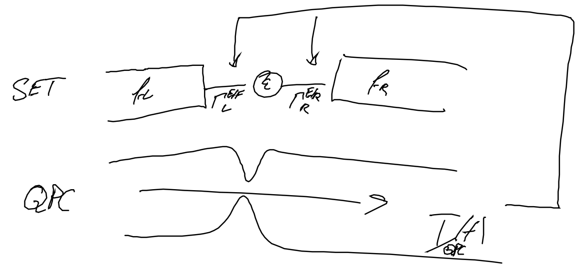
Wdh.



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

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

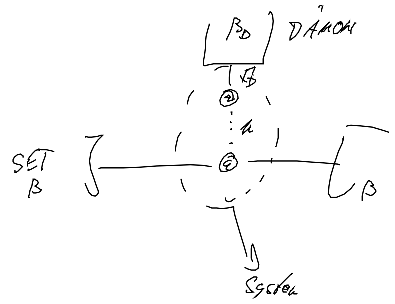
$$\mathcal{L}_{eff} = \sum_{\alpha \in \{L,R\}} \begin{pmatrix} -\Gamma_\alpha^E \cdot f_\alpha & +\Gamma_\alpha^F (1-f_\alpha) \\ +\Gamma_\alpha^E \cdot f_\alpha & -\Gamma_\alpha^F (1-f_\alpha) \end{pmatrix}$$

Verletzung det. GG

Umwandlung Info $\to$ 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.

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

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

enthält Verletzung lok. det. GG's

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

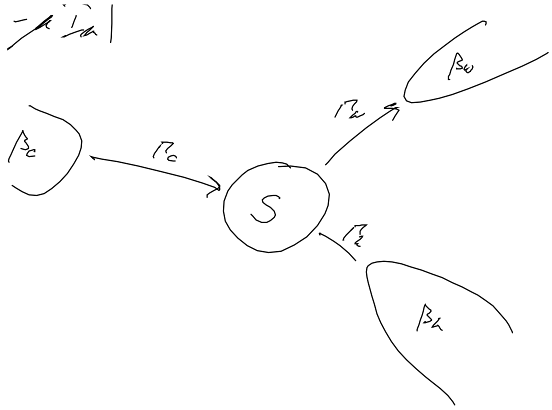
$$\hat{=} \frac{d}{dt} S_{sys} + \sum_\nu \frac{d}{dt} S_{res}^{(\nu)} \geq 0$$

Res. in GG: $\quad dU_{res} = T_{res} dS_{res} - \cancel{p\,dV}^{=0} + \mu\, dN_{res}$

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

$$= -k_B \cdot \beta_{res} (\dot I_E - \mu \dot I_N)$$

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

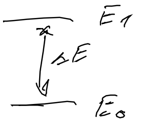
$$-\beta_c \bar I_E^{(c)} - \beta_h \bar I_E^{(h)} + \beta_w \left[\bar I_E^{(c)} + \bar I_E^{(h)}\right] \ge 0$$

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

$\bar I_E^{(c)} > 0$ für Kühlung

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

a) 2-Niveaus



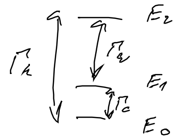
$$W = \sum_{\nu \in \{c,h,w\}} \Gamma_\nu \begin{pmatrix} -n_\nu & +(1+n_\nu) \\ +n_\nu & -(1+n_\nu) \end{pmatrix} \qquad n_\nu = \frac{1}{e^{\beta_\nu \Delta E} - 1}$$

lok. det. GG

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

$n_c < n_h \quad n_c < n_w \quad \longrightarrow \bar I_E^{(c)} < 0$ → funktioniert nicht

b) 3-Niveaus



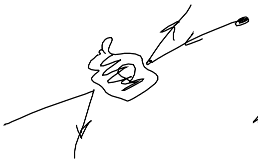
$$\Rightarrow W = \begin{pmatrix} -(\dots) & \Gamma_c (1+n_c) & \Gamma_h (1+n_c) \\ \Gamma_c \cdot n_c & -(\dots) & \Gamma_w (1+n_w) \\ \Gamma_h \cdot n_h & \Gamma_w \cdot n_w & -(\dots) \end{pmatrix}$$

$$\bar I_E^{(c)} \underset{n_w \to \infty}{=} (E_1 - E_0) \cdot \frac{\Gamma_c \cdot \Gamma_h (n_c - n_h)}{\Gamma_c (1 + 3n_c) + \Gamma_h (1 + 3n_h)}$$ ← 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 → Kühlung des kalten Reservoirs
"kleinste Kältemaschine braucht mind. 3 Niveaus"

4.2. Fokker-Planck-Gleichung



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

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

betrachte statt einzelner Trajektorie → WS-Verteilung → FP-Gleichung

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

Einstein-Smoluchowski-Beziehung

4.2.1. Unterdämpfte FPG

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

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

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

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

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

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)

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

- Entropie $\quad \frac{dS_{res}}{dt} = +\frac{1}{T_{res}}\frac{dU_{res}}{dt} = -k_B\cdot\beta\cdot I_E$ ← Energiestrom aus Reservoir

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

$$= \ldots = m \cdot D - \gamma \cdot \langle v^2 \rangle = \int \left[m \cdot D - \gamma \cdot v^2 \right] \cdot P(x,v,t)\, dx\, dv = I_E(t)$$

$$\lim_{t \to \infty} I_E(t) = 0$$

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

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

2. HS

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
- $I_E = \partial_t \langle V(x) \rangle = \int \left[\frac{m^2}{\gamma^2} D \left(\partial_x^2 V \right) - \frac{1}{\gamma} \left(\partial_x V \right)^2 \right] P(x,t)\, dx$

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