

Wdh • Rategl.:  $\dot{P}_k = \sum_j W_{kj} \cdot P_j$   $\sum_k \dot{P}_k = 0$   $-\sum_{i \neq k} W_{ik} = W_{kk}$   
↑ ↑ ↑  
Übergangsr. von j → k  $W_{ij, i \neq j} \geq 0$   
 WS für N-ten Zustand mit Energie  $E_N$  & TZ  $A_N$

$$W = \begin{pmatrix} -\sum_{i \neq 1} W_{i1} & W_{12} & W_{13} & \dots & W_{1N} \\ W_{21} & \dots & \dots & \dots & \dots \\ \vdots & \dots & \dots & \dots & \dots \\ W_{N1} & \dots & \dots & \dots & -\sum_{i \neq N} W_{iN} \end{pmatrix} \rightarrow \text{für stat. Zust.}$$

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

• Rateu z. B. aus Fermis Goldenen Regel

+ fern. R.  $W_{E \rightarrow E'}^{ferm} = \Gamma(\epsilon) \cdot f(\epsilon)$  Tunnelprozesse von  $e^-$   
↑  
Energieerhaltung  
 $W_{E \leftarrow E'}^{ferm} = \Gamma(\epsilon) [1 - f(\epsilon)]$

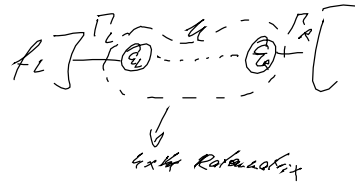
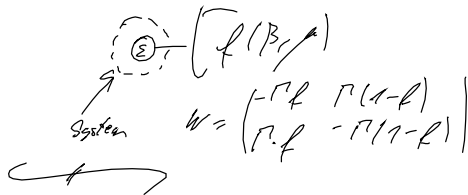
+ boson. Res  $W^{bos} = \Gamma(\Delta E) n_B(\Delta E)$   
 $W^{bos} = \Gamma(\Delta E) [1 + n_B(\Delta E)]$

$$\frac{W^{bos}}{W^{ferm}} = e^{-\beta(\Delta E - \mu)}$$

$$W_{ij} \bar{P}_j = W_{ji} \bar{P}_i$$

det. Gleichgewicht

• Beispiele

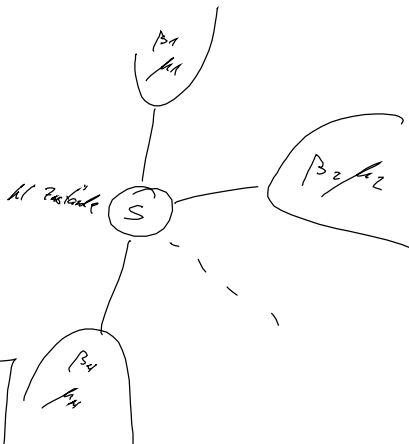


4.13 TD von RG

- viele Reservoirs
- Annahme:  $W_{ij} = \sum_k W_{ij}^{(k)}$ , zu sehr komplex, geht nicht
- $W_{ij}^{(k)} \geq 0$
- $\sum_j W_{ij}^{(k)} = 0 \quad \forall i, k$

• lokales det. GG

$$\frac{W_{ij}^{(k)}}{W_{ji}^{(k)}} = e^{-\beta \nu [E_j - E_i - \mu (N_j - N_i)]}$$



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

$$\begin{aligned} \frac{d}{dt} \langle E \rangle &= \sum_i \dot{E}_i P_i + \sum_{ij} E_i W_{ij}^{(M)} P_j - \sum_{ij} W_{ij}^{(M)} E_j P_i \\ &= \dot{W}_{\text{heat}} + \sum_{ij} \left[ \sum_{ii: i \neq j} E_i W_{ij}^{(M)} P_i + \sum_j E_j W_{ij}^{(M)} P_j \right] \\ &= \dot{W}_{\text{heat}} + \sum_{ij} \sum_{ii} (E_i - E_j) W_{ij}^{(M)} P_j \end{aligned}$$

Reservoir  $\uparrow$  Energiefluss in System  $\uparrow$  1. KS für Sprung  $j \rightarrow i$ , geg. dass 1. KS ist

$$\overline{I_E}^{(M)} = \sum_{ij} (E_i - E_j) W_{ij}^{(M)} \cdot P_j^{(M)}$$

Energiestrom aus Res. v

$$\overline{I_A}^{(M)} = \sum_{ij} (N_i - N_j) W_{ij}^{(M)} \cdot P_j$$

Teilchenstr. aus Res. v

$$\frac{d}{dt} \langle E \rangle = \frac{d}{dt} W_{\text{heat}} + \frac{d}{dt} W_{\text{chem}} + \sum_{ij} \dot{Q}_{ij}^{(M)} \quad \text{1. KS}$$

$\uparrow$  Wärmestr. aus Res. v

$$\frac{d}{dt} W_{\text{chem}} = \sum_{ij} \mu_j \cdot \overline{I_A}^{(M)}$$

$$\dot{Q}^{(M)} = \overline{I_E}^{(M)} - \mu \cdot \overline{I_A}^{(M)}$$

2. Hauptsatz

$$S = -k_B \sum_i P_i \ln P_i \quad \rightarrow \text{Z}$$

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

$$= -k_B \sum_{ij} \sum_{ii} W_{ij}^{(M)} P_j \ln \left( P_j \frac{W_{ij}^{(M)}}{P_j \cdot W_{ij}^{(M)}} \frac{P_j \cdot W_{ij}^{(M)}}{W_{ij}^{(M)}} \right)$$

Abspalten  $\downarrow$

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

$\rightarrow$  "S"  $\rightarrow$   $-k_B \sum_{ij} (E_i - E_j) - \mu (N_i - N_j)$

$$\begin{aligned} a_n, b_n \geq 0 \\ \sum_n a_n \ln \left( \frac{a_n}{b_n} \right) \geq a \ln \frac{a}{b} \\ a = \sum_n a_n \quad b = \sum_n b_n \end{aligned}$$

$$k_B \sum_{ij} \mu_j \left[ \overline{I_E}^{(M)} - \mu \cdot \overline{I_A}^{(M)} \right]$$

$\dot{Q}^{(M)}$

$$\left. \begin{aligned} (n) \equiv (ij) \\ a_n \rightarrow a_{ij} = W_{ij}^{(M)} P_j \\ b_n \rightarrow b_{ij} = W_{ij}^{(M)} P_i \end{aligned} \right\} \rightarrow a = \sum_{ij} W_{ij}^{(M)} P_j = b = \sum_{ij} W_{ij}^{(M)} P_i$$

$$\left. \begin{aligned} \dot{S}_i &= \dot{S} - k_B \sum_V \beta_V \dot{Q}^{(V)} \geq 0 \\ \text{2. HS in Nicht-GG} \\ \dot{S}_i &= \dot{S} + \sum_V \dot{S}_{res}^{(V)} \geq 0 \end{aligned} \right\}$$

$$T_V dS_V = dW_V - p_V dW_V$$

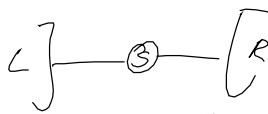
$$k_B \frac{dS_V}{dt} = \frac{1}{T_V} \left( \frac{dW_V}{dt} - p_V \frac{dW_V}{dt} \right) - \dot{Q}_V^{(in)}$$

$$\dot{Q}^{(V)} = \bar{I}_E^{(V)} - p_V \bar{I}_A^{(V)}$$

steady-state:  $\dot{S} = 0$

$$\left[ - \sum_V \beta^{(V)} \left( \bar{I}_E^{(V)} - p_V \bar{I}_A^{(V)} \right) \geq 0 \right]$$

#### 4.1.4. Stat. Transport



$$S_i \rightarrow \left[ \bar{I}_E (\beta_R - \beta_L) + \bar{I}_A (\beta_L p_L - \beta_R p_R) \geq 0 \right]$$

• AHS:  $\bar{I}_E^{(L)} + \bar{I}_E^{(R)} = 0$

• TE-Erh.:  $\bar{I}_A^{(L)} + \bar{I}_A^{(R)} = 0$

$$\left. \begin{aligned} \bar{I}_A &= +\bar{I}_R^{(L)} = -\bar{I}_R^{(R)} \\ \bar{I}_E &= +\bar{I}_E^{(L)} = -\bar{I}_E^{(R)} \end{aligned} \right\}$$

2. HS in steady state

a)  $p_L = p_R = p$

$$\left( \bar{I}_E - p \bar{I}_A \right) (\beta_R - \beta_L) \geq 0$$

Wärmestrom von links nach rechts "Wärme fließt von heiß nach kalt"

b)  $p_L = p_R = p$

$$\bar{I}_A (p_L - p_R) \geq 0$$

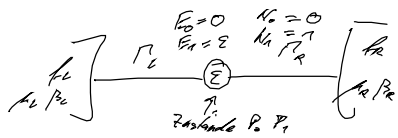
"T-Strom fließt von hohen zu niedrigen dem Potential"

c)  $p_L < p_R \quad \beta_L < \beta_R \quad (T_L > T_R)$

$$\eta = \frac{-\bar{I}_A (p_L - p_R)}{\bar{I}_E - p_L \bar{I}_A} = \frac{-(\beta_R - \beta_L) (p_L - p_R) \bar{I}_A}{(\beta_R - \beta_L) \bar{I}_E (\beta_R - \beta_L) p_L \bar{I}_A + (p_L \beta_L - p_R \beta_R) \bar{I}_A - (p_L \beta_L - p_R \beta_R) \bar{I}_A}$$

$$= \frac{-(\beta_R - \beta_L) (p_L - p_R) \bar{I}_A}{-(p_L \beta_L - p_R \beta_R) \bar{I}_A - (\beta_R - \beta_L) p_L \bar{I}_A} = 1 - \frac{\beta_L}{\beta_R} = 1 - \frac{T_R}{T_L} = 1 - \frac{T_C}{T_A} = \eta_{CA}$$

Handwritten: *Handwritten*

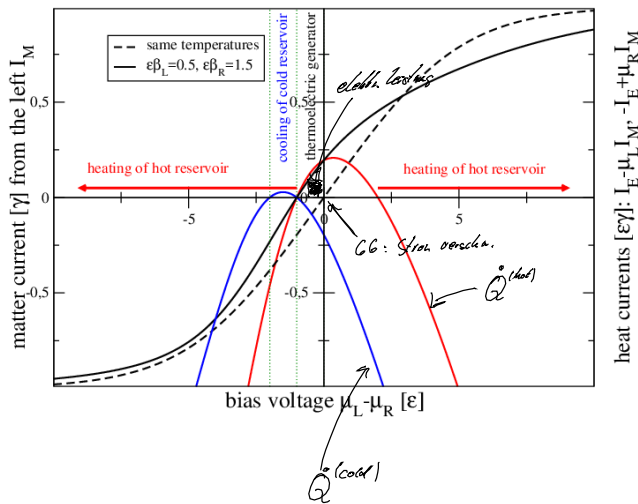


$$\frac{d}{dt} \begin{pmatrix} P_0 \\ P_1 \end{pmatrix} = \left[ \Gamma_L \begin{pmatrix} -f_L & 1-f_L \\ f_L & -(1-f_L) \end{pmatrix} + \Gamma_R \begin{pmatrix} -f_R & 1-f_R \\ f_R & -(1-f_R) \end{pmatrix} \right] \begin{pmatrix} P_0 \\ P_1 \end{pmatrix}$$

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

$$\begin{aligned} \bar{I}_M &= \bar{I}_M^{(M)} = \sum_{ij} (N_i - N_j) W_{ij}^{(M)} \bar{P}_i = (0-1)\Gamma_L(1-f_L)\bar{P}_1 + (1-0)\Gamma_L f_L \bar{P}_0 \\ &= \frac{\Gamma_L \Gamma_R}{\Gamma_L + \Gamma_R} (f_L - f_R) \quad f_\alpha = \frac{1}{e^{\beta_\alpha(\epsilon - \mu_\alpha)} + 1} \end{aligned}$$

$$\bar{I}_E = \epsilon \cdot \bar{I}_M$$



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