

	quantum	master equ.	elements:
description of state	$ \psi(t)\rangle$ vector in Hilbert space	$\vec{P}(t)$ vector in prob. space	$P_n(t)$
dynamical eqn.	$i\hbar \frac{\partial}{\partial t}  \psi(t)\rangle = \hat{H}  \psi(t)\rangle$	$\frac{\partial}{\partial t} \vec{P}(t) = \Omega \vec{P}(t)$	
solution	$ \psi(t)\rangle = \underbrace{e^{i\hat{H}t/\hbar}}_{\text{propagator } \hat{U}(t)}  \psi(0)\rangle$	$\vec{P}(t) = e^{-\Omega t} \vec{P}(0)$	
avg. of observable	$A(t) = \langle \psi(t)   \hat{A}   \psi(t) \rangle = \langle \psi(0)   \hat{A}^H(t)   \psi(0) \rangle$	$A(t) = \vec{A} \cdot \vec{P}(t) = \vec{A}^H(t) \cdot \vec{P}(0)$	$\vec{A}^H = \vec{A}^T e^{-\Omega t}$
Heis. dynamical equation	$\frac{d}{dt} \vec{A}^H(t) = \frac{i}{\hbar} [\hat{H}, \hat{A}^H(t)]$	$\frac{d}{dt} \vec{A}^H(t) = \vec{A}^H(t) \Omega$	

↓

if the graph is connected  $\Rightarrow A_n^H(t) \xrightarrow[t \rightarrow \infty]{} A^H_s$  constant

works for any  $\vec{A}^H(t)$  : choose an "indicator" observable

$$\vec{A}^{(k)} \Rightarrow A_n^{(k)} = \delta_{nk} = \begin{cases} 1 & \text{if } n=k \\ 0 & \text{if } n \neq k \end{cases}$$

avg.  $A^{(k)}(t) = \sum_n A_n^{(k)} p_n(t) = p_k(t) \xrightarrow[t \rightarrow \infty]{} A^{(k)H_s}$

$$\Rightarrow p_k(t) \xrightarrow[t \rightarrow \infty]{} p_k^s \quad \text{stationary value}$$

some limiting value

for constant  $\Omega$  + connected graph  $\Rightarrow$  we will go to a stationary state

$$F(t) = E(t) - T S(t) \quad \dot{F}(t) = \frac{d}{dt} F(t)$$

Combined 1st + 2nd law:  $\dot{W}(t) - T \dot{I}(t) = \dot{F}(t)$

$$t \rightarrow \infty : \text{stationary state} \quad p_n(t) \rightarrow p_n^s$$

$$\dot{E}, \dot{S}, \dot{F} \rightarrow 0 \quad E(t) = \sum_n p_n(t) E_n \rightarrow \text{const.}$$

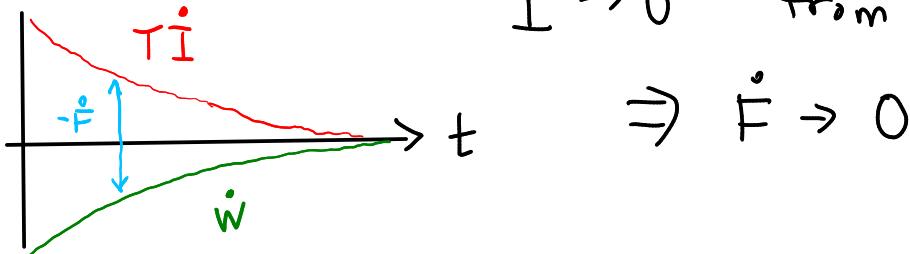
$$S(t) = -k_B \sum_n p_n(t) \ln p_n(t) \rightarrow \text{const.}$$

$$t \rightarrow \infty : \dot{W} - T \dot{I} \rightarrow 0$$

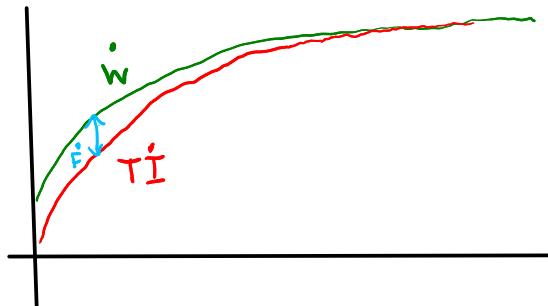
case I:  $\dot{W} < 0$  sys does net work on envir.

as  $t \rightarrow \infty$ :  $\dot{W} \rightarrow 0$  from below

$\dot{I} \rightarrow 0$  from above (ESS at  $t \rightarrow \infty$ )



case II:  $\dot{W} > 0$  as  $t \rightarrow \infty$  (continuous supply of work from outside, so that net work  $> 0$  on sys.)



$$\dot{W} > 0$$

$$\dot{I} > 0 \quad (\text{NESS})$$

$$\dot{W} - T \dot{I} \rightarrow 0 \Rightarrow \dot{W} = T \dot{I} > 0$$

$$\Rightarrow \dot{W} = P_{in} - P_{out} = \underbrace{T \dot{I}}_{P_{diss}} > 0 \quad (t \rightarrow \infty)$$

net power into sys

input power

(all > 0 terms)

output power

(all < 0 terms)

$P_{diss}$

dissipated (lost) power

anything interesting in biology:  $P_{diss} > 0$   
 $(\dot{I} > 0, \text{NESS})$

net:  $W_{nm}$  (work during  $m \rightarrow n$  trans.)

$$\dot{W} = \frac{1}{2} \sum_{nm} J_{nm}(+) W_{nm} \quad I_{nm} = k_B \ln \frac{\Omega_{nm} p_m}{\Omega_{mn} p_n}$$

$$\dot{I} = \frac{1}{2} \sum_{nm} J_{nm}(+) I_{nm} \geq 0$$

example: light-sensitive protein

$$+ \rightarrow \infty: J_{31}(+), J_{23}(+), J_{12}(+) \xrightarrow{+ \rightarrow \infty} J$$

$$J \propto (1 - e^{-\beta(E_{in} - E_{out})})$$

if  $E_{in} > E_{out} \Rightarrow J > 0 \quad (\text{NESS})$

$$\dot{W} = J_{31}(+) W_{31} + J_{12}(+) W_{12} + J_{23}(+) W_{23}^0$$

$$= J_{31}(+) E_{in} - J_{12}(+) E_{out}$$

$$\xrightarrow[+ \rightarrow \infty]{=} J E_{in} - J E_{out}$$

$$\text{if } E_{in} > E_{out}: P_{in} = J E_{in} \quad P_{out} = J E_{out}$$

$$\begin{aligned} \dot{W} &= P_{in} - P_{out} = J(E_{in} - E_{out}) = T \dot{I} > 0 \\ &= P_{diss} \end{aligned}$$