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Propriedades de simetria e dissipação:

i) Invariância por translação temporal:

$$\chi''_{ij}(t) = -\chi''_{ji}(-t) \Rightarrow \chi''_{ij}(\omega) = -\chi''_{ji}(-\omega)$$

ii) Hermiticidade de A:

$$\chi''^{*}_{ij}(t) = -\chi''_{ij}(t) \quad \text{ou} \quad \chi''^{*}_{ij}(\omega) = -\chi''_{ij}(-\omega)$$

$\Rightarrow \chi''_{ij}(t)$ é imaginário puro e $\chi''^{*}_{ij}(\omega) = -\chi''_{ij}(-\omega)$

iii) Invariância por inversão temporal

$$\chi''_{ij}(t) = -\epsilon_i\epsilon_j\chi''_{ij}(-t) \quad \text{ou} \quad \chi''_{ij}(\omega) = -\epsilon_i\epsilon_j\chi''_{ij}(-\omega)$$

onde ϵ_i é a paridade por inversão temporal do operador $\hat{A}_i$, ou seja:

$$\Theta\hat{A}_i(t)\Theta^{-1} = \epsilon_i\hat{A}_i(-t)$$

Dem: $C_{ij}(t) = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha \langle\hat{A}_i(t)\hat{A}_j(i\alpha)\rangle = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha\langle\hat{A}_i(0)\hat{A}_j(i\alpha-t)\rangle$

mas $C_{ij}(-t) = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha\langle\hat{A}_i(-t)\hat{A}_j(i\alpha)\rangle = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha\langle\hat{A}_i(0)\hat{A}_j(i\alpha+t)\rangle$

$= \epsilon_i\epsilon_j\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\alpha\langle\Theta\hat{A}_i(0)\Theta^{-1}\Theta\hat{A}_j(i\alpha-t)\Theta^{-1}\rangle = \frac{\epsilon_i\epsilon_j}{\hbar\beta}\int_0^{\hbar\beta} d\alpha\langle\hat{A}_i(0)\hat{A}_j(i\alpha-t)\rangle$

$= \epsilon_i\epsilon_j C_{ij}(t)$

$\Rightarrow \chi''_{ij}(t) = \frac{i\beta}{2}\dot{C}_{ij}$ e $C_{ij}(t) = \epsilon_i\epsilon_j C_{ij}(-t)$

$\Rightarrow \dot{C}_{ij} = -\epsilon_i\epsilon_j\dot{C}_{ij}(-t) \Rightarrow \chi''_{ij}(t) = -\frac{i\beta}{2}\epsilon_i\epsilon_j\dot{C}_{ij}(-t)$

$\Rightarrow \chi''_{ij}(t) = -\epsilon_i\epsilon_j\chi''(-t) \Rightarrow \chi''_{ij}(\omega) = -\epsilon_i\epsilon_j\chi''_{ij}(-\omega)$

Quando $A_i = A_j$, $\quad \epsilon_i \epsilon_j = 1 \Rightarrow \chi''_{ij}(\omega) = -\chi''_{ij}(-\omega)$

$\epsilon_i \epsilon_j = -1 \Rightarrow \chi''_{ij}(\omega) = +\chi''_{ij}(-\omega)$

Relação de χ'' com a dissipação.

Na versão de Schrödinger: $\hat{\rho}_S(t)$ e $\hat{V}_S(t) = -\sum_i f_i(t) \hat{A}_i$

$$i\hbar \frac{\partial \hat{\rho}_1^{(S)}}{\partial t} = [\hat{H}_1^{(S)}(t), \hat{\rho}_1^{(S)}(t)] = [\hat{H} + \hat{V}_S(t), \hat{\rho}_1^{(S)}]$$

$$\frac{dW}{dt} = \frac{dE}{dt} = \frac{d}{dt} \mathrm{Tr}\left(\hat{\rho}_1^{(S)}(t) \hat{H}_1^{(S)}\right)$$

$$= \mathrm{Tr}\left(\hat{\rho}_1^{(S)} \dot{\hat{H}}_1^{(S)}\right) + \mathrm{Tr}\left(\dot{\hat{\rho}}_1^{(S)} \hat{H}_1^{(S)}\right)$$

Mas $\mathrm{Tr}\left(\dot{\hat{\rho}}_1^{(S)} \hat{H}_1^{(S)}\right) = \mathrm{Tr}\left(\frac{1}{i\hbar} [\hat{H}_1^{(S)}(t), \hat{\rho}_1^{(S)}(t)] \hat{H}_1^{(S)}\right)$

$$= \mathrm{Tr} \frac{1}{i\hbar}\left(\hat{H}_1^{(S)}(t) \hat{\rho}_1^{(S)}(t) \hat{H}_1^{(S)}(t) - \hat{\rho}_1^{(S)}(t) \hat{H}_1^{(S)}(t) \hat{H}_1^{(S)}(t)\right)$$

$= 0$ //

$$\Rightarrow \frac{dW}{dt} = -\sum_i \mathrm{Tr}[\hat{\rho}_1^{(S)} \hat{A}_i] \dot{f}_i(t) = -\sum_i \bar{A}_i(t) \dot{f}_i(t)$$

$$\left\langle \frac{dW}{dt} \right\rangle_T = \frac{1}{2T} \int_{-T}^{T} \frac{dW}{dt} dt = \frac{-1}{2T} \sum_i \int_{-T}^{T} \bar{A}_i(t) \dot{f}_i(t) dt = \frac{1}{2T} \left[\sum_i f_i(t) \bar{A}_i(t) \right]_{-T}^{T}$$

$$+ \frac{1}{2T} \sum_i \int_{-T}^{T} f_i(t) \dot{\bar{A}}_i(t) dt = \frac{1}{2T} \sum_i \int_{-T}^{T} f_i(t) \dot{\bar{A}}_i(t) dt$$

$$\bar{A}_i(t) = \langle A_i \rangle + \sum_j \int_{-\infty}^{t} \chi_{ij}(t - t') f_j(t') dt'$$

$$\delta \mathring{A}_i(t) = \overbrace{\sum_j \chi_{ij}(0) f_j(t)}\ + \sum_j \dot{\chi}_{ij}(t-t') f_j(t') dt'$$

$$\Rightarrow \left\langle \frac{dw}{dt} \right\rangle_T = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} \sum_{ij} dt \int_{-\infty}^{\infty} f_i(t)\, \dot{\chi}_{ij}(t-t') f_j(t') dt' + \frac{1}{2T} \sum_{ij} \int f_i(t) \chi_{ij}(0) \frac{f_j(t)}{dt}$$

Mas quando $T \to \infty$ o 2º termo se anula.

$$\Rightarrow \left\langle \frac{dw}{dt} \right\rangle_T = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} dt \int_{-\infty}^{\infty} f_i(t)\, \dot{\chi}_{ij}(t-t') f_j(t') dt'$$

$$\chi_{ij}(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{-i\omega(t-t')} \chi_{ij}(\omega)$$

$$\Rightarrow \frac{d}{dt} \chi_{ij}(t-t') = \frac{-i}{2\pi} \int_{-\infty}^{\infty} \omega\, \chi_{ij}(\omega)\, e^{-i\omega t}\, e^{i\omega t'}\, d\omega$$

$$\Rightarrow \int_{-\infty}^{\infty} f_j(t')\, \dot{\chi}_{ij}(t-t') dt' = \int_{-\infty}^{\infty} \frac{-i}{2\pi} \omega \chi_{ij}(\omega) f_j(\omega) d\omega$$

$$\Rightarrow \lim_{T\to\infty} \int \frac{d\omega}{2T} \int_{-T}^{T} dt\, f_i(t)\, e^{-i\omega t} \left(\frac{-i}{2\pi}\right) \omega\, \chi_{ij}(\omega) f_j(\omega)$$

↳ extensão periódica

$$\left\langle \frac{dw}{dt} \right\rangle_T = \frac{-i}{2\pi} \int d\omega\, f_i^*(\omega)\, \omega\, \chi_{ij}(\omega) f_j(\omega)$$

Como $\chi_{ij}(\omega) = \chi'_{ij}(\omega) + i\chi''_{ij}(\omega)$

$$\left\langle \frac{dw}{dt} \right\rangle_T = -\frac{i}{2\pi} \int d\omega\, f_i^*(\omega)\, \omega\, \chi'_{ij}(\omega) f_j(\omega) + \frac{1}{2\pi} \int d\omega\, f_i^*(\omega)\, \omega\, \chi''_{ij}(\omega) f_j(\omega)$$

$$\chi''_{ij}(\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi'_{ij}(\omega')}{\omega'-\omega}\, d\omega'$$

$$\chi''_{ij}(-\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi'_{ij}(\omega')}{\omega'+\omega}\, d\omega'$$

$$= -\frac{1}{\pi}\int_{\infty}^{-\infty} -d\omega' \, \frac{\chi'_{ij}(-\omega')}{-\omega'+\omega} = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi'_{ij}(-\omega')}{\omega'-\omega}\, d\omega'$$

$$\chi''_{ij}(-\omega) = -\chi''_{ji}(\omega) \Rightarrow \chi''_{ji}(\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi'_{ij}(-\omega')}{\omega'-\omega}\, d\omega'.$$

$$\Rightarrow \chi'_{ij}(-\omega) = \chi'_{ji}(\omega)$$

$$\Rightarrow \int_{-\infty}^{\infty} d\omega \, f^*_i(\omega)\, \omega\, \chi'_{ij}(\omega)\, f_j(\omega) = +\int_{\infty}^{-\infty} -d\omega \, f^*_i(-\omega)\,(-\omega)\,\chi'_{ij}(-\omega)\, f_j(-\omega)$$

$$= \int_{-\infty}^{\infty} d\omega \, f_i(\omega)\,(-\omega)\,\chi'_{ji}(\omega)\, f^*_j(\omega)$$

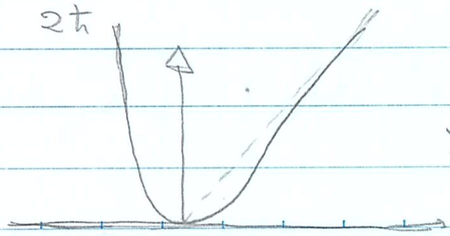
$$= -\int_{-\infty}^{\infty} d\omega \, f^*_i(\omega)\, \omega\, \chi'_{ij}(\omega)\, f_j(\omega)$$

$$\Rightarrow \int_{-\infty}^{\infty} d\omega \, f^*_i(\omega)\, \omega\, \chi'_{ij}(\omega)\, f_j(\omega) = 0 \, //$$

$$\Rightarrow \left\langle \frac{dW}{dt} \right\rangle_T = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \, f^*_i(\omega)\, \omega\, \chi''_{ij}(\omega)\, f_j(\omega)$$

Pelo TFD: $\omega\chi''_{ij}(\omega) = \frac{\omega}{2\hbar}\left(1-e^{-\beta\hbar\omega}\right) S_{ij}(\omega)$

$\omega\left(1-e^{-\beta\hbar\omega}\right) \longrightarrow$



≥ 0 !

Mas $\frac{1}{2T}\iint dt\, dt'\, f_i^*(t)\, \langle A_i^*(t)\, A_j(t')\rangle\, f_j(t')$

$= \langle A^* A\rangle \geq 0$

$$\hat{A} = \frac{1}{\sqrt{2T}}\int_{-T}^{T} \left[\hat{A}_i(t) - \langle A_i\rangle\right] f_i(t)\, dt$$

$$\Rightarrow \int d\omega\, f_i^*(\omega)\, S_{ij}(\omega)\, f_j(\omega) \geq 0$$

$\Rightarrow \left\langle \frac{dW}{dt}\right\rangle_T \geq 0$ o que é fisicamente plausível.

<u>Regras de soma:</u>

Como vimos: $\chi''_{ij}(t,t')\ \frac{1}{2\hbar}\left\langle \left[\hat{A}_i(t), \hat{A}_j(t')\right]\right\rangle$

$$\Rightarrow \left(i\frac{\partial}{\partial t}\right)^n \chi''_{ij}(t,t') = \frac{1}{2\hbar}\left\langle \left[\left(i\frac{\partial}{\partial t}\right)^n \hat{A}_i(t), \hat{A}_j(t')\right]\right\rangle$$

mas $i\hbar \frac{d\hat{A}}{dt} = [\hat{A}, \hat{H}] \Rightarrow i\frac{\partial}{\partial t}\hat{A} = \frac{1}{\hbar}[\hat{A}, \hat{H}]$

$$\left(i\frac{\partial}{\partial t}\right)^n \hat{A}\ \frac{1}{\hbar^n}\underbrace{\left[\ldots\left[\left[\hat{A}, \hat{H}\right], \hat{H}\right], \hat{H}\right]\ldots\hat{H}]}_{n} = \hat{A}^{(n)}$$

$$\Rightarrow \left(i\frac{\partial}{\partial t}\right)^n \chi''_{ij}(t) = \frac{1}{2\hbar}\left\langle\left[\hat{A}_i^{(n)}(t), \hat{A}_j(t')\right]\right\rangle$$

Como $\chi''_{ij}(t,t') = \frac{1}{2\pi}\int \chi''_{ij}(\omega)\, e^{-i\omega(t-t')}$