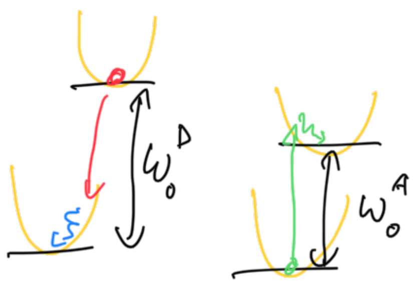
Detailní rovnováha ve Försterově teorii

Försterova teorie



$$\Delta\omega = \omega_0^D - \omega_0^A$$

Termodynamická rovnováha mezi energiemi
$\hbar(\omega_0^D - \lambda_D)$
a
$\hbar(\omega_0^A + \lambda_A)$

Rychlostní konstanta má tvar

$$K_{AD} = \varkappa \int \alpha_A(\omega)\, f_D(\omega) \qquad D \to A$$

$$K_{DA} = \varkappa \int \alpha_D(\omega)\, f_A(\omega) \qquad A \to D$$

mělo by platit

$$\boxed{\frac{K_{DA}}{K_{AD}} = e^{-\frac{\hbar(\omega_0^D - \omega_0^A)}{k_B T}}}$$

V přibližných teoriích jeden někdy není!

$$K_{AD} = \frac{|J_{AD}|^2}{\hbar^2}\, 2\mathrm{Re} \int_0^\infty dt\, \mathrm{tr}_B\{U_D^+(t) U_A(t) w_{eq}^D\}$$

$$= \frac{|J_{AD}|^2}{\hbar^2} \int_{-\infty}^{\infty} dt\, \mathrm{tr}_B\{U_D^+(t) U_A(t) w_{eq}^D\}$$

$$tr_B\{\dots\} = \sum_{\nu} \langle\nu| U_D^{\dagger}(t)|\nu\rangle\langle\nu| U_A(t)|\nu\rangle P(\nu)$$

↑ 'diagonální' v $|\nu\rangle$

↑ w_{eq}^{D} je také 'diagonální' v $|\nu\rangle$

$U_A(t)$ není 'diagonální' v $|\nu\rangle$

$$\langle\nu|U_A(t)|\nu\rangle = \sum_{\mu'\varkappa'} \langle\nu|\mu'\rangle \underbrace{\langle\mu'|U_A(t)|\varkappa'\rangle}_{\text{'diagonální' v } |\mu'\rangle} \langle\varkappa'|\nu\rangle$$

$$\langle\nu|U_A(t)|\nu\rangle = \sum_{\mu'} |\langle\nu|\mu'\rangle|^2 U^A_{\mu'}(t)$$

$$tr_B\{\dots\} = \sum_{\nu\mu'} e^{\frac{i}{\hbar}\varepsilon_\nu^D t} e^{-\frac{i}{\hbar}\varepsilon_{\mu'}^A t} |\langle\nu|\mu'\rangle|^2 P_D(\nu)$$

$$= \sum_{\nu\mu'} e^{i\omega^{DA}_{\nu\mu'} t} |\langle\nu|\mu'\rangle|^2 P_D(\nu)$$

$$K_{AD} \approx \int_{-\infty}^{\infty} dt \sum_{\nu\mu'} e^{i\omega^{DA}_{\nu\mu'} t} |\langle\nu|\mu'\rangle|^2 P_D(\nu)$$

$$\boxed{\approx \sum_{\nu\mu} \delta(\omega^{DA}_{\nu\mu'}) |\langle\nu|\mu'\rangle|^2 P_D(\nu)}$$

$$\boxed{K_{DA} \approx \int_{-\infty}^{\infty} dt \sum_{\nu\mu'} \delta(\omega^{AD}_{\nu\mu'}) |\langle\nu|\mu'\rangle|^2 P_A(\nu)}$$

$$\hbar\omega^{AD}_{\nu\mu'} = \hbar\omega_0^{AD} + \hbar\omega_\nu^A - \hbar\omega_{\mu'}^D = 0$$

$$\hbar\omega^{DA}_{\nu\mu'} = \hbar\omega_0^{DA} + \hbar\omega_\nu^D - \hbar\omega_{\mu'}^A = 0$$

$$K_{DA} \propto \sum_{\nu\mu'} \delta\left(\omega_0^{AD} + \omega_\nu^A - \omega_{\mu'}^D\right) |\langle \nu | \mu' \rangle|^2 e^{\frac{\hbar\omega_0^{AD} - \hbar\omega_{\mu'}^D}{k_B T}}$$

$$= \sum_{\nu\mu'} \delta\left(\omega_0^{AD} + \omega_\nu^A - \omega_{\mu'}^D\right) |\langle \nu | \mu' \rangle|^2 P_D(\mu') \, e^{\frac{\hbar\omega_0^{AD}}{k_B T}}$$

$$K_{AD} \approx \sum_{\nu\mu'} \delta\left(\omega_0^{DA} + \omega_\nu^D - \omega_{\mu'}^A\right) |\langle \nu | \mu' \rangle|^2 P_D(\nu) \qquad \begin{array}{l} \mu' \to \nu \\ \nu \to \mu' \end{array}$$

$$= \sum_{\nu\mu'} \delta\left(\omega_0^{DA} + \omega_{\mu'}^D - \omega_\nu^A\right) |\langle \nu | \mu' \rangle|^2 P_D(\mu') \qquad \delta(\omega) \to \delta(-\omega)$$

$$= \sum_{\nu\mu'} \delta\left(\omega_0^{AD} + \omega_\nu^A - \omega_{\mu'}^D\right) |\langle \nu | \mu' \rangle|^2 P_D(\mu')$$

$$K_{DA} = K_{AD} \, e^{\frac{\hbar\omega_0^{AD}}{k_B T}}$$

$$\boxed{\frac{K_{DA}}{K_{AD}} = e^{-\frac{\hbar\omega_0^{DA}}{k_B T}}}$$