ss}{=} e^{\beta \Delta\mu\, n}$$

Macroscopic ST

$\vec{m} = (m_1, m_2, \dots m_N)$
occupation number vetor

①

$i = 1, \dots N$ states

$$\vec{m} \to \vec{m} + \vec{\Delta}_\rho$$

$$\begin{pmatrix} m_1 \\ m_2 \\ \vdots \\ m_N \end{pmatrix} \to \begin{pmatrix} m_1 + \Delta_\rho^1 \\ m_2 + \Delta_\rho^2 \\ \\ m_N + \Delta_\rho^3 \end{pmatrix}$$

$$d_t P(m) = \sum_\rho \left[R_{-\rho}(m+\Delta_\rho) P(m+\Delta_\rho, t) - R_\rho(m) P(m,\right.$$
$$= \sum_\rho \left[R_\rho(m-\Delta_\rho) P(m-\Delta_\rho, t) - R_\rho(m) P(m,t\right.$$

$$\Sigma_\rho(m) \equiv \ln \frac{R_\rho(\bar{m})}{R_{-\rho}(\bar{m}+\Delta_\rho)} = -\phi(\bar{m}+\bar{\Delta}_\rho) + \phi(\bar{m} + a_\rho$$

$$a_\rho = \bar{X}_\rho \cdot \bar{\delta}_{mc}$$

$$\Delta_{-\rho} = \Delta_\rho$$
$$X_{-\rho} = -X_\rho$$
$$a_{-\rho} = a_\rho$$

$$\Sigma_{-\rho}(\bar{m}+\bar{\Delta}_\rho) = -\phi(\bar{m} + \cancel{\bar{\Delta}_{-\rho}} + \cancel{\bar{\Delta}_\rho}) + \phi(\bar{m}+\Delta_\rho - a_\rho$$
$$= -\Sigma_\rho(\bar{m})$$

$$J_\rho(t) = \sum_k \delta_{\rho\rho(t)} \delta(t-t_k)$$

$$\dot\Sigma(t) = \dot\Sigma_e(t) + \underbrace{d_t S(m(t),t)},$$
$$= \sum_\rho J_\rho(t) \Sigma_\rho(m(t)) - d_t S_{int}(m(t)) + d_t \left[S_{int}(m(t)) - \ln P(m(t),t) \right]$$
$$= \sum_\rho J_\rho(t) \ln \frac{R_\rho(m(t)) \; P(m(t),t)}{R_{-\rho}(m(t)+\Delta_{\rho(t)}) P(m(t)+\Delta_{\rho(t)}, t)} + d_t \ln P(m(t),t)$$

$$\langle \dot{I} \rangle = \sum_{m\rho} R_\rho(m) P(m,t) \ln \frac{R_\rho(m) P(m,t)}{R_{-\rho}(m+\Delta_\rho) P(m+\Delta_\rho,t)}$$
$$= \sum_{m\rho>0} \left[R_\rho(m) P(m,t) - R_{-\rho}(m+\Delta_\rho) \underset{P(m+\Delta_\rho,t)}{\wedge} \right] \ln \frac{R_\rho(m) P(m,t)}{R_{-\rho}(m+\Delta_\rho) P(m+\Delta_\rho,t)} \geq$$

$$\langle \dot{\tilde\Sigma} \rangle = \sum_{\substack{m\,\rho>0 \\ \rho:\Delta_\rho=\tilde\Delta_\rho}} \quad (R_\rho \to \tilde{R}_\rho)$$

$$\tilde{R}_\rho(m) = \sum_{\underbrace{\rho:\Delta_\rho=\tilde\Delta_\rho}} R_\rho(m)$$

→ all jumps of same size.

Other splittings :

$$\overset{\circ}{\dot{\Sigma}}(t) = \underset{\displaystyle\sum_s J_s(t)\, a_s}{\underset{\parallel}{\overset{\circ}{\dot{\Sigma}}_{mc}}} + \underset{\displaystyle\partial_t \Phi(m,t)\Big|_{m=m(t)}}{\underset{\parallel}{\dot{\Sigma}_d}} - d_t\left[\Phi(m(t),t) + \ln P(m(t),t)\right]$$

$$\overset{\circ}{\dot{\Sigma}}(t) = \overset{\circ}{\dot{\Sigma}}_a + \dot{\Sigma}_{ma}$$

$$\dot{\Sigma}_a = \sum_s J_s(t)\left(\underbrace{\sum_s (t) + \ln \frac{P_t^{ss}(m(t))}{P_t^{ss}(m(t)+\Delta_s)}}\right)$$

$$\dot{\Sigma}_{ma} = -d_t \ln P(m(t),t) - \sum_s J_s(t) \ln \frac{P_t^{ss}(m(t))}{P_t^{ss}(m(t)+\Delta_s)}$$

$$= -d_t \ln \frac{P(m(t),t)}{P^{ss}(m(t),t)} - \partial_t \ln P^{ss}_{(m,t)}\Big|_{m=m}$$

$$R_s(m) = \underset{\displaystyle\underset{\displaystyle\Gamma_{-s}(m+\Delta_s)}{\underset{\parallel}{\sqrt{R_s(m)\, R_{-s}(m+\Delta_s)}}}}{\underset{|||}{\overset{\text{Symmetric part}}{\overset{\Uparrow}{\Gamma_s(m)}}}} \; \underbrace{e^{\frac{1}{2}\left(-\Phi(m+\Delta_s) + \Phi(m) + a_s\right)}}_{\displaystyle\underset{\displaystyle\sqrt{\frac{R_s(m)}{R_{-s}(m+\Delta_s)}}}{\parallel}}$$

$$\Lambda(m) \equiv \sum_s \Big[\underset{\text{entrance rate}}{R(m-\Delta_s)} - \underset{\text{exit rate}}{R_s(m)}\Big] \qquad \text{inflow rate in } m$$

$$\ln \frac{R_s(m)\, P_t^{ss}(m)}{R_{-s}(m+\Delta_s)\, P_t^{ss}(m+\Delta_s)} \equiv \ln \frac{R_s(m)}{R_s^+(m)}$$

Give examples : CRNs Potts E circuits

Macroscopic limit

$$c = \frac{m}{V} \qquad \begin{matrix} m \to \infty \\ V \to \infty \end{matrix}$$

$$\phi(c) = \lim_{V\to\infty} \frac{\Phi(m)}{V}$$

$$r_s(c) = \lim_{V\to\infty} \frac{R_s(m)}{V} \overset{\circledast}{=} \gamma_s(c)\ e^{1/2\left[-\Delta_s \cdot \partial_c \phi(c) + a_s\right]}$$

where $\gamma_s(c) = \lim_{V\to\infty} \frac{\Gamma_s(m)}{V} = \gamma_{-s}(c)$

$$r_{-s}(c) = \gamma_s(c)\ e^{-1/2\left[-\Delta_s \cdot \partial_c \phi(c) + a_s\right]}$$

$$\sigma_s(c) = \lim_{V\to\infty} \Sigma_s(m) = \ln \frac{r_s(c)}{r_{-s}(c)} = -\Delta_s \cdot \partial_c \phi(c) + a_s$$

$\circledast$
$$-\Phi(m+\Delta_s) + \Phi(m) = V\left(\frac{\Phi(m)}{V} - \frac{\Phi(m+\Delta_s)}{V}\right)$$
$$= V\left(\phi(c) - \phi(c+\tfrac{\Delta_s}{V})\right) = -V\frac{\partial\phi}{\partial c}\frac{\Delta_s}{V} = -\Delta_s \cdot \partial_c \phi(c)$$

$$\lim_{V\to\infty} \frac{\Gamma_{-s}(m+\Delta_s)}{V} = \gamma_{-s}(c+\tfrac{\Delta_s}{V}) = \gamma_{-s}(c) + \underbrace{\frac{\partial\gamma}{\partial c}\frac{\Delta_s}{V}}_{\to 0}$$

prob density

$$p(c,t) = V^N P(m,t)$$

$$V^N \partial_t P(m,t) = V \sum_s \left[\frac{R_s(m-\Delta_s)}{V} V^N P(m-\Delta_s,t) - \frac{R_s(m)}{V} V^N P(m,t)\right]$$

$$\partial_t p(c,t) = V \sum_s \left[r_s(c-\tfrac{\Delta_s}{V})\, p(c-\tfrac{\Delta_s}{V},t) - r_s(c)\, p(c,t)\right]$$

$$p(c,t) \asymp e^{-VI(c,t)} \qquad \text{large deviation}$$

$$-\cancel{V}\partial_t I(c,t)\, \cancel{e^{-VI(c,t)}} = \cancel{V} \sum_s \left(r(c-\tfrac{\Delta_s}{V})\, e^{-V\left[\cancel{I(c)} - \frac{\Delta_s}{V}\cdot\frac{\partial I}{\partial c}\right]} - r_s(c)\, \cancel{e^{-VI(c)}} \right)$$

$$-\partial_t I(c,t) = \sum_s \left(e^{+\Delta_s \cdot \boxed{\partial_c I}} - 1\right) r_s(c) \qquad \text{Hamilton-Jacobi eq.}$$

$$-\partial_t I = H(c, \underset{\text{"momentum" } \pi}{\underset{\shortparallel}{\partial_c I}})$$

Steady state $H(c, \partial_c I_{ss}) = 0$ $\quad p^{ss}(c) \asymp e^{-V I_{ss}(c)}$

For detailed balanced $a_\varrho = 0$ $\quad r^0_\varrho(c) = e^{-\Delta_\varrho \cdot \partial_c \Phi(c)} r^0_{-\varrho}(c)$

This means
$$H(c, \partial_c I_{ss}) = 0 = \sum_\varrho \left(e^{+\Delta_\varrho \cdot \partial_c I_{ss}} - 1\right) r^0_\varrho(c)$$
$$= \sum_\varrho \left[e^{+\Delta_\varrho \cdot \partial_c I_{ss}} r^0_\varrho(c) - r^0_{-\varrho}(c)\right]$$
$$= \sum_\varrho \left[e^{\Delta_\varrho \cdot \partial_c [I_{ss} - \phi]} - 1\right] r^0_{-\varrho}(c)$$

$$\Rightarrow \quad I_{ss}(c) = \phi(c) + cte$$

if x_{eq} is min of I_{ss} : $I_{ss}(x_{eq}) = 0 \Rightarrow cte = -\phi(x_{eq})$

$$p^{eq}(c) = e^{-V[\phi(c) - \phi(x_{eq})]}$$

Einstein fluctuation formula

NB: $\sum_n e^{-\Phi(n)} \asymp e^{-V\phi(x^{eq})}$

Instantaneous ss : $H(c, \partial_c I^t_{ss}) = 0$ $\quad p^{ss}(c,t) = e^{-V I^t_{ss}(c)}$

$$r^+_\varrho(c) = \lim_{V \to \infty} \frac{R^+_\varrho(n)}{V} \equiv \lim_{V \to \infty} \frac{R_{-\varrho}(n + \Delta_\varrho)}{V} \frac{p^{ss}(n + \Delta_\varrho)}{p^{ss}(n)}$$
$$= \underline{r}_\varrho\left(c + \frac{\Delta_\varrho}{V}\right) \frac{p^{ss}\left(c + \frac{\Delta_\varrho}{V}\right)}{p^{ss}(c)} = \underline{r}_\varrho(c)\, e^{-V\left[I^{ss}\left(c + \frac{\Delta_\varrho}{V}\right) - I^{ss}(c)\right]}$$
$$= \underline{r}_\varrho(c)\, e^{-\Delta_\varrho \cdot \partial_c I^{ss}}$$

$$\frac{r_\varrho(c)}{r^+_\varrho(c)} = \frac{r_\varrho(c)}{r_{-\varrho}(c)} e^{+\Delta_\varrho \partial_c I^{ss}} = e^{\Delta_\varrho \cdot \partial_c (I^{ss} - \phi) + a_\varrho}$$

Deterministic dynamics

$$\partial_t P(c,t) = V \sum_s \left[r_s\!\left(c - \tfrac{\Delta_s}{V}\right) P\!\left(c - \tfrac{\Delta_s}{V}, t\right) - r_s(c) P(c,t) \right]$$

$$d_t \langle c \rangle = \int dc\, c\, \partial_t P(c,t) = \cancel{V} \sum_s \left[\int dc \left(\cancel{c} + \frac{\Delta_s}{\cancel{V}} \right) r_s(c) P(c,t) - \cancel{\int dc\, c\, r_s(c) P(c,t)} \right]$$

$$= \sum_s \Delta_s \langle r_s(c) \rangle$$

$$= \sum_{s>0} \Delta_s \left[\langle r_s(c) \rangle - \langle r_{-s}(c) \rangle \right]$$

Since $P(c,t) \asymp e^{-V I(c,t)}$ ⇒ narrows around global min $x(t) = \mathrm{argmin}_c\, I(c,t)$

$$I(x(t),t) = \partial_c I(x(t),t) = 0 \quad \partial_c^2 I(x(t),t) > 0$$

$$d_t x(t) = \overset{\text{drift field}}{F(x(t))} \quad \text{(typically nonlinear)}$$

where $F(c) \equiv \sum_s \Delta_s r_s(c) = \partial_\pi H(c,\pi)\big|_{\pi=0}$

$$H(c,\pi) = \sum_s \left(e^{\Delta_s \cdot \pi} - 1\right) r_s(c$$

$$\lambda(c) = \lim_{V\to\infty} \Lambda(m) = \lim_{V\to\infty} V \sum_s \left(\frac{R_s(m-\Delta_s)}{V} - \frac{R_s(m)}{V} \right)$$

$$= \lim_{V\to\infty} V \sum_s \left(r_s\!\left(c - \tfrac{\Delta_s}{V}\right) - r_s(c) \right)$$

$$= -\sum_s \Delta_s \partial_c r_s(c) = -\partial_c F(c)$$

divergence of drift field ⇒ Phase space volum contraction rate $-\sum_i \lambda_i$ Lyapunov exponents

I_{ss} is a Lyapunov fct of the det dynamics: (autonomous)

$$d_t I_{ss}(x_t) = \partial_c I_{ss} \cdot d_t x = \partial_c I_{ss} \cdot F(x)$$

$e^x - 1 \geq x$

Since $H(c, \partial_c I_{ss}) = 0 = \sum_s \left(e^{\Delta_s \cdot \partial_c I_{ss}} - 1\right) r_s(c)$

$$\geq \sum_s \Delta_s \cdot \partial_c I_{ss}\, r_s(c) = \partial_c I_{ss} \cdot F(x)$$

$$\Rightarrow d_t I_{ss}(x_t) \leq 0$$

For detailed balanced dynamics: $d_t \phi(x_t) \leq 0$

Det dynics goes down in thermo potential.

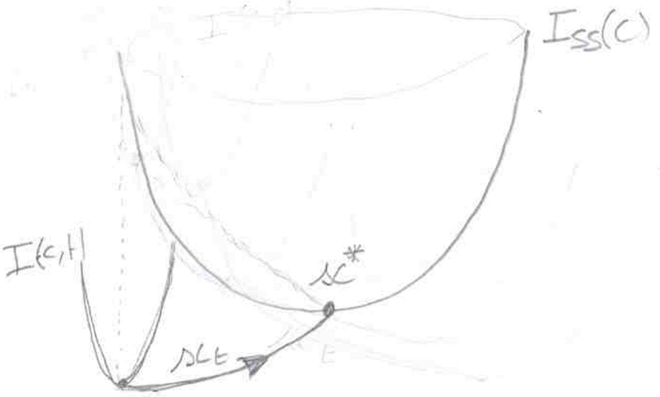
- Hamiltonian of dual dynmics: $H^+(c,\pi) = \sum_s \left(e^{\Delta_s \cdot \pi} - 1\right) r_s^+(c)$

its det drift $F^+(c) = \sum_s \Delta_s r_s^+(c) = \partial_\pi H^+(c,\pi)\big|_{\pi=0}$

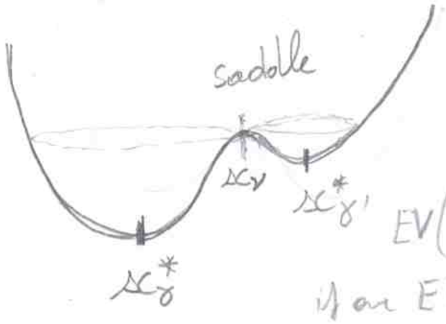
$F^+(x^*) = F(x^*) = 0$ same fixed point

$H^+(c, \partial_c I_{ss}) = -H(c, \partial_c I_{ss}) = 0$ same steady state

$d_t x^+ = F^+(x^+)$

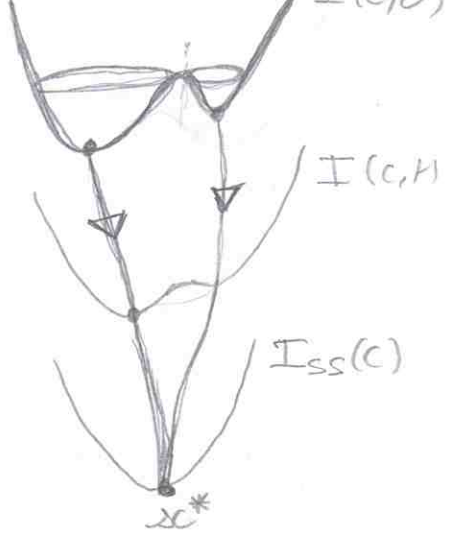


Multistability : →



Stable x^*: $EV\left(\partial_c F(x^*_\gamma)\right) < 0$

if an $EV > 0$ → unstabl x^*



- Other fixed points
- Attractors → limit cycles, → chaos

$$\text{Attractors} \begin{cases} \to \text{limit cycles} \\ \to \text{chaos} \end{cases}$$

Keizer paradox results from the fact that $t \to \infty$ and $V \to \infty$ do not commute.

I_{ss} locally non-differentiable on the saddle
- if $V \to \infty$ before $t \to \infty$
  initial condition fixes relative weigh
- if $t \to \infty$ before $V \to \infty$
  Markov jumps between attractors

Deterministic thermodynamics

$$\lim_{V\to\infty}\frac{1}{V}\underbrace{\left(-\sum_{m}\frac{P(m)}{V^N}\ln\frac{P(m)}{V^N}V^N\right)}_{S_{sh}}=-\lim_{V\to\infty}\frac{1}{V}\int dc\,P(c)\ln \overset{e^{-vI(c)}}{\overset{\uparrow}{P(c)}}+0$$

$$=\int dc\,P(c)I(c)=I(x_t)=0$$

$$\lim_{V\to\infty}\frac{1}{V}\sum_{m}P(m,t)S_{int}(m)=\int dc\,P(c,t)\,s(c)=s(x(t))$$

$$\lim_{V\to\infty}\frac{1}{V}\langle J_s(t)\rangle=\lim_{V\to\infty}\sum_m\frac{R_s(m)}{V}\frac{P(m)}{V^N}V^N=\int dc\,r_s(c)P(c)$$

$$=r_s(x(t))$$

$$\mathring{\sigma}=\lim_{V\to\infty}\frac{1}{V}\langle\mathring{\Sigma}\rangle=\lim_{V\to\infty}\frac{1}{V}\left[\sum_{m\,s}R_s(m)\frac{P(m)}{V^N}V^N\ln\frac{R_s(m)/V}{R_{-s}(m+\Delta_s)/V}+\cancel{d_t S_{sh}}\right]$$

$$=\sum_s\int dc\,r_s(c)P(c)\underbrace{\ln\frac{r_s(c)}{r_{-s}(c+\cancel{\Delta_s/V})}}_{\overset{|||}{\sigma_s(c)}}\quad \sigma_s(c)=\nearrow -\Delta_s\cdot\partial_c\phi(c)+a_s$$

$$=\sum_s r_s(x_t)\,\sigma_s(x_t)$$

$$=\sum_{s>0}\left(r_s(x_t)-r_{-s}(x_t)\right)\ln\frac{r_s(x_t)}{r_{-s}(x_t)}\geq 0$$

$$\mathring{\sigma}_{nc}=\lim_{V\to\infty}\langle\mathring{\Sigma}_{nc}\rangle=\sum_s r_s(x_t)\,a_s$$

$$\mathring{\sigma}_d=\lim_{V\to\infty}\langle\mathring{\Sigma}_d\rangle=\partial_t\phi(c,t)\big|_{c=x(t)}$$

$$\mathring{\sigma}=\mathring{\sigma}_{nc}+\mathring{\sigma}_d-d_t\phi(x_t,t)$$

$$\mathring{\sigma}=\mathring{\sigma}_a+\mathring{\sigma}_{na}\longrightarrow-\sum_s r_s(x_t)\,\Delta_s\cdot\partial_c I^{ss}(x_t)=-F(x_t)\cdot\partial_c I^{ss}(x_t)$$

$$=\partial_t I^{+}_{ss}(c)\big|_{c=x_t}-d_t I_{ss}(x$$

$$\mathring{\sigma}_a\downarrow$$

$$\sum_s r_s(x(t))\underbrace{\ln\frac{r_s(c)}{r^{+}_{s}(c)}}_{\overset{|||}{\sigma^a_s(c)=\Delta_s\cdot\partial_c(I^{ss}-\phi)+a_s=-\sigma^a_{-s}(c)}}=\sum_{s>0}\left[r_s(x_t)-r_{-s}(x_t)\right]\sigma^a_s(c)$$

$\boxed{\text{Drift-field decomposition}}$

$$\partial_t P(c) = V \sum_s \left[r_s\left(\bar{c} + \frac{\Delta_s}{V}\right) p\left(c - \frac{\Delta_s}{V}\right) - r_s(c) P(c) \right] \qquad f\left(c+\frac{\Delta_s}{V}\right) = f(c) + \sum_{k=1} \frac{\partial_c^k f}{k!}(c)\cdot\left(\frac{\Delta_s}{V}\right)^k$$

$$= V \sum_s \left[\sum_{k=1} \left(\frac{\partial_c^k}{k!} \left[r_s(c)\, p(c)\right]\right) \cdot \left(\frac{\bar{\Delta}_s}{V}\right)^k \right]$$

$$= \cancel{V} \sum_s \partial_c \sum_{k=1} \frac{\Delta_s}{\cancel{V}} \cdot \left(\frac{\bar{\Delta}_s}{V}\right)^{k-1} \frac{\partial_c^{k-1}}{k!} \left[r_s(c)\, p(c)\right]$$

$$= -\frac{\partial}{\partial c} \cdot \mathring{j}(c)$$

$$\mathring{j} = \sum_s \sum_{k=1} \frac{\bar{\Delta}_s}{V^{k-1}\, k!} \left(-\bar{\Delta}_s \cdot \bar{\partial}_c\right)^{k-1} \left[r_s(c)\, p(c)\right]$$

$$P_{ss}(c) = e^{-V I_{ss}(c)}$$

brings down V

$$\lim_{t\to\infty} \frac{j(c,t)}{P(c,t)} = \frac{j^{ss}(c)}{p^{ss}(c)} = \sum_s \sum_{k=1} \frac{\bar{\Delta}_s}{V^{k-1}\, k!}\, e^{V I_{ss}(c)} \left(-\Delta_s \cdot \partial_c\right)^{k-1} \left[r_s(c) \cdot e^{-V I_{ss}(c)}\right]$$

does not bring down enough V to survive V→∞

$|||$

$v_{ss}(c)$

probability velocity

$$= \sum_s \sum_{k=1} \bar{\Delta}_s\, r_s(c) \cdot \frac{e^{V I_{ss}(C)}}{V^{k-1}\, k!} \left(-\Delta_s \cdot \partial_c\right)^{k-1} e^{-V I_{ss}(c)}$$

$$= \sum_s \sum_{k=1} \bar{\Delta}_s\, r_s(c) \cdot \frac{\cancel{e^{V I_{ss}(C)}}}{\cancel{V^{k-1}}\, k!} \left(\Delta_s \cdot \partial_c I_{ss}\right)^{k-1} \cancel{V^{k-1}} \cancel{e^{-V I_{ss}}}$$

$$= \sum_s \bar{\Delta}_s\, r_s(c) \sum_{k=1} \frac{\left(\Delta_s \cdot \partial_c I_{ss}\right)^k}{k!\; \Delta_s \cdot \partial_c I_{ss}}$$

$$= \sum_s \bar{\Delta}_s\, r_s(c)\, \frac{e^{\Delta_s \cdot \partial_c I_{ss}} - 1}{\Delta_s \cdot \partial_c I_{ss}}$$

$$\underbrace{v_{ss}(c) \cdot \partial_c I_{ss}}_{\textcircled{1}} = \sum_s r_s(c) \left(e^{\Delta_s \cdot \partial_c I_{ss}} - 1\right) = \mathcal{H}(c, \partial_c I_{ss}) = 0$$

$$F(c) = \sum_s \Delta_s r_s(c) = v_{ss}(c) - \tilde{F}(c)$$

$$\tilde{F}(c) = \sum_s \bar{\Delta}_s r_s(c) \; \frac{e^{\Delta_s \cdot \partial_c I_{ss}} - \Delta_s \cdot \partial_c I_{ss} - 1}{\Delta_s \cdot \partial_c I_{ss}}$$

gradient -like vector field

$$\tilde{F}(c) = \underbrace{\sum_s \Delta_s \Delta_s r_s(c) \; \frac{e^{\Delta_s \cdot \partial_c I_{ss}} - \Delta_s \cdot \partial_c I_{ss} - 1}{(\Delta_s \cdot \partial_c I_{ss})^2}}_{M(c) \quad \text{"Mobility"}} \cdot \partial_c I_{ss}$$

nonlinear gradient descend

$$\frac{d\, I_{ss}(X_t)}{dt} = \frac{\partial I_{ss}}{\partial c} \cdot \frac{dc}{dt} = F(c) \cdot \partial_c I_{ss} = 0 - \tilde{F}(c) \cdot \partial_c I_{ss} \leq 0$$

$$\left[\text{since } \mathcal{H}(c, \partial_c I_{ss}) = 0 = \sum_s \big(\underbrace{e^{\Delta_s \cdot \partial_c I_{ss}} - 1}_{\geq \Delta_s \cdot \partial_c I_{ss}}\big)\, r_s(c) \right.$$

$$\left. \sum_s \Delta_s \cdot \partial_c I_{ss}\, r_s = F(c) \cdot \partial_c I_{ss} \leq 0 \right]$$

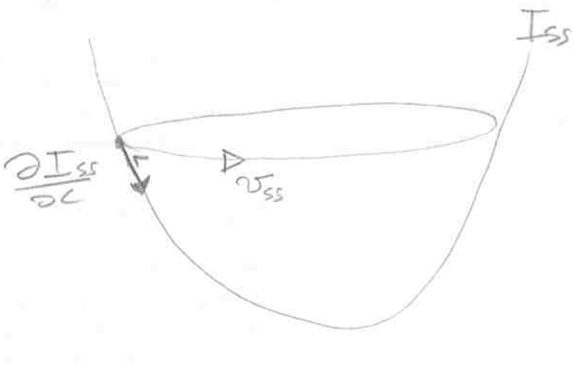
(since $j_{ss} = 0$)

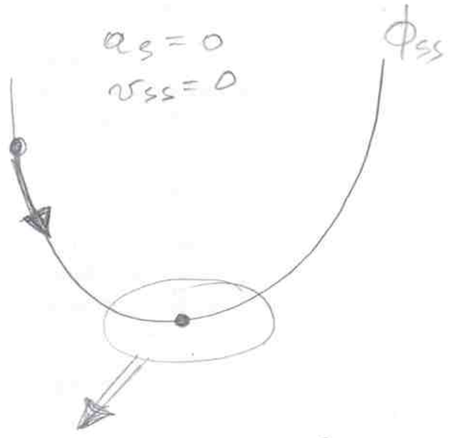
detailed balanced : $a_s = 0 \Rightarrow v_{ss} = 0 \Rightarrow I_{ss} = \phi$

$$F(c) = -\tilde{F}(c) = -\underbrace{\frac{1}{2} \sum_s \Delta_s \Delta_s \overset{o}{r}_s(c)}_{\equiv D^o(c) \text{ diffusion matrix}} \cdot \partial_c \phi + O(\partial_c^2 \phi)$$

nonlinear gradient descend

No limit cycle, no chaos





On any attractor $\tilde{F}(x^*) = 0$ since $\partial_I I_{ss}(x^*) = 0$

$\Rightarrow F(x^*(t)) = v_{ss}(x^*(t))$

For fixed point $v_{ss}(x^*) = 0$

$$\frac{d}{dt} \phi(x_t) = D^o(c) \cdot \partial_c \phi($$

Linearized dynamics and thermo (Det)

$$d_t \bar{x} = \overline{\overline{\partial_c F}}(x^*)\,(\bar{x}-\bar{x}^*) \qquad \text{because } F(x^*)=0$$

$$\xrightarrow{} \overline{\partial_c I_{ss}}(x^*) + \overline{\overline{\partial^2_c I_{ss}}}(x^*)\,(\bar{x}-\bar{x}^*) + \cancel{\tfrac{1}{2}\partial^3_c I_{ss}(x^*)\,(x-x^*)^2}$$
$$\overset{\shortparallel}{}$$

$$\to\infty \quad \langle \dot{\sigma}_{na} \rangle = -\overline{F}(x) \cdot \overline{\partial_c I}^{ss}(x)$$

$$\downarrow$$

$$\underset{\overset{\shortparallel}{0}}{\overline{F}(x^*)} + \overline{\overline{\partial_c F}}(x^*)\,(\bar{x}-\bar{x}^*) + \cancel{\tfrac{1}{2}\partial^2_c F(x^*)(x-x^*)^2}$$

$$-\overline{\overline{\frac{\partial F}{\partial c}}}^{T} \cdot \overline{\overline{\partial^2_c I_{ss}}}$$

$$\overset{\shortparallel\!\shortparallel\!\shortparallel}{}$$

$$V\to\infty \quad \langle \dot{\sigma}_{na} \rangle = (\bar{x}-\bar{x}^*)^T \cdot \overline{\overline{S}}(x^*) \cdot (\bar{x}-\bar{x}^*) \geq 0$$

$$\sinh x = \frac{e^{x}-e^{-x}}{2}$$
$$\simeq x + O(x^2)$$

$$\sum_{s>0} (\Delta_s r_s - \Delta_{s} r_{s})$$

$$\overline{F}(\bar{c}) = \sum_{s} \overline{\Delta}_s\, r_s(\bar{c}) = 2\sum_{s>0} \overline{\Delta}_s\, \gamma_s(c) \sinh\left[\tfrac{1}{2}\left(-\overline{\Delta}_s \cdot \overline{\partial_c \Phi}(c) + a_s\right)\right]$$

$$r_s = \gamma_s(c)\, e^{\frac{1}{2}\left[-\overline{\Delta}_s \cdot \overline{\partial_c\Phi} + a_s\right]} \qquad \text{whi } \gamma_s = \gamma_{-s}$$

⚠ Nonlinear fct of free

- If $\Delta_s \to$ small (continuous space) then it becomes linear.
  $a_s \to$ small
- When a_s small we can expand around x^{eq} $\qquad a_s = \tilde{X}_s \cdot \tilde{f}_{nc}$ # of nc forces

$$\overline{F}(x) = \underset{\overset{\shortparallel}{0}}{\overline{F}(x^{eq})} + \overline{\overline{\frac{\partial F}{\partial x}}}^{0 \,\to\, a_s=0}\Big|_{x^{eq}} (\bar{x}-\bar{x}^{eq}) + \overline{\frac{\partial F}{\partial a}}^{0}(x^{eq})\, X_s \cdot f_{nc}$$

$$\overline{\overline{\frac{\partial F}{\partial c}}}^{0}(x_{eq}) = -\sum_{s>0} \overline{\Delta}_s\, \gamma^0_s(x^{eq})\left(\overline{\Delta}_s \cdot \partial^2_c \Phi\right) + \underbrace{2\sum_{s>0} \Delta_s\, \partial_c \gamma_s(x_{eq}) \cdot 0}_{=0}$$

$$= -\boxed{\tfrac{1}{2}\sum_{s} \overline{\Delta}_s \overline{\Delta}_s\, \gamma^0_s(x^{eq})} \cdot \partial^2_c \Phi \qquad \text{(fluc - diss)}$$

rate of relax of eq syst ($a_s=0$)

$$\equiv \overline{\overline{D}}^0(x^{eq}) \quad \text{symmetric (Onsager)}$$

$$\overline{\frac{\partial F}{\partial a}}^{0}(x_{eq}) = \sum_{s>0} \overline{\Delta}_s\, \gamma^0_s(x_{eq}) + \underbrace{2\sum_{s} \overline{\Delta}_s \frac{\partial \gamma}{\partial a} \cdot 0}_{=0}$$

$$\overline{F}(x) \simeq \overline{\overline{D}}^0(x^{eq})\, \overline{\overline{\partial^2_c \Phi}}(x^{eq})\, (\bar{x}-\bar{x}^{eq}) + \overset{\sim}{\overline{M}}^0(x^{eq}) \cdot \tilde{f}_m$$

$$\overset{\sim}{\overline{\overline{M}}}^0(x^{eq}) = \sum_{s>0} \gamma^0_s(x^{eq})\, \overline{\Delta}_s\, \tilde{X}_s = \frac{1}{2}\sum_{s} \gamma^0_s(x^{eq})\, \overline{\Delta}_s\, \tilde{X}_s$$

⑪

$$\circledast \quad \text{In } x^* : \overline{F}(x^*) = 0 \Rightarrow -\frac{\overline{\overline{\partial F}}}{\partial x}^0 (x^{eq}) \cdot (\overline{x}^* - x^{eq}) = \overline{F}^0(x^{eq}) \; \jmath_{nc}$$

$$\Rightarrow d_t \overline{x} = \frac{\overline{\overline{\partial F}}}{\partial x}^0 (x^{eq})(\overline{x} - \cancel{\overline{x}^{eq}}) - \frac{\overline{\overline{\partial F}}}{\partial x}^0 (x^{eq})(\overline{x}^* - \cancel{\overline{x}^{eq}})$$

$$= \frac{\overline{\overline{\partial F}}}{\partial x}^0 (x^{eq})(\overline{x} - \overline{x}^*)$$

$$V \to \langle \dot{\sigma}_{na} \rangle = (x - x^*) \cdot \overline{\overline{S}}(x^*) \cdot (x - \overline{x}^*) \geq 0$$

$$\overline{\overline{S}}(x^*) = \frac{\overline{\overline{\partial F}}}{\partial x}(x^*) \cdot \partial_c^2 I_{ss}(x^*)$$

$$\overline{\overline{S}}^0(x^{eq}) = \boxed{\frac{\overline{\overline{\partial F}}}{\partial x}(x^{eq}) \cdot \partial_c^2 \phi(x^{eq})} + O(x^* - x^{eq})$$

$$= \overline{\overline{\partial_c^2}}^T \phi(x^{eq}) \; \overline{\overline{D}}^0(x^{eq}) \; \overline{\overline{\partial}}_c^2 \phi(x^{eq})$$

$$V \to \infty \quad \langle \dot{\sigma} \rangle = \frac{1}{2} \sum_s \left(r_s(x) - r_{-s}(x) \right) \underbrace{\ln \frac{r_s(x)}{r_{-s}(x)}}_{(-\Delta_s \cdot \partial_c \phi + a_s)}$$

Expend $X - x^{eq}$ and a_s

$$= \frac{1}{2} \sum_s \underset{\gamma_s^0(x^{eq}) + O(\,)^2}{\gamma_s(x)} \; e^{-\frac{1}{2}(-\Delta_s \cdot \partial_c \phi + a_s)} \left(e^{-\Delta_s \cdot \partial_c \phi + a_s} - 1 \right) (-\Delta_s \cdot \partial \phi + a_s)$$

$$= \frac{1}{2} \sum_s \gamma_s^0(x_{eq}) \left(-\Delta_s \cdot \partial_c^2 \phi(x^{eq}) \cdot (x - x^{eq}) + a_s \right) \left(-\Delta_s \cdot \partial_c^2 \phi(x^{eq})(x - x^{eq}) + a_s \right)$$

Using $x - x^{eq} = (x^* - x^{eq}) + (\overline{x} - \overline{x}^*)$

$$= \frac{1}{2} \sum_s \gamma_s^0(x_{eq}) \left(-\Delta_s \cdot \partial_c^2 \phi(x^{eq})(x^* - x^{eq}) + a_s \right) \left(-\Delta_s \cdot \partial_c^2 \phi(x^{eq})(x^* - x^{eq}) + a_s \right)$$

$$+ (x - x^*) \underbrace{\partial_c^2 \phi(x^{eq}) \overbrace{\sum_s \tfrac{1}{2} \gamma_s^0(x^{eq}) \overline{\Delta}_s \overline{\Delta}_s}^{\overline{\overline{D}}^0(x^{eq})} \partial_c^2 \phi(x^{eq})}_{\overline{\overline{S}}^0(x^{eq})} (x - x^*)$$

$$+ \underset{=0}{\text{Cross terms}} \xrightarrow{\text{using } \circledast} \frac{1}{2} \sum_s \gamma_s^0(x_{eq}) \left[-\overline{\Delta}_s \overline{\overline{\partial_c^2}} \phi(x_{eq}) \cdot (\overline{x} - \overline{x}^*) \right] \left[-\Delta_s \overline{\overline{\partial_c^2}} \phi(x_{eq})(\overline{x}^* - \overline{x}^{eq}) + \right.$$

$$(\overline{x} - \overline{x}^*) \overline{\overline{\partial_c^2}} \phi(x_{eq}) \underbrace{\overline{\overline{D}}^0(x_{eq}) \partial_c^2 \phi(x_{eq})}_{-\frac{\partial F^0}{\partial x}} (x^* - x^{eq}) = (\overline{x} - \overline{x}^*) \frac{\overline{\overline{\partial \phi}}}{\partial x} \overline{F}^0 \jmath = $$

Macroscopic fluctuations

$$\partial_t P(c,t) = V\sum_\rho \left[r_\rho\left(c-\tfrac{\Delta_\rho}{V}\right) P\left(c-\tfrac{\Delta_\rho}{V}\right) - r_\rho(c) P(c,t) \right]$$

$$= V \boxed{\sum_\rho \left[e^{-\frac{\Delta_\rho}{V}\cdot\partial_c} - 1 \right] r_\rho(c)} P(c,t)$$

$$\equiv H\left(c, -\tfrac{\partial_c}{V}\right)$$

trajectories

$$P\left[\{\overset{\downarrow}{c}(t)\} \mid c(0)\right] = \int \mathcal{D}\pi \; e^{V A[\{c(t)\},\{\pi(t)\}]}$$

→ Int will be dominated by traj that max the action fct.

↳ action functional

$$A[\{c(t)\},\{\pi(t)\}] = \int_0^\tau dt \left[\underbrace{-\pi(t)\cdot d_t c(t) + H(c(t),\pi(t))}_{} \right]$$

$$\left(= -\mathcal{L}(c(t),\dot{c}(t)) \quad \text{Lagrangian} \right).$$

$$d_t c = \partial_\pi H(c,\pi) = \sum_\rho \Delta_\rho r_\rho(c)\, e^{\Delta_\rho\cdot\pi} \qquad \pi = \frac{\partial \mathcal{L}}{\partial \dot{c}}$$

$$d_t \pi = -\partial_c H(c,\pi) = -\sum_\rho \partial_c r_\rho(c)\left(e^{\Delta_\rho\cdot\pi} - 1\right)$$

$$P[\{c(t)\} \mid c(0)] \asymp e^{V\left(A[\{c(t),\pi(t)\}] - I(c(0),0)\right)}$$

$$\downarrow$$

$$P(c(0),0)$$

EX: Propagating $\underset{I}{P(c(0),0)} \longrightarrow \underset{F}{P(c(t),t)}$

$$\left.\begin{array}{l} \pi(0) = \partial_c I(c(0),0) \\ c(t) \end{array}\right\}$$

Shooting method

$\pi(0)$, $c(0)$ $\longrightarrow$ $\pi(t)$, $c(t)$

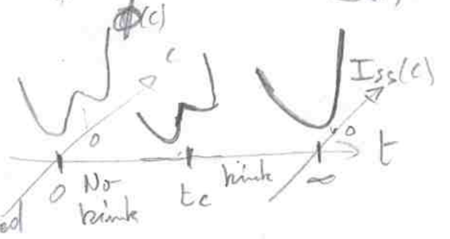
$\uparrow$ try #

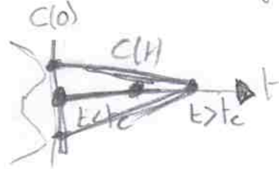
PRL 128 110603 (2022)

Ising Mean Field quench

$T_{low} \to T_{high}$

ordered disordered





Instantons: $c(0) = x^* \longrightarrow c(t)$

(autonomous)

$$H(c,\partial_c I^{ss}) = 0 \Rightarrow H(c(t),\pi(t)) = 0 \Rightarrow \pi(t) = \partial_c I^{ss}(c(t))$$

$$\Rightarrow d_t c(t) = \sum_\rho \Delta_\rho r_\rho(c(t))\, e^{\Delta_\rho\cdot\partial_c I_{ss}(c(t))} = -\sum_\rho \Delta_\rho r_{-\rho}\, e^{-\Delta_\rho\cdot\partial_c I_{ss}}$$

$$= \sum_\rho \Delta_\rho r_\rho^\dagger(c) = -F^\dagger(c)$$

$$\lim_{t\to\infty} P[c(t)=c \mid c(0)=x^*] = P_{ss}^{(\gamma)}(c) \asymp e^{-V\int_{c(0)}^{c(t)} dt\, \underset{\partial_c I_{ss}}{\underset{\downarrow}{\pi(t)}}\cdot d_t c(t)} = e^{-V\left(I_{ss}^{(\gamma)}(c) - I_{ss}^{(\gamma)}(x_\gamma^*)\right)}$$

$$\to \sum_k \delta_{s s(t)}\, \delta(t-t_k)$$

$$d_t \frac{n}{V} = \sum_s \Delta_s \frac{j_s}{V}$$

$$d_t c(t) = \sum_s \Delta_s \dot{\jmath}_s(t)$$

$$\dot\sigma(c(t)) = \sum_s j_s(t)\, \sigma_s(c(t)) + d_t I(c(t),t)$$

$$= \dot\sigma_{nd}(c(t)) + \dot\sigma_d(c(t)) - d_t(I-\phi)(c(t),t)$$

$$\underset{\displaystyle \sum_s j_s(t)\, a_s}{\shortparallel} \qquad \searrow\ -\partial_t \phi(c,t)\Big|_{c=c(t)}$$

$$\Delta_{sys}(c(t)) = I(c(t),t) - s_{int}(c(t))$$

$$\dot\sigma(c(t)) = \dot\sigma_a(c(t)) + \dot\sigma_{na}(c(t)) \geq \underbrace{d_t\left[I(c(t),t) - I^t_{ss}(c(t))\right] + \partial_t I_{ss}(c)\Big|_{c=c(t)}}_{=0 \text{ if stationary autonomous}}$$

$$\shortparallel$$

$$\sum_s j_s(t)\, \sigma_s^a$$

$$\downarrow$$

$$\underbrace{\Delta_s \cdot \partial_c\left[I_{ss}(c(t)) - \phi(c(t))\right] + a_s}_{=0}$$

iff $a_s = 0$ $\quad I^t_{ss}(c) = \phi^t(c)$

$$\lim_{V\to\infty} \langle\dot\sigma\rangle(x(t)) \geq d_t I(x(t)) + \underbrace{\partial_t I_{ss}(c)\Big|_{c=x(t)}}_{=0 \text{ autonomous}} \geq 0$$

Linear response on I

$$\partial_t I = \sum_s \left(e^{\Delta_s \cdot \partial_c I} - 1\right) r_s \qquad I = \phi + g$$

$$= -\sum_{s>0} \left[r_s \left(1 - e^{\Delta_s \partial_c I}\right) - r_{-s} \left(1 - e^{-\Delta_s \partial_c I}\right) \right]$$

$$= \sum_{s>0} \left(r_s \left(1 - e^{\Delta_s \partial_c I}\right) + \underbrace{r_{-s} \left(1 - e^{-\Delta_s \partial_c I}\right)}_{r_{-s}\, e^{-\Delta_s \partial_c I} \left(e^{+\Delta_s \partial_c I} - 1\right)} \right)$$

$$= -\sum_{s>0} \left(r_s - r_{-s} e^{-\Delta_s \partial_c I}\right) \left(1 - e^{\Delta_s \partial_c I}\right)$$

$$\overset{\text{LDB}}{=} -\sum_{s>0} r_s \left(1 - e^{+\Delta_s [\partial_c \phi - \partial_c I] - a_s}\right)\left(1 - e^{\Delta_s \partial_c I}\right)$$

Expand in g and a_s because $a_s = 0$ $\Rightarrow$

$$= + \sum_{s>0} r_s^0 \left(\Delta_s \partial_c g + a_s\right)\left(1 - e^{\Delta_s \partial_c \phi}\right) + O(g, a_s)$$

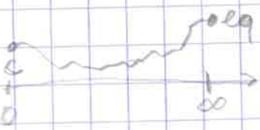
$$= \sum_{s>0} \left[r_s^0 \left(\Delta_s \partial_c g + a_s\right) - r_s^0 e^{\Delta_s \partial_c \phi} \left(\text{''} \right) \right] \qquad 0 : a_s \to 0$$

$$= \sum_{s>0} \left(r_s^0 - r_{-s}^0\right)\left(\Delta_s \partial_c g + a_s\right)$$

$$= F^0(c) \cdot \partial_c g + \underbrace{\sum_s r_s a_s}_{\dot{\sigma}_{nc}}$$

$$\partial_t I = \partial_t \phi + \partial_t g$$

SS : $I \to I^{ss}$ $\quad \partial_t \phi = 0 \qquad I_{ss} = \phi + g$



$$\int_{x(0)=c}^{x(\infty)=x_{eq}^{+}} dt \left(\underbrace{F^0(c)}_{\frac{dc}{dt}^0} \cdot \partial_c g = -\sum_s r_s a_s = -\dot{\sigma}_{nc} \right)$$

$$\cancel{I_{ss}(x_{eq})} - I_{ss}^{\gamma}(c) = \cancel{\phi(x_{eq})} - \phi(c) - \int_c^{x_{eq}} dt\, \dot{\sigma}_{nc}^0 (x(t))$$

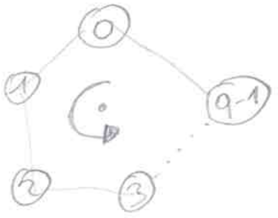
$$\phi(x_{eq})$$

$$I_{ss}(c) = \int_{x=c}^{x=x_{eq}} dt\, \dot{\sigma}^0 (x(t))$$

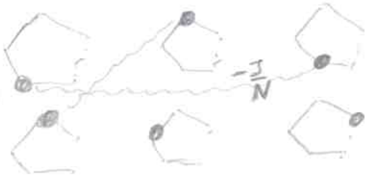
$$\partial_t g = F^0(c) \cdot \partial_c g - \partial_t \phi^0 + \dot{\sigma}_{nc}^0$$

PART III Applications

Nonequilibrium Potts model



q states units N units

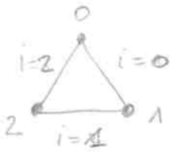


$$E(\vec{m}) = -\frac{1}{N}\sum_{i=0}^{q-1} J\,\frac{m_i(m_i-1)}{2}$$

$$S_{\text{int}}(\vec{m}) = \log \frac{N!}{m_0!\,m_1!\dots m_{q-1}!}$$

$$= -\frac{J}{2N}\left(\vec{m}\cdot\vec{m} - N\right)$$

$$\vec{m} \longrightarrow \vec{m} + \vec{\Delta}_i^{\pm} \qquad \left(\Delta_i^{\pm}\right)_j = \delta_{j\,i\pm1} - \delta_{ji} \quad \text{mod } q$$



q = 3

$$\begin{pmatrix} m_0 \\ m_1 \\ m_2 \end{pmatrix} \longrightarrow \begin{pmatrix} m_0 + (\Delta_i^{\pm})_0 \\ m_1 + (\Delta_i^{\pm})_1 \\ m_2 + (\Delta_i^{\pm})_2 \end{pmatrix}$$

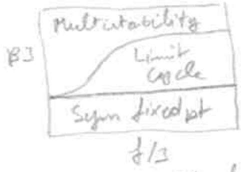
$$\Delta^+ = \begin{array}{c|ccc} & 0 & 1 & 2 \to i \\ \hline 0 & -1 & 0 & 1 \\ 1 & 1 & -1 & 0 \\ 2 & 0 & 1 & -1 \\ \downarrow j & & & \end{array}$$

$$\Delta^- = \begin{array}{c|ccc} & 0 & 1 & 2 \quad i \\ \hline 0 & -1 & 1 & 0 \\ 1 & 0 & -1 & 1 \\ 2 & 1 & 0 & -1 \\ j & & & \end{array}$$

$$F(\vec{m}) = E(\vec{m}) - \beta^{-1} S_{\text{in}}(\vec{m})$$

$$\ln \frac{R_i^{\pm}(\vec{m})}{R_{i\pm1}^{\mp}(\vec{m}+\Delta_i^{\pm})} = -\beta\left(F(\vec{m}+\Delta_i^{\pm}) - F(\vec{m}) \mp f\right)$$

$$R_i^{\pm}(\vec{m}) = m_i \begin{cases} \tau^{-1}\, e^{\frac{\beta}{2}\left[\frac{J}{N}(1\mp\xi)(m_{i\pm1} - m_i + 1) \pm f\right]} & \text{Arrhenius} \\[2ex] 2\tau^{-1}\, \dfrac{e^{\pm\beta\frac{f}{2}}}{e^{-\frac{J}{N}(m_{i\pm1} - m_i + 1)} + 1} & \text{Glauber} \end{cases}$$



Herpich Thingna ME PRX $\bar{8}$, 031056 (2018) 3 states

Herpich Cocconi Falasco ME NJP $\overline{22}$, 063005 (2020) → Macroscopic fluctuations (FT)

Meibohm ME 2401.14980 Any rate } full charact. of limit cycle close to bif.

2401.14982 Any q

chemical reactions

Rao ME JCP $\overline{149}$ 245101 (2018)

$$\sum_y \nu_{y\rho} Y_y + \sum_i \nu_{i\rho} X_i \underset{-\rho}{\overset{\rho}{\rightleftharpoons}} \sum_i \nu_{i-\rho} X_i + \sum_y \nu_{y-\rho} Y_y$$

$$R_\rho(m) = V\, k_\rho \prod_i \frac{1}{V^{\nu_{i\rho}}} \frac{m_i!}{(m_i-\nu_\rho)!} \prod_y c_y^{\nu_{y\rho}}$$

$$\Delta_\rho = \nu_{-\rho} - \nu_\rho$$

$$R_{-\rho}(m+\Delta_\rho) = V\, k_{-\rho} \prod_i \frac{1}{V^{\nu_{i-\rho}}} \frac{(m_i+\Delta_\rho^i)!}{(m_i+\underbrace{\Delta_\rho^i-\nu_{i-\rho}}_{-\nu_{i\rho}})!} \prod_y c_y^{\nu_{y-\rho}}$$

$$RT\ln\frac{R_\rho(m)}{R_{-\rho}(m+\Delta_\rho)} = \underbrace{RT\ln\frac{k_\rho}{k_{-\rho}}}_{-\sum_i \Delta_\rho^i(\mu_i^0-kT\ln c_s)-\sum_y \Delta_\rho^y(\mu_y^0-kT\ln c_s)} + \underbrace{RT\ln\prod_i V^{\Delta_\rho^i}\frac{m_i!}{(m_i+\Delta_\rho^i)!}}_{+RT(\sum_i\Delta_\rho^i)\ln V + RT\ln m_i! - RT\ln(m_i+\Delta_\rho^i)} + \underbrace{RT\ln\prod_y c_y^{-\Delta_{y\rho}}}_{-RT\Delta_\rho\cdot\ln c_y}$$

$$c_s = \frac{m_s}{V}$$

$$\Phi(m) = \sum_i\left[\mu_i^0 m_i + RT\ln m_i!\right] - RT\ln m_s\cdot\sum_i m_i$$

$$\Phi(m+\Delta_\rho) = \sum_i\left[\mu_i^0(m_i+\Delta_\rho) + RT\ln(m_i+\Delta_\rho)!\right] - RT\ln m_s\cdot\sum_i(m_i+\Delta_\rho^i)$$

$$\Phi(m)-\Phi(m+\Delta_\rho) = -\sum_i \mu_i^0\Delta_\rho^i + RT\ln m_i! - RT\ln(m_i+\Delta_\rho)! + RT\ln m_s\sum_i\Delta_\rho^i$$

$$RT\ln\frac{R_\rho(m)}{R_{-\rho}(m-\Delta_\rho)} = \Phi(m)-\Phi(m+\Delta_\rho) - \sum_y \Delta_y\,\mu_y$$

$\mu_y \to \mu_y^0 + RT\ln c_y$

$\mu_y^0 \leftarrow -RT\ln c_s$

$\ln m! = m\ln m - m$

$$\Phi(m) = \sum_i(\mu_i^0 m_i + RT m_i\ln m_i - m_i - RT\ln m_s\, m_i$$

$$\phi(c) = \frac{\Phi(m)}{V} = \sum_i(\mu_i^0 c_i + RT c_i\ln c_i V - c_i - RT\ln m_s\, c_i$$

$$= \sum_i \underbrace{(\mu_i^0 - RT\ln c_s)}_{\mu_i^\otimes} c_i + RT c_i\ln c_i - c_i)$$

$$= \sum_i c_i \underbrace{(\mu_i^\otimes + RT\ln c_i)}_{\mu_i} - \sum_i c_i$$

$$r_\rho(c) = \frac{R_\rho(m)}{V} = k_\rho \prod_i c_i^{\nu_{i\rho}} \prod_y c_y^{\nu_{y\rho}} \qquad \frac{dc_i}{dt} = \sum_\rho \Delta_\rho\, r_\rho(c)$$

No.
Date

Schlögl model:

$$\Delta_{-s} = -\Delta_s$$

$$2X + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3X \qquad B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X$$

$$\begin{array}{c|cc} & 1 & 2 \\ X & 1 & 1 \\ A & -1 & 0 \\ B & 3 & -1 \end{array}$$

$$R_1(m) = \frac{k_1}{V} a\, m(m-1)$$

$$R_{-1}(m) = \frac{k_{-1}}{V^2} m(m-1)(m-2)$$

$$R_2(m) = k_2 b$$

$$R_{-2}(m) = k_{-2} m$$

$r_1 = k_1 a c^2$
$r_{-1} = k_{-1} c^3$
$r_2 = k_2 b$
$r_{-2} = k_{-2} c$

$$\Rightarrow \frac{dx}{dt} = \sum_s \Delta_s^x r_s = r_1 - r_{-1} + r_2 - r$$

$$\frac{\dot{\sigma}}{RT} = (r_1 - r_{-1}) \ln \frac{r_1}{r_{-1}} - (r_2 - r_{-2}) \ln \frac{r_2}{r_{-2}}$$

$$\overset{ss}{=} (r_1 - r_{-1}) \ln \frac{r_1 r_{-2}}{r_{-1} r_2} \rightarrow \;= \frac{k_1 a \cancel{c^2}\, k_{-2} \cancel{c}}{k_{-1} \cancel{c^3}\, k_2 b}$$

$$\frac{k_1}{k_{-1}} = e^{\frac{\Delta_1 \mu^\circ}{RT}} \qquad \frac{k_{-2}}{k_2} = e^{-\frac{\Delta_2 \mu^\circ}{RT}}$$

$$= e^{(\mu_A - \mu_B)}$$

$\mu_A = \mu_A^\circ + RT \ln a$

$\mu_B = \mu_B^\circ + RT \ln b$

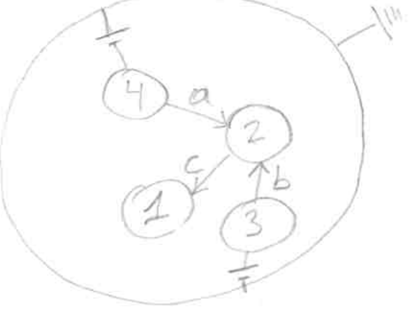
$\Delta_1 \mu^\circ = \mu_A^\circ - \mu_X^\circ$
$\Delta_2 \mu^\circ = \mu_B^\circ - \mu_X^\circ$

$$\frac{\dot{\sigma}}{RT} = \underbrace{(r_1 - r_{-1})}_{I} \underbrace{(\mu_A - \mu_B)}_{} \geq 0$$

if > I>0
if < I<0

E^- circuits

Freitas, Delvenne, ME PRX (2021)



$$\bar{q} = \begin{vmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \end{vmatrix} \qquad \bar{q} = q_e \bar{m}$$

↳ # of e^- on conductor

$$\bar{q} = \bar{\bar{C}} \cdot \bar{V}$$

↓ Maxwell capacitance matrix (Mutual + self capacitance) symmetric

$$\bar{q} \longrightarrow \bar{q} + q_e \bar{\Delta}_s$$

$$\Delta_s^i = -\delta_{i\alpha(s)} + \delta_{io(-s)}$$

$$\Delta = \begin{array}{c|ccc} & a & b & c \\ \hline 1 & 0 & 0 & 1 \\ 2 & 1 & 1 & -1 \\ 3 & 0 & -1 & 0 \\ 4 & -1 & 0 & 0 \end{array}$$

$$\begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \end{array} \begin{pmatrix} \bar{q} \\ \bar{q}_r \end{pmatrix} = \begin{pmatrix} \bar{\bar{C}} & \bar{\bar{C}}_m \\ \bar{\bar{C}}_m^T & \bar{\bar{C}}_r \end{pmatrix} \begin{pmatrix} \bar{V} \\ \bar{V}_r \end{pmatrix} \Rightarrow \begin{pmatrix} \bar{V} \\ \bar{q}_r \end{pmatrix} = \begin{pmatrix} \bar{\bar{C}}^{-1} & -\bar{\bar{C}}^{-1} C_m \\ \bar{\bar{C}}_m^T \bar{\bar{C}}^{-1} & \bar{\bar{C}}_r - \bar{\bar{C}}_m^T \bar{\bar{C}}^{-1} \bar{\bar{C}}_m \end{pmatrix} \begin{pmatrix} \bar{q} \\ \bar{V}_r \end{pmatrix}$$

↓ regulated conductors

$$\left(\begin{aligned} q &= CV + C_m V_r \longrightarrow V = C^{-1} q - C^{-1} C_m V_r \quad \circledast\circledast \\ q_r &= C_m^T V + C_r V_r \longrightarrow q_r = \underbrace{C_m^T C^{-1} q}_{\circledast} + (C_r - C_m^T C^{-1} C_m) V_r \end{aligned} \right)$$

$$E(\vec{\bar{q}}) = \frac{1}{2} \bar{q}^T \cdot \bar{V} + \frac{1}{2} \bar{V}_r^T \cdot q_r$$

$$= \frac{1}{2} \bar{q}^T \cdot \bar{\bar{C}}^{-1} \cdot \bar{q} - \cancel{\frac{1}{2} \bar{q}^T \cdot \bar{\bar{C}}^{-1}} \bar{\bar{C}}_m \cdot \bar{V}_r$$

$$+ \cancel{\frac{1}{2} V_r^T \cdot \bar{\bar{C}}_m^T} \bar{\bar{C}}^{-1} \cdot \bar{q} + \frac{1}{2} \bar{V}_r^T \cdot (\bar{\bar{C}}_r - \bar{\bar{C}}_m^T \bar{\bar{C}}^{-1} \bar{\bar{C}}_m) \cdot \bar{V}_r$$

symmetri

$$E(\bar{q} + q_e \bar{\Delta}_s) - E(\bar{q}) = \overset{0}{\cancel{\frac{1}{2}}} q_e \bar{q}^T \cdot \bar{\bar{C}}^{-1} \cdot \bar{\Delta}_s + \cancel{\frac{1}{2} q_e \Delta_s^T \cdot \bar{\bar{C}}^{-1} \cdot q}$$

$$+ \frac{1}{2} q_e^2 \bar{\Delta}_s^T \cdot \bar{\bar{C}}^{-1} \cdot \bar{\Delta}_s$$

Since we have regulated conductors, they will perform work on the system during the transition.

$$\delta W^s = \underbrace{- q_e \overline{V}_h^T \cdot \overline{\Delta}_s^r}_{\begin{array}{l}\text{work done by regulated}\\ \text{conductor to restore the}\\ \text{charge that is taken } (<0)\\ \text{or removed from it } (>0)\end{array}} \xleftarrow{} (\geq 0) \text{ pure on } r \quad + \underbrace{q_e \overline{V}_h^T \cdot \overline{\overline{C}}_m^T \overline{\overline{C}}^{-1} \cdot \overline{\Delta}_s}_{\begin{array}{l}\text{work done by regulated}\\ \text{conductors to restore the}\\ \text{charge that changes}\\ \text{by induction from a}\\ \text{transfer on a non-regulated}\\ \text{conductor (see ⊛)}\end{array}} \swarrow$$

$$\delta Q_s(\vec{q}) \equiv -RT \ln \frac{R_s(\vec{q})}{R_{-s}(\vec{q}+q_e\vec{\Delta}_s)} = -\delta Q_{-s}(\vec{q}+q_e\vec{\Delta}_s)$$

$$= E(\vec{q}+q_e\vec{\Delta}_s) - E(\vec{q}) - \delta W^s$$

$$= \phi(\vec{q}+q_e\vec{\Delta}_s) - \phi(\vec{q}) + q_e \vec{V}_h^T \vec{\Delta}_s^r$$

where $\phi(\vec{q}) = E(\vec{q}) - \vec{V}_h^T \cdot \overline{\overline{C}}_m^T \overline{\overline{C}}^{-1} \cdot \vec{q}$

Consistency check $\underset{\text{voltage}}{\overline{V}(\overline{q})} = \nabla_{\overline{q}} \phi(\overline{q}) \longrightarrow$ conservative part of the energy

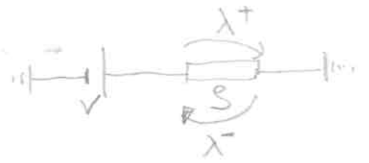
indeed $\nabla_{\overline{q}} \phi = \underbrace{\nabla_{\overline{q}} E(\overline{q})}_{\overline{\overline{C}}^{-1} \cdot \overline{q}} - \overline{\overline{C}}^{-1} \overline{\overline{C}}_m^T \cdot \overline{V}_h \underset{(**)}{=} \overline{V}$

Macro limit: elementary voltage $v_e = \frac{q_e}{C}$ where C is a characteristic capacitance

$v_e \to 0 \qquad V = \frac{1}{v_e} \to \infty$

How to get the rates:

Every channel ρ is modelled as a bipoisson process



We measure the I-V of the channel $\langle I\rangle(V)$

We impose local detailed balance (LDB)

$$\log \frac{\lambda^+(V)}{\lambda^-(V)} = \beta q_e V$$

Since $\langle I\rangle = q_e\left(\lambda_+(V) - \lambda_-(V)\right)$

$$\overset{\text{LDB}}{=} q_e\,\lambda_+(V)\left(1 - e^{-\beta q_e V}\right)$$

I-V + LDB specifies $\lambda_+(V)$ and $\lambda_-(V)$

How do we get the rates inside the circuit?

$$R_{\pm\rho}(\vec q) = \lambda_{\pm\rho}\left(\mp\frac{\delta Q_{\pm\rho}(q)}{q_e}\right)$$

$$R_\rho(\vec q) = \lambda_\rho\left(-\frac{\delta Q_\rho(\bar q)}{q_e}\right)$$

$$R_{-\rho}(\bar q) = \lambda_{-\rho}\left(\frac{\delta Q_{-\rho}(\bar q)}{q_e}\right) = \lambda_{-\rho}\left(-\frac{\delta Q_\rho(\vec q - q_e\vec\Delta_\rho)}{q_e}\right)$$

$$R_{-\rho}(\bar q + \Delta_\rho q_e) = \lambda_{-\rho}\left(\underbrace{\delta Q_{-\rho}(\bar q + \Delta_\rho q_e)/q_e}_{-\delta Q_\rho(\vec q)/q_e}\right)$$

$$-RT \ln \frac{R_{+\rho}(\bar q)}{R_{-\rho}(\bar q + \Delta_\rho q_e)} = \delta Q_\rho(\vec q)$$ They satisfy LDB

Which devices can be modelled like that? Devices that display shot noise

diodes, tunnel junctions, CMOS,

$$q(\Delta t) = q_e\left(N_+(\Delta t) - N_-(\Delta t)\right)$$

Poisson process with rate λ^+ or λ^-

$$I(\Delta t) = \frac{q(\Delta t)}{\Delta t}$$

$$\sigma_I^2(\Delta t) = \left\langle\left(I(\Delta t) - \langle I(\Delta t)\rangle\right)^2\right\rangle = \frac{q_e^2}{\Delta t}(\lambda^+ + \lambda^-)$$

$$= \frac{q_e}{\Delta t}\langle I(\Delta t)\rangle \coth\frac{\beta q_e V}{2}$$

if $\beta q_e V \gg 1$ $\quad \sigma_I^2(\Delta t) = 2q_e\langle I\rangle \overset{\Delta f}{\boxed{\frac{1}{2\Delta t}}}$ shot noise

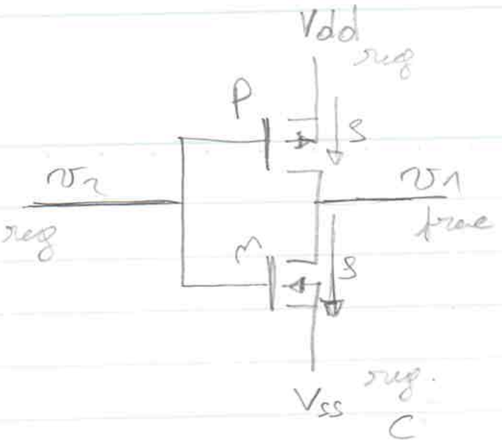
if $\beta e V \ll 1$ $\quad \sigma_I^2(\Delta t) = \frac{q_e}{\Delta t}\langle I\rangle\frac{2}{\beta q_e V} = \frac{2\langle I\rangle}{\beta V}$ Johnson -Nyquist

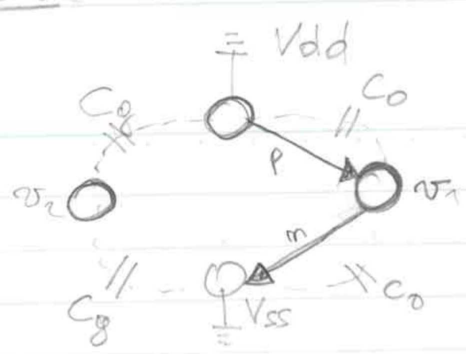
③

A. Gopal, ME, Freitas PRB (2022)

Inverter

$$\Delta = \begin{array}{c|cc|c} & p & m & \\ \hline & 1 & -1 & 1 \\ & 0 & 0 & 2 \\ & -1 & 0 & d \\ & 0 & 1 & ss \end{array}$$





$$\Delta^q_s = \begin{cases} +1 \\ -1 \end{cases}$$

$$\begin{pmatrix} q_1 \\ \hline q_2 \\ q_3 \\ q_4 \end{pmatrix} = \left(\begin{array}{c|ccc} \overbrace{2C_0}^{C} & \multicolumn{3}{c}{\overbrace{0 \quad -C_0 \quad -C_0}^{C_m}} \\ \hline 0 & 2C_g & -C_g & -C_g \\ -C_0 & -C_g & C_0+C_g & 0 \\ \underbrace{-C_0}_{C_m^T} & \multicolumn{3}{c}{\underbrace{-C_g \quad 0 \quad C_0+C_g}_{C_n}} \end{array}\right) \begin{pmatrix} v_1 \\ \hline v_2 \\ V_{dd} \\ V_{ss} \end{pmatrix}$$

$$-\frac{1}{2}(v_2\, V_{dd}\, V_{ss})\begin{pmatrix}0\\1\\1\end{pmatrix} \cdot \frac{(v_{dd}+v_{ss})}{2} C$$

$$\frac{C_0}{2}\begin{pmatrix}0&0&0\\0&1&1\\0&1&1\end{pmatrix}\begin{pmatrix}v_2\\v_{dd}\\v_{ss}\end{pmatrix} = \begin{pmatrix}0\\(v_{dd}+v_{ss})\\(v_{dd}+v_{ss})\end{pmatrix}$$

$$E(q) = \frac{1}{2}\, q \cdot C^{-1} \cdot q + \frac{1}{2} V_n^T \cdot \left(C_n - \underbrace{C_m^T C^{-1} C_m}\right) \cdot V_n \rightarrow \frac{C_0}{2}\begin{pmatrix}0&0&0\\0&1&1\\0&1&1\end{pmatrix}$$

$$= \frac{q_1^2}{4C_0} + \frac{1}{2}(v_2\ V_{dd}\ V_{ss}) \cdot \begin{pmatrix} 2C_g v_2 - C_g V_{dd} - C_g V_{ss} \\ -C_g v_2 + (C_0+C_g) V_{dd} \\ -C_g v_2 + (C_0+C_g) V_{ss} \end{pmatrix}$$

$$- \frac{1}{4} C_0 (V_{dd}+V_{ss})^2$$

$$= \frac{q_1^2}{4C_0} + C_g v_2^2 - \frac{C_g}{\cancel{2}} V_{dd} v_2 - \frac{C_g}{\cancel{2}} V_{ss} v_2 - \cancel{\frac{C_g}{2} v_2 V_{dd}} + \left(\frac{\cancel{C_0}+C_g}{2}\right) V_{dd}^2$$

$$- \cancel{\frac{C_g}{2} v_2 V_{ss}} + \left(\frac{\cancel{C_0}+C_g}{2}\right) V_{ss}^2$$

$$- \frac{1}{2} C_0 (V_{dd} + V_{ss})$$

$$- \frac{C_0}{4} V_{dd}^2 - \frac{C_0}{4} V_{ss}^2$$

$$= \frac{q_1^2}{4C_0} + C_g v_2^2 - C_g (V_{dd}+V_{ss}) v_2 + \frac{C_g}{2}(V_{dd}^2 + V_{ss}^2)$$

$$+ \frac{C_0}{4}(V_{dd}^2 + V_{ss}^2) - \frac{1}{2} C_0 V_{dd} V_{ss}$$

$$= \frac{q_1^2}{4C_0} + \frac{C_0}{4}(V_{dd}-V_{ss})^2 + \frac{C_g}{2}\left[(v_2-V_{dd})^2 + (v_2 - V_{ss})^2\right]$$

$$\phi(q) = E(q) - V_n^T \cdot C_m^T C^{-1} \cdot q = E(q) - (v_2\ V_{dd}\ V_{ss})\begin{pmatrix}0\\-C_0\\-C_0\end{pmatrix}\frac{q}{2C_0}$$

$$= E(q) + \frac{(V_{dd}+V_{ss})}{2} q$$

Rates mod

doesn't depend on q

$$R_+^p(q) = \frac{I_0}{q_e} e^{(V_{dd} - V_{th} - v_2)/mV_T}$$

$$R_-^p(q) = R_+^p(q)\, e^{-\left[\underbrace{-\frac{(q-\frac{q_e}{2})}{2C_0} + \frac{(V_{dd}-V_{ss})}{2}}_{-\delta Q_p (q-q_e)/q_e}\right]/V_T}$$

$$R_+^m(q) = \frac{I_0}{q_e} e^{(-V_{ss} - V_{th} + v_2)/mV_T}$$

$$R_-^m(q) = R_+^m(q)\, e^{-\left[\underbrace{\frac{(q+\frac{q_e}{2})}{2C_0} + \frac{(V_{dd}-V_{ss})}{2}}_{-\delta Q_m (q+q_e)/q_e}\right]/V_T}$$

+A

+A

Verifying that rates satisfy LDB

$$-\delta Q_p(q)$$

$$\parallel$$

$$RT \ln \frac{R_+^p(q)}{R_-^p(q+q_e)} = \overset{q_e}{\left(\frac{RT}{V_T}\right)} \left[-\frac{q+q_e/2}{2C_0} + \left(\frac{V_{dd}-V_{ss}}{2}\right) \right] \qquad V_T = \frac{k_B T}{q_e}$$

$$\Phi(q) - \Phi(q+q_e\Delta_s) = \underbrace{E(q) - E(q+\Delta_s q_e)} - \left(\frac{V_{dd}+V_{ss}}{2}\right) q_e$$

$$\frac{q^2-(q+q_e)^2}{4C_0}$$

$$-\frac{q_e(q_e+2q)}{4C_0}$$

$$-\frac{kT}{V_T}\left(\frac{q+q_e/2}{2C_0}\right)$$

: $-q_e V_r^T \Delta_s^r = +q_e V_{dd}$

$$\Phi(q) - \Phi(q+q_e) - q_e V_r^T \Delta_s^r = +\frac{kT}{V_T}\left[-\left(\frac{q+q_e/2}{2C_0}\right) + \left(\frac{V_{dd}-V_{ss}}{2}\right)\right] = -\delta Q_p$$

$$RT \ln \frac{R_+^m(q)}{R_-^m(q-q_e)} = \overset{q_e}{\left(\frac{RT}{V_T}\right)} \left[\frac{\left(q-\frac{q_e}{2}\right)}{2C_0} + \left(\frac{V_{dd}-V_{ss}}{2}\right) \right]$$

$$\parallel$$

$$-\delta Q_m(q)$$

$$\Phi(q) - \Phi(q-q_e) = \frac{q^2-(q-q_e)^2}{4C_0} + \frac{(V_{dd}+V_{ss})}{2}$$

$$\frac{-q_e^2+2qq_e}{4C_0}$$

$$+\frac{kT}{V_T}\left(\frac{q-q_e/2}{2C_0}\right)$$

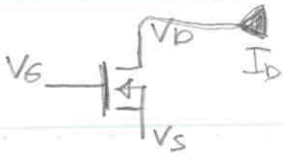
m: $-q_e V_r^T \Delta_s^n = -q_e V_{ss}$

$$\Phi(q) - \Phi(q-q_e) - q_e V_r^T \Delta_s^n = \frac{kT}{V_T}\left[\left(\frac{q-q_e/2}{2C_0}\right) + \left(\frac{V_{dd}-V_{ss}}{2}\right)\right]$$

Building rates from I-V and LDB

MOS transistors → saturation mode $V_{gat} > V_{th}$

→ subthreshold $V_G < V_{th} = \frac{kT}{q_e}$



nMOS : $\langle I_D \rangle_n = \lambda_+^n - \lambda_-^n$

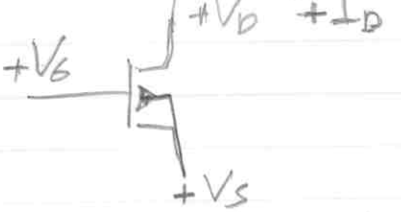
$\to v_2$ $\to V_{ss}$

$$\boxed{\lambda_+^n} = \frac{I_0}{q_e} e^{(V_G - V_S - V_{th})/nV_T}$$

$\to V_{ss}$

$$\lambda_-^n = \boxed{\frac{I_0}{q_e} e^{(V_G - V_S - V_{th})/nV_T}} e^{-(V_D - V_S)/V_T}$$

pMOS (same with inverted V and current)



$$\langle I_D \rangle_p = \lambda_+^p - \lambda_-^p$$

$\to V_{dd}$ $\to v_2$

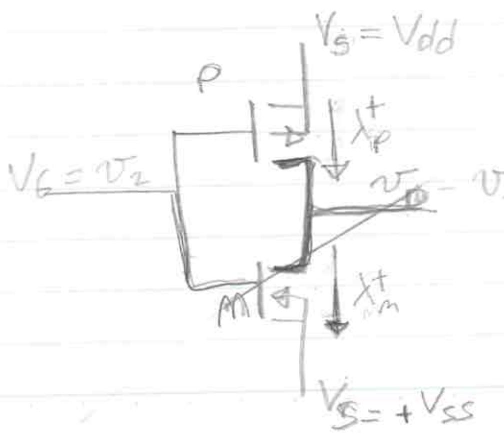
$$\boxed{\lambda_+^p} = \frac{I_0}{q_e} e^{(V_S - V_G - V_{th})/nV_T}$$

$\to V_{dd}$

$$\lambda_-^p = \boxed{\frac{I_0}{q_e} e^{(V_S - V_G - V_{th})/nV_T}} e^{-(V_S - V_D)/V_T}$$

$$-\frac{\delta Q_p(q)}{q_e} = -\left[\left(\frac{q + q_e/2}{2C_0}\right) - \left(\frac{V_{dd} - V_{ss}}{2}\right)\right]$$

$$-\frac{\delta Q_n(q)}{q_e} = +\left[\left(\frac{q - q_e/2}{2C_0}\right) + \left(\frac{V_{dd} - V_{ss}}{2}\right)\right]$$



~~$\lambda_+^p(q) = \frac{I_0}{q_e} e^{(V_{dd} - v_2 - V_{th})/nV_T}$~~

~~$\lambda_-^p(q) = \lambda_+^p(q)\, e^{-\left[\left(\frac{q + q_e/2}{2C_0}\right) - \frac{V_{dd}}{2} + \frac{V_{ss}}{2} - V_{ss}\right]/}$~~

~~$\lambda_+^n(q) = \frac{I_0}{q_e} e^{(-V_{ss} + v_2 - V_{th})/nV_T}$~~

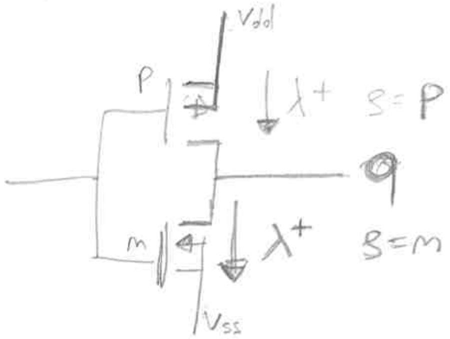
~~$\lambda_-^n(q) = \lambda_+^n(q)\, e^{-\left(\frac{q - q_e/2}{2C_0} + \frac{V_{dd}}{2} - \frac{V_{ss}}{2} - V_s\right.}$~~

$s = p$

$P+ : q \rightarrow q + q_e$

$$R_p(q) = \lambda_p^+(q)$$

$$R_{-p}(q + \underset{\overset{\|}{1}}{\Delta_p} q_e) = \lambda_p^-(q + q_e)$$



$$R_m(q) = \lambda_m^+(q)$$

$m+ : q \rightarrow q - q_e$

$$R_{-m}(q + \underset{\overset{\|}{-1}}{\Delta_m} q_e) = \lambda_m^-(q - q_e)$$

$$\Delta_s = \begin{array}{cc} p & m \\ \end{array}$$
$$\Delta_s = \begin{pmatrix} 1 & -1 \end{pmatrix}$$

$$R_p(q) = \lambda_+^p\left(V_S - V_D \rightarrow -\frac{\delta Q_p(q)}{q_e}\right) = \underbrace{\frac{I_0}{q_e} e^{(V_{dd} - v_2 - V_{th})/mV_T}}$$

$$R_{-p}(q) = \lambda_-^p\left(V_S - V_D \rightarrow \underbrace{-\frac{\delta Q_p(q - q_e)}{q_e}}\right) = \square\, e^{\left[\left(\frac{q - q_e/2}{2C_0}\right) - \frac{V_{dd}}{2} + \frac{V_{ss}}{2}\right]}$$

$$R_m(q) = \lambda_+^m\left(V_D - V_S \rightarrow -\frac{\delta Q_m(q)}{q_e}\right) = \underbrace{\frac{I_0}{q_e} e^{(v_2 - V_{ss} - V_{th})/mV_T}}$$

$$R_{-m}(q) = \lambda_-^m\left(V_D - V_S \rightarrow \underbrace{-\frac{\delta Q_m(q + q_e)}{q_e}}\right) = \square\, e^{-\left[\left(\frac{q + \frac{q_e}{2}}{2C_0}\right) + \frac{V_{dd}}{2} - \frac{V_{ss}}{2}\right]}$$

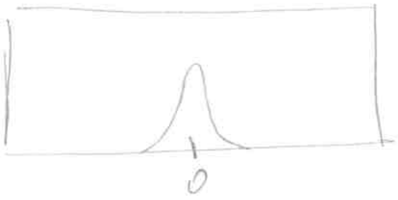
Master equation

$$d_t P(q) = P(q-q_e,t)\left(\lambda_-^n(q-q_e)+\lambda_+^p(q-q_e)\right)$$

$$P(q+q_e,t)\left(\lambda_+^n(q+q_e)+\lambda_-^p(q-q_e)\right)$$

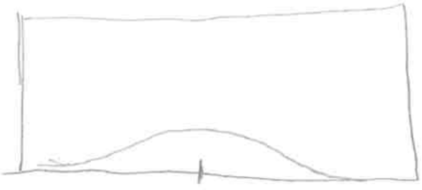
$$-P(q)\left[\lambda_-^n(q)+\lambda_+^n(q)+\lambda_-^p(q)+\lambda_+^p(q)\right]$$

$V_{ss} = -V_{dd}$



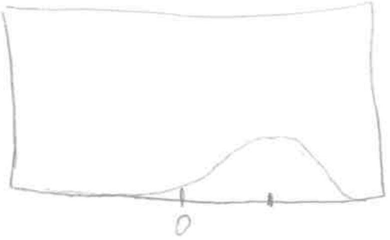
$V_{dd}/V_T = 0$

$V_2/V_{dd} = 0$



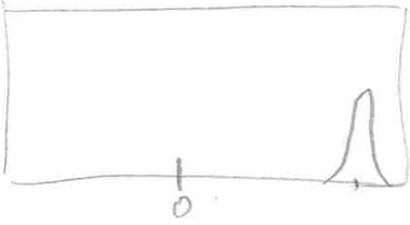
$V_{dd}/V_T = 5$

$V_2/V_{dd} = 0$



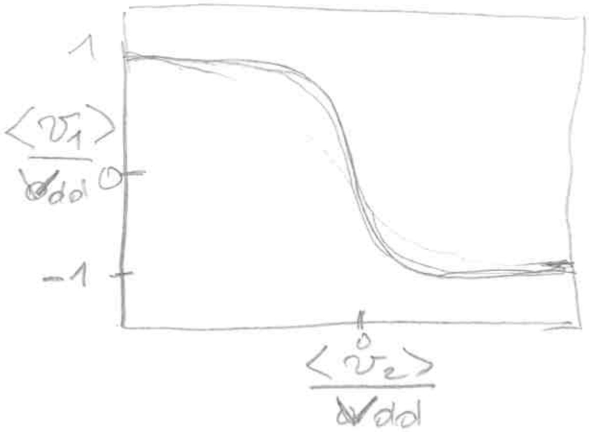
$V_{dd}/V_T = 5$

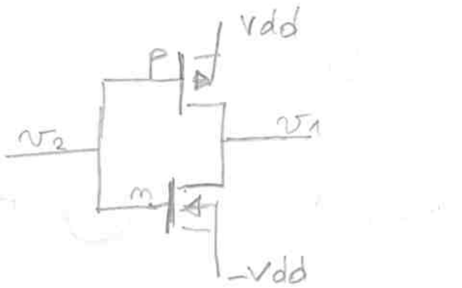
$V_2/V_{dd} = -0{,}01$



$V_{dd}/V_T = 5$

$V_2/V_{dd} = -0{,}2$





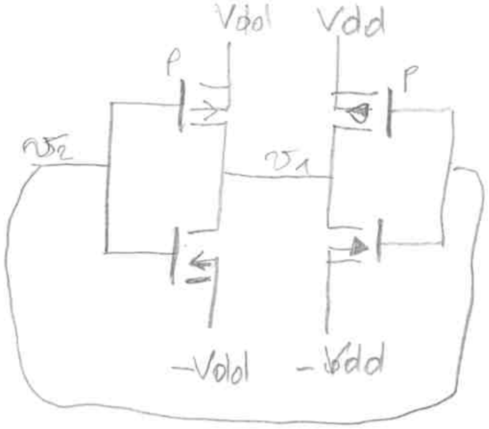
$v_2 \nearrow$ → p closes

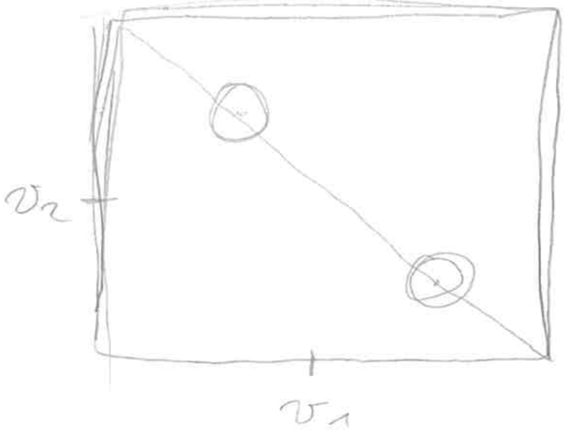
v_2 eq with $-V_{dd}$

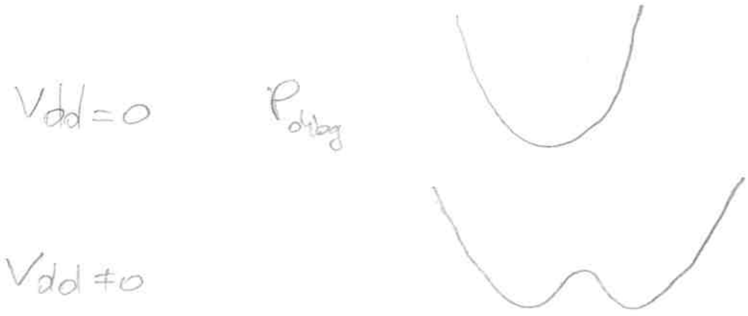
$v_2 \searrow$ → n closes

v_2 eq with V_{dd}

cMOS Memory



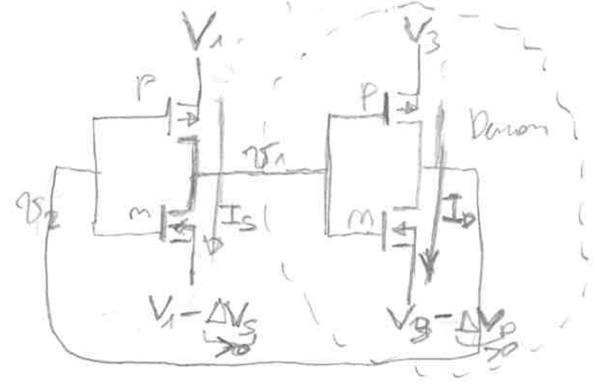


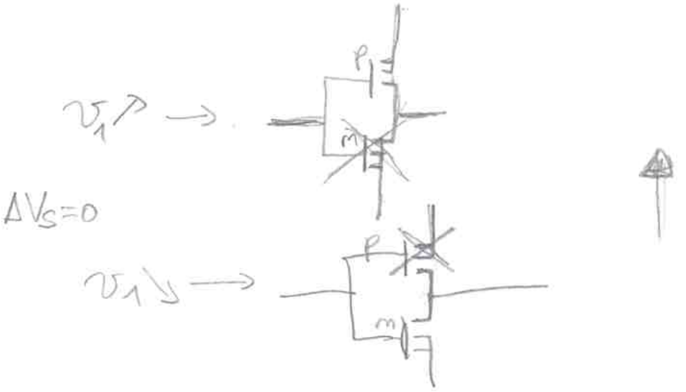


Freitas, Proesmans, ME PRE $\overline{106}$, 064121 (2022)

Maxwell demon

PRL $\overline{129}$ 120602 (2022) Freitas ME

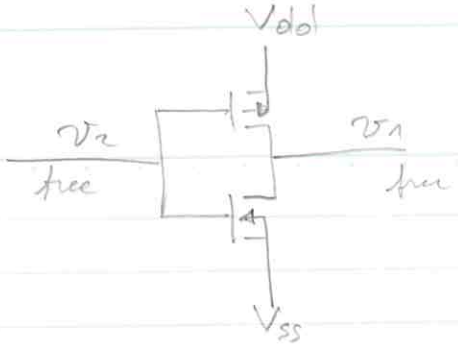




$$\underbrace{\Delta V_S}_{\geq 0}(I_S) \geq 0 \quad \text{if system alone}$$

$$\underbrace{\underbrace{\Delta V_S}_{\geq 0}(\underbrace{I_S}_{\substack{<0\\ \uparrow\\ \text{can be}}})}_{} + \underbrace{\underbrace{\Delta V_D}_{\geq 0}(\underbrace{I_D}_{\geq 0})}_{} \geq 0$$

<



$$\begin{pmatrix}q_1\\q_2\\\hline q_3\\q_4\end{pmatrix}=\left(\begin{array}{cc|cc}2C_o&0&-C_o&-C_o\\0&2C_g&-C_g&-C_g\\\hline -C_o&-C_g&C_o+C_g&0\\-C_o&-C_g&0&C_o+C_g\end{array}\right)\begin{pmatrix}v_1\\v_1\\\hline V_{dd}\\V_{ss}\end{pmatrix}$$

C $\quad C_m$

C_m^T $\quad C_r=(C_o+C_g)\mathbb{1}$

$$E(q_1,q_2)=\frac{1}{4C_o}q_1^2+\frac{1}{4C_g}q_2^2+\frac{1}{2}V_r^T\cdot\left(C_r-C_m^TC^{-1}C_m\right)V_r$$

$$C^{-1}C_m=\begin{pmatrix}\frac{1}{2C_o}&0\\0&\frac{1}{2C_g}\end{pmatrix}\begin{pmatrix}-C_o&-C_o\\-C_g&-C_g\end{pmatrix}=\begin{pmatrix}-1/2&-1/2\\-1/2&-1/2\end{pmatrix}$$

$$C_m^TC^{-1}C_m=\begin{pmatrix}C_o&C_g\\C_o&C_g\end{pmatrix}\begin{pmatrix}1/2&1/2\\1/2&1/2\end{pmatrix}=\begin{pmatrix}\frac{C_o+C_g}{2}&\frac{C_o+C_g}{2}\\\frac{C_o+C_g}{2}&\frac{C_o+C_g}{2}\end{pmatrix}$$

$$C_r-C_m^TC^{-1}C_m=\begin{pmatrix}\frac{C_o+C_g}{2}&-\frac{(C_o+C_g)}{2}\\-\frac{(C_o+C_g)}{2}&\frac{C_o+C_g}{2}\end{pmatrix}=\frac{C_o+C_g}{2}\begin{pmatrix}1&-1\\-1&1\end{pmatrix}$$

$$E(q_1,q_2)=\frac{q_1^2}{4C_o}+\frac{q_2^2}{4C_g}-\frac{C_o+C_g}{4}(V_{dd},V_{ss})\begin{pmatrix}V_{dd}-V_{ss}\\V_{ss}-V_{dd}\end{pmatrix}$$

$$=\frac{q_1^2}{4C_o}+\frac{q_2^2}{4C_g}-\frac{C_o+C_g}{4}(V_{dd}-V_{ss})^2$$

$$-V_r^T\cdot C_m^TC^{-1}\cdot q=(V_{dd}\ V_{ss})\begin{pmatrix}C_o&C_g\\C_o&C_g\end{pmatrix}\begin{pmatrix}\frac{1}{2C_o}q_1\\\frac{1}{2C_g}q_2\end{pmatrix}$$

$$=(V_{dd}\ V_{ss})\cdot\begin{pmatrix}\frac{q_1+q_2}{2}\\\frac{q_1+q_2}{2}\end{pmatrix}=\frac{1}{2}(q_1+q_2)(V_{dd}+V_{ss})$$

$$\Phi(q_1,q_2)=\underbrace{\frac{q_1^2}{4C_o}+\frac{q_2^2}{4C_g}-\frac{C_o+C_g}{2}(V_{dd}-V_{ss})^2}_{E(q_1,q_2)}+\frac{1}{2}(q_1+q_2)(V_{dd}+V_{ss})$$