WdH ∘ Rategl.: $\dot{P}_k = \sum_j W_{kj} \cdot P_j$ $\quad \sum_k \dot{P}_k = 0 \quad -\sum_{j \neq k} W_{jk} = W_{kk}$

Übergangs-Rate von $j \to k$ $\quad W_{kj : k \neq j} \geq 0$

WS für k-ten Zustand mit Energie E_k & TZ N_k

$$\underline{\underline{W}} = \begin{pmatrix} -\sum_{j \neq 1} W_{j1} & W_{12} & W_{13} & \dots & W_{1N} \\ W_{21} & \ddots & & & \\ \vdots & & \ddots & & \\ & & & \ddots & \\ W_{N1} & & & & -\sum_{j \neq N} W_{jN} \end{pmatrix} \longrightarrow \exists \text{ } v_{ein}^{\text{wird}} \text{ stat. Zust.}$$

$$\underline{\underline{W}}\, \bar{P} = 0$$

∘ Raten z.B. aus Fermis Goldener Regel

+ ferm. R. $\quad W^{\text{rein}}_{\substack{\Delta E = +\varepsilon \\ \Delta N = +1}} = \Gamma(\varepsilon) \cdot f(\varepsilon)$ $\qquad$ Tunnelprozesse von e^-

Energiedifferenz

$$W^{\text{raus}}_{\substack{\Delta E = -\varepsilon \\ \Delta N = -1}} = \Gamma(\varepsilon)\,[1 - f(\varepsilon)]$$

+ boson. Res $\quad W^{\text{Abs.}} = \Gamma(\Delta E)\, n_B(\Delta E)$

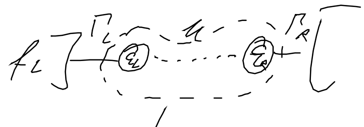
$$W^{\text{Em.}} = \Gamma(\Delta E)\,[1 + n_B(\Delta E)]$$

$$\frac{W^{\text{Abs}}}{W^{\text{Em}}} = e^{-\beta(\Delta E - \mu \Delta N)} \qquad W_{ij} \cdot \bar{P}_j = W_{ji} \cdot \bar{P}_i$$

det. Gleichgewicht

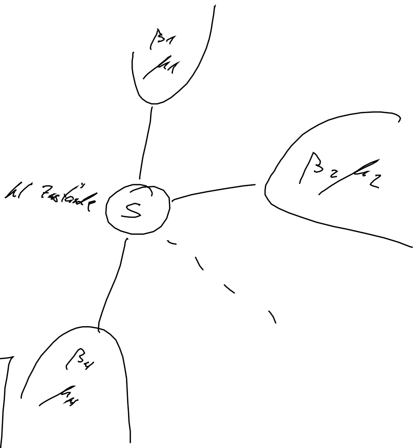
∘ Beispiele

$$W = \begin{pmatrix} -\Gamma f & \Gamma(1-f) \\ \Gamma f & -\Gamma(1-f) \end{pmatrix}$$



4x4 Ratenmatrix

4.1.3 TD von RG



• viele Reservoire

• Annahme: $W_{ij} = \sum_\nu W_{ij}^{(\nu)}$, in schw. Kopplung gut erfüllt

$$W_{i \neq j}^{(\nu)} \geq 0$$

$$\sum_i W_{ij}^{(\nu)} = 0 \quad \forall j, \nu$$

∘ lokales det. GG

$$\boxed{\frac{W_{ji}^{(\nu)}}{W_{ij}^{(\nu)}} = e^{-\beta_\nu [E_j - E_i - \mu_\nu (N_j - N_i)]}}$$

1. Hauptsatz $\langle E \rangle = \sum_i E_i \cdot P_i$

$$\frac{d}{dt}\langle E \rangle = \underbrace{\sum_i \dot{E}_i P_i}_{\dot{W}_{mech}} + \sum_{ij}\sum_\nu E_i W_{ij}^{(\nu)} P_j \qquad -\sum_{i\neq j} W_{ij}^{(\nu)}$$

$$= \dot{W}_{mech} + \sum_\nu \left[\sum_{ij: i\neq j} E_i W_{ij}^{(\nu)} P_j + \sum_j E_j W_{jj}^{(\nu)} P_j\right]$$

$$= \dot{W}_{mech} + \sum_\nu \sum_{ij} (E_i - E_j) W_{ij}^{(\nu)} \cdot P_j$$

Reservoire

Energiediff. in System

$\frac{1}{dt}$ WS für Sprung $j \to i$, geg. dass AZ j ist

$$\boxed{I_E^{(\nu)}(t) = \sum_{ij} (E_i - E_j) W_{ij}^{(\nu)} \cdot P_j(t)}$$

Energiestrom aus Res ν

$$\boxed{I_n^{(\nu)} = \sum_{ij} (N_i - N_j) W_{ij}^{(\nu)} \cdot P_j}$$

Teilchenstr. aus Res. ν

$$\boxed{\frac{d}{dt}\langle E \rangle = \frac{d}{dt} W_{mech} + \frac{d}{dt} W_{chem} + \sum_\nu \dot{Q}^{(\nu)} \quad \text{1. HS}}$$

Wärmestr. aus Res. ν

$$\frac{d}{dt} W_{chem} = \sum_\nu \mu_\nu \cdot I_n^{(\nu)}$$

$$\dot{Q}^{(\nu)} = I_E^{(\nu)} - \mu_\nu \cdot I_n^{(\nu)}$$

2. Hauptsatz

$$S = -k_B \sum_i P_i \ln P_i$$

$$\frac{d}{dt} S = -k_B \sum_i \left(\dot{P}_i \ln P_i + \cancel{P_i \frac{1}{P_i} \dot{P}_i} \right) \quad = 0$$

$$= -k_B \sum_{ij} \sum_\nu W_{ij}^{(\nu)} P_j \ln\left(P_i \frac{W_{ji}^{(\nu)}}{P_j \cdot W_{ij}^{(\nu)}} \frac{P_j \cdot W_{ij}^{(\nu)}}{W_{ji}^{(\nu)}} \right)$$

Abspalten

$$= +k_B \sum_{ij} \sum_\nu W_{ij}^{(\nu)} P_j \ln\left(\frac{P_j \cdot W_{ij}^{(\nu)}}{P_i \cdot W_{ji}^{(\nu)}} \right) + k_B \sum_{ij} \sum_\nu W_{ij}^{(\nu)} P_j \cdot \ln\left(\frac{W_{ji}^{(\nu)}}{W_{ij}^{(\nu)}} \frac{1}{P_j} \right)$$

$$= +k_B \underbrace{\sum_{ij} \sum_\nu W_{ij}^{(\nu)} P_j \ln\left(\frac{W_{ij}^{(\nu)} P_j}{W_{ji}^{(\nu)} \cdot P_i} \right)}_{\geq 0 \;\to\; \text{"}\dot{S}_i\text{"}} + \underbrace{k_B \sum_{ij} \sum_\nu W_{ij}^{(\nu)} P_j \underbrace{\ln\left(\frac{W_{ji}^{(\nu)}}{W_{ij}^{(\nu)}} \right)}_{-\beta_\nu [(E_j - E_i) - \mu_\nu (N_j - N_i)]}}_{k_B \sum_\nu \beta_\nu \underbrace{\left[I_E^{(\nu)} - \mu_\nu \cdot I_n^{(\nu)} \right]}_{\dot{Q}^{(\nu)}}}$$

$$\boxed{\begin{gathered} a_n, b_n \geq 0 \\ \sum_n a_n \ln\left(\frac{a_n}{b_n}\right) \geq a \cdot \ln \frac{a}{b} \overset{a=b}{=} 0 \\ a = \sum_n a_n \qquad b = \sum_n b_n \end{gathered}}$$

$$(n) \hat{=} (i,j) \qquad \left.\begin{aligned} a_n &\to a_{ij} = W_{ij}^{(\nu)} P_j \\ b_n &\to b_{ij} = W_{ji}^{(\nu)} P_i \end{aligned}\right\} \to a = \sum_{ij} W_{ij}^{(\nu)} P_j = b = \sum_{ij} W_{ji}^{(\nu)} P_i$$

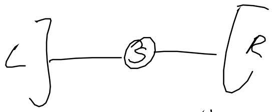
$$\boxed{\begin{aligned}&\dot S_i = \dot S - k_B \sum_\nu \beta_\nu \dot Q^{(\nu)} \ge 0\\ &\text{2. HS im Nicht-GG}\\ &\dot S_i = \dot S + \sum_\nu \dot S^{(\nu)}_{res} \ge 0\end{aligned}}$$

$$T_\nu dS_\nu = dU_\nu - \mu_\nu dN_\nu \qquad \dot Q^{(\nu)} = I_E^{(\nu)} - \mu_\nu I_M^{(\nu)}$$

$$k_B \frac{dS_\nu}{dt} = \frac{1}{T_\nu}\underbrace{\left(\frac{dU_\nu}{dt} - \mu_\nu \frac{dN_\nu}{dt}\right)}_{-\dot Q^{(\nu)}}$$

steady-state: $\dot S = 0$ $\qquad \boxed{-\sum_\nu \beta^{(\nu)} \left[I_E^{(\nu)} - \mu_\nu I_M^{(\nu)}\right] \ge 0}$

4.1.4. Stat. Transport



$$\dot S_i \to \boxed{I_E(\beta_R-\beta_L) + I_M(\beta_L\mu_L - \beta_R\mu_R) \ge 0}$$

2. HS in steady state

- 1. HS: $I_E^{(L)} + I_E^{(R)} = 0$
- Tz-Erh.: $I_M^{(L)} + I_M^{(R)} = 0$

$$\left.\begin{aligned} I_M &= +I_M^{(L)} = -I_M^{(R)}\\ I_E &= +I_E^{(L)} = -I_E^{(R)}\end{aligned}\right.$$

a.) $\mu_L=\mu_R=\mu$

$$\underbrace{(I_E - \mu I_M)}_{\text{Wärmestrom von links nach rechts}}(\beta_R-\beta_L) \ge 0$$

"Wärme fließt von heiß nach kalt"

b.) $\beta_L=\beta_R=\beta$

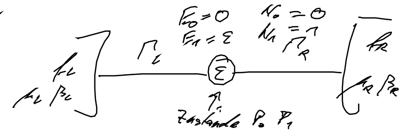
$I_M(\mu_L-\mu_R)\ge 0$ "T-Strom fließt von hohen zum niedrigen chem. Potential"

c.) $\mu_L<\mu_R$ $\quad \beta_L<\beta_R$ $\quad (T_L > T_R)$

$$\eta = \frac{-I_M(\mu_L-\mu_R)}{I_E - \mu_L I_M} = \frac{-(\beta_R-\beta_L)(\mu_L-\mu_R)I_M}{(\beta_R-\beta_L)I_E - (\beta_R-\beta_L)\mu_L I_M + (\mu_L\beta_L-\mu_R\beta_R)I_M - (\mu_L\beta_L-\mu_R\beta_R)I_M}$$

$$\le \frac{-(\beta_R-\beta_L)(\mu_L-\mu_R)I_M}{-(\mu_L\beta_L-\mu_R\beta_R)I_M - (\beta_R-\beta_L)\mu_L I_M} = 1-\frac{\beta_L}{\beta_R} = 1-\frac{T_R}{T_L} = 1-\frac{T_c}{T_h} = \eta_{CA}$$

Modell



$$\frac{d}{dt}\begin{pmatrix} P_0 \\ P_1 \end{pmatrix} = \left[\Gamma_L \begin{pmatrix} -f_L & 1-f_L \\ f_L & -(1-f_L) \end{pmatrix} + \Gamma_R \begin{pmatrix} -f_R & 1-f_R \\ f_R & -(1-f_R) \end{pmatrix}\right] \begin{pmatrix} P_0 \\ P_1 \end{pmatrix}$$

$$\bar{P}_0 = \frac{\Gamma_L (1-f_L) + \Gamma_R (1-f_R)}{\Gamma_L + \Gamma_R} \qquad \bar{P}_1 = \frac{\Gamma_L \cdot f_L + \Gamma_R \cdot f_R}{\Gamma_L + \Gamma_R}$$

$$I_M = I_M^{(L)} = \sum_{ij} (N_i - N_j)\, W_{ij}^{(L)} \bar{P}_j = (0-1)\,\Gamma_L (1-f_L) \cdot \bar{P}_1 + (1-0)\,\Gamma_L \cdot f_L \cdot \bar{P}_0$$

$$= \frac{\Gamma_L \cdot \Gamma_R}{\Gamma_L + \Gamma_R} (f_L - f_R) \qquad f_\alpha = \frac{1}{e^{\beta_\alpha (\varepsilon - \mu_\alpha)} + 1}$$

$$I_E = \varepsilon \cdot I_M$$

$$\gamma = \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R}$$