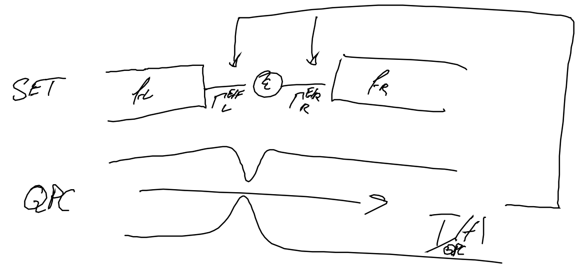
WdH



$$\underline{P}(t+\Delta t) = \left[e^{\mathcal{L}_E \Delta t} \cdot \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + e^{\mathcal{L}_F \Delta t} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \right] \underline{P}(t)$$

$$\frac{\underline{P}(t+\Delta t) - \underline{P}(t)}{\Delta t} \approx \dot{\underline{P}} = \mathcal{L}_{eff} \cdot \underline{P}(t)$$

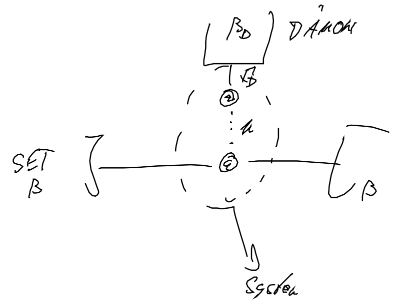
$$\mathcal{L}_{eff} = \sum_{\alpha \in \{L,R\}} \begin{pmatrix} -\Gamma_\alpha^E \cdot f_\alpha & +\Gamma_\alpha^F (1-f_\alpha) \\ +\Gamma_\alpha^E \cdot f_\alpha & -\Gamma_\alpha^F (1-f_\alpha) \end{pmatrix}$$

Verletzung det. GG

Umwandlung Info $\rightarrow$ elektr. Leistung $\beta = \beta_L = \beta_R$ $\quad \mu_L \neq \mu_R \quad \mu_L - \mu_R = V$

$$P = -\bar{I}_M^{(L)} (\mu_L - \mu_R) = -\dot{W}_{chem}$$

- autonome Variante



$T_D < T_{SET}$

$\Gamma_L(\varepsilon+U) \gg \Gamma_R(\varepsilon+U)$

$\Gamma_L(\varepsilon) \ll \Gamma_R(\varepsilon)$

$\boxed{\Gamma_D(\varepsilon), \Gamma_D(\varepsilon+U) \gg \Gamma_{LR}(\varepsilon+U), \Gamma_{LR}(\varepsilon)}$ Zeitskalensep.

$$\dot{P}_{ij} = \sum_{kl} \mathcal{L}_{ij,kl} \cdot P_{kl} \rightarrow P_i := \sum_j P_{ij} \ \hat{=}\ \text{WS für SET-Besetzung}$$

Zeitskalensep. $\dot{P}_i \approx \sum_k W_{ik}^{eff} \cdot P_k$

enthält Verletzung lok. det. GG's

- 2HS: $\frac{d}{dt} S_{sys} - \sum_\nu \beta^{(\nu)} \left[\bar{I}_E^{(\nu)} - \mu_\nu \bar{I}_M^{(\nu)} \right] \geq 0$

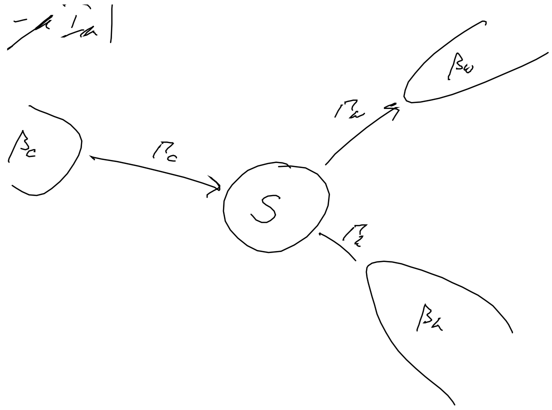
$$\hat{=} \frac{d}{dt} S_{sys} + \sum_\nu \frac{d}{dt} S_{res}^{(\nu)} \geq 0$$

Res. in GG: $dU_{res} = T_{res} dS_{res} - \underbrace{p\,dV}_{\to 0} + \mu\, dN_{res}$

$$\frac{dS_{res}}{dt} = \frac{1}{T_{res}} \left(\frac{dU_{res}}{dt} - \mu \frac{dN_{res}}{dt} \right)$$

$$= -k_B \cdot \beta_{res} \left(\bar{I}_E - \mu \bar{I}_M\right)$$

4.1.6 Kältemaschine



- über Energieaustausch
- 2 Terminal geht nicht (2. HS)
- 3 Terminal könnte gehen
- Energie-Erhaltung in SS

$$\bar{I}_E^{(c)} + \bar{I}_E^{(h)} + \bar{I}_E^{(w)} = 0$$

- 2HS in SS

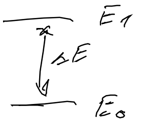
$$-\beta_c \bar{I}_E^{(c)} - \beta_h \bar{I}_E^{(h)} + \beta_w \left[\bar{I}_E^{(c)} + \bar{I}_E^{(h)}\right] \ge 0$$

$$= (\beta_w - \beta_c) \cdot \bar{I}_E^{(c)} + (\beta_w - \beta_h) \cdot \bar{I}_E^{(h)} \ge 0$$

$\bar{I}_E^{(c)} > 0$ für Kühlung

$$\beta_c > \beta_w, \beta_h \longrightarrow \beta_c > \beta_h > \beta_w$$

a) 2-Niveaus



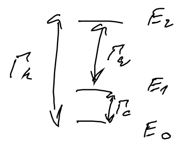
$$W = \sum_{\nu \in \{c,h,w\}} \Gamma_\nu \begin{pmatrix} -n_\nu & +(1+n_\nu) \\ +n_\nu & -(1+n_\nu) \end{pmatrix} \qquad n_\nu = \frac{1}{e^{\beta_\nu \Delta E} - 1}$$

lok. det. GG

$$\bar{I}_E^{(c)} = \Delta E \, \frac{\Gamma_c \left\{\Gamma_h \left[(n_c - n_h)\right] + \Gamma_w \left[(n_c - n_w)\right]\right\}}{\Gamma_c (1+2n_c) + \Gamma_h (1+2n_h) + \Gamma_w (1+2n_w)}$$

$n_c < n_h \quad n_c < n_w \rightsquigarrow \bar{I}_E^{(c)} < 0 \longrightarrow$ funktioniert nicht

b) 3-Niveaus



$$\Rightarrow W = \begin{pmatrix} -(\ldots) & \Gamma_c (1+n_c) & \Gamma_h (1+n_c) \\ \Gamma_c \cdot n_c & -(\ldots) & \Gamma_w (1+n_w) \\ \Gamma_h \cdot n_h & \Gamma_w \cdot n_w & -(\ldots) \end{pmatrix}$$

$$\underset{n_w \to \infty}{\bar{I}_E^{(c)}} = (E_1 - E_0) \cdot \frac{\Gamma_c \cdot \Gamma_h (n_c - n_h)}{\Gamma_c (1+3n_c) + \Gamma_h (1+3n_h)}$$

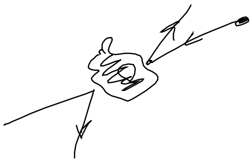
$\longleftarrow$ Unterschied

$$n_c = \frac{1}{e^{\beta_c (E_1 - E_0)} - 1} \qquad n_h = \frac{1}{e^{\beta_h (E_2 - E_0)} - 1}$$

kann positiv werden $\longrightarrow$ Kühlung des kalten Reservoirs

"kleinste Kältemaschine braucht mind. 3 Niveaus"

4.2. Fokker-Planck-Gleichung



Brown'sche Bewegung — Reibung — WW mit Reservoir — stochast. Kraft

$$m \cdot \ddot{x} + \gamma \cdot \dot{x} = F_{ext}^{kons}(x) + F^{stoch}(t)$$ Langevin-Gleichung

betrachte statt einzelner Trajektorie $\rightarrow$ WS-Verteilung $\rightarrow$ FP-Gleichung

$$\boxed{D = \frac{\gamma \cdot k_B \cdot T}{m^2}}$$

Einstein-Smoluchowski-Beziehung

4.2.1. Unterdämpfte FPG

$$\boxed{\partial_t P(x,v,t) = \Big[\frac{\gamma}{m} \underbrace{- v \cdot \partial_x + \Big(\frac{1}{m}\frac{\partial V}{\partial x} + \frac{\gamma}{m} \cdot v\Big)\partial_v}_{\text{Drift}} + \underbrace{D\,\partial_v^2}_{\text{Diffusionsterm}}\Big] P(x,v,t)}$$

Kramers-Gleichung

$P(x,v,t) \cdot \Delta x \cdot \Delta v \hat{=}$ WS für Teilchen am Ort x mit Geschw. v zur Zeit t

- WS ist erhalten

$$1 = \int P(x,v,t)\, dx\, dv$$

$$\int \partial_t P(x,v,t)\, dx\, dv = \frac{\gamma}{m}\int P(x,v,t)\, dx\, dv - \frac{\gamma}{m}\int (\partial_v v)\, P(x,v,t)\, dx\, dv$$
$$= \frac{\gamma}{m}\int P\, dx\, dv - \frac{\gamma}{m}\int P\, dx\, dv = 0$$

- $\langle x \rangle = \int x \cdot P(x,v,t)\, dx\, dv$

$$\partial_t \langle x \rangle = \cancel{\frac{\gamma}{m}\langle x \rangle} + \langle v \rangle - \cancel{\frac{\gamma}{m}\langle x \rangle}$$ gekoppelte Hierarchie von BwGL

$$\partial_t \langle v \rangle = -\frac{\gamma}{m}\langle v \rangle - \frac{1}{m}\left\langle \frac{\partial V}{\partial x} \right\rangle$$

Ansatz: $V = \frac{k}{2} \cdot x^2 \rightsquigarrow \frac{\partial V}{\partial x} = \underbrace{k}_{\text{Federkonst.}} \cdot x$ $\longrightarrow$ Mittelwerte $\hat{=}$ ged. harmon. Oszillator

- Diffusion kommt in höheren Momenten zum Tragen $\qquad D = \frac{\gamma \cdot k_B T}{m^2}$

für $V = \frac{k}{2}x^2$

$$\left.\begin{aligned}
\partial_t \langle x^2 \rangle &= 2 \cdot \langle x \cdot v \rangle \\
\partial_t \langle v^2 \rangle &= 2 \cdot D - 2\frac{\gamma}{m}\langle v^2 \rangle - \frac{2k}{m}\langle x \cdot v \rangle \\
\partial_t \langle x \cdot v \rangle &= \langle v^2 \rangle - \frac{k}{m}\langle x^2 \rangle - \frac{\gamma}{m}\langle x \cdot v \rangle
\end{aligned}\right\}$$ geschl. System

$$\overline{\langle x \cdot v \rangle} = 0$$

$$\overline{\langle x^2 \rangle} = \frac{k_B T}{k} \qquad \overline{\langle v^2 \rangle} = \frac{k_B T}{m}$$

$$\langle \bar{E} \rangle = \frac{1}{2} m \langle \bar{v}^2 \rangle + \frac{1}{2} k \langle \bar{x}^2 \rangle = k_B T$$

- man kann zeigen (Einsetzen)

$$\bar{P}(x,v) \propto e^{-\beta\left(\frac{1}{2}mv^2 + V(x)\right)}$$ Teilchen equilibriert mit Reservoir (Lösung)

- Entropie $\qquad \frac{d S_{res}}{dt} = +\frac{1}{T_{res}}\frac{d U_{res}}{dt} = -k_B \cdot \beta \cdot I_E$ $\leftarrow$ Energiestrom aus Reservoir

$$\dot{I}_E = \partial_t \langle E \rangle = \frac{m}{2} \partial_t \langle v^2 \rangle + \frac{k}{2} \partial_t \langle x^2 \rangle$$

$$= \dots = m \cdot D - \gamma \cdot \langle v^2 \rangle = \int \left[m \cdot D - \gamma \cdot v^2 \right] \cdot P(x,v,t)\, dx\, dv = \dot{I}_E(t)$$

$$\lim_{t\to\infty} \dot{I}_E(t) = 0$$

$$\dot{S}_i = \dot{S}_{sys} - k_B \cdot \beta \cdot \dot{I}_E$$

$$= \dots = k_B \underbrace{\int \frac{\left[\gamma \cdot v \cdot P(x,v,t) + D \cdot m \cdot \partial_v P(x,v,t) \right]^2}{D \cdot m^2 \cdot P(x,v,t)}}_{\geq 0} dx\, dv \overset{\text{2. HS}}{\geq} 0$$

4.2.2. Überdämpfte FPG

$$\underbrace{m \ddot{x}}_{\approx 0} + \gamma \dot{x} = F_{kons}(x) + F_{stoch}(t)$$

$$\boxed{\partial_t P(x,t) = \partial_x \left[\frac{1}{\gamma} \cdot (\partial_x V) P(x,t) \right] + \frac{m^2}{\gamma^2} D \cdot \partial_x^2 P(x,t)}$$

- $\int \partial_t P(x,t)\, dx = 0$
- $\partial_t \langle x \rangle = -\frac{1}{\gamma} \langle \partial_x V \rangle$
- $\bar{P} \propto e^{-\beta V(x)}$ ist stat. Lösung
- $\dot{I}_E = \partial_t \langle V(x) \rangle = \int \left[\frac{m^2}{\gamma^2} D \left(\partial_x^2 V \right) - \frac{1}{\gamma} \left(\partial_x V \right)^2 \right] P(x,t)\, dx$

$$\dot{S}_i = -k_B \int \left[\partial_t P(x,t) \right] \ln P(x,t)\, dx - \beta \cdot \dot{I}_E \geq 0$$